ORGANIC CHEMISTRY FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Check for updates

Cite this: *Org. Chem. Front.*, 2023, **10**, 2752

Base-catalyzed addition of silylacetylenes to ketones: a route to protected tertiary propargyl alcohols†

Krzysztof Kuciński, * Alicja Łuczak, Aliaksei Mankouski and Grzegorz Hreczycho

Received 18th April 2023,
Accepted 7th May 2023

DOI: 10.1039/d3qo00579h

rsc.li/frontiers-organic

The base-catalyzed addition of alkynylsilanes to ketone derivatives enables the formation of various silyl-protected propargylic alcohols. Commercially available and inexpensive potassium bis(trimethylsilyl)amide (KHMDS) serves as an efficient transition metal-free catalyst and permits the functionalization of a variety of derivatives, including pharmaceuticals and biorelevant compounds. Overall, the presented system complements classical routes to protected tertiary propargylic alcohols that mainly rely on stoichiometric processes or fluoride-mediated reactions.

Introduction

Propargyl alcohols are ubiquitous building blocks in chemical synthesis, being highly valued for their widespread application as valuable synthetic intermediates or medicinally relevant molecules themselves.[1–15] They participate in a diverse array of transformations, owing this to their multifunctionality, and thereby being the subject of numerous studies. Protected propargyl alcohols can be accessed *via* well-developed stoichiometric methods, including mainly the use of a combination of propargyl alcohol, chlorosilane and organolithium reagent (Fig. 1).[16] Such approaches are not without some disadvantages, including the need for an excess of both corrosive halosilane and hazardous *n*-butyllithium, little accessibility to commercial propargyl alcohol derivatives (compared with ubiquitous ketones), and the purification requiring high amounts of solvents (column chromatography). Moreover, the final isolating yields could be improved. For example, the reaction of 1-diphenyl-2-propyn-1-ol (Merck – 25 g per 139 €) gave the desired product in 81% yield, whereas our methodology using benzophenone as the starting reagent (Merck – 25 g per 11 €) led to identical product **3t** in 97% yield. Furthermore, an analogous stoichiometric reaction utilizing ketones requires a two-step pathway (the reaction with *in situ* generated (trimethylsilyl)acetylide followed by the subsequent *O*-silylation).[17] On the other hand, the concept of using silylacetylenes and ketones as the substrates has also been studied in the presence of fluorine reagents (*e.g.*, tetrabutylammonium fluoride – TBAF,[18–20] cesium fluoride – CsF,[21] *etc.*[22,23]). However, also these strategies have several drawbacks including lower selectivity and efficiency (formation of byproducts[19,21,22] and moderate yields[19,21,24,25]), the need for expensive crown ethers (CsF),[21] and narrow substrate scope.

In this context, it is also worth noting the classical alkynylation of carbonyl compounds for the generation of unprotected propargylic alcohols, originally discovered by Alexei Favorskii in the early 1900s.[26] Here, besides stoichiometric approaches, several catalytic protocols were developed as well.[27–37]

The application of Earth-abundant species as catalysts have gained recent significant attention in organic chemistry.[38–49] Considering our recent success in activating organometalloids under sustainable catalysis,[50–56] we reasoned that an appropriate catalytic manifold could provide an efficient platform to generate diversified libraries of protected propargyl alcohols. To address the limitations of previously mentioned methods, herein we report the KHMDS-catalyzed addition of silylacetylenes to ketones. Examples of biorelevant molecules transformed to the corresponding protected alkynols include camphor (topical medication), (*R*)-(−)-carvone (food additive), nabumetone (nonsteroidal anti-inflammatory drug), *etc.* Thereby, the mentioned late-stage functionalization may lead to potentially biologically interesting compounds.

Results and discussion

In optimization studies, summarized in Table 1, we investigated the addition of bis(trimethylsilyl)acetylene to acetophenone.

Faculty of Chemistry, Adam Mickiewicz University, Poznań, Uniwersytetu Poznańskiego St. 8, 61-614 Poznań, Poland. E-mail: kucinski.k@amu.edu.pl

† Electronic supplementary information (ESI) available: Characterization data including NMR spectra. See DOI: https://doi.org/10.1039/d3qo00579h

 This journal is © the Partner Organisations 2023

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

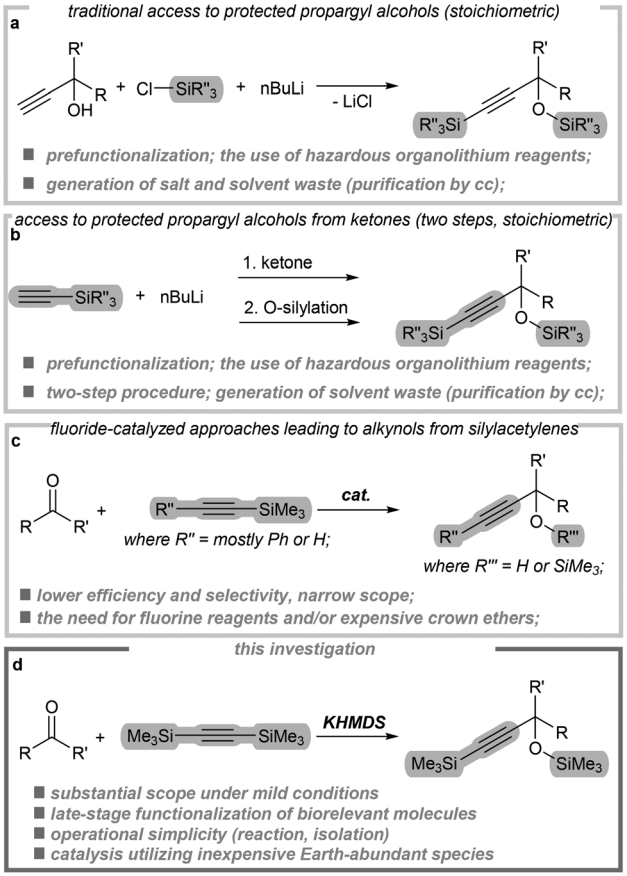
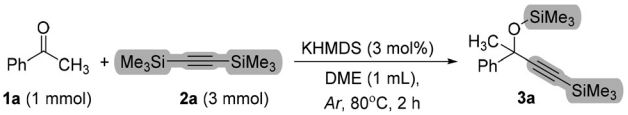


Fig. 1 Context of the investigation.

Table 1 Optimization of addition of silylacetylene **2a** to ketone **1a** [a]



Entry	Variation from standard conditions	Conversion of **1a** [a] [%]
1	No change	99 (95)
2	No catalyst	0[c]
3	Under solvent-free conditions	58[b]
4	1 mmol of **2a**	19
5	2 mmol of **2a**	90
6	Trimethylsilylacetylene instead of **2a**	80[b]
7	1.5 mol% of KHMDS	60[b]
8	3 mol% of KOH at 80 °C	0[b]
9	3 mol% of *t*-BuOK at 80 °C	20[b]
10	3 mol% of KF at 80 °C	0[b]
11	3 mol% of NaHMDS at 80 °C	0[b]
12	In toluene	0
13	In 1,4-dioxane	30[b]
14	Phenylacetylene instead of **2a**	0[c,d]

[a] Conversion determined *via* GC, with *n*-dodecane as internal standard. Isolated yield in parenthesis. [b] After 2 h. [c] After 24 h. [d] Solvent-free cond.

After several attempts, the ideal reaction conditions were identified (Table 1, entry 1), giving product **3a** in a 95% isolated yield. Control reactions revealed that the reaction does not proceed without the catalyst (entry 2). Instead, it was found that the reaction still works fine under solvent-free reaction conditions (entry 3). To ensure full conversion of **1a**, it is needed to use an excess of **2a** (entries 1, 5, and 6). What is more, such an excess of bis(trimethylsilyl)acetylene (BTMSA) excludes the formation of small amounts of diadduct. Please note, that **2a** can be readily recovered. For details, please see Fig. 8 (part D). Next, the attempt to replace the silylating source with trimethylsilylacetylene gave an inferior result (entry 7). Further experiments showed that other main-group mediators were mostly inactive under the tested conditions (entries 9–12). Considering the Favorskii reaction, we also checked simple phenylacetylene as the reaction partner with **1a** in the presence of KHMDS. However, no product was observed after 2 and 24 h (entry 14).

Next, a variety of different ketones were tested to evaluate the generality and functional-group tolerance of our protocol (Fig. 2). A wide range of 1-substituted ethanones worked efficiently under the reaction conditions (**3a–3i**). As an initial example **3a**, ketones bearing electron-donating alkyl groups were readily converted (**3b–3c**), as well as phenanthrene derivative **3e** (70% yield). Gratifyingly, halogenated acetophenones were readily adopted in this protocol (**3g–3j**, 76–79% yield), however, they required a higher amount of the catalyst (6 mol%). Moreover, other useful derivatives were also well tolerated, and led to protected alkynols **3k–3m** in good to excellent yields (79–99%). Notably, 5-hexen-2-one also participated effectively in this reaction (**3n**, 75% yield), while preserving the ene-functionality untouched. Encouraged by these results, we then investigated the use of heterocyclic ketones. All of them afforded the expected products in good yields (**3o–3p**, 62–70%). Subsequently, we tested our methodology on variously substituted propyl ketones. Simple nonan-3-one, as well as propiophenone and its fluoro-substituted derivative reacted well, providing **3q**, **3r**, and **3s** respectively in high yields (70–99%). Gratifyingly, two different benzophenones as well as cyclohexyl ketones were also readily adopted in this protocol (**3t–3w**, 94–99% yield). Finally, cyclohexanone was also well tolerated, and led to protected alkynol **3x** in excellent yield (91%).

Having demonstrated the unique robustness and versatility of our strategy, we sought to explore the late-stage functionalization of biorelevant compounds including drugs. Pleasingly then, camphor, (*R*)-(−)-carvone, and nabumetone were isolated in good to excellent yield (**4a–4c**; 72–96%; Fig. 3). Intrigued by the high efficiency and selectivity of the transformation, we next pursued the development of further applications of our catalytic system. Encouragingly, this strategy can also be applied to silylacetylenes other than bis(trimethylsilyl)acetylene (**2a**).

As shown in Fig. 4, the addition of 1-phenyl-2-trimethylsilylacetylene (**2b**), ((2-fluorophenyl)ethynyl)-trimethylsilane (**2c**), 2-((trimethylsilyl)ethynyl)pyridine (**2d**), and trimethyl (thiophen-3-ylethynyl)silane (**2e**) was performed, successfully

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

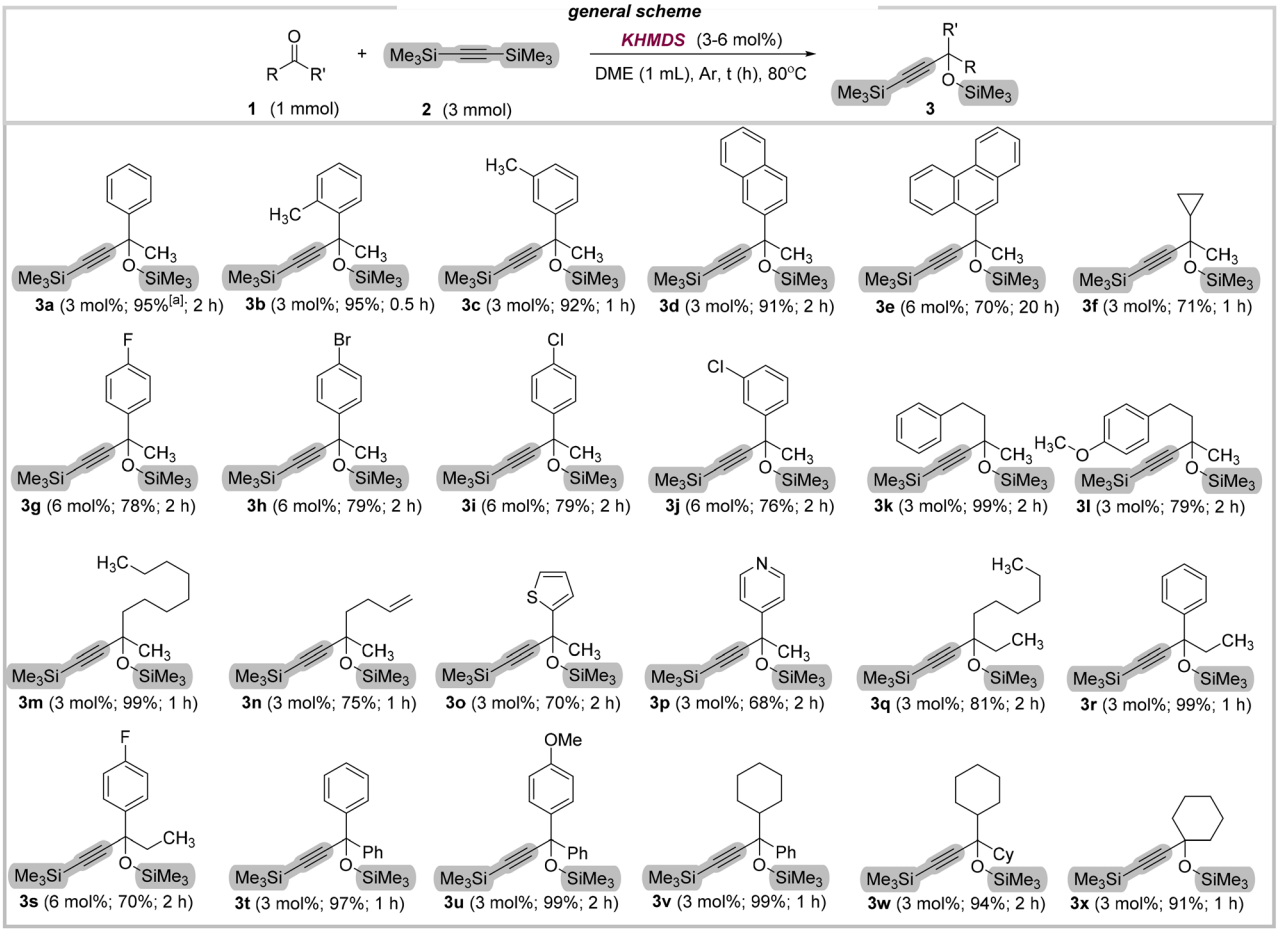


Fig. 2 Substrate scope for the addition of bis(trimethylsilyl)acetylene to ketones in the presence of KHMDS.

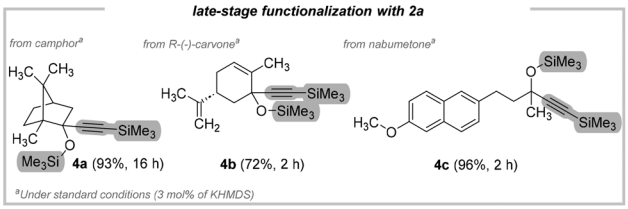


Fig. 3 Late-stage functionalization of biorelevant ketones.

providing protected alkynols **5a–5j**, in very good yields (up to 99%).

With these outcomes in mind, and given the similarity of aldehydes, we hypothesized that the presented addition reaction might allow convenient access to various protected secondary alkynols. In contrast to ketones, the reactions with the corresponding aldehydes were less selective and efficient, and somehow, this is in accordance with TBAF-mediated protocol (Fig. 5).[19]

For instance, the reaction of 3.0 eq. of **2a** with 1.0 eq. of benzaldehyde led to the mixture of mono- and diadduct (4 : 3). Notably, in the case of more sterically hindered ketones, we observed only traces of the above-mentioned diadducts (<1%).

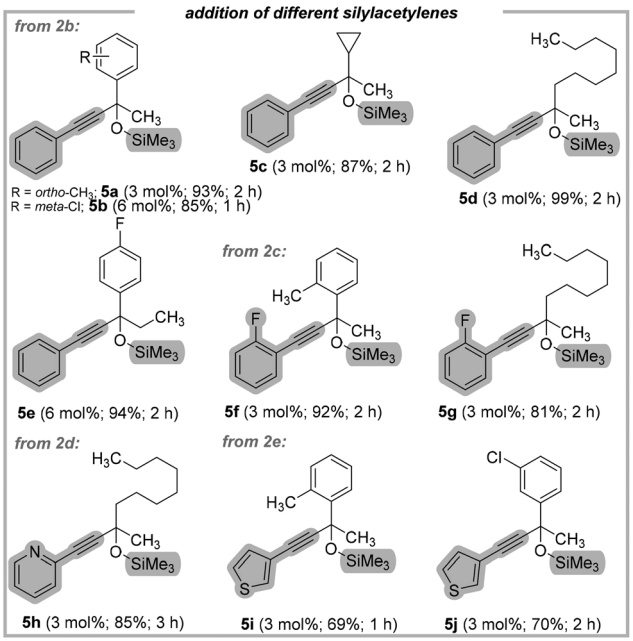


Fig. 4 Substrate scope for the addition of different silylacetylenes to ketones in the presence of KHMDS.

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

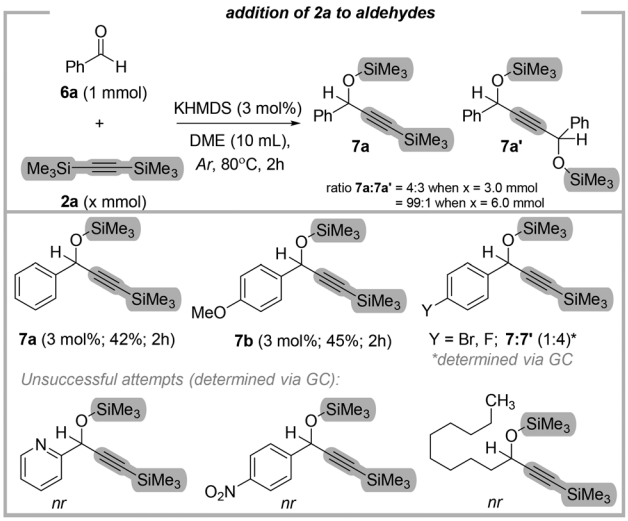


Fig. 5 Initial reaction between aldehydes and BTMSA under standard conditions.

Their formation suggests that protected secondary alkynols can serve as competitive substrates toward bis(trimethylsilyl)-acetylene. The same result was obtained for the reaction of 3.0 eq. of **2a** with 1.0 eq. of 4-bromobenzaldehyde. Specifically, a mixture of mono- and diadduct was also observed (1 : 4). Considering this, we decided to check the influence of higher amounts of BTMSA.

Indeed, when 6.0 eq. of **2a** was used, we observed the corresponding products **7a** and **7b** exclusively. Unfortunately, the aldehydes with the electron-withdrawing group still gave the mixture of mono- and diadduct. What is more, picolinaldehyde, 4-nitrobenzaldehyde, and decanal were non-reactive. Next, we were wondering that reaction of benzaldehyde with 1-phenyl-2-trimethylsilylacetylene (**2b**) should resolve the issue of selectivity. Surprisingly, we did not observe any conversion of benzaldehyde. The reason for the observed difference is not apparent at the moment. However, further investigations involving aldehydes and silylacetylenes are ongoing in our laboratory.

The key goals of this study were to simplify the synthesis and isolation of the protected tertiary alkynols, as well as show the scalability of the proposed methodology. Therefore, our protocol was successfully scaled up to a 10 mmol scale yielding 98% (2.84 g) of product **3a** (Fig. 6).

Once the scope of carbonyls was identified, our KHMDS-promoted addition was compared with other established methods leading to protected/unprotected tertiary alkynols (Fig. 7).

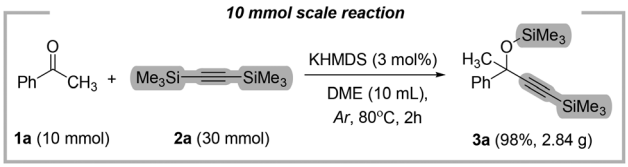


Fig. 6 Scaled up synthesis of **3a**.

comparison of base-mediated reactions leading to tertiary alkynols (protected/unprotected)

method A - Kuwajima [ref. 18 and 19]
Catalyst: 3-5 mol% of TBAF;
Scope (Si): mainly 1-phenyl-2-trimethylsilylacetylene, one example with BTMSA;
Scope (C=O): 4 aldehydes, 5 ketones;
Products: *O*-silylated alkynols;
Yields: 62-84% from aldehydes; 67-83% from ketones;
Important notes: *one reaction of BTMSA with benzaldehyde gives a mixture of mono- and diadduct (~1:1); no reaction with acetophenone and conjugated ketones; no example of gram-scale reaction;*

method B - Verkade [ref. 20] - Expansion of Kuwajima's work
Catalyst: 10 mol% of TBAF;
Scope (Si): mainly 1-phenyl-2-trimethylsilylacetylene and 1-trimethylsilyl-1-hexyne
Scope (C=O): 11 aldehydes, 7 ketones;
Products: *O*-silylated alkynols or Unprotected alkynols;
Yields: 69-99% from aldehydes; 44-98% from ketones;
Important notes: *no knowledge about the reaction with BTMSA as a substrate; no examples of reactions with acetophenone derivatives; no examples of conjugated carbonyls; no example of gram-scale reaction;*

method C - Lukevics [ref. 21]
Catalyst: 20 mol%/10 mol% of CsF/18-crown-6;
Scope (Si): only 1-phenyl-2-trimethylsilylacetylene and trimethylsilylacetylene;
Scope (C=O): 3 aldehydes, 8 ketones;
Products: mainly *O*-silylated alkynols;
Yields: 57-66% from aldehydes; 15-99% from ketones (mainly less than 70%);
Important notes: *no knowledge about the reaction with BTMSA as a substrate; low chemoselectivity in the case of trimethylsilylacetylene (the formation of: O-silylated alkynols, O- and C-silylated monoadducts, and O-silylated diadducts); no examples of conjugated carbonyls; no example of gram-scale reaction;*

method D - Scheidt [ref. 23]
Catalyst: 10-20 mol%/20 mol% of KOEt/18-crown-6;
Scope (Si): triethoxysilylacetylenes (in total 6 different trialkoxysilylacetylenes);
Scope (C=O): 12 aldehydes, 7 ketones;
Products: Unprotected alkynols (*via* one-pot hydrolysis of *O*-silylated alkynols);
Yields: 56-96% from aldehydes; 54-85% from ketones;
Important notes: *no knowledge about the reaction with BTMSA as a substrate; notably, the use of trialkylsilylacetylenes with KOEt afforded only traces of the product; trialkoxysilylalkynes are not commercial; no example of gram-scale reaction;*

this method
Catalyst: 3-6 mol% of KHMDS; *no additives*
Scope (Si): silylacetylenes - mainly BTMSA (in total 5 different silylacetylenes);
Scope (C=O): 2 aldehydes, 28 ketones;
Products: Exclusively fully protected *O*-silylated and/or *O,C*-silylated alkynols;
Yields: 42-45% from aldehydes; 68-99% from ketones;
Important notes: *low reactivity of aldehydes, the use of commercially available reagents (BTMSA and KHMDS); late-stage functionalization of biorelevant derivatives; excellent chemoselectivity; gram-scale reaction; further derivatization;*

Fig. 7 Applications of varied addition methods leading to protected or unprotected alkynols.

Admittedly, all mentioned strategies are not without their own disadvantages. In the case of this protocol, the main drawback is the low reactivity of aldehydes, unlike ketones. But apart from that, several salient benefits of our strategy should be outlined. First of all, this is the first chemoselective method utilizing BTMSA as the substrate – leading exclusively to mono-adduct products. There are two important facets. Firstly, bis(trimethylsilyl)acetylene is commercially available and inexpensive. Secondly, its use leads to *O*- and *C*-protected alkynols in a one-step procedure. Furthermore, the addition of BTMSA into carbonyls followed by selective deprotection can lead to terminal alkynols. Thus, being an indirect addition of acetylene. The other noteworthy feature of our strategy is the remarkable reactivity of ketones. It enabled the synthesis of a variety of protected tertiary alkynols including biorelevant compounds such as pharmaceuticals. Moreover, this protocol was scaled up to a 10 mmol scale. This once again makes it clear that the proposed methodology has significant application potential. Lastly, considering its operational simplicity, this reaction system provides a sustainable alternative to exist-

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

ing synthetic solutions. Notably, the exclusion of column chromatography leads to savings in many areas (*e.g.*, solvents, silica, time consumption, *etc.*).

In the end, we turned our attention to further applications of our methodology, as well as its sustainability and mechanistic insights (Fig. 8–10).

The KF/methanol system usually results in the deprotection of trimethylsilyl moiety, while the bulky triisopropylsilyl group remains untouched. By subjecting 2.5 mmol of potassium fluoride to the solution of **3a** (Fig. 8A) or **5k** (Fig. 8B) in methanol, the quantitative amounts of unprotected alkynol **8a** and *C*-protected alkynol **8b** were isolated. We could then successfully transform the silyl-protected alkynols into different products, thus showing the possibility to synthesize more complex products with challenging substitution patterns. Furthermore, the broader utility of our strategy is highlighted by the facile conversion of previously obtained *O*-silylated alkynol **5e** to a highly important enyne derivative (Fig. 8C). To the best of our knowledge, this is the first example of direct elimination of –OTMS group from alkynols leading to enynes (please note that recently, Vasilyev reported on similar acid-mediated elimination of TMS ethers of CF_3-benzyl alcohols).[57] To date, unprotected alkynols were generally converted to enynes by using methanesulfonyl chloride/triethylamine system. Lastly, our initial idea was to deliver a sustainable synthetic protocol. Thus, an excess of silylacetylene (mainly **2a**)

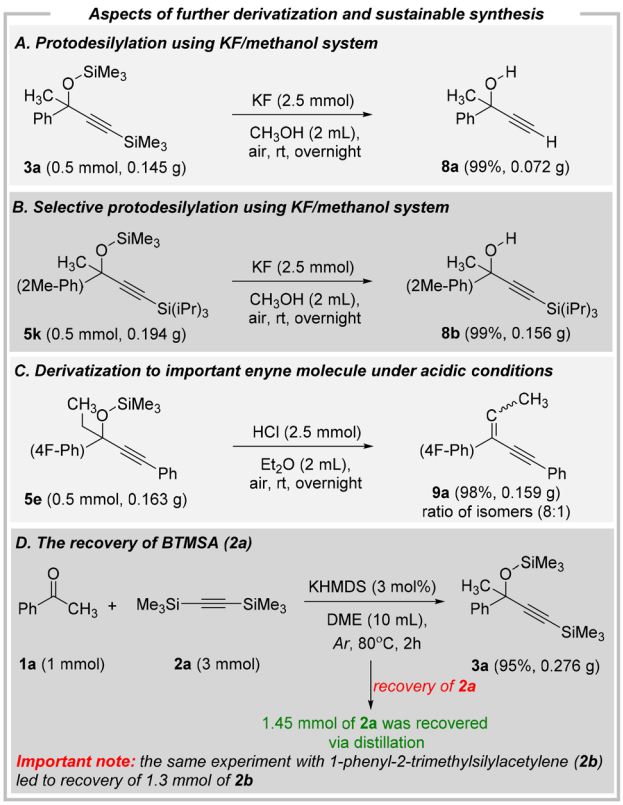


Fig. 8 Potential pathways for derivatizations and rationale for the excess amount of silylacetylene.

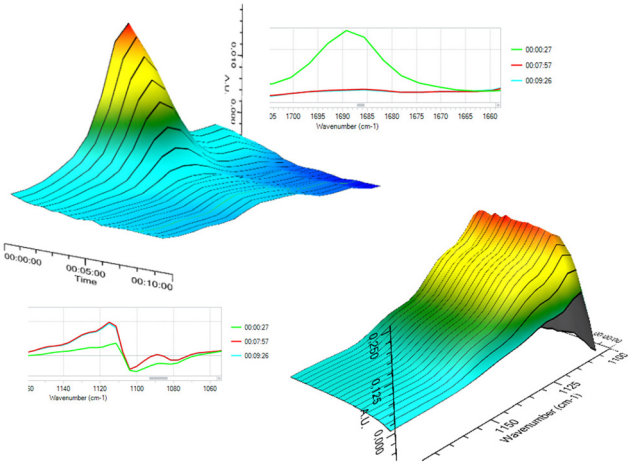


Fig. 9 Illustrations of carbonyl band disappearance (top) recorded using realtime FT-IR spectroscopy during the addition of **2a** to **1b** at 80 °C.

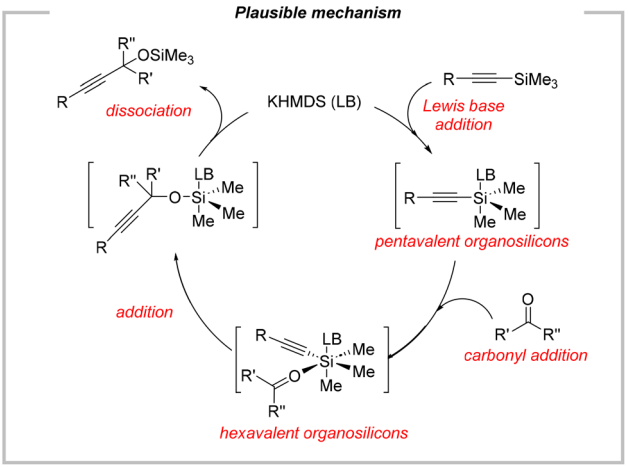


Fig. 10 Plausible mechanism for KHMDS-catalyzed addition of silylacetylenes to carbonyls.

could be regarded as a significant drawback of our methodology. Fortunately, this issue should not be considered problematic because bis(trimethylsilyl)acetylene (as well as 1-phenyl-2-trimethylsilylacetylene) can be readily recovered at the isolation stage (Fig. 8D).

Next, to get some mechanistic insights into this base catalysis, we conducted preliminary experiments. For instance, the addition was performed in the presence of a typical radical scavenger such as TEMPO (100 mol%), giving the desired product (with almost the same efficiency), thereby implying that radical pathways were likely not operative. Moreover, we monitored the reaction system using real-time *in situ* FT-IR spectroscopy. The kinetic plots obtained for the addition of BTMSA (**2a**) to 2-methylacetophenone (**1b**) confirmed a rapid disappearance of the distinguishing band at 1689 cm^{-1} of the carbonyl moiety (Fig. 9, top) with the simultaneously increased intensity of the Si–O band at 1115 cm^{-1} (Fig. 9, bottom).

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Previously, Scheidt presented very convincing evidence for hypervalent silicon intermediates resulting from the reversible addition of potassium ethoxide. Considering this, we performed ^{29}Si NMR analysis of the mixture containing stoichiometric amounts of BTMSA and KHMDS (ratio 1 : 1) in acetonitrile-d_3. In this particular experiment, we still observe the signal corresponding to BTMSA (−19.2 ppm, lit. val. = −19.2 ppm in $CDCl_3$). Moreover, two additional signals appeared at −17.3 ppm and 7.5 ppm. The former could be assigned to trimethylsilylacetylene. However, ^{1}H NMR analysis excluded such a situation (no signal for the acetylenic proton, lit. val. = 2.3 ppm (ref. 58)), suggesting more likely the presence of different, hypervalent silylacetylene species. However, in the case of pentacoordinated silicon species it is not so clear. Especially, there is little knowledge concerning pentavalent trialkylsilyl species resulting from the reversible addition of disilazide anion. In general, all the previous protocols for the base-catalyzed addition of silylacetylenes to carbonyls were assuming the intermediacy of hypervalent silicon species. In our specific case, it is also the most probable pathway. Thus, a plausible catalytic cycle is presented in Fig. 10.

Conclusions

In conclusion, the base-catalyzed addition of silylacetylenes to ketones has been enabled using commercially available reagents. The employment of inexpensive potassium bis(trimethylsilyl)amide as the catalyst and bis(trimethylsilyl)-acetylene not only provides a mild and economical alternative to canonical catalysis by fluoride anions, but also represents a highly chemoselective approach with an exceptional scope that is currently absent in other methods. Hence, late-stage derivatization of biorelevant compounds, as well as selective protodesilylation and OTMS elimination, further demonstrated the synthetic potential of the transformation. The scalability and practicality of this reaction were also demonstrated by both gram-scale and recovery experiments. We expect that our strategy will streamline the synthesis of different organosilicons and enable the development of new synthetic pathways involving potassium bis(trimethylsilyl)amide and bis(trimethylsilyl)acetylene as the reagents.‡

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by a National Science Centre (Poland) Grant UMO-2021/43/D/ST4/00132 (K.K.). This work was also supported by the Adam Mickiewicz University (KK-ID-UB project no. 038/04/NŚ/0001). We owe a very special thanks to Dr Rafał Januszewski (AMU Poznań) for his invaluable assistance involving FT-IR analyses.

‡The authors have cited additional references within the ESI.[59–61]

References

1 S. Jiang, S. Du, R. Yang, F. Jin, Z.-Z. Zhou, W.-F. Tian, X.-R. Song and Q. Xiao, Brønsted Acid Promoted Sulfonylation of Propargylic Alcohols: Synthesis of Triaryl Allenyl Sulfones under Mild Conditions, *Eur. J. Org. Chem.*, 2023, e202201377.
2 A. R. Pandey, D. K. Tiwari, A. Prakhar, D. P. Mishra and S. K. Sharma, A review towards synthesis of heterocycles using propargyl alcohols and propargyl amines, *Monatsh. Chem.*, 2022, **153**, 383–407.
3 T. A. C. Goulart, A. M. S. Recchi, D. F. Back and G. Zeni, Selective 5-Exo-Dig versus 6-Endo-Dig Cyclization of Benzoimidazole Thiols with Propargyl Alcohols, *Adv. Synth. Catal.*, 2022, **364**, 1989–1997.
4 S. Mishra, S. R. Nair and B. Baire, Recent approaches for the synthesis of pyridines and (iso)quinolines using propargylic Alcohols, *Org. Biomol. Chem.*, 2022, **20**, 6037–6056.
5 H. Zhu, Q. Zhou, N. Liu, J. Xing, W. Yao and X. Dou, Relay Rhodium(I)/Acid Catalysis for Rapid Access to Benzo-2H-Pyrans and Benzofurans, *Adv. Synth. Catal.*, 2022, **364**, 1162–1167.
6 S. Du, A.-X. Zhou, R. Yang, X.-R. Song and Q. Xiao, Recent advances in the direct transformation of propargylic alcohols to allenes, *Org. Chem. Front.*, 2021, **8**, 6760–6782.
7 S. Liu, Y. Tanabe, S. Kuriyama, K. Sakata and Y. Nishibayashi, Ruthenium- and Copper-Catalyzed Propargylic Substitution Reactions of Propargylic Alcohol Derivatives with Hydrazones, *Chem. – Eur. J.*, 2021, **27**, 15650–15659.
8 X.-R. Song, R. Yang and Q. Xiao, Recent Advances in the Synthesis of Heterocyclics via Cascade Cyclization of Propargylic Alcohols, *Adv. Synth. Catal.*, 2021, **363**, 852–876.
9 G. R. Kumar, M. Rajesh, S. Lin and S. Liu, Propargylic Alcohols as Coupling Partners in Transition-Metal-Catalyzed Arene C–H Activation, *Adv. Synth. Catal.*, 2020, **362**, 5238–5256.
10 U. M. Gonela and J. S. Yadav, Synthesis of chiral propargyl alcohols following the base-induced elimination protocol: application in the total synthesis of natural products, *New J. Chem.*, 2020, **44**, 4972–4986.
11 H. Tsuji and M. Kawatsura, Transition-Metal-Catalyzed Propargylic Substitution of Propargylic Alcohol Derivatives Bearing an Internal Alkyne Group, *Asian J. Org. Chem.*, 2020, **9**, 1924–1941.
12 H. Qian, D. Huang, Y. Bi and G. Yan, 2-Propargyl Alcohols in Organic Synthesis, *Adv. Synth. Catal.*, 2019, **361**, 3240–3280.
13 R. Roy and S. Saha, Scope and advances in the catalytic propargylic substitution reaction, *RSC Adv.*, 2018, **8**, 31129–31193.

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

14 Y. Miyake, S. Uemura and Y. Nishibayashi, Catalytic Propargylic Substitution Reactions, *ChemCatChem*, 2009, **1**, 342–356.
15 R. J. Detz, H. Hiemstra and J. H. van Maarseveen, Catalyzed Propargylic Substitution, *Eur. J. Org. Chem.*, 2009, 6263–6276.
16 T. Ishikawa, M. Okano, T. Aikawa and S. Saito, Novel Carbon–Carbon Bond-Forming Reactions Using Carbocations Produced from Substituted Propargyl Silyl Ethers by the Action of TMSOTf, *J. Org. Chem.*, 2001, **66**, 4635–4642.
17 T. Ishikawa, T. Aikawa, Y. Mori and S. Saito, Lewis Acid-Catalyzed Nucleophilic Substitutions of Propargylic and Allylic Silyl Ethers with Enol Silyl Ethers, *Org. Lett.*, 2003, **5**, 51–54.
18 E. Nakamura and I. Kuwajima, Fluoride Catalyzed Addition of Silylacetylenes to Carbonyl Compounds, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 498–499.
19 I. Kuwajima, E. Nakamura and K. Hashimoto, Fluoride catalyzed reaction of silylacetylenes with carbonyl compounds, *Tetrahedron*, 1983, **39**, 975–982.
20 V. R. Chintareddy, K. Wadhwa and J. G. Verkade, Tetrabutylammonium Fluoride (TBAF)-Catalyzed Addition of Substituted Trialkylsilylalkynes to Aldehydes, Ketones, and Trifluoromethyl Ketones, *J. Org. Chem.*, 2011, **76**, 4482–4488.
21 E. Abele, K. Rubina, R. Abele, J. Popelis, I. Mazeika and E. Lukevics, Fluoride-ion-mediated reactions of trimethylsilylacetylene with carbonyl compounds and terminal acetylenes, *J. Organomet. Chem.*, 1999, **586**, 184–189.
22 A. B. Holmes, C. L. D. Jennings-White, A. H. Schulthess, B. Akinde and D. R. M. Walton, Selective desilylation of bis (trimethylsilyl)acetylenes, *J. Chem. Soc., Chem. Commun.*, 1979, 840–842.
23 R. B. Lettan and K. A. Scheidt, Lewis Base-Catalyzed Additions of Alkynes Using Trialkoxysilylalkynes, *Org. Lett.*, 2005, **7**, 3227–3230.
24 A. Mori, A. Fujita, K. Ikegashira, Y. Nishihara and T. Hiyama, $TBAHF_2$ and $TBAH_2F_3$ as Activating Agents of Organosilanes, *Synlett*, 1997, 693–694.
25 T. Kitazawa, T. Minowa and T. Mukaiyama, Lewis Base-catalyzed Alkynylation of Carbonyl Compounds with Trimethylsilylacetylenes, *Chem. Lett.*, 2006, **35**, 1002–1003.
26 A. E. Favorskii and M. P. Skosarevskii, About the Reaction of Powdered Potassium Hydroxide on a Mixture of Phenylacetylene and Acetone, *Zh. Russ. Khim. O-va.*, 1900, **32**, 652.
27 H. Miyamoto, S. Yasaka and K. Tanaka, Solvent-Free Addition of Ethynylbenzene to Ketones, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 185–186.
28 P. G. Cozzi, J. Rudolph, C. Bolm, P.-O. Norrby and C. Tomasini, Me_2Zn-Mediated Addition of Acetylenes to Aldehydes and Ketones, *J. Org. Chem.*, 2005, **70**, 5733–5736.
29 D. N. Tomilin, O. V. Petrova, L. N. Sobenina, A. I. Mikhaleva and B. A. Trofimov, A convenient synthesis of hetarylethynyl ketones from hetarylcarbaldehydes and acetylene, *Chem. Heterocycl. Compd.*, 2013, **49**, 341–344.
30 E. Yu. Shmidt, I. A. Bidusenko, N. I. Protsuk, A. I. Mikhaleva and B. A. Trofimov, Improved synthesis of tertiary propargyl alcohols by the Favorskii reaction of alkyl aryl (hetaryl) ketones with acetylene, *Russ. J. Org. Chem.*, 2013, **49**, 8–11.
31 Y. N. Sum, D. Yu and Y. Zhang, Synthesis of acetylenic alcohols with calcium carbide as the acetylene source, *Green Chem.*, 2013, **15**, 2718–2721.
32 B. A. Trofimov and E. Y. Schmidt, Reactions of acetylenes in superbasic media. Recent advances, *Russ. Chem. Rev.*, 2014, **83**, 600.
33 E. Yu. Schmidt, N. A. Cherimichkina, I. A. Bidusenko, N. I. Protzuk and B. A. Trofimov, Alkynylation of Aldehydes and Ketones Using the Bu_4NOH/H_2O/DMSO Catalytic Composition: A Wide-Scope Methodology, *Eur. J. Org. Chem.*, 2014, 4663–4670.
34 A. Hosseini, D. Seidel, A. Miska and P. R. Schreiner, Fluoride-Assisted Activation of Calcium Carbide: A Simple Method for the Ethynylation of Aldehydes and Ketones, *Org. Lett.*, 2015, **17**, 2808–2811.
35 V. V. Voronin, M. S. Ledovskaya, A. S. Bogachenkov, K. S. Rodygin and V. P. Ananikov, Acetylene in Organic Synthesis: Recent Progress and New Uses, *Molecules*, 2018, **23**, 2442.
36 K. S. Rodygin, M. S. Ledovskaya, V. V. Voronin, K. A. Lotsman and V. P. Ananikov, Calcium Carbide: Versatile Synthetic Applications, Green Methodology and Sustainability, *Eur. J. Org. Chem.*, 2021, 43–52.
37 N. A. Sitte, F. Ghiringhelli, G. A. Shevchenko, F. Rominger, A. S. K. Hashmi and T. Schaub, Copper-Catalysed Synthesis of Propargyl Alcohol and Derivatives from Acetylene and other Terminal Alkynes, *Adv. Synth. Catal.*, 2022, **364**, 2227–2234.
38 E. M. Leitao, T. Jurca and I. Manners, Catalysis in service of main group chemistry offers a versatile approach to p-block molecules and materials, *Nat. Chem.*, 2013, **5**, 817–829.
39 R. L. Melen, Dehydrocoupling routes to element–element bonds catalysed by main group compounds, *Chem. Soc. Rev.*, 2016, **45**, 775–788.
40 L. C. Wilkins and R. L. Melen, Enantioselective Main Group Catalysis: Modern Catalysts for Organic Transformations, *Coord. Chem. Rev.*, 2016, **324**, 123–139.
41 K. Kuciński and G. Hreczycho, Hydrosilylation and hydroboration in a sustainable manner: from Earth-abundant catalysts to catalyst-free solutions, *Green Chem.*, 2020, **22**, 5210–5224.
42 M. M. D. Roy, A. A. Omaña, A. S. S. Wilson, M. S. Hill, S. Aldridge and E. Rivard, Molecular Main Group Metal Hydrides, *Chem. Rev.*, 2021, **121**, 12784–12965.
43 T. R. Puleo, S. J. Sujansky, S. E. Wright and J. S. Bandar, Organic superbases in recent synthetic methodology research, *Chem. – Eur. J.*, 2021, **27**, 4216–4229.
44 T. X. Gentner and R. E. Mulvey, Alkali–Metal Mediation: Diversity of Applications in Main–Group Organometallic Chemistry, *Angew. Chem., Int. Ed.*, 2021, **60**, 9247–9262.
45 H. Gao, A. Battley and E. M. Leitao, The ultimate Lewis acid catalyst: using tris (pentafluorophenyl) borane to create

Open Access Article. Published on 09 May 2023. Downloaded on 11/10/2025 10:25:21 AM.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

bespoke siloxane architectures, *Chem. Commun.*, 2022, **58**, 7451–7465.

46 M. Magre, M. Szewczyk and M. Rueping, s-Block metal catalysts for the hydroboration of unsaturated bonds, *Chem. Rev.*, 2022, **122**, 8261–8312.

47 K. Kuciński, H. Stachowiak-Dłużyńska and G. Hreczycho, Catalytic silylation of O–nucleophiles via Si–H or Si–C bond cleavage: A route to silyl ethers, silanols and siloxanes, *Coord. Chem. Rev.*, 2022, **459**, 214456.

48 S. E. Wright and J. S. Bandar, A Base-Promoted Reductive Coupling Platform for the Divergent Defluorofunctionalization of Trifluoromethylarenes, *J. Am. Chem. Soc.*, 2022, **144**, 13032–13038.

49 S. P. Pajk, Z. Qi, S. J. Sujansky and J. S. Bandar, A base-catalyzed approach for the anti-Markovnikov hydration of styrene derivatives, *Chem. Sci.*, 2022, **13**, 11427–11432.

50 K. Kuciński and G. Hreczycho, Lithium triethylborohydride as catalyst for solvent-free hydroboration of aldehydes and ketones, *Green Chem.*, 2019, **21**, 1912–1915.

51 K. Kuciński, H. Stachowiak and G. Hreczycho, Silylation of silanols with hydrosilanes via main-group catalysis: the synthesis of unsymmetrical siloxanes and hydrosiloxanes, *Inorg. Chem. Front.*, 2020, **7**, 4190–4196.

52 K. Kuciński, H. Stachowiak and G. Hreczycho, Silylation of Alcohols, Phenols, and Silanols with Alkynylsilanes – an Efficient Route to Silyl Ethers and Unsymmetrical Siloxanes, *Eur. J. Org. Chem.*, 2020, 4042–4049.

53 K. Kuciński and G. Hreczycho, Transition Metal-Free Catalytic C–H Silylation of Terminal Alkynes with bis(Trimethylsilyl)acetylene Initiated by KHMDS, *ChemCatChem*, 2022, **14**, e202200794.

54 K. Kuciński and G. Hreczycho, Silicon–nitrogen bond formation via dealkynative coupling of amines with bis(trimethylsilyl)acetylene mediated by KHMDS, *Chem. Commun.*, 2022, **58**, 11386–11389.

55 E. Szafoni, K. Kuciński and G. Hreczycho, Cobalt-catalyzed synthesis of silyl ethers via cross-dehydrogenative coupling between alcohols and hydrosilanes, *Green Chem. Lett. Rev.*, 2022, **15**, 757–764.

56 H. Stachowiak-Dłużyńska, K. Kuciński, K. Broniarz, E. Szafoni, M. Gruszczyński, D. Lewandowski, G. Consiglio and G. Hreczycho, Access to germasiloxanes and alkynylgermanes mediated by earth-abundant species, *Sci. Rep.*, 2023, **13**, 5618.

57 O. V. Khoroshilova, I. A. Boyarskaya and A. V. Vasilyev, Synthesis of α-(Trifluoromethyl)styrenes and 1,3-Di(trifluoromethyl)indanes via Electrophilic Activation of TMS Ethers of (Trifluoromethyl)benzyl Alcohols in Brønsted Acids, *J. Org. Chem.*, 2022, **87**, 15845–15862.

58 A. J. Pearce, X. Y. See and I. A. Tonks, Oxidative nitrene transfer from azides to alkynes via Ti(II)/Ti(IV) redox catalysis: formal [2 + 2 + 1] synthesis of pyrroles, *Chem. Commun.*, 2018, **54**, 6891–6894.

59 V. Maraval, C. Duhayon, Y. Coppel and R. Chauvin, The Intricate Assembling of gem-Diphenylpropargylic Units, *Eur. J. Org. Chem.*, 2008, 5144–5156.

60 I. Kownacki, B. Marciniec, B. Dudziec, A. Kownacka, M. Majchrzak, M. Szulc and B. Orwat, New (Triorganosilyl) Alkynes and Their Derivatives and a New Catalytic Method for Obtaining New and Conventional Substituted (Triorganosilyl)Alkynes and Their Derivatives, *US Patent*, US2014005427A1, 2014.

61 M. R. Hall, M. Korb, S. A. Moggach and P. J. Low, Further Chemistry of Ruthenium Alkenyl Acetylide Complexes: Routes to Allenylidene Complexes via a Series of Electrophilic Addition Reactions, *Organometallics*, 2020, **39**, 2838–2853.