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# Electrochemical synthesis of allenyl silanes and allenyl boronic esters

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Allenyl silanes and boronates are pivotal building blocks in organic synthesis. Nevertheless, their synthesis requires the manipulation of transition metal or highly reactive species. Hence, the development of more sustainable protocol is highly sought after. Here we show the electrochemical synthesis of allenyl silanes and allenyl boronic esters. This catalyst-free method proceeds under mild reaction conditions. The protocol for the synthesis of allenyl silanes shows an excellent efficiency and a good functional group tolerance. The allenyl silanes are isolated in good yields (28 examples, 45–95% yields) without the use of a transition metal catalyst and under mild reaction conditions. A similar protocol is developed for the synthesis of allenyl boronates, which are obtained in low to moderate yields (13 examples, 5–55% yields). Finally, a mechanism based on an oxidative generation of the silyl and boryl radicals is suggested to access these classes of allenes.

Since 1887 and the first documented allene synthesis by Burton and Pechmann[1], this peculiar class of cumulene has fascinated the organic practitioners. Indeed, the allene motif is found in a plethora of natural products[2], which stimulated the development of synthetic approaches. In addition, over the years allenes found applications in medicinal chemistry programs and in material chemistry[3,4].

Besides, allenes proved to be excellent synthetic building blocks to forge more complex structures[5–9], upon further synthetic manipulations[10–14]. Among them, allenyl silanes are an important class of versatile synthetic intermediates[15], which could be for instance used as propargylic anion surrogate, as pioneered by Danheiser[16,17]. These compounds are linchpin in organic synthesis and were used in strategic transformations in natural product synthesis, for instance[18]. Therefore, it is not surprising that significant efforts were devoted to elaborate practical reaction manifold to forge these compounds. The synthetic approaches mostly rely on the metal catalyzed silylation of propargylic derivatives, using Cu, Ni, Rh or Pd catalysts (Fig. 1, Eq. (1))[19–34]. Complementary, the electrophilic silylation of metaled allenes, generated from either carbometallation or direct metalation, offers a straightforward access to this scaffold (Fig. 1, Eq. (2))[35–37]. As another approach, the Wittig reaction on silylated ketene was also depicted (Fig. 1, Eq. (3))[38]. Finally, the formation of the allene moiety was reported starting from silylated substrates (Fig. 1, Eq. (4))[39–42]. Importantly, most of these methods require either the use of transition metal catalysts (Cu, Ni, Rh, Pd, Ir), stoichiometric amount of strong bases or harsh reaction conditions. Hence, the development of mild and more sustainable reaction conditions to forge this class of compounds is highly sought after.

Over the last decades, organic electrosynthesis has known a significant resurgence[43–55]. This renewal is mainly due to the impact of organic electrosynthesis on the development of sustainable process. Indeed, synthetic organic electrochemistry contributes to the reduction of waste generation, since it can replace hazardous oxidizing or reducing reagents by simple electrons. On the other hand, electrosynthesis usually provides high chemoselectivity with mild reaction conditions and could allow access to new reactivity[56–58]. Moreover, if electricity arises from renewable source, electrosynthesis fulfills the criteria of sustainability. Hence, organic electrosynthesis is a pivotal research area to offer alternative sustainable reaction manifold by decreasing the environmental footprint, a contemporary concern of the community for the public welfare.

Quite surprisingly, few electrochemical approaches to synthesize allenes were reported to date[59,60]. In addition, to our knowledge, the electrochemical synthesis of allenyl silanes remained scarce and mostly relied on the use of transition metal catalysts. In 2023, Li reported an electrochemical approach using a Cobalt catalyst and a

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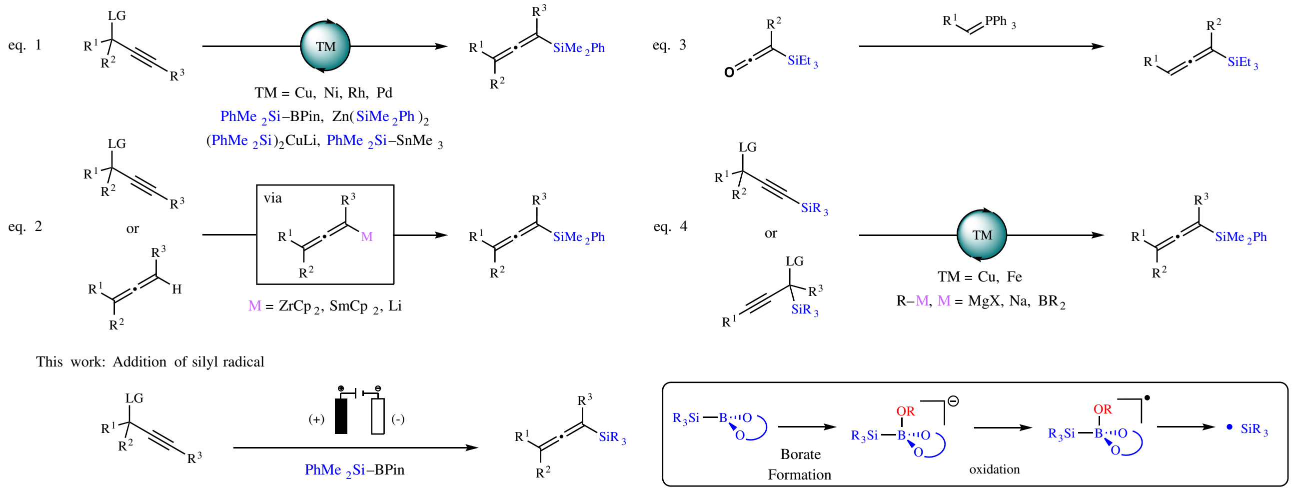


**Fig. 1 | State of the art and present work.** Eq. (1). Transition metals catalyzed synthesis of allenyl silanes. Eq. (2). Metallated allenes as precursors of allenyl silanes. Eq. (3). Silylated ketene as precursor of allenyl silane (Wittig approach). Eq. (4). Silylated alkynes of propargyl derivatives as precursor of allenyl silanes.

sacrificial anode to forge allenyl silanes from propargylic derivatives[61]. Concomitantly, Yue and Rueping described an electroreductive coupling to forge allenyl silanes from 1,3-enynes using a Nickel catalyst[62].

Thus, as part of our ongoing research program dedicated to organic electrosynthesis[63–69], we sought to elaborate a versatile electrochemical method to synthesize allenyl silanes. Indeed, based on our experience on the oxidative electrogeneration of silyl radical[70,71], and other reports[72–81], we surmised that a plausible addition of the latter on a propargylic derivative would lead to the formation of the desired allenyl silanes[82]. This approach, using a borosilane, avoids the use of electromediators, usually required for the formation of silyl radical from silanes, or harsh reductive conditions[71]. Indeed, the formation of the silyl radical using silane usually needs the addition of a HAT catalyst, while the use of chlorosilane required strong reductive conditions[72–81]. Our approach focuses on the oxidation of a boronate intermediate, which has a low oxidation potential, proving a smooth formation of the silyl radical[70].

In this work, we develop the electrochemical synthesis of allenyl silanes under oxidative conditions, using the Suginome reagent. This approach is also extended to the synthesis of allenyl boronated using a similar strategy.

## Results and discussion

### Optimization of the allenyl silane synthesis

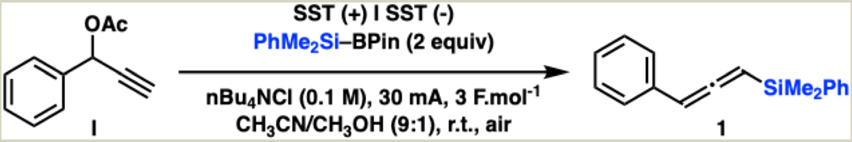
At the outset of our investigations, we studied the reaction of the propargyl acetate derivative **I** with the Suginome reagent ($PhMe_2Si$–BPin). After a meticulous set of optimizations[83], we were pleased to delineate the optimal reaction conditions. Using 2 equivalents of the Suginome reagent, $nBu_4NCl$ as the electrolyte (0.1 M), stainless steel electrodes at both the cathode and the anode in a 9:1 mixture of $CH_3CN$ and $CH_3OH$ with a constant current of 30 mA and a charge of 3 $F.mol^{-1}$, the allenyl silane **1** was obtained in a 74% NMR yield and a pleasant 68% isolated yield (Table 1, entry 1). From this optimization, we found that the 9:1 mixture of $CH_3CN$ and $CH_3OH$ was crucial for the outcome of the reaction (entries 2 and 3). Then, the replacement of the SST anode led to no reaction (entry 4), while the use of a platinum cathode furnished a lower yield (entry 5). A current of 30 mA was the optimum (entry 6). Our attempt to decrease the amount of electrolyte was deleterious for the reaction outcome (entry 7). Interestingly, the reaction conditions were compatible with methyl and *tert*-butyl carbonate propargyl derivatives, in place of the acetate, albeit with slightly lower yields (entries 8 and 9).

### Scope and limitations of the reaction

Then, with the settled optimized reaction conditions we decided to explore the scope and limitations of the method (Fig. 2).

First, we introduced substituents on the aromatic ring of the secondary propargyl acetate. The presence of halogens was well tolerated, giving access to the corresponding di-substituted allenes **2**–**4** in very good yields. Then, the methyl substituent, whatever its position on the phenyl ring did not alter the reaction outcome and allenes **5**–**7** were obtained in very good yields. The allenyl silane **8** having a methoxy group on the aromatic ring was obtained in a moderate 50% yield, while the benzodioxolane derivative **9** was obtained in a low 21% yield. The heteroaromatic ring (i.e. benzothiophene) was tolerated and the allene **10** was isolated in 45% yield. Then, the reactions with alkyl derivatives were performed. Pleasingly, allenyl silanes **11**–**13** were isolated in moderate to very good yields. The presence of an olefin was also tolerated affording the allene **14** in 45% yield, showcasing a faster addition on the alkyne than on the alkene. Cycloalkyl substituents did not hamper the reaction and allenyl silanes **15** and **16** were obtained in 56% and 53%. In addition, the reaction was tolerant to the presence of a thioether moiety, as observed with allene **17**, which was isolated in 74% yield. Then, we tested our reaction conditions on tertiary propargyl acetates to access trisubstituted allenyl silanes. Pleasingly, the method allowed the formation of the allenes **18** and **19**, bearing aromatic or alkyl substituent in very good yields (82% and 78%, respectively). The presence of a chlorine atom, a TBS-protected alcohol or an ester group was tolerated, as showcased with allenes **20, 21** and **22**. The cyclic derivatives **23, 24** and **25** were obtained in moderate to good yields. This straightforward protocol was then used to synthesize complex allenyl silanes. The Mestranol derived allenyl silane **26** was isolated in an excellent 95% yield. The procedure was then applied to propargyl acetates derived from Dehydroepiandrosterone and Pregnenolone. The corresponding allenyl silanes **27** and **28** were formed in very good yields, 69% and 79% respectively, the allene **28** obtained as a 9:1 mixture of diasteroisomer[83]. Interestingly, the reaction can be scale up. The allenyl silanes **11** and **19** were obtained in 46% and 63% isolated yield, on a 1.5 mmol and 1.2 mmol scale respectively. Overall, the reaction proceeded well and highlighted a good functional group tolerance, although some substrates remained reluctant in our hand (Fig. 2). Indeed, the presence of nitrile motif was not tolerated, resulting in the decomposition of the starting propargylic acetate. The reaction was sensitive to the steric hindrance, as shown with the fluorenone derivatives. Unfortunately, the substitution of the alkyne was not tolerated, hampering the access to tetrasubstituted allenyl

**Table 1 | Optimization of the reaction conditions**



| Entry | Deviation from standard conditions | % Yield[a] |
|---|---|---|
| 1 | None | 74, 68[b] |
| 2 | $CH_3OH$ as the sole solvent | 49 |
| 3 | $CH_3CN$ as the sole solvent | 0 |
| 4 | RVC, Graphite rod or Pt as the anode | NR |
| 5 | Pt as the cathode | 38 |
| 6 | 20 or 40 mA | 51 |
| 7 | $nBu_4NCl$ 0.05 M instead of 0.1 M | 53 |
| 8 | $OCO_2Me$ instead of OAc | 44 |
| 9 | OBoc instead of OAc | 67 |

[a] Determined by $^1H$ NMR yield using 1,3,5-trimethoxybenzene as the internal standard.
[b] Isolated yield.

silanes. Finally, primary propargyl acetates were also reluctant under our reaction conditions.

Then, we sought to extend our strategy to the synthesis of the synthetically useful allenyl boranes[84–91], using $B_2Pin_2$ as the boron source. Indeed, inspired by our initial foray in the electrooxidative generation of boryl radical[66,67,69], we hypothesized that the boryl radical[92–111] would have a similar reactivity and would lead to the formation of the allenyl boronate from an appropriate propargylic derivative. This approach would complement the existing state of the art and would offer a metal free and sustainable approach toward this versatile class of compound. Indeed, the seminal synthetic access to these compounds relied on the electrophilic borylation of allenyl metals (MgX, Li…). The metal catalyzed borylation reaction on propargylic derivatives (Cu, Pd, Au, Fe, Ag)[112–120], along with the hydrometallation/borylation sequence on enynes[121–125] remain the most popular approaches. Complementary, Studer and Friese recently reported the unique radical approach to these compounds, taking advantage of the redox properties of oxalic ester derived from tertiary propargylic alcohols[126]. Hence, we tested our electrochemical approach with the reaction of $B_2Pin_2$ with the propargyl carbonate **II**.

## Optimization of the allenyl boronated synthesis

After an extensive set of optimizations[83], we devised the optimal reaction conditions (Table 2, entry 1). Using stainless steel electrodes (cathode and anode), $Et_4NBF_4$ (0.05 M) as the electrolyte, $NaOCH_3$ as the additive (1 equiv) in $CH_3OH$, a constant current of 25 mA and rapid alternating polarity (rAP, 150 ms) at room temperature, the allenyl boronic ester **29** was obtained in a decent 56% NMR yield and a 46% isolated yield. The use of rapid alternating polarity was crucial to avoid the electrodes passivation and degradation of the product.

During the optimization study, we found that $NaOCH_3$ was the best additive, since the other bases (NaOH or $Na_2CO_3$) did not improve the yield (entry 2). The use of stainless-steel cathode and anode was the optimal setup, as other electrodes gave either poor yield or no reaction (entries 3 and 4). The screening of solvent highlights methanol as the best solvent, since other combinations led to lower yields (entries 6 and 7). Finally, the pulse duration of rapid alternating polarity was investigated and an optimal rAP of 150 ms was found (entries 8 and 9). Then, with these optimized reaction conditions in hand we explored the scope and the limitations of this catalyst-free electrochemical synthesis of allenyl boronic esters (Fig. 3).

## Scope of the reaction with $B_2Pin_2$

First, other diborane were tested. Pleasingly, the PinB–Baam was tested and the corresponding allenyl borane **30** was isolated in a modest 20%. The PinB–Bdan was also tested, however the reaction led a complex reaction mixture without trace of the desired allene. Then, the reaction conditions were then applied to other propargylic derivatives with longer alkyl chain on the alkyne. The allenyl boranes **31** and **32** were isolated in moderate yields (28% and 32%), despite a good NMR yield in the case of **32**, mainly due to tedious purification of the products due to their moderate stability over silica gel. The cyclohexyl derivative **33** was obtained in a modest 48% isolated yield and a 69% NMR yield. Interestingly, the allenyl boranes **34** was isolated in a pleasant 52% yield. Likewise, the boronate **35** was obtained in a 50% isolated yield. The reaction with dimethylated propargyl derivatives led to the formation of allenes **36, 37, 38** and **39** in low to modest yields (12% to 40%). Finally, other disubstituted allenes were synthesized with very low yields (**40** and **41**, 10% and 5% isolated yields). The observed low yields are mainly explained by the stability of the allenyl boranes in the reaction media. Indeed, these substrates can readily be subjected to a protodeboration event. Then, we sought to get insight into the reaction mechanism (Fig. 4).

## Study of the reaction mechanism

First, the stereoretentive nature of the process was studied. Thus, we conducted the reaction with the enantioenriched propargylic derivatives **(*S*)-III** and **(*R*)-III** (Fig. 4A). Under standard reaction conditions, the corresponding allene **11** was obtained in similar yields with a complete enantiospecificity in the case of **(*R*)-III** and a slight alteration of the e.r., when the (*S*) isomer was used (e.r. = 93:7, e.s. = 96%). Likewise, **(*S*)-IV** was used as a model substrate and the enantioenriched product **12** was obtained in a similar e.r. (e.s. = 98%) These results demonstrate the enantiospecificity of the reaction and a possible access to enantioenriched allenes from enantioenriched chiral propargylic acetates. To confirm the presence of the silyl radical in the reaction mixture, the reaction of the model substrate in the presence of 1,1-diphenylethene was conducted under standard conditions (Fig. 4B). The HRMS analysis of the crude reaction mixture allowed the detection of the silyl radical addition product on the 1,1-diphenylethene, confirming the involvement of the silyl radical[83].

Then, we conducted cyclic voltammetry (CV) measurements to support a plausible reaction mechanism (Fig. 4C). First, the CV

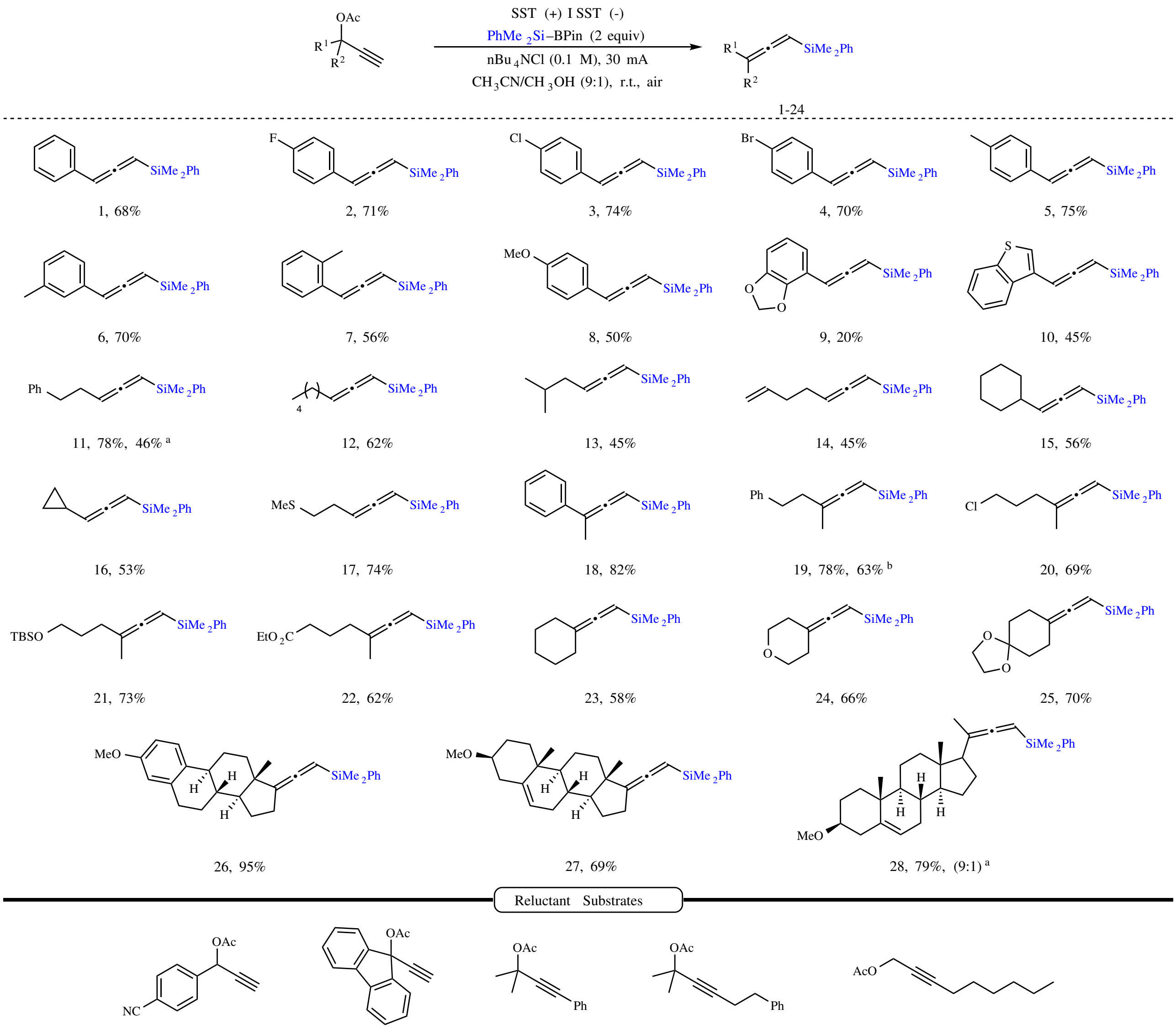
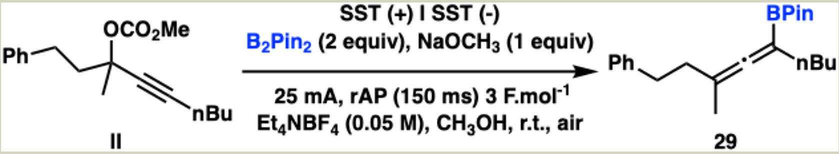


**Fig. 2 | Electrochemical synthesis of allenyl silanes – scope and limitations.** Reaction conditions: propargyl acetate (0.3 mmol), $PhMe_2Si$–BPin (0.6 mmol), nBu4NCl (0.4 mmol), $CH_3CN/CH_3OH$ (9:1, 4 mL), 30 mA, r.t., air.[a] diasteroisomeric ratio determined by $^1H$ NMR.

measurements of the model proparylic acetate **I**[83], and carbonate **II** did not showcase an oxidation nor a reduction event under our conditions. These results preclude an initial reduction of the propagylic derivatives under our conditions (Cheng, Li and co-workers (reference 59) described a possible initial reduction of the propargylic acetate ($E°_{1/2}$ = −2.24 V to −2.50 V vs Ag/$Ag^+$) in DMF, which has a larger electroactivity field). The measurement of a mixture of $B_2Pin_2$ and NaOMe, to mimic the cathodic formation of methoxide from methanol, revealed a single oxidation event (blue curve, $E_p$ = +1.26 V vs SCE). Thus, a possible oxidation of an in situ formed borate species from $B_2Pin_2$ and methoxide, which eventually would lead to the formation of a boryl radical, since this oxidation appears irreversible. Likewise, and in agreement with previous reports[70,71,127], a plausible oxidation of a borate formed from the Suginome reagent could lead to the formation of the corresponding silyl radical (despite all our effort, we have not been able to collect the CV measurement of the Suginome reagent ($Me_2PhSi$–BPin), using NaOMe, mainly due to a fast decomposition of the borosilane). Finally, the CV measurement in the presence of all reaction partners highlights a similar profile as the one observed with $B_2Pin_2$ and NaOMe (Fig. 2C, green curve).

Hence, with all these data in hand and previous reports[69,70,111], we suggested the following mechanism (Fig. 4D). First, $B_2Pin_2$ reacted with methoxide, generated from the reduction of the solvent (i.e MeOH) at the cathode to form the corresponding borate **A**. The latter is then oxidized to generate **B**, which collapse into the boryl radical **C** (the boryl radical is probably stabilized by the solvent or a methoxide anion to form a stable 7 electrons boryl radical. For clarity, the solvent or the Lewis base was omitted from Fig. 4C). This radical was reacted with the propargylic derivative to form a transient vinyl radical **D**. This radical might then react through two distinct pathways to forge the desired allene. First, the β-scission of the C–O bond could form the allene and the corresponding methoxycarbonyloxy radical (MeOCOO•) (path a). This radical, which highlights a very slow decarboxylation rate ($3.8 \times 10^3 M s^{-1}$)[128,129], can be reduced at the cathode to form the corresponding anion. This anion might then quickly extrude $CO_2$ to form methoxide[130]. Even though this class of C–O fragmentation has been scarcely reported, some examples might support this pathway[131–135]. Alternatively, a radical ionic pathway, similar to the well-known fragmentation of β-(phosphatoxy)alkyl radical[136], might lead to the formation of a radical cation **E** along with methoxide and $CO_2$ (generated from $MeOCO_2^-$) (path b). This cation **E** could be reduced at the cathode to deliver the targeted allene. Although, the mechanistic elucidation of this final event is yet impossible in our hand, we presume that the β-scission of the C–O bond might be the favored pathway. Indeed, the

**Table 2 | Optimization of the reaction conditions for the synthesis of 29**



| Entry | Deviation from standard conditions | % Yield[a] |
|---|---|---|
| 1 | None | 56, 46[b] |
| 2 | $Na_2CO_3$ or NaOH instead of MeONa | 46, 30 |
| 3 | Graphite at both the anode and the cathode | NR |
| 4 | Platinum anode instead of SST | 17 |
| 5 | $LiClO_4$ instead of $Et_4NBF_4$ | 23 |
| 6 | $CH_3OH/CH_3CN$ (4:1) instead of $CH_3OH$ | 39 |
| 7 | $CH_3OH$/acetone (4:1) instead of $CH_3OH$ | 42 |
| 8 | rAP = 50 ms instead of 150 ms | 12 |
| 9 | rAP = 300 ms instead of 150 ms | 39 |

*NR* no reaction.

[a] Determined by $^1$HNMR yield using $CH_3NO_2$ as the internal standard. bIsolated yield.

[b] Isolated yield.

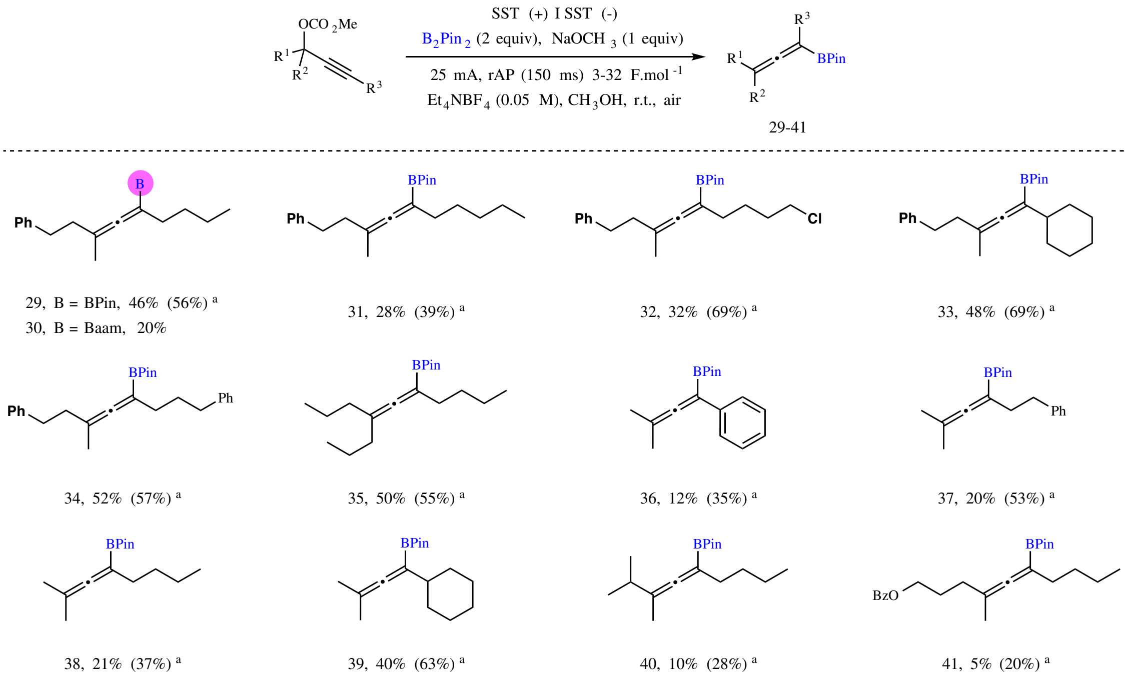


**Fig. 3 | Electrochemical synthesis of allenyl boranes.** Reaction conditions: propargyl carbonate (0.2 mmol), $B_2Pin_2$ (0.4 mmol), $nBu_4NBF_4$ (0.02 mmol), $CH_3ONa$ (0.2 mmol), $CH_3OH$ (4 mL), 25 mA, rAP (150 ms) r.t., air.[a] determined by $^1$H NMR using $CH_3NO_2$ as the internal standard.

formation of the methoxycarbonyloxy radical MeOCOO• radical, resulting from the fragmentation, is prompt to be reduced and then undergo a fast decarboxylation[136,137]. Moreover, the stereoretentive nature of the process (see Fig. 4A), supports a concerted mechanism, without the involvement of a radical cation prompt to racemize. Note that an anionic pathway, resulting from the direct borylation of the substrates has been ruled out[138,139]. Indeed, control experiments without current in the presence of $B_2Pin_2$ and NaOMe, led to no reaction[83]. In the case of $PhMe_2Si–BPin$ a complete decomposition of the reagent was observed without trace of the allenyl silane.

Finally, to showcase the synthetic utility of the products some transformations were carried out (Fig. 5).

## Synthetic utility of the products

First, the regioselective hydroboration catalyzed by copper was attempted on allenyl silane **11**. Pleasingly, the vinyl boronate **42** was obtained in 40% yield with a 2:1 *Z*:*E* selectivity. The allenyl silane **19** was then used to access the alkenyl silane **43** with a propargylic quaternary carbon center. Then, the protodesilylation of **10** and **18** was achieved in moderate yields, 40% and 49%, respectively, mainly due to the volatility of the final allenes. The synthetic utility of allenyl boranes was also demonstrated. First, the Suzuki cross coupling of **33** with iodotoluene provided the tetrasubstituted allene **46** in a 45% yield. Then, the hydroxymethylation of **33** gave the primary alcohol **47** in an excellent 97% yield. Finally, the

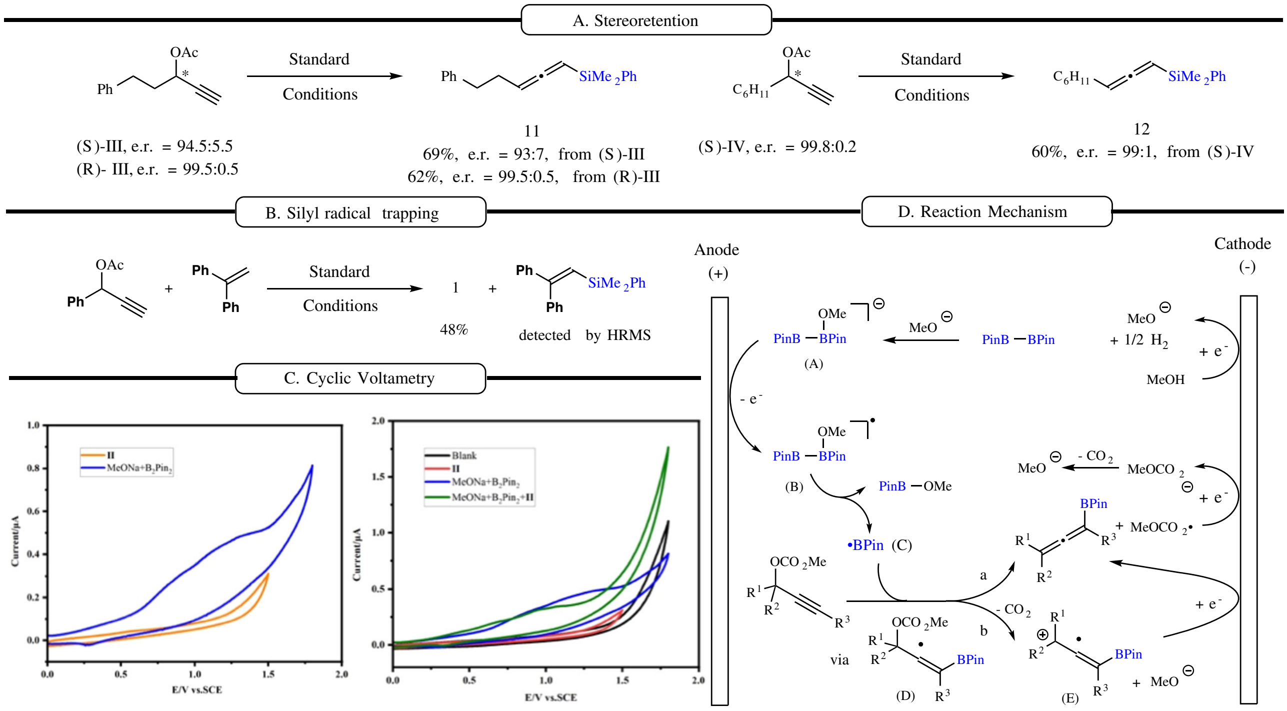


**Fig. 4 | Mechanistic investigations and plausible reaction mechanism. A** Study of the stereoretention of the process. **B** Radical trapping experiment. **C** Cyclic voltammetry studies. **D** Plausible reaction mechanism—for the sake of clarity ligand on the boryl radical was omitted.

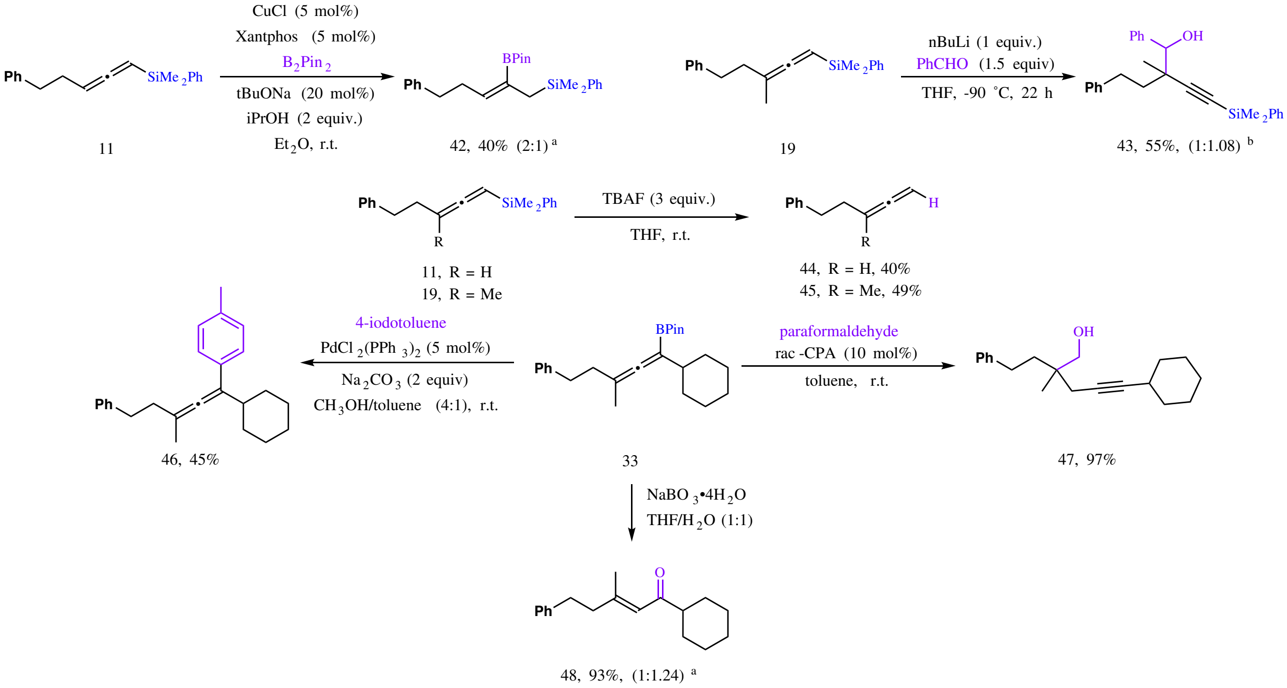


**Fig. 5 | Synthetic utility of the products.** $^a$*Z*:*E* ratio determined by $^1$H NMR. $^b$ Diastereoisomeric ratio determined by $^1$H NMR.

oxidation of **33** allows the formation of the trisubstituted alkene **48** in a 93% yield and a 1:1.24 *Z*:*E* ratio.

In summary, we reported herein the mild and catalyst-free electrochemical synthesis of allenyl silanes and allenyl boronates. The formation of allenyl silanes proceeded smoothly with a good functional group tolerance. The reaction conditions were applied to the synthesis of a large panel of allenyl silanes, which were isolated in good yields (28 examples, 45–82%). This practical method allows the formation of di- and trisubstituted allenyl silanes and avoids the use of sensitive reagents or expensive transition metal catalyst. Under modified reaction conditions, the electrochemical synthesis of allenyl boronic esters was developed. The applicability of the method was illustrated through the synthesis of 13 examples, which were isolated in low to moderate yields (5–57%). Finally, a mechanistic analysis of the reaction supported a plausible addition of a silyl or boryl radical, generated from an oxidation of a transient borate, on the propargylic precursor. These original approaches toward the synthesis of allenyl silanes and boranes, broaden the current arsenal of the organic chemist. We believe that these novel manifolds will inspire further developments toward the sustainable synthesis of silicon- and boron-containing building blocks.

## Methods

### General procedure for the synthesis of allenyl silanes

$PhMe_2Si$–BPin (0.6 mmol, 157.3 mg, 2.0 equiv.) and $nBu_4NCl$ (0.4 mmol, 111.2 mg, 0.1 M) were weighted under Argon in a glovebox and added in an ElectraSyn vial (5 mL) with a stir bar. The propargylic acetate (0.3 mmol, 1.0 equiv.) solubilized in anhydrous $CH_3CN$ (3.6 mL) and $CH_3OH$ (0.4 mL) was added. The ElectraSyn vial cap equipped with anode (Stainless steel, SST, 8 mm × 52 mm × 2 mm, immersion length is 25 mm) and cathode (SST) was inserted into the mixture. After pre-stirring for 5 minutes, the reaction mixture was electrolyzed under air and a constant current of 30 mA. The reaction is monitored by TLC and stopped until total conversion of the starting material substrate was observed. The reaction mixture was then concentrated under reduced pressure. The residue was diluted with ethyl acetate, filtered through a pad of silica and celite and concentrated. The crude mixture was purified by flash column chromatography on silica gel or preparative thin layer chromatography (PTLC).

### General procedure for the synthesis of allenyl boronates

The ElectraSyn 5 mL vial was wrapped with parafilm to improve sealing. Then the ElectraSyn vial (5 mL) with a stir bar was charged with propargylic carbonate (0.2 mmol, 1.0 equiv.), $B_2Pin_2$ (0.4 mmol, 101.6 mg, 2.0 equiv.), tetraethylammonium tetrafluoroborate ($Et_4NBF_4$, 0.2 mmol, 43.4 mg, 0.05 M) and $CH_3ONa$ (0.2 mmol, 10.8 mg, 1.0 equiv.) was added anhydrous $CH_3OH$ (4 mL). After the resulting mixture was purged with an argon balloon for ca 10 s. An ElectraSyn vial cap equipped with anode (SST) and cathode (SST) was inserted into the mixture. The mixture was electrolyzed at room temperature under a constant current of 25 mA with rapid alternating polarity (150 ms, 3.33 Hz) until the completion of the reaction monitored by TLC. The reaction mixture was concentrated under reduced pressure. The residue was diluted with ethyl acetate, filtered through a pad of silica and celite and concentrated. $CH_3NO_2$ (1.0 equiv.) was added as an internal standard to the mixture, the NMR yield of the product was determined by $^1H$ NMR. Then the resulting mixture was purified by flash column chromatography on silica gel (Santai Tech. Inc., 25 g), flow rate: 25 mL/min (pentane/ethyl acetate, gradient: 100:0 to 95:5).

## Data availability

The authors declare that the data to support the findings of this study are available within the paper and its Supplementary Information. All other data are available from the corresponding author upon request.

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## Author contributions

T.F., P.J., and T.P. conceived and designed the experiments. T.F. optimized the silylation reaction, developed the borylation reaction and extended the scope of these transformations. T.F., P.J., and T.P. analyzed the data. T.B. discovered the silylation reaction. T.P. wrote the manuscript with the input from all the authors.

## Competing interests

The authors declare no competing interests.

## Additional information

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