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A facile access to mono-C-alkynylated-*o*-carboranes from *o*-carboranes and arylsulfonylacetylenes



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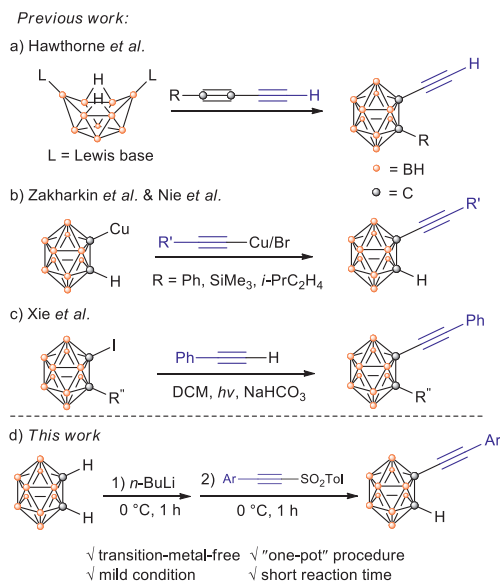
ABSTRACT

A facile access to mono-C-alkynyl-*o*-carboranes from *o*-carboranes and arylsulfonylacetylenes was developed. This facile process tolerates a wide variety of functional groups, occurs at mild conditions in one-pot procedure with short reaction time. The obtained mono-C-alkynyl-*o*-carboranes can be easily derivatized to synthesize 1,2-difunctionalized *o*-carboranes. This work provides a useful tool for the functionalization of *o*-carboranes.

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o-Carborane is an electron-deficient icosahedral boron cluster compound of formula $C_2B_{10}H_{12}$, in which two carbon atoms are adjacent to each other. *o*-Carborane has 26 delocalized valence electrons, exhibits special three-dimensional aromaticity, and extraordinary chemical and thermal stability [1,2]. The different electronegativity between carbon and boron makes the C–H bond of *o*-carboranes partially acidic, which can work as a useful reaction site to obtain functionalized *o*-carboranes. During the past few decades, *o*-carboranes and their derivatives have broad applications in many fields [3–19]. Among them, some C-alkynyl-*o*-carboranes have special luminescence and can be used in optoelectronic functional materials as electron-accepting motifs to tune the LUMO and HOMO energy levels [20–25]. Some of them have remarkable aggregation-induced emission (AIE) property and/or stimuli-responsivity and/or environment-sensitivity [26–28] with potential for application in novel functional materials. In addition, alkynyl groups are fundamental structural units in organic synthesis, and can be easily further derivatized [29–33]. Thus, the synthesis and performance of C-alkynyl-*o*-carboranes have received considerable attention.

Currently, there are mainly three methods for the synthesis of C-alkynyl-*o*-carboranes. In 1964, Dupont and Hawthorne synthesized C-alkynyl-*o*-carboranes from decaborane and corresponding diynes for the first time (Scheme 1a) [34,35]. In 1973, Hawthorne



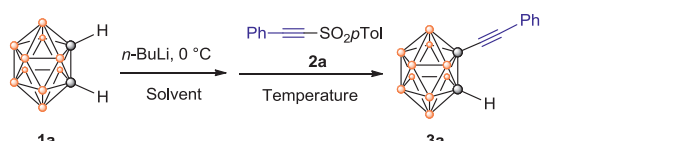
Scheme 1. Synthesis of C-alkynyl-*o*-carboranes.

modified the method [36,37]. In 1976, Zakharkin and coworkers prepared C-alkynyl-*o*-carboranes by the reaction of bromoalkynes with 1-Cu-*o*- $C_2B_{10}H_{11}$ to give C-alkynyl-*o*-carboranes in moderate

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Table 1
Optimization of the reaction conditions for the synthesis of **3a**.^a



Entry	2a (equiv.)	Solvent	T (°C)	Time (min)	Yield (%) ^b
1	1	THF	-78	60	12
2	1	THF	0	60	23
3	2	THF	0	60	57
4	2	THF	r.t.	60	20
5	3	THF	0	60	56
6	2	DME	0	60	53
7	2	Et ₂ O	0	60	50

^a Reaction conditions: **1a** (0.5 mmol), solvent (5.0 mL), the reaction flask, in nitrogen atmosphere, GC was used to monitor the reaction process;

^b Isolated yields.

yields. 1-Cu-*o*-C₂B₁₀H₁₁ was obtained from the corresponding 1-carboranylolithium and 1.25 equiv. of CuCl in a THF-ether solution (Scheme 1b) [38,39]. In 2013, Nie and co-workers reported the cross-coupling of 1-Cu-*o*-C₂B₁₀H₁₁ and Cu-C≡C-R to give C-alkynyl-*o*-carboranes with more excess amount of *n*-BuLi and CuCl (4 equiv. respectively, Scheme 1b) [40]. For a long period of time, C-alkynyl-*o*-carboranes were synthesized by these methods, the use of hypertoxic decaborane and diynes or stoichiometric amounts of transition-metal salts encumbers their broader applications. Very recently, Xie and coworkers reported a very efficient approach to synthesize C-alkynyl-*o*-carboranes by the reaction of iodocarboranes and terminal alkynes in the presence of base under UV-light (Scheme 1c) [41]. However, this method is more suitable for *o*-carborane with substituents such as methyl on the ortho position. Until now, there are only a few reported mono-C-alkynyl substituted *o*-carboranes and the methods for synthesizing those mono-C-functional carboranes are still very limited. Therefore, it is of great significance to develop simple and efficient methods to synthesize mono-C-alkynyl-*o*-carboranes.

Sulfones are important intermediates in synthetic applications due to their strong electron-withdrawing property. Alkynyl sulfones have broad applications in the alkylation and other fields including building complex organic molecules or naturally occurring products [42–47]. They could be readily obtained from varied synthetic methods [42,48–52]. In 2012, García Ruano's group reported a strategy that acetylenic sulfones were used as alkynylating reagents for the construction of the C_{Ar}-C_{sp} bonds [53–55]. Inspired by these results, we wonder if arylacetylenic sulfones could be used to synthesize mono-C-alkynyl-*o*-carboranes. It should be noted that the carbon of *o*-carborane is sp hybridized, and the alkylation of C_{sp} with acetylenic sulfones is unknown. Herein, we wish to report our findings toward the construction of various mono-C-alkynyl-*o*-carboranes from *o*-carboranylolithiums and arylacetylenic sulfones (Scheme 1d).

The starting arylacetylenic sulfones were synthesized according to a modified literature's procedure [48–52]. At the outset of our studies, *o*-carborane **1a** and phenylethynyl sulfone **2a** were chosen as model substrates to optimize the reaction conditions (Table 1). Initially, *n*-BuLi (1.2 equiv.) was added dropwise to *o*-carborane **1a** in THF at 0 °C, and the reaction mixture was stirred for an hour. Then phenylethynyl sulfone **2a** (1 equiv.) was added and the reaction mixture was stirred for another hour at -78 °C, the desirable product **3a** was obtained with an isolated yield of 12% and some **1a** was recovered (Table 1, entry 1). When the reaction temperature at the second step was kept at 0 °C, the reaction can be finished within 2 h also, but the isolated yield of **3a** is only 23%

(Table 1, entry 2). If 2 equiv. of **2a** was used, the reaction can be finished in 2 h also, and the yield of **3a** is up to 57% (Table 1, entry 3). Adding 3 equiv. of **2a** did not improve the yield and the reaction was worse when it was run at room temperature (Table 1, entries 4 and 5). At last, solvent effects on the reaction were studied, dimethyl ether (DME) and Et₂O can also give comparable yields (Table 1, entries 6 and 7).

After establishing the optimized conditions (Table 1, entry 3), we examined the substrate scope and limitation of this alkylation reaction and the results are summarized in Scheme 2. Gratifyingly, a variety of arylacetylenic sulfones **2a–2n** were smoothly coupled to *o*-carborane **1a**, delivering the corresponding mono-C-alkynyl-*o*-carboranes **3a–3n** in moderate yields. This reaction tolerated a wide variety of functional groups, such as Me or Ph, electron-donating groups OMe, NPh₂ or electron-withdrawing groups F, Cl and CF₃. Moreover, the electronic properties of the substituents have no significant effect on the products yield. The positions of substituents on the Phenyl ring have no obvious impact on the yield also. In addition, alkyne with heteroaryl was compatible with this reaction, affording the product in a relatively lower yield (**3n**, 32%). The obtained products **3a–3n** were characterized by ¹H NMR, ¹³C NMR, ¹¹B NMR and HRMS (Supporting information).

1,2-Difunctionalized *o*-carboranes have some unique photoelectric properties [56–60]. After successful preparation of a variety of mono-C-alkynyl-*o*-carboranes, we turned our attention to synthesize 1,2-difunctionalized *o*-carboranes. Unfortunately, the attempt to synthesize the bisalkynylation compound under the similar method was failed. But the alkylation and iodination reactions proceeded smoothly and provided the corresponding difunctionalized *o*-carboranes **4a** and **4b** and C-alkynyl-*o*-iodocarborane **4c** in 65%–72% yields (Scheme 3). Even iodoalkane bearing the hindered isopropyl group proved to be effective for furnishing the product **4b** in 65% yield. The further derivatization reaction of C-I in compound **4c** and applications of the new mono-C-alkynyl-*o*-carboranes are currently in progress in our laboratory.

To investigate the utility of this synthetic method, methyl, ethyl and isopropyl substituted *o*-carboranes were synthesized according to the literature [61]. When R¹ is methyl or ethyl or isopropyl, **4d**, **4a** and **4b** were obtained in yields of 51%, 61% and 67% respectively (Scheme 4). It demonstrates the new synthetic method is applicable with *o*-substituted *o*-carboranes also.

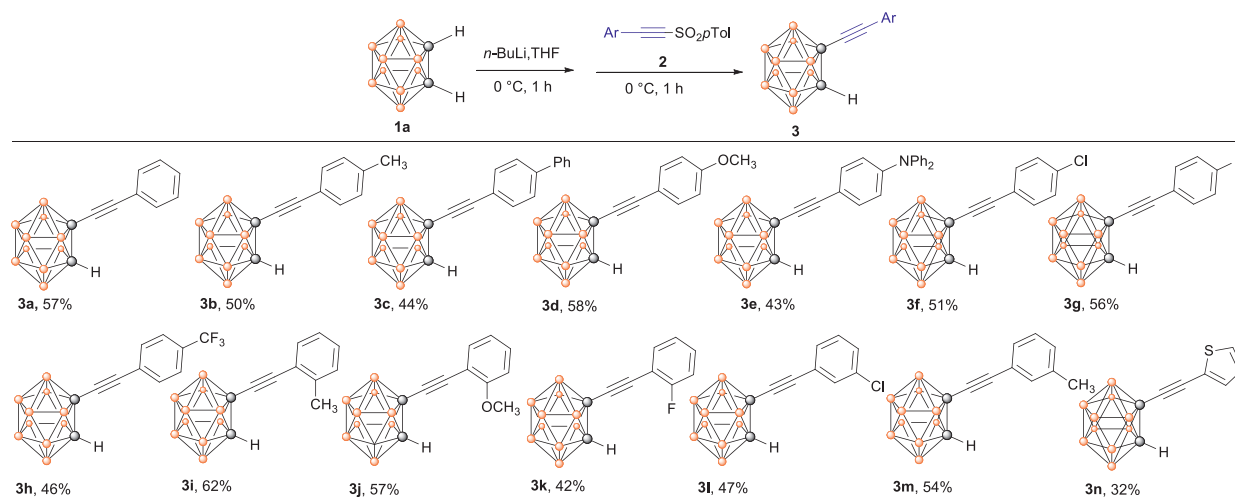
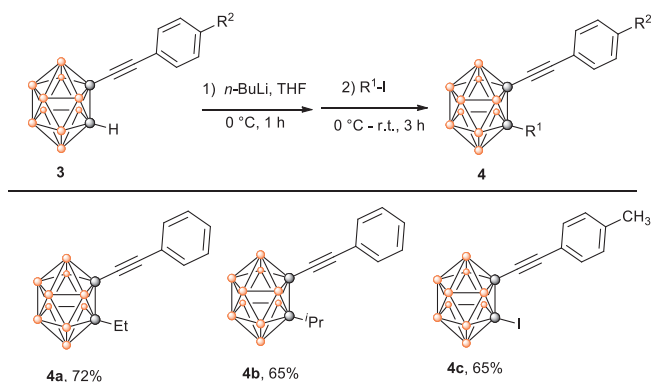
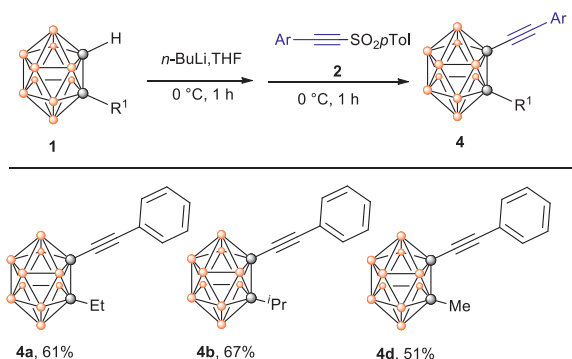
In summary, a facile synthetic route to mono-C-alkynyl-*o*-carboranes from *o*-carboranes and arylsulfonylacetylenes was developed. This new method tolerates a wide variety of functional groups, and the process occurs at mild conditions in one-pot procedure with short reaction time. The obtained mono-C-alkynyl-*o*-carboranes can be further derivatized to synthesize 1,2-difunctionalized *o*-carboranes. This work provides a very useful tool for the functionalization and practical applications of *o*-carboranes.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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Scheme 2. Synthesis of mono-C-alkynyl-*o*-carboranes.Scheme 3. Synthesis of 1,2-difunctionalized *o*-carboranes.Scheme 4. *Ortho*-substituted *o*-carborane alkynyl functionalization.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2021.05.062.

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