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1,2-Carbopentafluorophenylation of Alkynes: The Metallomimetic Pull-Push Reactivity of Tris(pentafluorophenyl)borane

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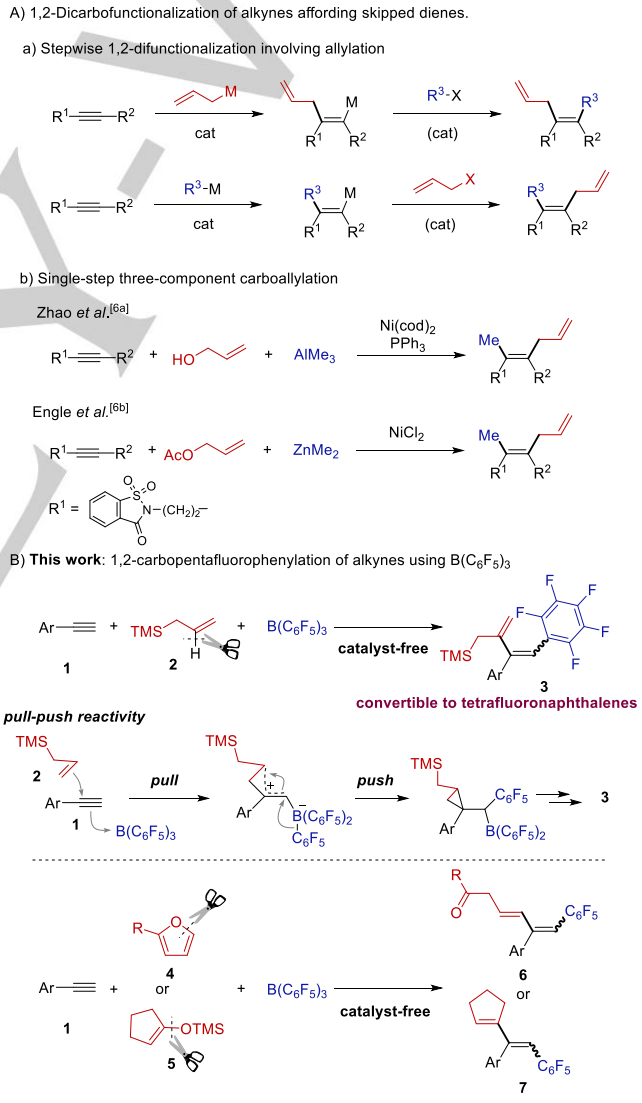
Abstract: We report the novel single-step 1,2-dicarbofunctionalization of an arylacetylene with an allylsilane and tris(pentafluorophenyl)borane [$B(C_6F_5)_3$], involving C–C bond formation with C–H bond scission at the β-position to the silicon atom of an allylsilane and B→C migration of a C_6F_5 group. The 1,2-carbopentafluorophenylation reaction occurs smoothly without the requirement for a catalyst or heating. Mechanistic studies suggest that the metallomimetic "pull-push" reactivity of $B(C_6F_5)_3$ imparts consecutive electrophilic and nucleophilic characteristics to the benzylic carbon of the arylacetylene. Subsequent photochemical 6π-electrocyclization affords tetrafluoronaphthalenes, which are important in the pharmaceutical and materials sciences. Owing to the unique reactivity of $B(C_6F_5)_3$, the 1,2-carbopentafluorophenylation using 2-substituted furan proceeded with ring opening, and the reaction using silyl enolates formed C–C bond with C–O bond scission at the silyloxy-substituted carbon.

Introduction

Multicomponent-coupling reactions enable the construction of advanced molecules in a single step, thereby facilitating the rapid syntheses of complex molecules.[1] In this context, the three-component 1,2-difunctionalization of an alkyne is a powerful reaction for the preparation of tri- and tetra-substituted alkenes. The carbometallation of an alkyne results in the formation of an alkenylmetal species, and subsequent transition-metal-catalyzed cross-coupling with an aryl halide or reaction with an electrophile facilitates the stepwise 1,2-difunctionalization.[2] A single-step 1,2-difunctionalization reaction based on a three-component coupling process enables a more facile and practical access to tri- and tetra-substituted alkenes.[3,4] Owing to the versatility of an allyl moiety in organic synthesis, 1,2-difunctionalization involving allylation has been intensively studied (Scheme 1A). Thus, a variety of the stepwise allylative 1,2-difunctionalization reactions have been developed.[3,5] Very recently, Zhao *et al.* and Engle *et al*. independently reported the nickel-catalyzed allylmethylations of alkynes which are three-component allylative 1,2-dicarbofunctionalizations. [6]

As a strong and unique Lewis acid, tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] has been used in a variety of organic reactions since its first report in the 1960s,[7,8]



Scheme 1. Allylative 1,2-dicarbofunctionalization of alkynes and this work.

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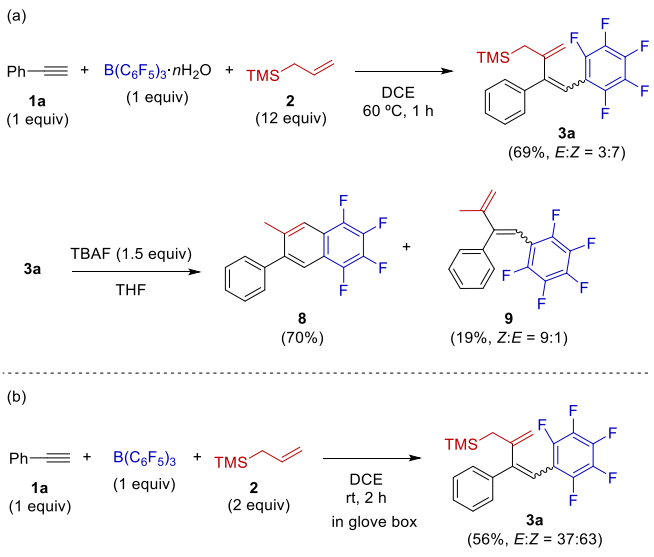
wherein its use as the Lewis acid component of frustrated Lewis pairs (FLPs) is the most representative.[8] FLPs consisting of $B(C_6F_5)_3$ and Lewis bases exhibit synergic reactivities between an electrophilic boron-centered vacant orbital and a nucleophilic filled orbital of the Lewis base,[9] which facilitates the heterolytic cleavage of H_2 and reactions with a variety of small molecules.[10] $B(C_6F_5)_3$ also promotes several distinguishable reactions of alkynes.[11–15] More specifically, the 1,2-additions of $B(C_6F_5)_3$ and Lewis bases such as phosphines, pyrroles, and amines to alkynes were reported.[11] We therefore surmised that if $B(C_6F_5)_3$ and allylsilanes can add to alkynes, the subsequent coupling of the resultant alkenylborates will facilitate the 1,2-allylboration process. However, to the best of our knowledge, allylsilanes are less nucleophilic than the Lewis bases that have been reported for such 1,2-additions.[16] $B(C_6F_5)_3$ was reported to readily facilitate the 1,1-carboborations of alkynes in the absence of a Lewis base,[14] thereby indicating that the nucleophilicity of the Lewis base is important for promoting the 1,2-addition prior to the 1,1-carboboration reaction.[13c,14e] In this article, we report that $B(C_6F_5)_3$ and allylsilanes **2** do add arylacetylenes **1** to yield novel 1,2-carbopentafluorophenylation products **3** rather than the simple allylsilylated or hydroallylated compounds which are produced from alkenylborate intermediates (Scheme 1B). Interestingly, C–C bonds are formed at the β-position to silicon of the allylsilane, and this is accompanied by C–H bond scission without elimination of the silyl group to afford conjugated 1,3-dienes instead of skipped dienes. We also demonstrate that the resultant pentafluorophenyl-substituted 1,3-dienes can be converted into the corresponding tetrafluoronaphthalenes by a photochemical 6π-electrocyclization process. In addition, reactions using 2-substituted furans **4** or silyl enolate **5** as Lewis bases were also examined, with novel 1,2-carbopentafluorophenylation products **6** and **7** being obtained. To reasonably understand the mechanism of the observed novel 1,2-carbopentafluorophenylations, we herein introduce a metallomimetic "pull-push" reactivity concept involving $B(C_6F_5)_3$ toward alkynes (see Scheme 1B). This "pull-push" reactivity is known to be responsible for the reactivities of carbophilic transition metal catalysts, such as gold and platinum catalysts, in reactions with alkynes.[17] The transition-metal catalyst not only electrophilically activates the alkyne ("pull"), but the electron density is also back-donated to the vicinal carbon atom ("push"). This "pull-push" nature imparts a consecutive electrophillic and nucleophilic characteristics to the vicinal carbon atom of the alkyne substrate and enables characteristic reactions to take place such as the cyclopropanation reaction of enynes and the acetylenic Schmidt reaction.[17b,c] Similarly, $B(C_6F_5)_3$ electrophilically activates an alkyne ("pull") to facilitate the addition of a Lewis base. The electron density is consecutively donated to the vicinal carbon atom by the migration of a C_6F_5 group from the boron to the adjacent carbon atom ("push") to form a cycopropane ring. This reactivity enables the observed novel 1,2-carbopentafluorophenylations. Several previously reported reactions also implicate such a metallomimetic pull-push reactivity.[13a,b]

Results and Discussion

We initially examined the reaction of $B(C_6F_5)_3$•$n$$H_2O$ (1 equiv) and allylsilane **2** (12 equiv) with phenylacetylene (**1a**) (1 equiv) in dichloroethane (DCE) at 60 °C (Scheme 2), wherein the unpredicted three-component coupling product **3a** was obtained. The structure of **3a** was determined by $^1H/^{13}C/^{19}F$ and 2D NMR spectroscopy, and by mass spectrometry. In addition, the treatment of **3a** with TBAF promoted the intramolecular nucleophilic aromatic substitution reaction of the *Z*-isomer to afford tetrafluoronaphthalene **8** together with desilylated compound **9**. A single crystal of **8** was obtained and its structure was unambiguously confirmed by X-ray diffractometry (Figure S5). The structure of **3a** reveals that two C–C bonds were formed during the reaction, namely one bond between the benzylic C1 position of **1a** and the β-position to the silicon atom of **2**, which is accompanied by cleavage of the $C_β$–H bond, and a second bond between the terminal C2 position of **1a** and the C_6F_5 group from $B(C_6F_5)_3$.

Because **2** was consumed by the dehydration of $B(C_6F_5)_3$•$n$$H_2O$, an excess amount of **2** was used for the initial experiment.[15] Hence, we examined the reaction using anhydrous $B(C_6F_5)_3$ and 2 equiv of **2** in a glove box, which efficiently proceeded at room temperature to afford **3a** in 56% yield after 2 h (Scheme 2).

Several control experiments were conducted to gain insight into the mechanism of the novel 1,2-carbopentafluorophenylation reaction (Schemes 3 and S1, Figures S1-S4). Initially, to evaluate the possibility of a reaction through 1,1-carboboration,[14] **2** was added to a solution of 1,1-carboboration product **10** in CD_2Cl_2, which was prepared *in situ* from **1a** and $B(C_6F_5)_3$ in the absence of a Lewis base; unreacted **10** remained as a major compound after 4 h (Scheme 3a, Figure S1). This result suggests that 1,1-carboboration is, at least, not a major reaction pathway for the 1,2-carbopentafluorophenylation. Subsequently, the reaction was performed using deuterium-labeled phenylacetylene (**1a**-***d***), with deuterium-labeled coupling product **3a**-***d*** being formed (Scheme 3b). The level of deuterium incorporation did not decrease in the product (Figure S2), which suggests that the methine proton of **1a** is not abstracted during the reaction. After stirring the reaction mixture of $B(C_6F_5)_3$•$n$$H_2O$, **1a**, and **2** in DCE for 0.5 h at rt, basic aqueous H_2O_2 was then added, and alcohol **11** was



Scheme 2. Initial results. a) Reaction of $B(C_6F_5)_3$•$n$$H_2O$ and allylsilane **2** with phenylacetylene (**1a**) and the treatment of the obtained product **3a** with TBAF. b) Reaction using anhydrous $B(C_6F_5)_3$ in glove box.

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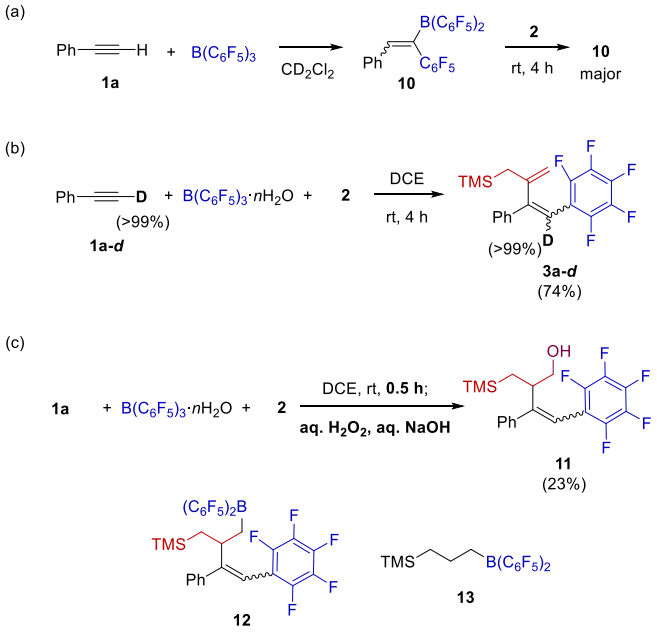

Scheme 3. Gaining insight into the reaction mechanism. a) Reaction of 1,2-carboboration product **10** with allylsilane **2**. b) 1,2-Carbopentafluorophenylation of deuterium-labeled phenylacetylene (**1a-*d***). c) Treatment of the reaction mixture with basic aqueous H_2O_2.

obtained in a moderate yield (Scheme 3c, Figure S3). This result suggests that alkylborane **12** is an intermediate and that the retro-hydroboration of **12** forms **3a** and $HB(C_6F_5)_2$. The generation of $HB(C_6F_5)_2$ was supported by the fact that **13**, which is a hydroboration product of $HB(C_6F_5)_2$ and allylsilane, was detected by ^{19}F NMR spectroscopy of the reaction mixture (Figure S4).

To further probe the reaction mechanism, the 1,2-carbopentafluorophenylation reaction was examined using density functional theory (DFT) calculations [SMD (DCE) B3LYP/6-311G++(d,p)//B3LYP/6-31G(d)]. The calculated energy surface for the overall process is depicted in Figure 1. More specifically, the first step is a formation of zwitterionic intermediate **B**, which is nearly identical with the structure of the zwitterionic intermediate in 1,1-carboboration.[14b,c,18] Although **B** is 11.3 kcal/mol less stable than **A**, the subsequent addition of allylsilane **2** proceeds readily with a very small energy barrier ($\Delta G^{\ddagger}$ = +0.1 kcal/mol) to afford intermediate **C**. The calculations suggest that **C** is a non-classical cation; the positive charge is stabilized by the silicon β-effect as well as through delocalization involving the double bond, which enables **C** to be preorganized in a conformation conducive for the subsequent migration of a C_6F_5 group and cyclopropane formation. Natural bond orbital (NBO) analysis of **C** suggests that a σ orbital is present between C_β and C_1 with an electronic occupancy of 1.72 e, and that a vacant p-orbital of C_2 is stabilized by electronic delocalization from $\sigma_{C\beta-C1}$ ($E^{(2)}$ = 24.0 kcal/mol) (Tables S4 and S5). It should be noted that σ_{B-C6F5} donates its electron density to a vacant p-orbital on C_2 with a stabilization energy of 15.6 kcal/mol, while $\sigma_{Si-C\alpha}$ donates its electron density to $\sigma^*_{C\beta-C1}$ with a relatively lower stabilization energy ($E^{(2)}$ = 7.5 kcal/mol). These results support that the "push" effect of the electron density through the migration of a C_6F_5 group facilitated cyclopropane formation.

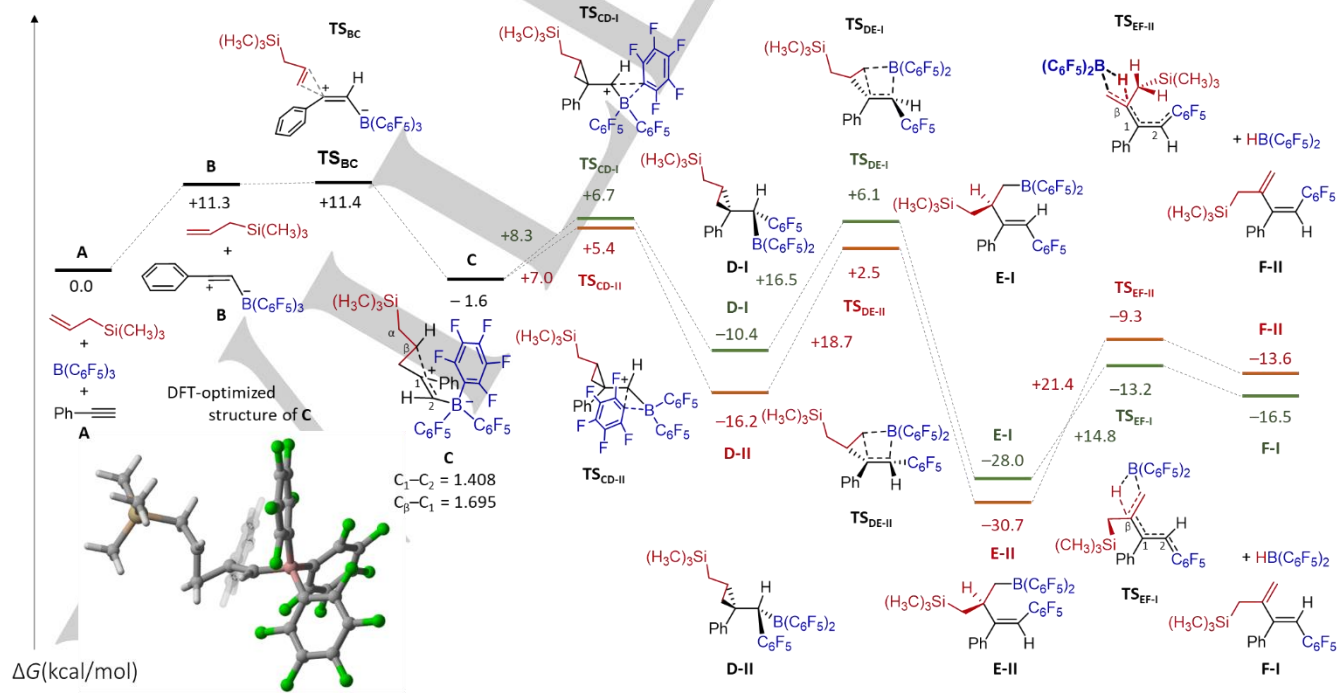

Figure 1. Gibbs free energy diagram for the 1,2-carbopentafluorophenylation reaction [SMD (DCE) B3LYP/6-311G++(d,p)//B3LYP/6-31G(d)] (CYLview (Ver. 1.0b)[19] was used for visualization of the optimized structure of **C**).

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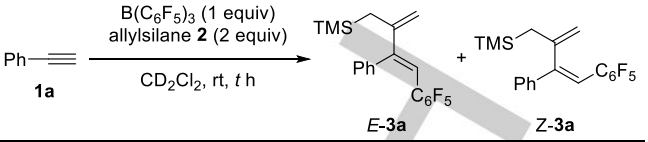
Cyclopropane formation with the migration of a C_6F_5 group on boron to the adjacent carbon atom proceeded with energy barriers ($\Delta G^{\ddagger}$) of +7.0 and +8.3 kcal/mol, respectively, and this stage represents the diastereoselectivity-determining step. Intermediates **D-II** and **D-I** are formed, which in turn lead to *Z*-**3a** and *E*-**3a**, respectively. The energy barrier for the formation of **D-II** is 1.3 kcal/mol lower than that for **D-I**; hence *Z*-**3a** is predicted to be the major product. Steric repulsion between the $TMSCH_2$ moiety and the migrating C_6F_5 group presumably affects the difference in the energy barriers. Retro-carboborations involving a cyclopropane ring-opening via four-membered transition states $\mathbf{TS_{DE\text{-}I}}$ and $\mathbf{TS_{DE\text{-}II}}$ then convert **D-I** and **D-II** to homoallylboranes **E-I** and **E-II** with activation barriers ($\Delta G^{\ddagger}$) of +16.5 and +18.7 kcal/mol, respectively, and these processes are exergonic. A similar cyclopropanation and retro-carboboration process was proposed by Hansmann and co-workers for the intramolecular reaction of an enyne with $B(C_6F_5)_3$.[13a] In our case, the final retro-hydroborations of **E-I** and **E-II** proceed via four-membered transition states $\mathbf{TS_{EF\text{-}I}}$ and $\mathbf{TS_{EF\text{-}II}}$ with energy barriers of +14.8 and +21.4 kcal/mol to provide **F-I** and **F-II**, respectively.[20] The Si-C_α bonds are oriented anti-parallel to the C_β–H bonds in both $\mathbf{TS_{EF\text{-}I}}$ and $\mathbf{TS_{EF\text{-}II}}$. NBO analyses indicated that electron donation from $\sigma_{Si-C\alpha}$ and π_{C1-C2} to the cleaving C_β–H antibonding orbital in $\mathbf{TS_{EF\text{-}I}}$ occurs more effectively than in $\mathbf{TS_{EF\text{-}II}}$ (Tables S6 and S7). The final steps are endergonic. Presumably, the consumption of $HB(C_6F_5)_2$ by hydroboration to the remaining **2** drives the reaction forward. The retro-carboboration and retro-hydroboration energy barriers involved in the formation of **F-II** are higher than those for **F-I**. These calculation results suggest that the consecutive arylacetylene/allylsilane cyclopropanation, retro-carboboration, and retro-hydroboration process enables novel 1,2-carbopentafluorophenylation with C–H functionalization at the β-position to silicon in **2**.

Following the addition of an allylsilane to an electrophile, the elimination of the silyl group generally occurs to afford the corresponding allylated product.[21] In contrast, our reaction proceeds without elimination of the silyl group following the electrophilic addition of the allylsilane to the alkyne. This reaction is enabled by the effective donation of the electron density of a vinylborate moiety to the formed carbocation, which is supported by the optimized structure of **C** and its NBO calculation results (vide supra).

We next monitored the reaction by ^{1}H NMR spectroscopy to provide a temporal profile (Table 1). The reaction was carried out in CD_2Cl_2 in an NMR tube, and the yields were determined from the ^{1}H NMR spectra using mesitylene as an internal standard. It was found that the starting material **1a** was completely consumed within 15 min, and *E*-**3a** and *Z*-**3a** were formed in yields of 17 and 8% at this time. Greater amounts of *Z*-**3a** were formed upon increasing the reaction time until completion was reached. On the other hand, although the yield of *E*-**3a** was slightly increased after 30 min, it remained constant beyond that point. Consequently, the major product changed to *Z*-**3a** after 1 h and the reaction reached completion after 4 h, giving *Z*-**3a** as the major isomer in 42% yield together with *E*-**3a** (21%). The DFT results also suggest that *Z*-**3a** is formed as a major isomer as mentioned above. In addition, *Z*-**3a** is formed more slowly than *E*-**3a** because the energy barriers for the conversion of **D-II** into **F-II** via **E-II** are higher than those for the conversion of **D-I** into **F-I** (Figure 1).

Table 1. Temporal profile of the 1,2-carbopentafluorophenylation reaction.



	yield (%)[a]		
t (h)	*E*-**3a**	*Z*-**3a**	*E*-**3a** + *Z*-**3a**
0.25	17	8	25
0.5	20	16	36
1	21	25	46
2	20	34	54
4	21	42	63
6	21	42	63

[a] Yields determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

Following the proposal of a plausible mechanism and the revelation of a temporal profile for the reaction, we moved on to investigate the substrate scope. The reaction of $B(C_6F_5)_3$ (1 equiv) and **2** (2 equiv) with **1a** (1 equiv) in DCE at room temperature afforded **3a** in 75% isolated yield with a 30:70 *E*/*Z* ratio after 6 h (Scheme 4). In terms of the allylsilane, the coupling reaction using allyltriethylsilane (**14**) proceeded to provide **15** in 78% yield with almost the same *E*/*Z* ratio, whereas the reaction using allyl(*tert*-butyl)dimethylsilane (**16**) did not afford the desired product **17**. We then examined the effect of the substituent at the 4-position of the phenylacetylene using **2** as a nucleophile. The reactions of phenylacetylenes bearing electron-donating substituents (CH_3-, CF_3O-, BzO-, PhO-, CH_3S-) efficiently proceeded to afford the desired products **3b**–**3f** in yields of 69–87%. The *E*/*Z* ratios of **3b**–**3f** were slightly higher than that of **3a.** Interestingly, the reaction using (4-methoxyphenyl)acetylene (**1g**) afforded **3g** in 58% yield (76:24 *E*/*Z* ratio), with *E*-**3g** being formed as the major isomer. Reactions of phenylacetylenes bearing weakly electron-withdrawing halogen atoms (F-, Cl-, Br-, I-), phenyl, and vinyl groups also efficiently proceeded to afford the corresponding products **3h**–**3m** in yields of 61–80%. It should be noted here that products **3j**, **3k**, and **3m** bearing substituents useful for further derivatization or polymerization (bromo, iodo, and vinyl) can be readily prepared. The reactions of phenylacetylenes **1n** and **1o** bearing strongly electron-withdrawing groups (CF_3-, CH_3OCO-) were slow; **3n** and **3o** were obtained in 39% isolated and 36% NMR yields after 22 and 24 h, respectively. The use of 4 equivs of **2** resulted in improved yields of **3n** and **3o** (74 and 60%, respectively). Phenylacetylenes **1p** and **1q** substituted with electron-donating methoxy- and electron-withdrawing trifluoromethyl-groups at their 3-positions efficiently afforded **3p** and **3q** in high yields (76 and 71%), while the reactions of (3,5-dimethoxyphenyl)acetylene (**1r**) and 3,5-bis(trifluoromethyl)phenylacetylene (**1s**) provided **3r** and **3s** in moderate yields (39 and 37%). The use of 4 equivs of **2** improved the yields of **3r** and **3s** to 67 and 69%, respectively. The reactions

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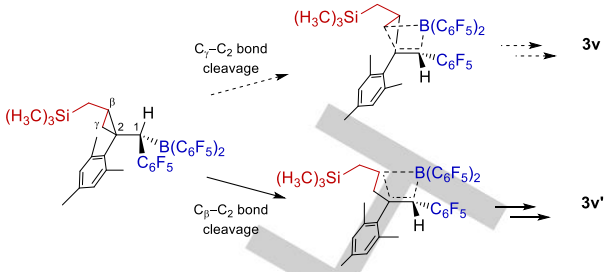
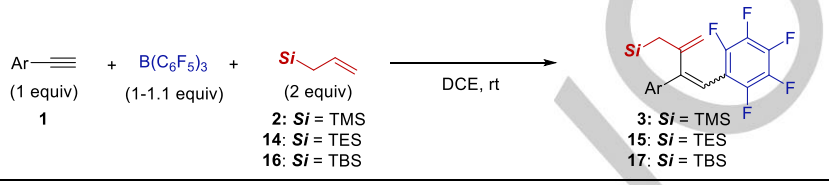
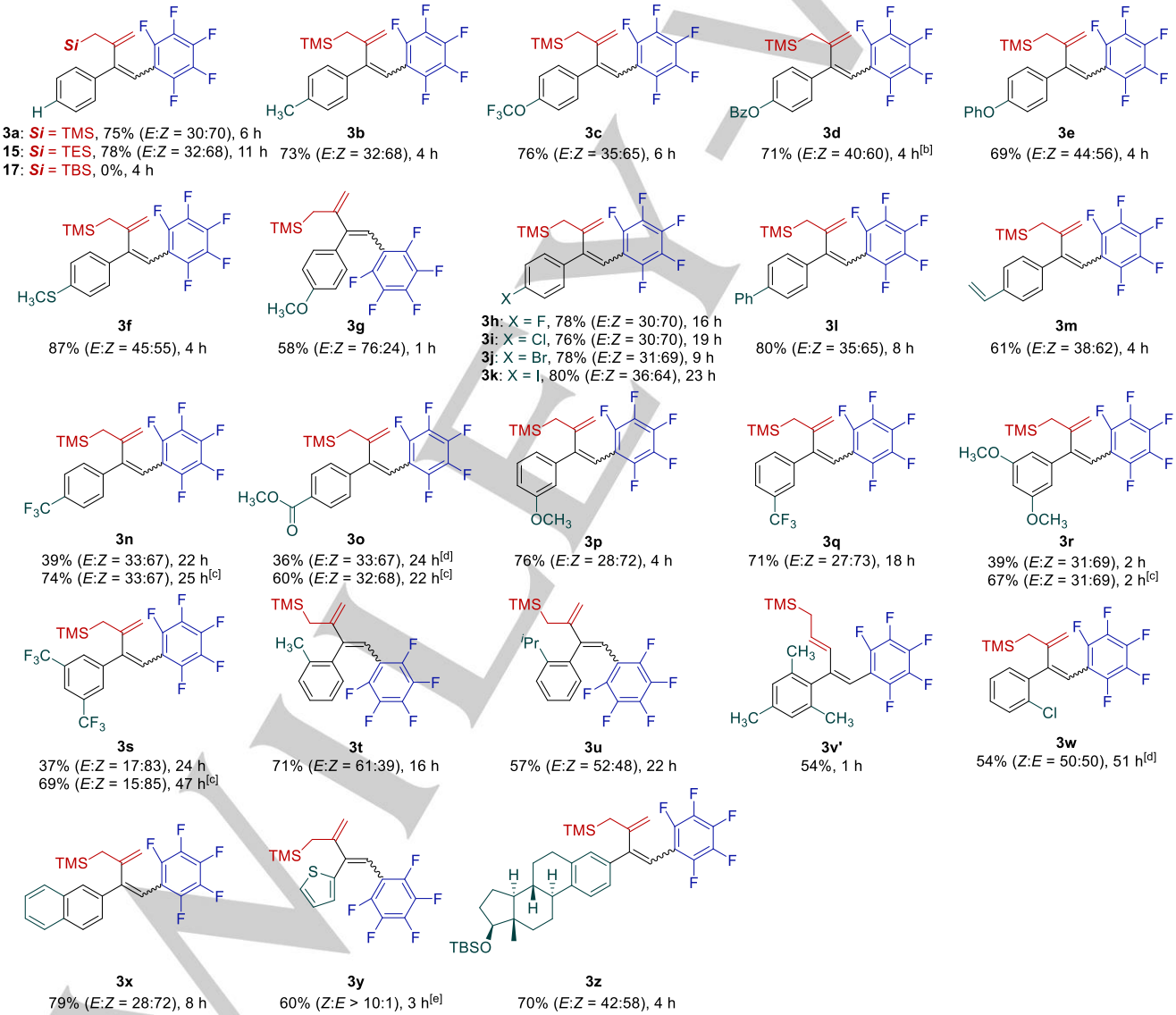
of (2-methylphenyl)acetylene (**1t**) and (2-isopropylphenyl)acetylene (**1u**) afforded **3t** and **3u** in yields of 71 and 57%, respectively, wherein *E*-**3t** and *E*-**3u** were formed as the major isomers, although the selectivity was low. These results suggest that steric hindrance associated with the substituent at the 2-position affects the direction of C_6F_5-migration in the diastereoselectivity-determining step. Interestingly, the reaction of (2,4,6-trimethylphenyl)acetylene (**1v**) was complete within 1 h to afford **3v'** instead of **3v** in 54% yield. This result suggests that C–C bond cleavage of the



Scheme 5. Reaction pathway to produce **3v'** in the reaction of (2,4,6-trimethylphenyl)acetylene **1v**.





Scheme 4. Scope of the 1,2-carbopentafluorophenylation reactions of arylacetylenes with $B(C_6F_5)_3$ and allysilanes.[a] [a] Isolated yield. [b] Obtained as a mixture with <10% of a byproduct. [c] 4 equivs of **2** were used. [d] 2% of **3w'** was contained. [e] As small amounts of inseparable impurities were contained, the yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

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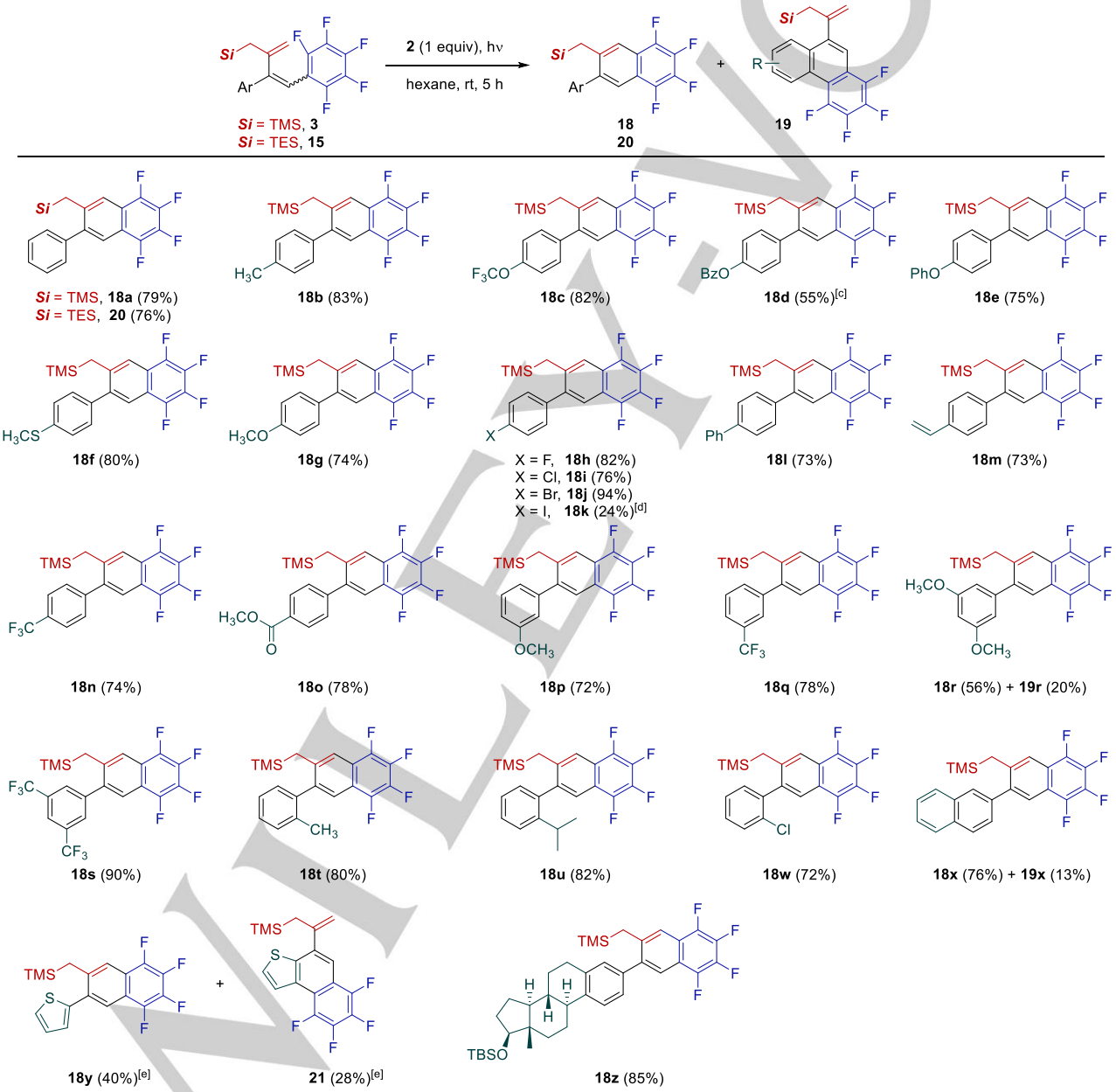
corresponding cyclopropane intermediate occurred at the β-position to silicon prior to cleavage at the γ-position owing to steric repulsion between the $TMSCH_2$ moiety and the CH_3 substituents at the 2,6-positions on the benzene ring during the retro-carboboration step (Scheme 5). In addition, the reaction of (2-chlorophenyl)acetylene (**1w**) slowly proceeded to afford **3w** in 54% yield. 2-Naphthylacetylene **1x** smoothly underwent the desired reaction to provide **3x** in 79% yield. The reaction of 2-thienylacetylene (**1y**) afforded **3y** in 60% yield with high *Z*-selectivity (*Z*:*E* >10:1). Finally, to demonstrate the applicability of this 1,2-carbopentafluorophenylation to late-stage functionalization during the synthesis of a complex molecule, estradiol derivative **1z** was subjected to the reaction to successfully afford **3z** in 70% yield.

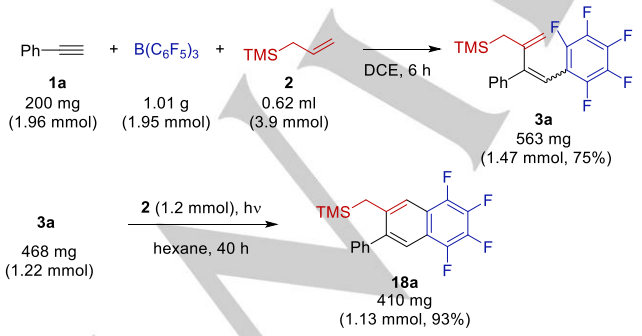
In our initial studies, tetrafluoronaphthalene **8** was obtained when **3a** was treated with TBAF (Scheme 2). Perfluoroarenes are widely used in pharmaceutical sciences, since the hydrophobicities of fluorinated compounds, the thermal stability of the C–F bond, and the π-π stacking interactions between the fluorinated and non-fluorinated aryl moieties affect the biological and physical properties.[22] These compounds are also commonly employed in electronic materials due to the ability of



Scheme 6. Scope of the photochemical 6-electrocyclization Reaction.[a,b] [a] A 300 W xenon light source (250–385 nm) was used. [b] Isolated yield. [c] As small amounts of inseparable impurities were contained, the yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [d] **18k** was obtained as a mixture of inseparable impurities. The yield was determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [e] **3y** (4%) was also present.

the fluorine atom to lower the HOMO and LUMO energy levels.[23] Owing to the importance of fluorinated aromatic compounds,[24] we explored an optimal method for the preparation of tetrafluoronaphthalenes from the abovementioned 1,2-dicarbofunctionalization products. An intramolecular nucleophilic aromatic substitution reaction can be used to convert *Z*-**3** to tetrafluoronaphthalenes, whereas *E*-**3** should afford the corresponding uncyclized desilylated product. We surmised that a photochemical 6π-electrocyclization reaction followed by HF elimination could convert both *Z*- and *E*-**3** to the corresponding tetrafluoronaphthalenes due to the fact that *E*/*Z* isomerization occurs concurrently under irradiation.[25] In addition, the remaining silyl group is useful for the further derivatization of tetrafluoronaphthalenes (Scheme S2).[26] Hence, **3a** was irradiated in the presence of allylsilane **2** (1 equiv) as a HF scavenger in DCE (Table S1). As expected, the desired compound **18a** was produced in 78% yield (NMR) together with 8% of tetrafluorophenanthrene **19a** after 5 h. Various solvents were then examined, with hexane being found to be optimal; tetrafluoronaphthalene **18a** was produced in 80% yield (NMR), while the yield of **19a** was <3%. With the optimal conditions in hand, **3a**–**3u**, **3w**–**3z,** and **15** were subjected to the photochemical 6π-cyclization reaction (Scheme 6). In most cases, the reactions, including that of estradiol derivative **3z**, proceeded efficiently to afford the corresponding tetrafluoronaphthalenes **18a**–**18j**, **18l**–**18q**, **18s**–**18u**, **18w**, **18z**, and **20** in yields of 55–94%. The reactions of **3r**, **3x**, and **3y** afforded tetrafluorophenanthrene **19r**, tetrafluorobenz[α]anthracene **19x**, and tetrafluoronaphto[2,1-b]thiophene **21** in yields of 20, 13, and 28%, respectively, along with tetrafluoronaphthalenes (**18r**, **18x**, and **18y**). The reaction of **3k** unfortunately afforded **18k** in 24% yield (NMR) as a mixture with remaining **3k** and several impurities due to the occurence of uncontrollable side reactions. Although **3v'** was subjected to the reaction conditions, it did not appear to react. Steric hindrance associated with the $TMSCH_2$ group likely prevented the 1,3-diene moiety from adopting the s-*cis* conformation required for the 6π-electrocyclization reaction.

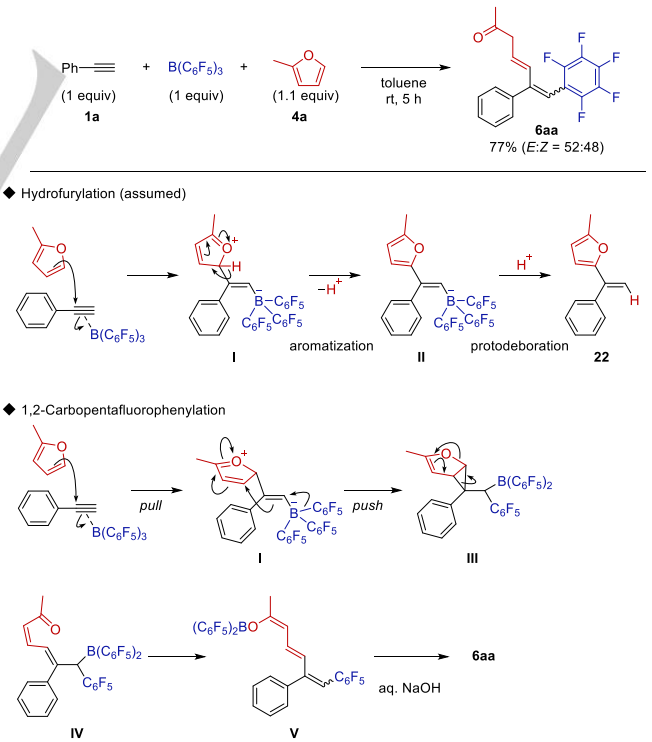
To demonstrate the amenability of the two-step sequence to scale up, the 1,2-carbopentafluorophenylation reaction was performed on a 1.95-mmol scale (Scheme 7). The reaction smoothly proceeded to afford **3a** in 75% yield; 1.22 mmol of **3a** was subsequently subjected to the 6π-electrocyclization reaction to afford **18a** in 93% yield.



Scheme 7. Synthesis of tetrafluoronaphthalene **18a** on a 1 mmol scale.

We subsequently examined the reaction of phenylacetylene (**1a**) (1 equiv) with $B(C_6F_5)_3$ (1 equiv) and 2-methylfuran (**4a**) (1.1 equiv) in toluene (Scheme 8). As **4a** is more nucleophilic than allylsilane **2**, we assumed that **4a** would add to **1a**,[16] and the formed intermediate **I** readily aromatizes to produce the hydrofurylation product **22** via alkenylborate **II**. Indeed, Au(I) catalysts are known to promote the hydrofurylation of arylacetylenes through an electrophilic activation of **1a**.[27] As a result, the unexpected 1,2-carbopentafluorophenylation product **6aa** was produced through the ring opening of furan[28] in 77% yield instead of **22,** with the following plausible mechanism being proposed. Following the formation of zwitterionic intermediate **I** by the addition of **4a** and $B(C_6F_5)_3$ to **1a**, the electron density is efficiently donated to form 2-oxabicyclo[3.1.0]hexene intermediate **III**, driven by the migration of a C_6F_5 group to the adjacent carbon atom.[29] The ring opening of **III** then produces intermediate **IV**, and a $B(C_6F_5)_2$ group of **IV** migrates onto the oxygen atom to form boron enolate **V**. Finally, workup using aqueous NaOH produces **6aa**. It should be noted that a mechanism involving the direct ring opening of **I** to produce **IV** cannot be excluded. In any case, this reaction is also enabled by the "pull-push" reactivity of $B(C_6F_5)_3$. Because the electron-donation through the migration of a C_6F_5 group is more efficient than that involving the Au(I) catalysts, cyclopropanation or ring-opening occurs prior to aromatization to reform the furan.[27]

To examine scope of the reaction with 2-substituted furans, phenylacetylenes **1b**, **1g**, and **1i**, substituted with electron-donating methyl- and methoxy-groups and electron-withdrawing chloro-group at their 4-positions were subjected to the reaction (Scheme 9). In all cases, the coupling reaction effectively



Scheme 8. Reaction of $B(C_6F_5)_3$ and 2-methylfuran with phenylacetylene and its plausible mechanism.

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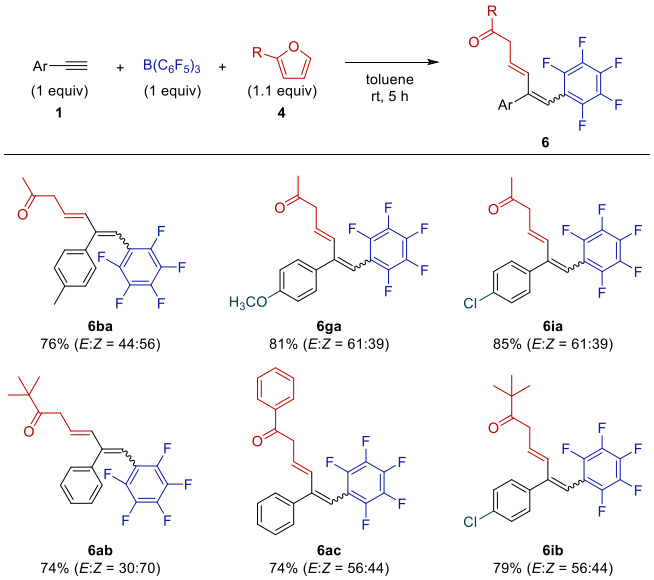
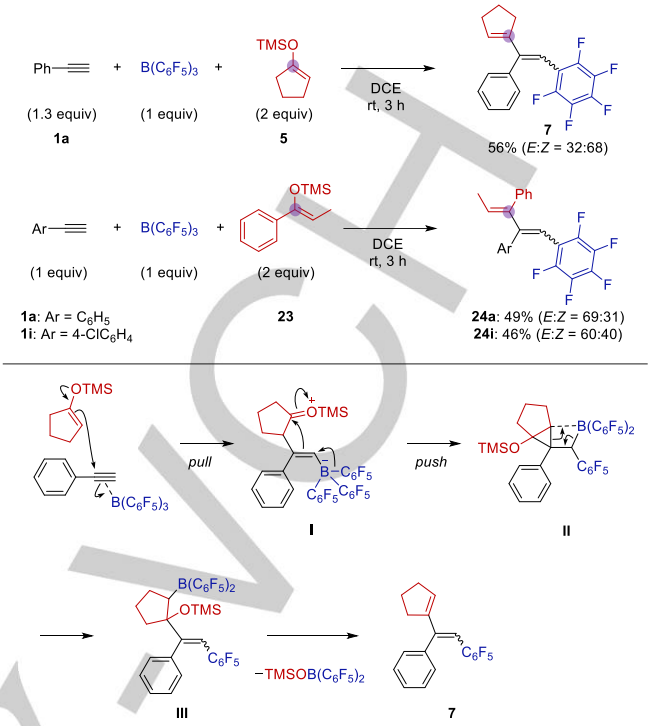


Scheme 9. Scope of the 1,2-carbofunctionalization of arylacetylenes with $B(C_6F_5)_3$ and 2-substituted furans.

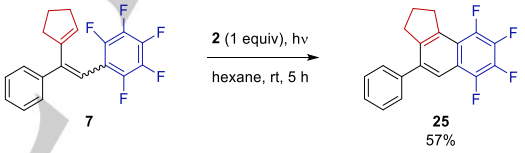
proceeded to afford **6ba**, **6ga**, and **6ia** in yields of 76, 81, and 85%, respectively. 2-*tert*-Butyl- and 2-phenylfurans (**4b** and **4c**) were also examined as nucleophiles, with **6ab**, **6ac**, and **6ib** being obtained in high yields (74–79%). These results suggest the broad scope of this reaction with respect to both arylacetylenes and 2-substituted furans.

Finally, we examined the reaction of arylacetylenes (1.0–1.3 equiv) with $B(C_6F_5)_3$ (1 equiv) and silyl enolates **5** and **23** (2 equiv) in DCE, with novel 1,2-carbopentafluorophenylation products **7**, **24a**, and **24i** being obtained in yields of 56, 49, and 46%, respectively (Scheme 10). In this process, C–C bonds are formed in associated with C–O bond cleavage between the alkenyl moiety and the silyloxy group. A plausible mechanism for the formation of **7** and **24** also involves the donation of the electron density driven by the migration of a C_6F_5 group. This enables cyclopropanation to form intermediate **II** after the formation of zwitterionic intermediate **I**. Subsequent retro-carboboration involving cyclopropane ring-opening produces intermediate **III**, with the elimination of $TMSOB(C_6F_5)_2$ affording **7**.

The 6π-electrocyclization reaction of **7** was also examined, with cyclopentane-fused tetrafluoronaphthalene **25** being obtained in 57% yield (Scheme 11).



Scheme 10. Reactions of $B(C_6F_5)_3$ and silyl enolates with phenylacetylenes and its plausible mechanism.



Scheme 11. Photochemical 6π-electrocyclization of **7**.

Conclusion

In conclusion, we examined the reaction of arylacetylenes with $B(C_6F_5)_3$ and three types of carbon nucleophile including allylsilanes, 2-substituted furans, and silyl enolates. We revealed that novel 1,2-dicarbofunctionalization products bearing a C_6F_5 group were obtained following the addition of $B(C_6F_5)_3$ and the carbon nucleophiles to the arylacetylenes. Mechanistic studies suggest that the observed 1,2-carbopentafluorophenylation reactions are enabled by the metallomimetic “pull-push” reactivity of $B(C_6F_5)_3$ toward the alkyne. More specifically, the arylacetylenes are electrophilically activated by $B(C_6F_5)_3$ to enable additions of the carbon nucleophiles. Subsequent migration of a C_6F_5 group from boron to the adjacent carbon atom donates electron density to the vicinal carbon, which results in the facile cyclopropanation or ring-opening of the furan-derived moiety. These 1,2-carbopentafluorophenylation reactions have a broad substrate scope and occur smoothly at room temperature without the requirement of a catalyst. A variety of unique compounds, each bearing a C_6F_5 group, can be prepared, which are difficult to access by other means. Moreover, the 1,2-carbopentafluorophenylation products obtained using allylsilanes

and silyl enolate as carbon nucleophiles were amenable to photochemical 6π-electrocyclization reactions to afford tetrafluoronaphthalenes, which are important in the pharmaceutical and materials sciences. The concept of the metallomimetic "pull-push" reactivity, which we propose herein, helpfully enables the unique property of $B(C_6F_5)_3$ to be understood, and will lead to the further development of unique methodologies using $B(C_6F_5)_3$.

Experimental Section

1,2-Carobopentafluorophenylation reactions were carried out in nitrogen-filled grove box, and photochemical cyclizations were performed under an atmosphere of Ar. Solvents and other reagents were purchased from chemical suppliers and used as receive. Experimental procedures for the preparations of arylacetylenes and derivatization of **18a**, characterizations, NMR charts, DFT calculations, and crystallographic data are described in the Supporting Information.

Representative procedure for 1,2-carobopentafluorophenylation with allylsilane: $B(C_6F_5)_3$ (51.9 mg, 0.1 mmol) and allylsilane **2** (32 µl, 0.2 mmol) were dissolved in DCE (1.0 ml). After the mixture was stirred for 20 min at room temperature, phenylacetylene (**1a**) (11 µl, 0.1 mmol) was added. The reaction mixture turned dark red and was stirred for 6 h. The color changed to yellow. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and was extracted with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane) to afford **3a** (28.6 mg, 75%) as a colorless oil.

Representative procedure for photochemical 6π-electrocyclization: A PP tube was charged with **3a** (11.3 mg, 0.03 mmol), allylsilane **2** (4.7 µl, 0.03 mmol), and hexane (1 ml). After the solution was degassed, it was irradiated with a 300 W xenon light source (250–385 nm) at an argon atmosphere at room temperature for 5 h. The reaction mixture was transferred to a flask and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane) to afford **18a** (8.56 mg, 79%) as a colorless solid.

Synthesis of tetrafluoronaphthalene 18a on 1 mmol scale: $B(C_6F_5)_3$ (1.00 g, 1.95 mmol) and allylsilane **2** (0.62 ml, 1.95 mmol) were dissolved in DCE (19.5 ml). After the mixture was stirred for 20 min at room temperature, phenylacetylene (**1a**) (200 mg, 1.96 mmol) was added. The reaction mixture turned dark red and was stirred for 6 h. The color changed to yellow. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and was extracted with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane) to afford **3a** (563 mg, 75%) as a colorless oil.

A test tube was charged with **3a** (468 mg, 1.22 mmol), allylsilane **2** (194 µl, 1.22 mmol), and hexane (3 ml). After the solution was degassed, it was irradiated with a 300 W xenon light source (250–385 nm) at an argon atmosphere at room temperature for 40 h. The reaction mixture was transferred to a flask and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane) to afford **18a** (410 mg, 93%) as a colorless solid.

Representative procedure for 1,2-carobopentafluorophenylation with 2-substituted furan: After $B(C_6F_5)_3$ (51.8 mg, 0.1 mmol) and 2-methylfuran **4a** (10 µl, 0.11 mmol) were dissolved in toluene (1.0 ml), a solution of **1a** (11 µl, 0.1 mmol) in toluene (0.5 mol) was added. The reaction mixture turned yellow, and was stirred at room temperature for 5 h. The reaction mixture was quenched with 10% aq. NaOH, and was extracted with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane:EtOAc = 10:1) to afford **6aa** (27.3 mg, 77%) as a yellow oil.

Representative procedure for 1,2-carobopentafluorophenylation with silyl enolate: After $B(C_6F_5)_3$ (51.8 mg, 0.1 mmol) and silyl enolate **5** (32 mg, 0.2 mmol) were dissolved in DCE (1.0 ml), **1a** (11 µl, 0.1 mmol) was added. The reaction mixture turned orange, and was stirred for 3 h at room temperature. The reaction mixture was quenched with sat. aq. $NaHCO_3$, and was extracted with EtOAc. The combined organic layer was washed with brine and dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane) to afford **7** (18.9 mg, 56%) as a colorless oil.

Photochemical 6π-electrocyclization of 7: A PP tube was charged with **7** (13.2 mg, 0.039 mmol), allylsilane **2** (6.2 µl, 0.039 mmol), and hexane (1 ml). After the solution was degassed, it was irradiated with a 300 W xenon light source (250–385 nm) under an argon atmosphere at room temperature for 5 h. The reaction mixture was transferred to a flask and concentrated in vacuo. The crude product was recrystallized from hexane and EtOAc to afford **25** (7.1 mg, 57%) as a colorless solid.

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Keywords: alkynes • boranes• 1,2-difunctionalization • metallomimetic• multicomponent reactions

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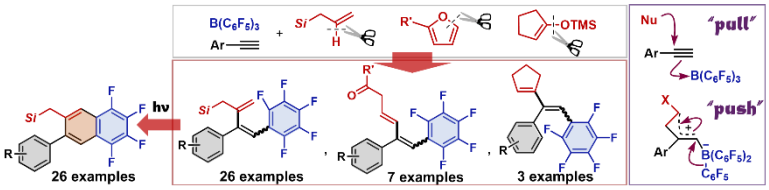

The pull-push reactivity of tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] enables the novel three-component coupling of an allylsilane, an arylacetylene, and a C_6F_5 group from $B(C_6F_5)_3$. Tetrafluoronaphthalenes can be prepared from the resultant C_6F_5-substituted 1,3-dienes by a photochemical 6π-electrocyclization. The reaction using a 2-substituted furan or a silyl enolate instead of an allylsilane also affords a novel three-component coupling product.