Direct Brønsted Acid-Catalyzed Functionalization of Benzhydryl Alcohols and 2-Ethoxytetrahydrofuran using Potassium Trifluoroborate Salts

by

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Metal-free transformations of organotrifluoroborates are advantageous since they avoid using frequently expensive and sensitive transition metals. Lewis acid-catalyzed reactions involving organotrifluoroborates have emerged as an alternative to metal-catalyzed protocols. However, these methods rely on generating unstable boron dihalide species thereby resulting in low functional group tolerance.

A Brønsted acid-catalyzed carbon-carbon bond forming methodology involving alkenyl- and alkynyltrifluoroborates and in situ generated carbocations has been developed. In the presence of HBF₄, we have shown that organotrifluoroborates react with benzhydryl alcohols to afford alkenes and alkynes in good to excellent yields. This protocol features excellent atom economy since alcohols and organotrifluoroborates react in a 1:1 ratio. Functional group tolerance superior to Lewis acid- and metal-catalyzed approaches was demonstrated.

Furthermore, we were able to extend this method to 2-ethoxytetrahydrofuran which underwent direct substitution to afford functionalized furans in moderate to excellent yields. A variety of alkenyl- and alkynyltrifluoroborates readily participated in this transformation.
Firstly, I would sincerely like to thank my supervisor, Dr. Yuri Bolshan, for all of his guidance and support throughout this project. I have gained invaluable knowledge from him since joining his laboratory in May 2013. Working under his management has been a great opportunity and I look forward to applying my acquired knowledge and skills in an industrial setting.

I would also like to thank all of the lab members (past and present). Not only did they provided their assistance in the laboratory, but they made the lab environment very pleasant. We have shared a lot of laughs throughout this, oftentimes, stressful process, which was greatly appreciated.

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well, I would like to thank my little sisters (Krista and Jenna) for being my best friends and for always being so supportive.

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“There’s a drive in me that won’t allow me to do certain things that are easy.”

- JOHNNY DEPP -
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<table>
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<th>Description</th>
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<tbody>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalents</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>Et₂O</td>
<td>diethyl ether</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>THP</td>
<td>tetrahydropyran</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>potassium permanganate</td>
</tr>
<tr>
<td>PMA</td>
<td>phosphomolybdic acid</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>EI</td>
<td>electron impact</td>
</tr>
<tr>
<td>DART</td>
<td>direct analysis in real time</td>
</tr>
<tr>
<td>TOF</td>
<td>time-of-flight</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Boc</td>
<td>tert-butyloxy carbonyl</td>
</tr>
<tr>
<td>vs</td>
<td>versus</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>IR</td>
<td>infrared spectroscopy</td>
</tr>
<tr>
<td>HBF₄</td>
<td>tetrafluoroboric acid</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and Drug Administration</td>
</tr>
<tr>
<td>MOM</td>
<td>methoxymethyl</td>
</tr>
<tr>
<td>HF</td>
<td>hydrogen fluoride</td>
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<tr>
<td>TfOH</td>
<td>trifluoromethanesulfonic acid</td>
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<tr>
<td>FDA</td>
<td>Food and Drug Administration</td>
</tr>
<tr>
<td>NDA</td>
<td>New Drug Application</td>
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1. INTRODUCTION

1.1 POTASSIUM TRIFLUOROBORATE SALTS

1.1.1 ORGANOBORON COMPOUNDS

In recent years, organoboron compounds have been increasingly used as reagents for carbon-carbon bond formation. Namely, this is due to the fact that these reagents have a low toxicity. In addition, these reagents are compatible with a wide range of functional groups\(^\text{[11]}\). The relative non-toxic nature of organoboron-containing compounds can be further supported by their presence in prescription pharmaceuticals (Figure 1). Bortezomib was initially approved by the FDA in 2003 for the treatment of multiple myeloma and mantle cell lymphoma. More recently, tavaborole was approved by the FDA in 2014 for the treatment of onychomycosis, a fungal infection of toenails. Additionally, earlier this year, the FDA accepted Anacor Pharmaceutical’s New Drug Application (NDA) for the approval of crisaborole for the potential treatment of atopic dermatitis. Results from the FDA with regards to this review are anticipated early next year.

Figure 1: Organoboron-containing pharmaceuticals

Boronic acids and boronate esters are two popular subclasses of organoboron compounds (Figure 2). However, their prolonged storage is not without issues. Boronic acids usually contain boroxines, also known as boronic acid anhydrides, resulting in
difficulties in stoichiometry determination\cite{2}. When the hydroxyl groups of boronic acids are replaced by alkoxy or aryloxy groups, this results in the formation of boronate esters. This is advantageous since with the hydroxyl groups removed, boronate esters lose the capability of acting as hydrogen bond donors and are, therefore, less polar and easier to handle\cite{3}. However, although they display a higher stability as compared to free boronic acids, they are generally less reactive\cite{2}. Furthermore, both boronic acids and boronate esters are sensitive to air and moisture due to the presence of an empty p-orbital on the boron atom\cite{1}.

![Organoboron compounds](image)

**Figure 2: Organoboron compounds**

In contrast, organotrifluoroborate salts have been gaining popularity as they have been shown to overcome the limitation of stability. Present as crystalline solids, they are both air and moisture stable, since they are not hygroscopic, which allows for indefinite storage at room temperature\cite{2}. Organotrifluoroborates also exhibit greater intrinsic nucleophilicity than their boronic acid and boronate ester counterparts due to their tetracoordinated nature\cite{4}. Furthermore, a wide variety are commercially available or can be easily prepared on a gram scale from inexpensive materials\cite{1,2,5,6}.

Potassium hydrogen difluoride, KHF$_2$, has been shown to serve as an appropriate fluorinating agent towards the synthesis of organotrifluoroborates and is compatible with many functional groups\cite{2}. Over the years, several one-pot methods have been developed for the synthesis of trifluoroborate salts and several procedures are being continuously reported. Three general methods that use the inexpensive KHF$_2$ reagent are shown below and are widely used today\cite{6} (Scheme 1). Firstly, organotrifluoroborates can be prepared from organolithium or Grignard reagents through reaction with trialkylborates and then subsequent reaction with KHF$_2$ (Scheme 1, Method A). Alternatively, hydroboration of alkenes or alkynes with catecholborane followed by reaction with KHF$_2$ would afford
alkanyl- or alkenyltrifluoroborates (Scheme 1, Method B). Lastly, treatment of boronic acids with aqueous KHF$_2$ is another popular method to furnish organotrifluoroborates (Scheme 1, Method C).

\[
\begin{align*}
\text{Method A} & \quad R^-\text{MgX} \\
& \quad \text{or} \quad R^-\text{Li} \\
& \quad \xrightarrow{B(OR)_3} \quad KHF_2 \quad \text{acetone (aq)} \\
& \quad \xrightarrow{} \quad R^-\text{BF}_3\text{K}
\end{align*}
\]

\[
\begin{align*}
\text{Method B} & \quad \begin{array}{c}
\text{R}\equiv \text{BH} \\
\text{O} \\
\text{O}
\end{array}
\quad \xrightarrow{} \quad KHF_2 \quad \text{acetone (aq)} \\
& \quad \xrightarrow{} \quad \text{R}^-\text{BF}_3\text{K}
\end{align*}
\]

\[
\begin{align*}
\text{Method C} & \quad \begin{array}{c}
\text{R}^-\text{B(OH)}_2 \\
\text{OH}
\end{array}
\quad \xrightarrow{KHF_2} \quad \text{MeOH/H}_2\text{O} \\
& \quad \xrightarrow{} \quad \text{R}^-\text{BF}_3\text{K}
\end{align*}
\]

Scheme 1: General methods for the preparation of organotrifluoroborates

Although KHF$_2$ is safe to handle, the HF$_2^-$ anion can cause extensive etching of glassware. As a result, Guy Lloyd-Jones and coworkers recently reported a new method for organotrifluoroborate preparation (Scheme 2). Through the use of KF and L-(-)-tartaric acid, a variety of aromatic, vinylic, allylic and alkyl boronic acids were converted to the corresponding organotrifluoroborate$^{[7]}$. Filtration of the product mixture to remove residual KF and potassium bitartrate byproduct, followed by evaporation resulted in directly obtaining the organotrifluoroborate product. The methodology was also applied to pinacol boronates.

\[
\begin{align*}
\text{R}^-\text{B(OH)}_2 \\
\text{OH}
\quad \xrightarrow{i) KF (4.0 equiv.), CH}_3\text{CN/H}_2\text{O, rt} \\
\quad \xrightarrow{ii) L-(-)-tartaric acid, THF} \quad \xrightarrow{iii) filter} \quad \text{R}^-\text{BF}_3\text{K} \quad + \quad \text{K salts} \\
\quad \xrightarrow{iv) evaporate}
\end{align*}
\]

Scheme 2: Preparation of organotrifluoroborates salts under non-etching conditions
1.1.2 METAL-FREE REACTIONS OF TRIFLUOROBORATES

Organotrifluoroborates have been shown to act as boronic acid equivalents in palladium-catalyzed Suzuki-Miyaura couplings\(^8\). However, our research is focused on the development of metal-free reactions of organotrifluoroborates. Metal-free transformations of organotrifluoroborates are becoming increasingly prevalent due to the cost and toxicity associated with transition metals\(^9\). Namely, Lewis acid-catalyzed reactions have emerged as an alternative to metal-catalyzed protocols.

1.1.2.1 LEWIS ACID-CATALYZED REACTIONS OF TRIFLUOROBORATES

In 2002, Matteson and coworkers developed a mild and efficient route to the synthesis of asymmetric secondary amines via an intramolecular reaction between azides and alkyltrifluoroborates (Scheme 3). In this method, the Lewis acidic tetrachlorosilane defluorinates the alkyltrifluoroborate salt to yield the reactive alkyldifluoroborane intermediate\(^{10}\).

Scheme 3: Lewis acid-catalyzed reaction of azide and difluoroborane intermediate

More recently, our group has described a straightforward method for the preparation of ynones from acyl chlorides and alkynyltrifluoroborate salts in the presence of a Lewis acid (Scheme 4). Reactive organodichloroborane intermediate is formed upon exposure of alkynyltrifluoroborates with BCl\(_3\)\(^{11}\).
Scheme 4: Lewis acid-catalyzed alkynylation of acyl chlorides

Our group was then able to employ a similar BCl$_3$ catalyzed protocol for the synthesis of sterically hindered ortho-demethylated ynones from mixed anhydrides and potassium alkynyltrifluoroborate salts (Scheme 5). The 2-hydroxy substituted ynone products were then converted to biologically active natural product scaffolds.$^{[12]}$

Scheme 5: Lewis acid-catalyzed preparation of sterically hindered ynones and their application to the synthesis of aurones and flavones

Additionally, organotrifluoroborates have also been shown to react with boron trifluoride (BF$_3$·OEt$_2$). In 2009, Bode and coworkers developed a method for the synthesis of dialkyl ethers from O-methoxymethyl (MOM) acetics and aryl-, alkenyl- or alkynyltrifluoroborate salts (Scheme 6)$^{[13]}$. In this method, interaction of trifluoroborate with BF$_3$·OEt$_2$ resulted in the formation of Lewis acidic organodifluoroborane species. Although this reaction tolerated aryl-, alkenyl- and alkynyltrifluoroborates, electron-deficient substrates resulted in poor yields. Later in 2011, Bode and coworkers were able
to improve the reaction conditions through the use of a hydroxamate leaving group. This resulted in improved regioselectivity of challenging substrates, higher yields of the dialkyl ether products, reduction of the equivalents of Lewis acid and organotrifluoroborate as well as allowed for electron-withdrawing (hetero)-aryls to be present\cite{14}.

![Scheme 6: Lewis acid-catalyzed synthesis of dialkyl ethers from organotrifluoroborates and acetals](image)

Stefani and coworkers developed a highly stereoselective and mild method for the C-glycosidation of 3,4,6-tri-O-acetyl-d-glucal with alkynyltrifluoroborates (Scheme 7). This reaction was mediated by BF$_3$·OEt$_2$ Lewis acid. They proposed that reaction of BF$_3$ and alkynyltrifluoroborate facilitates the generation of the organodifluoroborane Lewis acid. Activation of 3,4,6-tri-O-acetyl-d-glucal with organodifluoroborane results in the formation of an oxocarbenium ion and a nucleophilic tetracoordinated boron species. Attack at the C-1 position resulted in the formation of a variety of α-C-glycosides\cite{15}.

![Scheme 7: Lewis acid-catalyzed synthesis of α-C-glycosides from potassium alkynyltrifluoroborates and d-glucals](image)
Liu and coworkers were also able to employ a BF₃·OEt₂ mediated C-glycosylation approach through the coupling of organotrifluoroborates and glycosyl fluorides (Scheme 8). Alkenyl and alkynyl C-glycosides were obtained in good to excellent yields with high diastereoselectivity. 

Scheme 8: Lewis acid-catalyzed direct C-glycosylation of glycosyl fluorides with organotrifluoroborates

1.1.2.1.1 REACTIONS OF ORGANODICHLOROBORANES WITH BENZHYDRYL ALCOHOLS

In 2006, Kabalka and coworkers have shown that the substitution of hydroxyl groups of benzhydryl alcohols can occur using alkynylboron dihalides (Scheme 9). They reported a novel method for directly converting aryl and aliphatic alkynes to the corresponding alkynylboron dichlorides without the necessity to pre-form alkynyltrifluoroborates. Migration of the alkynyl group from boron to carbon occurs forming a variety of internal acetylenes in moderate to excellent yields.

Scheme 9: Substitution of hydroxyl groups of benzhydryl alcohols with Lewis acidic alkynylboron dihalides
In summary, metal-free Lewis acid-catalyzed reactions of organotri fluoroborates have been extensively studied. However, the limitations of these protocols include the necessity to preform unstable boron dihalide intermediates thereby resulting in a narrow substrate scope.

1.1.2.2 REACTIONS OF TRIFLUOROBORATES WHICH OCCUR IN THE PRESENCE OF BRØNSTED ACIDS

Contrary to the previously outlined methods for the Lewis acid-catalyzed reactions of organotri fluoroborates, Brønsted acid catalyzed reactions of organotri fluoroborates are uncommon. A literature survey only resulted in the findings that organotri fluoroborates have been shown to participate in reactions whereby Brønsted acids are present.

In the reaction shown by MacMillan and coworkers, vinyl and heteroaryl trifluoroborate salts were viable substrates for amine-catalyzed conjugate additions\textsuperscript{[18]}. They found that exposing crotonaldehyde to organotri fluoroborates in the presence of an imidazolidinone catalyst and hydrofluoric acid resulted in the formation of the desired aldehyde products (Scheme 10). The authors suggest that the presence of HF is necessary for the sequestration of boron trifluoride by-product, by forming a BF\textsubscript{3}K precipitate, which they confirmed by \textsuperscript{19}F NMR. Notably, HF has been used for the preparation of trifluoroborate salts. Therefore, it may also act as a stabilizing agent for the trifluoroborates.

Scheme 10: Organocatalytic conjugate addition of trifluoro(organo)borates to \(\alpha,\beta\)-unsaturated aldehydes in the presence of a Brønsted acid
In 2013, Carreira and coworkers showed an iridium-catalyzed asymmetric substitution reaction of allylic alcohols with vinyl trifluoroborates (Scheme 11). Although catalyzed by an Ir-(P,olefin) complex, the reaction took place in the presence of 2.0 equivalents a Brønsted acid, HF. Interestingly, in this case the authors suggested that HF was present as a trifluoroborate activator\(^\text{19}\). Later on, they showed that direct enantioselective substitution of allylic alcohols was possible with alkynyltrifluoroborates\(^\text{20}\). Notably, they were able to avoid the use of hazardous and corrosive HF in this protocol by using KHF\(_2\) as an alternative fluoride source. Through the use of KHF\(_2\) and CF\(_3\)COOH, they were able to generate HF \textit{in situ}.

![Scheme 11: Iridium-catalyzed enantioselective allylic vinylation using allylic alcohols and alkenyltrifluoroborates in the presence of a Brønsted acid](image)

Aggarwal and coworkers reported the allylation-like addition of trifluoroborates to aldehydes in the presence of trifluoromethanesulfonic acid (Scheme 12). However, although a Brønsted acid was used, the procedure was mechanistically similar to Lewis acid-catalyzed transformations since a difluoroborane intermediate was formed\(^\text{21}\).

![Scheme 12: Addition of benzylic trifluoroborates to aldehydes in the presence of a Brønsted acid](image)
1.2 RESEARCH OBJECTIVE

At the outset, we wanted to develop a set of metal-free Brønsted acid catalyzed reactions of organotrifluoroborates. By doing this, we would hopefully avoid issues associated with typical Lewis acid-catalyzed protocols, which involve the generation of unstable boron dihalide species. By avoiding the generation of Lewis acidic intermediates, there was promise to extend the substrate scope beyond ether, halide and alkyl substituents.

Inspired by the work described by Kabalka and coworkers (Section 1.1.2.1.1), we proposed that activation of benzhydryl alcohols could instead be accomplished via a Brønsted acid. Subsequently, in the presence of a nucleophilic organotrifluoroborate, reaction at the benzhydryl center could be possible. Unlike Lewis acidic boron dihalides, organotrifluoroborates do not need to be activated since they already have a tetracoordinated boron center and will readily react as nucleophiles.
1.3 BENZHYDRYL SCAFFOLDS

Development of methods for the synthesis of compounds which contain benzhydryl scaffolds are synthetically useful. Namely, the diphenylmethane scaffold is prevalent in natural products, bioactive compounds and several pharmaceuticals. The following Figure 3 illustrates three prescription pharmaceuticals present in the market which contain the benzhydryl scaffold.

![Figure 3: Benzhydryl scaffolds present in pharmaceuticals](image)

1.3.1 SYNTHEISIS OF BENZHYDRYL COMPOUNDS

1.3.1.1 METAL-CATALYZED REACTIONS OF BENZHYDRYL ALCOHOLS

Several protocols have been described for the functionalization of benzhydryl centers\textsuperscript{22}. However, direct metal-catalyzed dehydrative coupling reactions involving diarylmethanols have recently gained attention for several reasons. Firstly, a vast amount of diarylmethanol derivatives are commercially available or can be easily prepared. Secondly, the atom economy associated with these protocols is favourable as water is a major byproduct\textsuperscript{23}.
In 2009, Jiao and coworkers developed a sp-sp\(^3\) carbon-carbon bond forming methodology between terminal alkynes and benzhydryl alcohols via a Fe(OTf)\(_3\)/TfOH co-catalyzed coupling reaction\(^{[24]}\). In this protocol, water was the sole byproduct (Scheme 13).

Scheme 13: Metal-catalyzed dehydrative coupling of benzhydryl alcohols with terminal alkynes

As well, metal-catalyzed alkenylation of benzhydryl alcohols are known\(^{[25]}\). Specifically, Gandon and coworkers have shown that the direct alkenylation of a variety of alcohols, including benzhydrols, occurs in the presence of 2.0 equivalents of vinylboronic acids through the use of a Ca(NTf\(_2\))\(_2\) catalyst\(^{[26]}\) (Scheme 14).

Scheme 14: Ca\(^{II}\)-catalyzed alkenylation of benzhydryl alcohols with vinylboronic acids

However, several disadvantages are present for these metal-catalyzed approaches. Specifically, these protocols oftentimes require the use of expensive, sensitive and toxic metal catalysts. As a result, low functional group tolerance is observed.
1.3.1.2 METAL-FREE REACTIONS OF BENZHYDRYL ALCOHOLS

To avoid these limitations, metal-free reactions of benzhydryl alcohols is of interest. Previously mentioned in Section 1.1.2.1.1, Kabalka and coworkers demonstrated that the substitution of hydroxyl groups of benzhydryl alcohols can occur using alkynylboron dihalides\(^\text{[17]}\) (Scheme 9). They have also developed a similar metal-free methodology using benzhydryl alcohols and pre-formed alkenylboron dihalides\(^\text{[27]}\) (Scheme 15). In both cases, the use of \(n\)-BuLi as well as the necessity to form unstable boron dihalide intermediates resulted in a narrow substrate scope.

![Scheme 15: Metal-free substitution of benzylic hydroxyl groups with vinyl moieties using vinylboron dihalides](image)

Other methods for the alkenylation of benzhydryl alcohols under metal-free conditions are known\(^\text{[28]}\). However, of interest, Schaus and coworkers illustrated that the enantioselective addition of alkenylboronates to benzhydryl alcohols and ethers occurs via a chiral biphenol catalyst\(^\text{[29]}\) (Scheme 16). However, the necessity to use 2.0 equivalents of unstable alkenylboronates and the requirement of a 2-hydroxy substituted benzhydryl alcohol limits this methodology.
Scheme 16: Enantioselective addition of boronates to benzhydryl alcohols and ethers catalyzed by chiral biphenols

Although methods for the alkenyl- and alkynylation of benzhydryl alcohols under metal-free conditions are known, an operationally simple method, which avoids the use of n-BuLi, the necessity to pre-form unstable boron dihalide intermediates and avoid the use of unstable starting materials has not been developed. Furthermore, narrow substrate scopes for a number of these methods is observed.

1.3.1.3 METAL-FREE REACTION OF BENZHYDRIUM ION AND ORGANOTRIFLUOROBORATE

In 2012, Mayr and coworkers conducted a study which looked at determining the relative nucleophilicity of organoboron compounds in comparison with related nucleophiles\(^{[4a]}\). In this paper, they were able to show a single example of a pre-formed benzhydrylium carbocation reacting with a single potassium 5-methylfuran-2-yltrifluoroborate in the absence of a catalyst (Scheme 17).
1.4 α-FUNCTIONALIZED CYCLIC ETHER SCAFFOLDS

In addition to benzhydryl scaffolds, application of a Brønsted acid-catalyzed reaction of organotrifluoroborates towards the synthesis of ether scaffolds was also of interest. Ethers are an important functional group in organic chemistry as they are found among several bioactive compounds and pharmaceutical agents[30]. Tetrahydrofuran (THF) and tetrahydropyran (THP) rings are being increasingly observed in structures of new bioactive compounds and natural products[31]. Additionally, several bioactive molecules which contain α-functionalized cyclic ethers are known[32] (Figure 4).

![Figure 4: Bioactive molecules which contain α-functionalized cyclic ethers](image)

1.4.1 METHODS FOR THE SYNTHESIS OF α-FUNCTIONALIZED TETRAHYDROFURANS AND TETRAHYDROPYRANS

C-glycosides are present in a number of natural products and enzymatically stable analogs of pharmaceutical importance. As a result, a number of protocols for their preparation has increased over the past several decades[33]. Namely, the carbon-carbon glycosidic bond shows an increased stability toward chemical and/or enzymatic hydrolysis. Thus, the development of new methodologies for the creation of anomeric carbon-carbon
bonds is of interest. Specifically, the synthesis of 2-alkenyl and 2-alkynyl tetrahydrofurans and tetrahydropyrans have been explored.

Ley and coworkers have shown that a direct substitution of 2-benzenesulfonyl cyclic ethers occurs by treatment with the corresponding organozinc reagents to afford alkynylated products (Scheme 18). Both 2-(phenylsulfonyl)tetrahydropyran and 2-(phenylsulfonyl)tetrahydrofurans participated in the transformations[34].

![Scheme 18: Direct substitution of 2-benzenesulfonyl cyclic ethers using organozinc reagents](image)

Later in 2004, Ley and coworkers demonstrated that anomeric oxygen to carbon rearrangements of alkynylstannane derivatives of furan and pyran rings occur in the presence of a BF₃·OEt₂ Lewis acid (Scheme 19). This rearrangement resulted in the formation of the corresponding carbon linked alkynol products[35].

![Scheme 19: Rearrangements of alkynylstannane derivatives of furan and pyran rings catalyzed by BF₃·OEt₂](image)

In 1996, Fuchs and coworkers showed that the alkynylation of C-H bonds occurs via reaction of THF or THP with acetylenic triflones[36]. Alkynylated furan and pyran derivatives were obtained in good to excellent yields (Scheme 20). The C-H functionalization protocol was later extended to the domain of olefins using THF and vinyl triflones[37].
Scheme 20: Alkynylation of C-H bonds via reaction with acetylenic triflones

Several additional methods for the synthesis of 2-alkenyl and 2-alkynyl tetrahydrofurans and tetrahydropyrans have been explored. However, all of these methods occur through tetrahydrofuranyl and tetrahydropyranyl α-oxy radical intermediates similar to the method described above\[^{38}\].

Also, Anderson and coworkers were able to prepare 2-alkynyl tetrahydrofurans and tetrahydropyrans from cyclic and acyclic carbonates (Scheme 21). These cyclizations were achieved through the use of palladium catalysts\[^{39}\].

Scheme 21: Palladium-catalyzed cyclizations of cyclic and acyclic carbonates

In addition, when looking at methods for the synthesis of 2-alkenyl and 2-alkynyl tetrahydrofurans and tetrahydropyrans, the use of boron-based compounds is limited. Namely, Hall and coworkers employed a boronic acid catalysis approach for the direct
cyclization of free allylic alcohols (Scheme 22). Mechanistic studies suggested that complete or near-complete ionization of allylic alcohols into allylic carbocation intermediates occurs when exposed to the boronic acid catalyst\[^{[40]}\].

![Scheme 22](image)

**Scheme 22: Boronic acid catalyzed heterocyclizations of allylic alcohols**

Additionally, Liu and coworkers illustrated that organotrifluoroborates and trityl ions can be used for the C-H functionalization of THF (Scheme 23). Trityl salts were generated by exposing trityl chlorides to GaCl\(_3\) Lewis acid. This method was tolerant to alkanyl, alkynyl and aryltrifluoroborates. Mechanistic studies suggested that for THF and other saturated ethers, the trityl ion functioned as a hydride acceptor\[^{[41]}\].

![Scheme 23](image)

**Scheme 23: C-H functionalization of THF using trifluoroborates and trityl ions**

Although there are several protocols, which describe the preparation of these desired products, the necessity to use expensive metal catalysts, stoichiometric amounts of Lewis acid as well as sensitive reagents is what hinders the practicality of these methods. As a result, we wanted to develop an operationally simple protocol involving a metal-free transformation of organotrifluoroborates.
1.4.2 METAL-FREE REACTIONS OF TRIFLUOROBORATES (CONTINUED)

In addition to the methods described in Section 1.1.2 regarding metal-free reactions of trifluoroborates, our group recently developed a Brønsted-acid catalyzed methodology for the alkynylation of acetals and ketals with alkynyl trifluoroborates (Scheme 24). After the findings, which are described in the following Chapter 3 were obtained[^42], this protocol for the preparation of propargylic ethers was developed as an extension of the substrates, which reacted under similar Brønsted acid-catalyzed conditions[^43]. Similar to Lewis acid catalyzed methods shown by Bode[^13,14] and Stefani[^15], this Brønsted acid-catalyzed transformation was also proposed to occur through an oxocarbenium ion intermediate.

![Scheme 24: Brønsted acid-catalyzed alkynylation of acetals and ketals with alkynyl trifluoroborates](image)

In showing that the alkynylation of acetals and ketals occurs via a Brønsted acid catalyst, we wanted to probe at similar scaffolds, which could undergo an analogous transformation. Therefore, we envisioned that the synthesis of α-functionalized ethers could be possible if the described methodology could be extended to tetrahydrofuranyl and/or tetrahydropyranyl acetals.
2. EXPERIMENTAL METHODS

2.1 GENERAL SYNTHETIC METHODS

All reactions were set up in 2 dram glass vials at room temperature under air. Unless otherwise noted, all other reagents and materials were obtained from commercial suppliers and used without further purification. Potassium trifluoroborate salts were synthesized according to published procedures\cite{11,15,42,43,44}. Reaction progress was monitored via thin layer chromatography (TLC) on silica gel (60 Å) with visualization using ultraviolet light (254 nm) and by staining with potassium permanganate (KMnO₄) or phosphomolybdic acid (PMA). NMR characterization data was collected at 25°C on an Oxford AS400 NMR as solutions in deuterated solvents (CDCl₃, acetone-d₆ and DMSO-d₆ obtained from Cambridge Isotope Laboratories, Inc.). ¹H and ¹⁹F NMR spectra were collected at 400 and 376 MHz, respectively, while ¹³C {¹H} and ¹¹B {¹H} NMR spectra were collected at 100 and 128 MHz, respectively. Chemical shifts are expressed in ppm values. IR spectra were recorded on a Bruker ALPHA-P FTIR spectrometer using a platinum ATR with a diamond ATR crystal. Spectra are reported in terms of frequency of absorption (cm⁻¹) and only partial data is provided. Melting points were measured with a melting point apparatus and are uncorrected. High resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI), electron impact ionization (EI), direct analysis in real time (DART) ion source, and time-of-flight (TOF) mass analysis. Automated flash chromatography was conducted using a Biotage Isolera flash chromatography system using silica gel (60 Å, low acidity, obtained from SiliCycle) and reagent grade solvents.
2.2 SYNTHESIS OF POTASSIUM ALKYNYLTRIFLUOROBORATE SALTS

Potassium alkynyltrifluoroborate salts were prepared according to a known procedure\cite{15}.

\[
\begin{align*}
\text{R} & \equiv \equiv \text{H} \quad \xrightarrow{1. \text{n-BuLi or } t\text{-BuLi, } -70^\circ\text{C, 1h}} \quad \xrightarrow{2. \text{B(OMe)}} \equiv \equiv \text{BF}_3\text{K} \\
& \quad \xrightarrow{3. \text{aq. } KHF_2, -20^\circ\text{C to rt, 2 h}} \quad \text{1}
\end{align*}
\]

**General Procedure 1:** To a solution of the indicated terminal alkyne (1.0 equiv.) in dry THF at \(-70^\circ\text{C}\) under argon atmosphere was added either \(n\)-BuLi or \(t\)-BuLi (1.0 equiv.) dropwise, and the solution was stirred for 1 h at this temperature. Trimethylborate (1.5 equiv.) was added dropwise at \(-60^\circ\text{C}\). The solution was stirred at this temperature for 2 h. A saturated aqueous solution of \(KHF_2\) (6.0 equiv.) was added at \(-20^\circ\text{C}\). The mixture was allowed to stir for 1 h at \(-20^\circ\text{C}\) and for 1 h at room temperature. The solvent was removed under reduced pressure, and the resulting solid was placed under vacuum overnight to remove any remaining water. The solid was washed several times with hot acetone (\(4 \times 10\) mL), which was collected and concentrated to a volume of \(\sim 10\) mL. The product was precipitated with diethyl ether (30 mL) and cooled to \(4^\circ\text{C}\) to complete precipitation. The crystalline solids were collected by gravity filtration and further dried under vacuum to afford alkynyltrifluoroborate salts \(1\text{a-k}\) (Figure 5).
Figure 5: Potassium alkynyltrifluoroborate salts
2.3 SYNTHESIS OF POTASSIUM (E)-ALKENYLTRIFLUOROBORATE SALTS

Potassium (E)-alkenyltrifluoroborate salts were prepared according to a procedure modified from Molander and coworkers\textsuperscript{[44]}.

\[
\text{R} = \text{BF}_3\text{K} \quad \text{OH} \quad \text{OH} \quad \text{KHF}_2 \text{ (aq.)} \quad \text{Et}_2\text{O, rt, 3h} \quad \text{R} = \text{BF}_3\text{K}
\]

**General Procedure 2:** To a solution of the indicated boronic acid (1.0 equiv.) in Et\(_2\)O (6 mL) was added KHF\(_2\) (2.8 equiv.), followed by H\(_2\)O (2.7 mL) over a period of 30 min. After stirring at rt for 3 h, the solvent was removed under reduced pressure, and the resulting solid was placed under vacuum overnight to remove any remaining water. The solid was washed several times with hot acetone (4 × 10 mL), which was collected and concentrated to a volume of ∼10 mL. The product was precipitated with diethyl ether (30 mL) and cooled to 4 °C to complete precipitation. The crystalline solids were collected by gravity filtration and further dried under vacuum to afford (E)-alkenyltrifluoroborate salts 2a-d (Figure 6).

---

**Figure 6:** Potassium (E)-alkenyltrifluoroborate salts
2.4 SYNTHESIS OF BENZHYDRYL ALCOHOLS

**General Procedure 3:** A solution of the indicated benzaldehyde (1.0 equiv.) in dry THF was treated with the indicated phenylmagnesium bromide solution (1.1-4.0 equiv.) at 0 °C. After addition was complete, the mixture was allowed to stir at room temperature for 30–120 min. The reaction was quenched with aqueous 1 M HCl solution and extracted with 50 mL of EtOAc. The organic layer was washed with water (3 × 30 mL) followed by brine (1 × 25 mL). The organic layer was dried with MgSO₄ and concentrated. Purification by flash chromatography with hexanes/ethyl acetate afforded products 3a-i (Figure 7).

![Synthesis Diagram](image)

**Figure 7:** Benzhydryl alcohols
2.5 SYNTHESIS OF INTERNAL ALKENES AND ALKYNES

General Procedure 4: In a 2 mL vial containing a stir bar, the indicated benzhydrol alcohol (1.0 equiv.) and potassium trifluoroborate salt (1.0 equiv.) were added followed by addition of anhydrous acetonitrile (0.3 mL). HBF$_4$·OEt$_2$ (1.3-2.6 equiv.) was added dropwise, and the reaction was allowed to stir at room temperature for 15 min. The reaction was quenched with water and extracted in 20 mL of ethyl acetate. The organic layer was washed with water (3 × 15 mL) followed by brine (1 × 10 mL). The organic layer was dried with MgSO$_4$ and concentrated. The products were purified by flash chromatography with hexanes/ethyl acetate. In the cases where a CH$_3$CN/hexanes extraction was required, the product was solubilized in 5 mL of anhydrous acetonitrile in a 20 mL vial. Then, 1 mL of hexanes was added, forming a bilayer. The two layers were thoroughly mixed and then allowed to settle. The bottom acetonitrile layer was then removed and concentrated to afford the product. In the cases where a pentane wash was required, in a minimum of chloroform, the product was washed with 5 mL of pentane on a pipet column and eluted with diethyl ether to afford the product.
2.6 PROCEDURE FOR THE DEMETHYLATION OF 7

Phenol 8 was prepared according to a procedure modified from Hanson and coworkers\textsuperscript{[45]}.

![Chemical structure of 7 and 8](image)

**General Procedure 5**: A solution of the indicated ortho-methoxy-substituted product 7 (1.0 equiv.) in dry DCM (0.1 M) was treated with boron tribromide solution (3.0 equiv.) at 0 °C. After addition was complete, the mixture was allowed to stir at room temperature for 30 min. The reaction was quenched with water and extracted with 20 mL of EtOAc. The organic layer was washed with water (3 × 15 mL) followed by brine (1 × 10 mL). The organic layer was dried with MgSO\textsubscript{4} and concentrated. The product was purified by flash chromatography with hexanes/ethyl acetate and concentrated. Further purification via a CH\textsubscript{3}CN/hexanes extraction afforded the desired demethylated product 8.
2.7 CYCLIZATION OF INTERNAL ALKYNE 8

Benzofuran 9 was prepared according to a procedure by Luo and coworkers\textsuperscript{[46]}.

![Chemical structure]

**General Procedure 6:** The indicated ortho-hydroxy-substituted product 8 (1.0 equiv.) was dissolved in anhydrous dioxane. Then, potassium tert-butoxide (2.0 equiv.) was added, and the reaction mixture was stirred at ambient temperature for 1.75 h. The reaction solution was then diluted with DCM (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with DCM (2 × 10 mL). The combined organic phase was washed with water (3 × 15 mL) and brine (1 × 10 mL). The organic layer was dried with MgSO\textsubscript{4} and concentrated. The product was purified by flash chromatography with hexanes/diethyl ether and concentrated. Further purification via a CH\textsubscript{3}CN/hexanes extraction afforded the desired demethylated product 9.
2.8 SYNTHESIS OF 2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS AND TETRAHYDROPYRANS

General Procedure 7: In a 2 dram vial containing a stir bar, the indicated potassium trifluoroborate salt (1.5 equiv.) was added at room temperature followed by the addition of anhydrous acetonitrile (C = 0.1 M). The indicated THF or THP (1.0 equiv.) was then added to the solution, and the solution was stirred at -10°C for 5 minutes. HBF₄·OEt₂ (1.5 equiv.) was added to the stirring solution at -10°C. The solution was stirred at this temperature for 15 minutes. The reaction was quenched with water and extracted with 20 mL of ethyl acetate. The organic layer was washed with water (3 x 15 mL) followed by brine (1 x 10 mL). The organic layer was dried with MgSO₄ and concentrated. The crude product was purified by flash chromatography and concentrated. In the cases where a CH₃CN/hexanes extraction was required, the product was solubilized in 5 mL of acetonitrile and 1 mL of hexanes was added forming a bi-layer. The two layers were thoroughly mixed and cooled to 0°C in an ice bath to promote separation. The bottom acetonitrile layer was then removed and the extraction was performed again on the same hexanes layer. The acetonitrile extractions were then concentrated to afford products 10-12.
3. METHODOLOGY DEVELOPMENT FOR THE ALKENYLATION AND ALKYNYLATION OF BENZHYDRYL ALCOHOLS WITH ORGANOTRIFLUOROBORATES

3.1 METHODOLOGY DEVELOPMENT

3.1.1 OPTIMIZATION OF REACTION CONDITIONS

Our initial efforts were focused on the preparation of secondary alkylacetylene 4a from potassium phenylacetylenetrifluoroborate salt 1a and commercially available diphenylmethanol (Table 1). After careful consideration, we chose to use tetrafluoroboric acid (HBF₄) as the catalyst. With a pKₐ of 0.5 in water, this Brønsted acid has been shown to be strong enough to promote the formation of benzhydrylium carbocations from diarylmethanols. Additionally, this Brønsted acid has a non-nucleophilic counter ion (BF₄⁻) which will not react with the benzhydrylium carbocation once it is generated.

We initially began with a screen of solvents and found that the desired product 4a was not formed in DCM (Table 1, entry 1) and DMSO (Table 1, entry 2). Alternatively, we found that when CH₃CN was used as the solvent, the reaction yielded alkyne 4a solely in 35% yield (Table 1, entry 3).

We then focused our attention on determining the optimal equivalents of each starting material. We found that a slight excess of either diphenylmethanol (Table 1, entry 4) or potassium phenylacetylenetrifluoroborate salt (Table 1, entry 5) resulted in the formation of an inseparable mixture of product 4a and the undesired dibenzhydryl ether byproduct 13.
Table 1: Optimization of Conditions for the Preparation of Secondary Alkylacetylene 4a

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Benzhydrol (equiv.)</th>
<th>BF₃K (equiv.)</th>
<th>Acid (equiv.)</th>
<th>Acid (equiv.)</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>Ratio 4a:13</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>HBF₄·OEt₂</td>
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<td>DCM</td>
<td>trace</td>
<td></td>
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<tr>
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<td>1.0</td>
<td>HBF₄·OEt₂</td>
<td>1.6</td>
<td>DMSO</td>
<td>trace</td>
<td></td>
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<td>1.0</td>
<td>HBF₄·OEt₂</td>
<td>1.0</td>
<td>CH₃CN</td>
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<td>1:0</td>
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<td>1.0</td>
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<td>CH₃CN</td>
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<td>1.0</td>
<td>1.2</td>
<td>HBF₄·OEt₂</td>
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<td>CH₃CN</td>
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<td>1.0</td>
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<td>CH₃CN</td>
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<td>41</td>
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<td>1:0</td>
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<tr>
<td>12</td>
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<td>4.0 M HCl</td>
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<td>CH₃CN</td>
<td>trace</td>
<td></td>
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<td>1.0</td>
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<td>CH₃CN</td>
<td>trace</td>
<td></td>
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<td>14ᵇ</td>
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<td>1.0</td>
<td>HBF₄·OEt₂</td>
<td>1.6</td>
<td>CH₃CN</td>
<td>36</td>
<td>1:0</td>
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<tr>
<td>15ᶜ</td>
<td>1.0</td>
<td>1.0</td>
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<td>CH₃CN</td>
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</tr>
<tr>
<td>16ᵈ</td>
<td>1.0</td>
<td>1.0</td>
<td>HBF₄·OEt₂</td>
<td>1.6</td>
<td>CH₃CN</td>
<td>34</td>
<td>1:0</td>
</tr>
<tr>
<td>17ᵉ</td>
<td>1.0</td>
<td>1.0</td>
<td>HBF₄·OEt₂</td>
<td>1.6</td>
<td>CH₃CN</td>
<td>25</td>
<td>20:1</td>
</tr>
</tbody>
</table>

ᵃThe ratio has been determined by NMR analysis of crude reaction mixtures. ᵇReaction run at 0°C. ᶜReaction run at 40°C. Product and unidentified by-product synthesized. ᵇAnhydrous conditions. ᵈ1.5 equiv. H₂O added.
Next, we looked at the effect of the acid catalyst loading on the reaction. Initially, we observed that using a substoichiometric amount of HBF₄ resulted in the formation of a 50/50 mixture of 4a and 13 (Table 1, entry 6). By gradually increasing the amount of HBF₄, we observed that the yield of the desired product 4a was increasing, and that the formation of the undesired dibenzhydryl ether byproduct 13 was suppressed (Table 1, entries 7, 8). These observations were consistent with the findings that increasing the equivalents of HBF₄ results in inhibition of the formation of the dimer byproduct 13\(^{[48]}\). In further increasing HBF₄ to 1.6 equivalents, we obtained a 41% yield of 4a (Table 1, entry 9). Additional gradual increases in the amount of HBF₄ resulted in a decrease in product formation (Table 1, entries 10-11).

Efforts were then focused on seeing if alternative Brønsted acids could catalyze the reaction. HCl was initially tried since it could be purchased as an anhydrous solution in dioxane. This was important since the HBF₄ acid was purchased as an anhydrous complex with diethyl ether. However, only trace amounts of product was formed when HCl was used (Table 1, entry 12). Work-up NMR indicated that chlorodiphenylmethane emerged as a byproduct due to the competing reaction of the nucleophilic Cl\(^-\) anion with the benzhydrylum carbocation. Consequently, we realized that having an acid with a non-nucleophilic counter ion was important. As a result, we then wanted to see if HSbF₆·6H₂O could catalyze the reaction. This acid, like HBF₄, also contains a non-nucleophilic counter ion (SbF₆\(^-\)) which should not react with the benzhydrylum carbocation. However, this acid also only allowed for the formation of trace amounts of product 4a to form (Table 1, entry 13). In this case, however, the starting material was not consumed. Neither the product nor the byproduct were observed.

With the tentatively optimized conditions at hand (Table 1, entry 9), we then focused our attention on manipulation of other reaction variables (Table 1, entries 14-17). With the reaction occurring within fifteen minutes at room temperature, we wanted to see the effect of reduced temperature. We observed that running the reaction at 0°C (Table 1, entry 14) resulted in the disappearance of diphenylmethanol within thirty minutes, however, the yield decreased by 5%. We then wanted to see the effect of running the reaction at increased temperature. When the reaction was conducted at 40°C (Table 1, entry
15), diphenylmethanol starting material disappeared within fifteen minutes, however, this resulted in the formation of an inseparable mixture of product 4a and a new unidentified byproduct. Interestingly, the yield decreased from 41% to 34% when the reaction flask was dried and the reaction was conducted under argon (Table 1, entry 16). We then looked to see what the effect was of adding a controlled quantity of water. The yield decreased dramatically to 25% of product 4a and trace amounts of the dibenzhydryl ether byproduct 13 was formed when 1.5 equivalents of water was introduced (Table 1, entry 17).

### 3.1.2 INVESTIGATION INTO THE ORDER OF ADDITION OF REAGENTS

The order of addition of reagents in this method was deemed to be very important. Initially, 4-methylbenzhydrol and potassium phenylacetylenetrifluoroborate salt 1a were pre-stirred in acetonitrile for one minute at room temperature. No evidence of a reaction between the two starting materials was observed on TLC in the absence of the acid catalyst. Once HBF$_4$ was added, the reaction solution turned from a colourless transparent solution to bright yellow solution, which was translucent. Product formation was clearly evident on TLC. When the order of addition was changed, the reaction did not result in significant product formation (Scheme 25).

---

**Scheme 25: Analyzing the order of addition of reagents**
When potassium phenylacetylenetrifluoroborate salt and HBF$_4$ were pre-mixed, which was followed by the addition of 4-methylbenzhydrol, the reaction resulted in trace amounts of product 4b. Several byproducts were observed on TLC. It turned out that potassium phenylacetylenetrifluoroborate salt 1a decomposed in the presence of HBF$_4$. This was confirmed by a set of NMR studies (Figure 8 and Appendix III). Firstly, in deuterated acetonitrile solvent (CD$_3$CN), potassium phenylacetylenetrifluoroborate salt 1a shows a signal at -134.90 ppm in a $^{19}$F NMR (Figure 8, NMR A). HBF$_4$ shows a signal at -150.49 ppm (Figure 8, NMR B). Then, potassium phenylacetylenetrifluoroborate salt 1a and HBF$_4$ were mixed in CD$_3$CN in an NMR tube and a $^{19}$F NMR of the mixture was taken immediately. We observed that the fluorine peak of the potassium phenylacetylenetrifluoroborate salt 1a had disappeared but that the fluorine peak for HBF$_4$ was still observed (Figure 8, NMR C). From looking at the proton and carbon NMRs of this reaction mixture, characteristic peaks from phenylacetylene were observed (see Appendix III for additional spectra). Therefore, we propose that when potassium phenylacetylenetrifluoroborate salt is exposed to HBF$_4$ in the absence of 4-methylbenzhydrol, protodeboronation occurs. As a result of the decomposition, the reaction does not take place once 4-methylbenzhydrol is added to the reaction mixture since only trace amounts of 4b were observed.

<table>
<thead>
<tr>
<th>NMR A</th>
<th>NMR B</th>
<th>NMR C</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="NMR A" /></td>
<td><img src="image" alt="NMR B" /></td>
<td><img src="image" alt="NMR C" /></td>
</tr>
<tr>
<td>phenylacetylene-trifluoroborate 1a</td>
<td>HBF$_4$·OEt$_2$</td>
<td>HBF$_4$·OEt$_2$ + trifluoroborate 1a</td>
</tr>
</tbody>
</table>

Figure 8: $^{19}$F NMR study of potassium phenylacetylenetrifluoroborate 1a and HBF$_4$·OEt$_2$ in CD$_3$CN
Similarly, when potassium phenylacetylenetri fluoroborate 1a was added to a mixture of 4-methylbenzhydrol and HBF₄, only trace amounts of desired product 4b were observed on TLC (Scheme 25). After leaving the reaction for several hours, a significant amount of 4-methylbenzhydrol was still observed on TLC and only a faint product spot had appeared. After no change in the TLC after several hours, this illustrated that pre-mixing 4-methylbenzhydrol and HBF₄ was not advantageous.

Therefore, we found that it was imperative to add the HBF₄ catalyst as the last reagent in order for significant formation of the desired product.

### 3.2 PROPOSED MECHANISTIC PATHWAY

Illustrated in the following Scheme 26 is our proposed mechanistic pathway for the formation of internal alkenes and alkynes. We suggest that a Brønsted acid would protonate the hydroxyl group of the benzhydryl alcohol (I). Subsequently, the protonated alcohol, will dissociate in the form of a water molecule from the diphenylmethane compound (II) thus generating the benzhydridium ion (III). The nucleophilic trifluoroborate present in the solution will then react with the electrophilic center, thus forming the final product (IV).

![Scheme 26: Proposed mechanistic pathway for the preparation of internal alkenes and alkynes](image-url)
3.3 RESULTS AND DISCUSSION

With the developed reaction conditions at hand, our next step was to look at the scope of benzhydryl alcohols and organotrifluoroborate salts that are capable of participating in the reaction.

3.3.1 REACTIONS OF PHENYLACETYLENETRIFLUOROBORATE SALT WITH BENZHYDRYL ALCOHOLS

Initial investigation into the substitution effects revealed that benzhydryl alcohols containing electron-donating substituents resulted in higher yields of the desired products as compared to when electron-withdrawing substituents were present (Figure 9). As previously discovered, when unsubstituted benzhydryl was used, product 4a was obtained in 41% yield. Furthermore, the yield of 4b was 67% when an electron-donating 4-methyl substituent was present. The reaction exhibited mild sensitivity to the steric hindrance. Electron-donating methyl group in the 2-position resulted in modest 51% yield of product 4c.
Figure 9: Reactions of phenylacetylenetrifluoroborate salt with benzhydryl alcohols. 

*Using 1.3 equiv of HBF₄

The yield further increased when stronger electron-donating 4-methoxy group was present. Product 4d was obtained in excellent 87% yield. Notably, a scale-up reaction afforded 0.20 g of 4d with a yield erosion of only 10%. Product 4e was obtained in an even higher 91% yield when two methoxy groups were present in the para-positions. Conversely, a low 19% yield of product 4f was obtained when an electron-withdrawing 4-
chloro group was present. We propose that destabilization of the carbocation intermediate occurs in the presence of electron-withdrawing groups. As a result, several unidentified byproducts were observed.

Next, we then wanted to explore into whether the destabilizing electron-withdrawing effect of one substituent in the 4-position could be off-set if an electron-donating group was present in the 4’-position. When (4-chlorophenyl)(4-methoxyphenyl)methanol was used, product 4g was obtained in excellent 84% yield. Seemingly, the negative effect of an electron-withdrawing group can be overcome by applying this method.

Furthermore, we were pleased to see that we were able to expand the scope to unprotected protic functional groups. Free phenol- and amide-containing substrates afforded products 4h and 4i in 66 and 61% yields, respectively. When a carboxylic acid functional group was present, modest 42% yield of 4j was observed. However, we proposed that the carboxylic acid moiety could act as a source of protons during the reaction. As a result, we thought that in combination with the HBF₄ acid catalyst, excessive amounts of acid present could have been responsible for the poor yield of 4j. Consequently, we found that the yield increased to 62% when the amount of HBF₄ was reduced to 1.3 equivalents.
Next, we looked to investigate into the scope of potassium alkynyltrifluoroborate salts that were tolerant to this method (Figure 10). A wide range of phenylacetylenetrifluoroborate salts that contained trifluoromethyl, chloro and fluoro functional groups acted as sufficient coupling partners to afford the desired products 5a-5e in excellent yields. Notably, product 5e was obtained in 82% yield when an unprotected aldehyde group was present on the benzhydryl alcohol. Furthermore, unsubstituted biphenyl- and naphthylacetylenetrifluoroborates afforded the desired products (5f-5h) in good yield.

We then looked to examine other substituents which were tolerant to the methodology. More specifically, we were able to expand the substrate scope to benzhydryl alcohols, which contained an amine functional group. The presence of a dimethylamine functional group resulted in a modest 53% yield of 5i. In the presence of acid, the basic amine functional group could undergo protonation. As a result, we decided to increase the acid-to-substrate ratio with the expectation of obtaining an increased product yield. With the addition of 2.6 equivalents of HBF$_4$ (one equivalent more than the usual acid loading), we were able to improve the yield of 5i to 61%. We then applied the same conditions to a benzhydryl alcohol, which contained a Boc-protected amine. We obtained a 51% yield of the deprotected product 5j. This was to be expected since the Boc group is stable towards most bases and nucleophiles, however, it is acid-labile.

Hexynyltrifluoroborate salt was a good coupling partner in addition to the previously observed phenylacetylenetrifluoroborate derivatives. Desired product 5k was formed in 73% yield.
Figure 10: Reactions of various alkynyltrifluoroborates with benzhydryl alcohols. aUsing 2.6 equivalents of HBF₄. For 5j, Boc-protected amine was used as the starting material.
3.3.3 REACTIONS OF TRANS-STYRYLTRIFLUOROBORATES WITH BENZHYDRYL ALCOHOLS

To our delight, we observed that potassium alkenyl trifluoroborate salts readily participated in the developed methodology (Figure 11). More specifically, alkenyl trifluoroborates such as potassium trans-styryl and 2-(3-fluorophenyl)vinyl trifluoroborate salts afford the desired products in good to excellent yields (6a-6e). Consistent with our previous findings, increasing the amount of HBF$_4$ from 1.6 to 2.6 equivalents in the presence of a dimethylamine substituent translated to a yield increase of $6d$ from 67% to 84%. As well, decreasing the amount of HBF$_4$ from 1.6 to 1.3 equivalents in the presence of a carboxylic acid containing benzhydryl alcohol resulted in a modest yield increase of $6e$ from 71% to 77%.

Figure 11: Reactions of trans-styryltrifluoroborates with benzhydryl alcohols. Using $^a$2.6 or $^b$1.3 equiv of HBF$_4$. 
3.3.4 UNSUCCESSFUL TRIFLUOROBORATE SALT COUPLING PARTNERS

When looking into the substrate scope of organotrifluoroborates, a few did not prove to be successful coupling partners (Figure 12). More specifically, potassium phenylacetylenetri fluoroborate salts that contained para-methoxy (1b) or para-butyl (1c) groups did not react to form the desired products. Instead, the reactions resulted in the consumption of the benzhydrol starting material and subsequent formation of multiple unidentified byproducts. This illustrates that the method is not tolerant to phenylacetylenetri fluoroborates containing electron donating groups. This is contrary to what was observed in the above substrate scope, whereby, electron withdrawing halide groups on the phenylacetylenetri fluoroborates proved to be successful coupling partners. As a result, electron-rich trifluoroborates were poor coupling partners.

![Figure 12: Organotrifluoroborates that did not participate in the developed methodology](image)

With hopes to expand the substrate scope to aryl trifluoroborates, we attempted the coupling reaction with potassium phenyl trifluoroborate salt. However, these efforts were unproductive as multiple byproduct spots were observed on a TLC plate. Moreover, benzhydrol starting material was still present after leaving the reaction for several hours. Due to no change in the concentration of starting material estimated by TLC, potassium phenyl trifluoroborate salt was likely decomposed by HBF₄.

Lastly, we observed that alkenyl trifluoroborate salts proved to be successful coupling partners in the developed methodology (Figure 11). Therefore, we wanted to see
if potassium vinyltrifluoroborate salt would react to afford the desired product. However, similar results were observed as in the case of potassium phenyltrifluoroborate, whereby, multiple byproducts were formed and benzhydrol starting material was still present after several hours.

### 3.3.5 APPLICATION OF THE DEVELOPED METHODOLOGY TO THE SYNTHESIS OF BENZOFURAN 9

To illustrate the utility of the established method, we developed a preparation of synthetically useful benzofurans. Annulations of ortho-propargyl phenols have been shown to occur in the presence of bases to form 2,3-disubstituted benzofurans\[^{[46]}\]. We decided to apply this cyclization procedure to a product synthesized via our methodology. Our retrosynthetic analysis gave rise to a three-step approach illustrated in the following Scheme 27.

**Scheme 27: Retrosynthetic analysis towards the synthesis of benzofuran**

Initially, we proposed that the reaction of 2-hydroxybenzaldehyde with 4-methoxyphenylmagnesium bromide would result in the synthesis of 2-(hydroxy(4-
methoxyphenyl)methyl)phenol (V). This benzhydryl alcohol could then react with phenylacetylenetriﬂuoroborate salt 1a under the developed methodology to afford ortho-propargyl phenol (VI). After application of the known cyclization procedure[46], benzofuran (VII) should be obtained.

However, issues arose when trying to conduct the first step of the synthesis (Scheme 28). More specifically, when the reaction was initially run with 2.0 equivalents of 4-methoxyphenylmagnesium bromide, the 2-hydroxybenzaldehyde starting material was not completely consumed over the course of the reaction. However, a product spot had developed and was isolated after observing that the reaction was no longer progressing. NMR analysis showed that product had formed, however, inseparable byproducts co-eluted with the benzhydryl alcohol. A final attempt at the reaction resulted in the use of 3.0 equivalents of 4-methoxyphenylmagnesium bromide with the intentions of it reacting completely with 2-hydroxybenzaldehyde. Although complete consumption of 2-hydroxybenzaldehyde was observed, inseparable byproducts still contaminated the benzhydryl alcohol. As a result, we hypothesized that the hydroxyl group from 2-hydroxybenzaldehyde interfered during the reaction with the Grignard reagent, thus resulting in the formation of byproducts.

![Scheme 28: Unsuccessful synthesis of 2-(hydroxy(4-methoxyphenyl)methyl)phenol](image)

We then had to devise a new route towards the synthesis of 2,3-benzofurans. The 2-hydroxyl group is imperative for the cyclization to occur in the final step, however, we envisioned that demethylation of a 2-methoxy group could be a viable alternative. As a result, we looked to apply a Grignard reaction to 2-methoxybenzaldehyde as an alternative (Scheme 29).
Scheme 29: Application of the developed methodology to the synthesis of benzofuran 9

Successful reaction between 2-methoxybenzaldehyde and p-tolylmagnesium bromide resulting in benzhydryl alcohol 3i in 79% yield. Applying the developed methodology to benzhydryl alcohol 3i using phenylacetylene trifluoroborate salt 1a and HBF₄ catalyst afforded compound 7 in 67% yield. The additional step involved the demethylation[45] of 7 using boron tribromide to afford ortho-propargyl phenol 8 in 73% yield. Applying the potassium tert-butoxide cyclization procedure by Luo and coworkers[46] to compound 8 resulted in 2,3-disubstituted benzofuran 9 in 47% yield.
4. METHODOLOGY DEVELOPMENT FOR THE PREPARATION OF 2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS

4.1 SUBSTRATE SCOPE FOR THE SYNTHESIS OF 2-ALKENYL AND 2-ALKYNYL TETRAHYDROPYRANS

Recently, our group has also shown that acetals and ketals act as suitable starting materials under similar Brønsted acid-catalyzed conditions\cite{43}. This methodology has also been optimized for 2-methoxytetrahydropyran, a cyclic acetal substrate\cite{49}. Previously, compounds 10a and 10b were successful synthesized using this method\cite{49} (Figure 13). Phenylacetylenetrifluoroborate was a good coupling partner which resulted in the synthesis of 10a in excellent 82% yield. However, when trans-styryltrifluoroborate salt was used, product 10b was synthesized in poor 36% yield.

\[
\begin{align*}
\text{CH}_3\text{CN} & \quad -10^\circ\text{C}, 15 \text{ min.} \\
& \quad \text{HBF}_4\text{OEt}_2 (1.5 \text{ eq.}) \\
\text{R}^1 & \quad \text{BF}_3\text{K} (1.5 \text{ eq.}) \\
\text{(1.0 eq.)} & \quad \text{(1.5 eq.)} \\
\end{align*}
\]

\[
\begin{align*}
& \quad \text{OCH}_2\text{Me} \\
& \quad \text{(1 eq.)} \\
& \quad \text{R}^1\text{Me} \\
& \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
& \quad \text{Ph} \\
& \quad \text{(1 eq.)} \\
\end{align*}
\]

\[
\begin{align*}
& \quad \text{O} \\
& \quad \text{OMe} \\
\end{align*}
\]

\[
\begin{align*}
& \quad \text{F} \\
& \quad \text{O} \\
\end{align*}
\]

Figure 13: Reactions of organotri fluoroborates with 2-methoxytetrahydropyran
We then wanted to look into exploring other organotrifluoroborate salts, which were tolerant to this method. With poor results obtained from the use of an alkenyltrifluoroborate salt, we decided to focus on alkynyltrifluoroborates. We found that hexynyltrifluoroborate salt (1d) afforded 10c in excellent 84% yield which was comparable to when phenylacetylenetrifluoroborate was used. We then looked to pursue reactions with other phenylacetylenetrifluoroborate derivatives. However, these efforts only provided products 10d and 10e in meager 48% and 34% yields, respectively. Evidently, both electron-poor and electron-rich alkynyltrifluoroborates proved to be problematic towards the developed methodology, whereas, sterically unhindered neutral organotrifluoroborates (such as phenylacetylenetrifluoroborate and hexynyltrifluoroborate) were successful.

4.2 TETRAHYDROFURAN VS TETRAHYDROPYRAN

With the substrate scope of organotrifluoroborates and 2-methoxytetrahydropyran looking discouraging due to only two products being synthesized in excellent yield, we looked to determine the rationale behind this observation. In 1992, Woods and coworkers proposed the six-membered oxocarbenium ring transition state model[50]. Later, in 1999, Woerpel and coworkers developed a general model, which explains the stereoselective reactions involving five-membered-ring oxocarbenium ions[51].

\[
\begin{array}{c}
\text{proposed 6-membered oxocarbenium transition state} \\
\text{versus} \\
\text{proposed 5-membered oxocarbenium transition state}
\end{array}
\]

Figure 14: Transition state models for five- and six-membered oxocarbenium rings

In looking at the two transition states, it is evident that the 5-membered oxocarbenium ring transition state allows for easier approach of nucleophiles in terms of steric accessibility, as compared to the 6-membered oxocarbenium ion (Figure 14). Due to this revelation, we looked at applying the above methodology towards tetrahydrofuran cyclic acetals.
4.3 OPTIMIZATION REACTIONS FOR THE PREPARATION OF 2-ALKYNYLTETRAHYDROFURAN 11a

Initially, we looked to investigate into the efficiency of the HBF$_4$ Brønsted acid-catalyst towards the substitution of 2-ethoxytetrahydrofuran by using unsubstituted potassium phenylacetylenetrifluoroborate salt 1a as a model substrate (Table 2).

Table 2: Optimization of Conditions for the Synthesis of Tetrahydrofuran 11a

<table>
<thead>
<tr>
<th>Entry</th>
<th>BF$_3$K (equiv.)</th>
<th>Brønsted Acid</th>
<th>Brønsted Acid (equiv.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1</td>
<td>HBF$_4$·OEt$_2$</td>
<td>1.1</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>1.1</td>
<td>CF$_3$COOH</td>
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<td>trace</td>
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<tr>
<td>3</td>
<td>1.5</td>
<td>HBF$_4$·OEt$_2$</td>
<td>1.5</td>
<td>92</td>
</tr>
</tbody>
</table>

Previously, it has been found that when using acyclic acetals, a slight excess of 1.1 equivalents of both the organotrifluoroborate and HBF$_4$ acid catalyst afforded the desired products in good to excellent yields.$^{[43]}$ Therefore, we began our optimization with identical stoichiometry (Table 2, entry 1). We found that the substitution was achieved with 75% of the desired product 11a. Attempts to use trifluoroacetic acid, a Brønsted acid with a similar $pK_a$ to that of HBF$_4$, only resulted in trace amounts of product formation (Table 2, entry 2). However, increasing the amount of the organotrifluoroborate and HBF$_4$ catalyst to 1.5 equivalents resulted in higher yields when using the six-membered ring substrate, 2-methoxytetrahydropyran.$^{[49]}$ In applying these reaction conditions to 2-ethoxytetrahydrofuran, we were able to obtain product 11a in an excellent 92% yield (Table 2, entry 3). Since other reaction conditions, such as reaction temperature and solvent were already extensively studied in our previous methodologies.$^{[42,43,49]}$ we decided to explore the organotrifluoroborate substrate scope.
**4.4 PROPOSED MECHANISTIC PATHWAY**

Illustrated in the following Scheme 30 is our proposed mechanistic pathway for the formation of 2-alkenyl and 2-alkynyl tetrahydrofurans. We propose that initial protonation of 2-ethoxytetrahydrofuran occurs in the presence of the Brønsted acid catalyst. Subsequent elimination of ethanol from compound VII results in the formation of the 5-membered-ring oxocarbenium ion intermediate (IX). Reaction at the 2-position by nucleophilic organotrifluoroborate results in the generation of the desired product (X). With boron trifluoride being a byproduct, we propose that the in situ generation of ethanol is advantageous since it can act as a sequestering agent. Previously, McMillian and co-workers had to externally add hydrofluoric acid in order to sequester the boron trifluoride byproduct\[^{[18]}\].

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**Scheme 30: Proposed mechanistic pathway for the preparation of 2-alkenyl and 2-alkynyl tetrahydrofurans**
4.5 RESULTS AND DISCUSSION

With the developed reaction conditions at hand, our next step was to look at the scope of organotrifluoroborate salts that are capable of participating in the reaction.

4.5.1 REACTIONS OF ALKYNYLTRIFLUOROBORATE SALTS WITH 2-ETHOXYTETRAHYDROFURAN

Neutral naphthylacetylenetrifluoroborate salt proved to be a good coupling partner as product \(11b\) was obtained in a nearly quantitative yield (Figure 15). Both electron-rich \(p\)-butyl and \(p\)-methoxy substituted derivatives of phenylacetylenetrifluoroborate salt afforded products \(11c\) and \(11d\) in 93% and 78% yields, respectively. Remarkably, a scale-up reaction afforded 0.18 g of \(11c\) in essentially identical yield to the small-scale synthesis. The developed methodology was also tolerant to phenylacetylenetrifluoroborate derivatives, which contained electron-withdrawing substituents such as dichloro, fluoro and trifluoromethyl. Products \(11e-11g\) were obtained in good to excellent yields. Lastly, hexynyltrifluoroborate salt effectively participated in the reaction to afford 64% of product \(11h\).
To our delight, we discovered that potassium alkenyltrifluoroborate salts also participated in the reaction. Namely, potassium trans-styryltrifluoroborate salts afforded the desired products in moderate to excellent yields (Figure 16).

**4.5.2 REACTIONS OF STYRYLTRIFLUOROBORATE SALTS WITH 2-ETHOXYTETRAHYDROFURAN**

To our delight, we discovered that potassium alkenyltrifluoroborate salts also participated in the reaction. Namely, potassium trans-styryltrifluoroborate salts afforded the desired products in moderate to excellent yields (Figure 16).
When unsubstituted potassium trans-styryltrifluoroborate salt was used, product 12a was obtained in 74% yield. We then looked at the effect of aromatic substituents on the styryltrifluoroborates. We found that potassium 2-(3-fluorophenyl)vinyltrifluoroborate and potassium (E)-trifluoro(4-(trifluoromethyl)styryl)borate (2a) reacted similarly to the unsubstituted trans-styryltrifluoroborate salt. Desired products 12b and 12c were formed in 78% yield. Conversely, electron-rich trans-styryltrifluoroborate salt derivative containing a methyl group in the para-position only resulted in a modest 54% yield of product 12d. Additionally, product 12e was obtained in 72% yield from reaction of 2-ethoxytetrahydrofuran with potassium (E)-4-phenylstyryltrifluoroborate salt (2c). Lastly, when potassium trifluoro(1H-inden-2-yl)borate (2d) was used, product 12f was obtained in 79% yield.
5. CONCLUSIONS AND FUTURE WORK

A novel set of Brønsted acid-catalyzed reactions has been developed. At the outset, the preparation of internal alkenes and alkynes from benzhydryl alcohols and organotrifluoroborates has been shown\textsuperscript{[42]}. This transformation was shown to proceed rapidly in the presence of a HBF\textsubscript{4} Brønsted acid without the necessity to exclude air or moisture. Excellent atom economy was illustrated as organotrifluoroborates and benzhydryl alcohols were shown to react in a 1:1 ratio. Additionally, functional group tolerance superior to that of Lewis acid- and metal-catalyzed approaches was demonstrated. Namely, this method was tolerant to a variety of unprotected functional groups such as free hydroxyl, amide, aldehyde and carboxylic acid.

Additionally, Brønsted acid-catalyzed direct substitution of 2-ethoxytetrahydrofuran has been demonstrated\textsuperscript{[52]}. Specifically, alkenyl- and alkynylation of 2-ethoxytetrahydrofuran readily occurred in the presence of alkenyl- and alkynyltrifluoroborates and HBF\textsubscript{4}. Functionalized furans were obtained in moderate to excellent yields.

In future, further investigation into the scope of this reaction is of interest. We plan to look at other \textit{in situ} generated carbocations that could participate in this reaction, as well as additional nucleophiles tolerant to this method. Furthermore, application of this method towards C-glycosylation of sugars is of interest. Currently, direct C-glycosylation of organotrifluoroborates with glycosyl fluorides is known\textsuperscript{[16]}. However, this method requires the use of BF\textsubscript{3} OEt\textsubscript{2} Lewis acid. Furthermore, C-glycosylation of 5-membered ring sugars using alkenyltrifluoroborates was not shown. Therefore, development of a Brønsted acid-catalyzed method involving organotrifluoroborates for C-glycosylation is of interest.
6. APPENDICES

APPENDIX I: COMPOUND CHARACTERIZATION DATA

POTASSIUM TRIFLUOROBORATE SALTS

Potassium trifluoro(phenylethynyl)borate (1a)
The title compound was derived from phenylacetylene (2.45 g, 24.0 mmol, 1.0 equiv), n-BuLi (1.54 g, 24.0 mmol, 1.0 equiv), B(OMe)₃ (3.75 g, 36.1 mmol, 1.5 equiv), and aqueous KHF₂ (11.26 g, 144.2 mmol, 6.0 equiv) in 50 mL of THF. 1a was obtained as a white crystalline solid (1.190 g, 24% yield). ¹H NMR (DMSO) δ 7.27-7.29 (m, 4H), 7.21-7.26 (m, 1H); ¹³C {¹H} NMR (DMSO) δ 130.9, 128.2, 126.7, 125.5; ¹⁹F NMR (DMSO) δ -131.71 (br. s, 3F); ¹¹B {¹H} NMR (DMSO) δ -1.55 (s, 1B); HRMS (ESI/M-) calcd. for C₈H₅BF₃ 169.0442, found 169.0438.

Potassium trifluoro((4-methoxyphenyl)ethynyl)borate (1b)
The title compound was derived from 4-ethynylanisole (1.00 g, 7.34 mmol, 1.0 equiv.), n-BuLi (0.470 g, 7.34 mmol, 1.0 equiv.), B(OMe)₃ (1.14 g, 11.0 mmol, 1.5 equiv.), and aqueous KHF₂ (3.462 g, 44.3 mmol, 6.0 equiv.) in 25 mL THF. 1b was obtained as a white crystalline solid (2.609 g, 55% yield). ¹H NMR (DMSO) δ 7.20-7.22 (m, 2H), 6.83-6.85 (m, 2H), 3.73 (s, 3H); ¹³C {¹H} NMR (DMSO) δ 158.0, 132.2, 117.8, 113.8, 55.0; ¹⁹F NMR (DMSO) δ -131.50 (br. s, 3F); ¹¹B {¹H} NMR (DMSO) δ -1.67 (s, 1B); HRMS (ESI/M-) calcd. for C₉H₇OBF₃ 199.0548, found 199.0543.

Potassium ((4-butylphenyl)ethynyl)trifluoroborate (1c)
The title compound was derived from 1-butyl-4-ethynylbenzene (3.00 g, 18.0 mmol, 1.0 equiv.), n-BuLi (1.15 g, 18.0 mmol, 1.0 equiv.), B(OMe)₃ (2.81 g, 27.0 mmol, 1.5 equiv.), and aqueous KHF₂ (8.463 g, 108 mmol, 6.0 equiv.) in 50 mL THF. 1c was obtained as a white crystalline solid (2.609 g, 55% yield). ¹H NMR (DMSO) δ 7.17-7.20 (m 2H), 7.08-7.10 (m, 2H), 2.54 (t, J = 7.4 Hz
Potassium trifluoro((3-chlorophenyl)ethynyl)borate (1f)
The title compound was derived from 3-chloro-1-ethynylbenzene (0.44 g, 3.25 mmol, 1.0 equiv), t-BuLi (0.21 g, 3.25 mmol, 1.0 equiv), B(OMe)_3 (0.51 g, 4.87 mmol, 1.5 equiv), and aqueous KHF_2 (1.52 g, 19.5 mmol, 6.0 equiv) in 10.0 mL of THF. 1f was obtained as a white crystalline solid (0.460 g, 59% yield). \[^{1}H\] NMR (DMSO) δ 7.30-7.32 (m, 3H), 7.24-7.28 (m, 1H); \[^{13}C\] \[^{1}H\] NMR (DMSO) δ 132.8, 131.0, 129.7, 127.4, 126.9; \[^{19}F\] NMR (DMSO) δ -131.98 (br. s, 3F); \[^{11}B\] \[^{1}H\] NMR (DMSO) δ -1.67 (s, 1B); HRMS (ESI/M-) calcd. for C\textsubscript{12}H\textsubscript{13}BF\textsubscript{3} 225.1068, found 225.1065.

Potassium trifluoro(hex-1-yn-1-yl)borate (1d)
The title compound was derived from 1-hexyne (2.0 g, 23.6 mmol, 1.0 equiv), n-BuLi (1.51 g, 23.6 mmol, 1.0 equiv), B(OMe)_3 (3.68 g, 35.4 mmol, 1.5 equiv), and aqueous KHF\textsubscript{2} (11.06 g, 142 mmol, 6.0 equiv) in 25 mL of THF. 1d was obtained as a white crystalline solid (1.659 g, 36% yield). \[^{1}H\] NMR (DMSO) δ 1.98 (m, 2H) 1.33 (m, 4H), 0.85 (m, 3H); \[^{13}C\] \[^{1}H\] NMR (DMSO) δ 31.1, 21.4, 18.5, 13.5; \[^{19}F\] NMR (DMSO) δ -131.01 (br. s, 3F); \[^{11}B\] \[^{1}H\] NMR (DMSO) δ -1.30 (s, 1B); HRMS (ESI/M-) calcd. for C\textsubscript{6}H\textsubscript{9}BF\textsubscript{3} 149.0755, found 149.0749.

Potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (1e)
The title compound was derived from 3,4-dichloro-1-ethylbenzene (0.894 g, 5.22 mmol, 1.0 equiv), n-BuLi (0.335 g, 5.22 mmol, 1.0 equiv), B(OMe)_3 (0.81 g, 7.84 mmol, 1.5 equiv), and aqueous KHF\textsubscript{2} (2.45 g, 31.3 mmol, 6.0 equiv) in 17.5 mL of THF. 1e was obtained as an off-white crystalline solid (0.618 g, 43% yield). \[^{1}H\] NMR (DMSO) δ 7.51-7.54 (m, 2H), 7.26 (dd, J = 2.0, 8.2 Hz, 1H); \[^{13}C\] \[^{1}H\] NMR (DMSO) δ 132.8, 131.7, 131.4, 130.9, 130.0, 126.4, 109.9; \[^{19}F\] NMR (DMSO) δ -132.12 (br. s, 3F); \[^{11}B\] \[^{1}H\] NMR (DMSO) δ -1.70 (s, 1B); HRMS (ESI/M-) calcd. for C\textsubscript{8}H\textsubscript{3}BCl\textsubscript{2}F\textsubscript{3}: calculated: 236.9662, found 236.9664.

Potassium trifluoro((3-chlorophenyl)ethynyl)borate (1f)
The title compound was derived from 3-chloro-1-ethylbenzene (0.44 g, 3.25 mmol, 1.0 equiv), t-BuLi (0.21 g, 3.25 mmol, 1.0 equiv), B(OMe)_3 (0.51 g, 4.87 mmol, 1.5 equiv), and aqueous KHF\textsubscript{2} (1.52 g, 19.5 mmol, 6.0 equiv) in 10.0 mL of THF. 1f was obtained as a white crystalline solid (0.460 g, 59% yield). \[^{1}H\] NMR (DMSO) δ 7.30-7.32 (m, 3H), 7.24-7.28 (m, 1H); \[^{13}C\] \[^{1}H\] NMR (DMSO) δ 132.8, 130.3, 129.7, 127.4, 126.9; \[^{19}F\] NMR (DMSO) δ -131.98 (br. s, 3F); \[^{11}B\] \[^{1}H\] NMR (DMSO) δ -1.51 (s, 1B);
Potassium trifluoro((3-fluorophenyl)ethynyl)borate (1g)
The title compound was derived from 1-ethynyl-3-fluorobenzene (0.67 g, 5.44 mmol, 1.0 equiv), n-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), B(OMe)₃ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF₂ (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. 1g was obtained as a white crystalline solid (1.038 g, 84% yield). ¹H NMR (DMSO) δ 7.30-7.35 (m, 1H), 7.07-7.14 (m, 3H); ¹³C {¹H} NMR (DMSO) δ 161.8 (d, J = 243.1 Hz), 130.3 (d, J = 9.2 Hz), 127.5 (d, J = 9.2 Hz), 127.3 (d, J = 3.1 Hz), 117.3 (d, J = 22.2 Hz), 114.0 (d, J = 21.5 Hz); ¹⁹F NMR (DMSO) δ -113.49 (q, J = 6.6 Hz, 1F), -131.97 (br. s, 3F); ¹¹B {¹H} NMR (DMSO) δ -1.56 (s, 1B); HRMS (ESI/M-) calcd. for C₈H₄BF₄ 187.0348, found 187.0348.

Potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl)borate (1h)
The title compound was derived from 1-ethynyl-2-trifluoromethylbenzene (1.00 g, 5.70 mmol, 1.0 equiv), n-BuLi (0.365 g, 5.70 mmol, 1.0 equiv), B(OMe)₃ (0.89 g, 8.55 mmol, 1.5 equiv), and aqueous KHF₂ (2.67 g, 34.2 mmol, 6.0 equiv) in 17.0 mL of THF. 1h was obtained as a white crystalline solid (0.879 g, 56% yield). ¹H NMR (DMSO) δ 7.65 (d, J = 7.4 Hz, 1H), 7.51-7.58 (m, 2H), 7.39-7.44 (m, 1H); ¹³C {¹H} NMR (DMSO) δ 134.1, 132.0, 129.4 (q, J = 29.1 Hz), 126.9, 125.5 (q, J = 5.4 Hz), 123.7 (q, J = 273.0 Hz), 123.6; ¹⁹F NMR (DMSO) δ -60.85 (s, 3F), -132.09 (br. s, 3F); ¹¹B {¹H} NMR (DMSO) δ -1.61 (s, 1B); HRMS (ESI/M-) calcd. for C₈H₄BF₄ 237.0316, found 237.0318.

Potassium trifluoro((3,5-bis(trifluoromethyl)phenyl)ethynyl)borate (1i)
The title compound was derived from 1-ethynyl-3,5-bis(trifluoromethyl)benzene (1.00 g, 4.07 mmol, 1.0 equiv), n-BuLi (0.261 g, 4.07 mmol, 1.0 equiv), B(OMe)₃ (0.63 g, 6.11 mmol, 1.5 equiv), and aqueous KHF₂ (1.90 g, 24.4 mmol, 6.0 equiv) in 12.2 mL of THF. 1i was obtained as a white crystalline solid (0.444 g, 32% yield). ¹H NMR (DMSO) δ 7.92-7.93 (m, 3H); ¹³C {¹H} NMR (DMSO) δ
Potassium trifluoro(naphthalen-1-ylethynyl)borate (1j)
The title compound was derived from 1-ethynlnaphthalene (0.854 g, 5.44 mmol, 1.0 equiv), $n$-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), B(OMe)$_3$ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF$_2$ (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. 1j was obtained as a slightly pink crystalline solid (0.876 g, 62% yield). $^1$H NMR (DMSO) $\delta$ 8.33 (d, $J = 8.2$ Hz, 1H), 7.91 (d, $J = 8.6$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.51-7.61 (m, 3H), 7.42-7.45 (m, 1H); $^{13}$C {$^1$H} NMR (DMSO) $\delta$ 132.9, 132.8, 128.9, 128.1, 126.9, 126.3, 126.2, 126.1, 125.5, 123.1; $^{19}$F NMR (DMSO) $\delta$ -131.46 (br. s, 3F); $^{11}$B {$^1$H} NMR (DMSO) $\delta$ -1.61 (s, 1B); HRMS (ESI/M-) calcd. for C$_{10}$H$_3$BF$_3$ 305.0190, found 305.0193.

Potassium trifluoro([1,1'-biphenyl]-4-ylethynyl)borate (1k)
The title compound was derived from 4-ethynlbiphenyl (1.00 g, 5.44 mmol, 1.0 equiv), $n$-BuLi (0.349 g, 5.44 mmol, 1.0 equiv), B(OMe)$_3$ (0.85 g, 8.16 mmol, 1.5 equiv), and aqueous KHF$_2$ (2.55 g, 32.7 mmol, 6.0 equiv) in 17.0 mL of THF. 1k was obtained as an off-white crystalline solid (0.201 g, 13% yield). $^1$H NMR (DMSO) $\delta$ 7.65-7.67 (d, $J = 7.03$ Hz, 2H), 7.58-7.61 (d, $J = 8.6$ Hz, 2H), 7.44-7.47 (m, 2H), 7.33-7.39 (m, 3H); $^{13}$C {$^1$H} NMR (DMSO) $\delta$ 139.5, 138.3, 131.5, 128.9, 127.5, 126.48, 126.45, 124.7; $^{19}$F NMR (DMSO) $\delta$ -131.70 (br. s, 3F); $^{11}$B {$^1$H} NMR (DMSO) $\delta$ -1.22 (s, 1B); HRMS (ESI/M-) calcd. for C$_{14}$H$_9$BF$_3$ 245.0755, found 245.0755.

Potassium (E)-trifluoro(4-(trifluoromethyl)styryl)-borate (2a)
The title compound was derived from trans-2-[4-(trifluoromethyl)phenyl]vinylboronic acid (0.65 g, 3 mmol, 1.0 equiv.) and aqueous KHF$_2$ (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et$_2$O. 2a was obtained as a white crystalline solid (0.694 g, 83% yield). $^1$H-NMR (DMSO) $\delta$ 7.58–7.60 (m, 2H), 7.51–7.53 (m, 2H), 6.56 (d, $J = 18.0$ Hz, 1H), 6.39 (dq,
$J = 3.5, 18.0 \text{ Hz, 1H}$; $^{13}$C $^{1}$H NMR (DMSO) $\delta 144.3, 131.8 \text{ (q, } J = 4.6 \text{ Hz), 125.9, 125.2 \text{ (q, } J = 3.8 \text{ Hz), 124.7 \text{ (q, } J = 300.6 \text{ Hz); }^{19}$F NMR (DMSO) $\delta -60.60 \text{ (s, 3F), -138.31 (br. s, 3F).}$

Potassium (E)-trifluoro(4-methylstyryl)borate (2b)

The title compound was derived from trans-2-(4-methylphenyl) vinylboronic acid (0.49 g, 3 mmol, 1.0 equiv.) and aqueous KHF$_2$ (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et$_2$O. 2b was obtained as a white crystalline solid (0.562 g, 84% yield). $^{1}$H-NMR (DMSO) $\delta 7.19 \text{ (d, } J = 8.2 \text{ Hz, 2H), 7.05 \text{ (d, } J = 7.8 \text{ Hz, 2H), 6.42 \text{ (d, } J = 18.0 \text{ Hz, 1H), 6.10 \text{ (dq, } J = 3.5, 18.0 \text{ Hz, 1H), 2.25 \text{ (s, 3H); }^{13}$C $^{1}$H NMR (DMSO) $\delta 137.6, 134.7, 132.8, 128.8, 125.3, 20.7; }^{19}$F NMR (DMSO) $\delta -137.73 \text{ (br. s, 3F).}$

Potassium (E)-(2-((1,1′-biphenyl)-4-yl)vinyl)trifluoro-borate (2c)

The title compound was derived from trans-2-(4-biphenyl) vinylboronic acid (0.67 g, 3 mmol, 1.0 equiv.) and aqueous KHF$_2$ (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et$_2$O. 2c was obtained as a white crystalline solid (0.108 g, 13% yield). $^{1}$H-NMR (DMSO) $\delta 7.63–7.66 \text{ (m, 2H), 7.55–7.58 \text{ (m, 2H), 7.39–7.46 \text{ (m, 4H), 7.30–7.35 \text{ (m, 1H), 6.52 \text{ (d, } J = 18.0 \text{ Hz, 1H), 6.25 \text{ (dq, } J = 3.5, 18.0 \text{ Hz, 1H); }^{13}$C $^{1}$H NMR (DMSO) $\delta 140.1, 139.5, 137.5, 132.5, 128.9, 127.0, 126.6, 126.3, 125.9; }^{19}$F NMR (DMSO) $\delta -137.85 \text{ (br. s, 3F).}$

Potassium trifluoro(1H-inden-2-yl)borate (2d)

The title compound was derived from 1H-indene-2-boronic acid (0.48 g, 3 mmol, 1.0 equiv.) and aqueous KHF$_2$ (0.66 g, 8.4 mmol, 2.8 equiv.) in 6 mL Et$_2$O. 2d was obtained as an off-white crystalline solid (0.537 g, 81% yield). $^{1}$H-NMR (DMSO) $\delta 7.33–7.35 \text{ (m, 1H), 7.19–7.20 \text{ (m, 1H), 7.08–7.12 \text{ (m, 1H), 6.94–6.98 \text{ (m, 1H), 6.55 \text{ (s, 1H), 3.16 \text{ (s, 1H); }^{13}$C $^{1}$H NMR (DMSO) $\delta 147.5, 145.7, 129.8, 125.4, 123.1, 122.2, 119.0, 41.7; }^{19}$F NMR (DMSO) $\delta -137.30 \text{ (br. s, 3F); HRMS (ESI/M-) calcd. for C$_9$H$_7$BF$_3$ 183.0598, found 183.0609.}$
4-(hydroxy(phenyl)methyl)phenol (3a)
The title compound was derived from 4-hydroxybenzaldehyde (0.153 g, 1.25 mmol, 1.0 equiv) and phenylmagnesium bromide (0.453 g, 2.50 mmol, 2.0 equiv) in 5.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (3:1) afforded product 3a (0.196 g, 79% yield) as a white solid. IR (Diamond-ATR) ν 3393, 3154, 1595, 1447, 1171, 1000, 815, 695, 556 cm⁻¹; ¹H NMR (DMSO) δ 9.22 (s, 1H), 7.26-7.34 (m, 4H), 7.12-7.19 (m, 3H), 6.67 (d, J = 8.6 Hz, 2H), 5.67 (d, J = 3.9 Hz, 1H), 5.59 (d, J = 3.9 Hz, 1H); ¹³C {¹H} NMR (DMSO) δ 156.1, 146.1, 136.1, 127.9, 127.5, 126.4, 126.1, 114.7, 73.9.

Bis(4-methoxyphenyl)methanol (3b)
The title compound was derived from 4-methoxybenzaldehyde (0.139 g, 1.02 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.649 g, 3.07 mmol, 3.0 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel column chromatography using hexanes/EtOAc (5:1) afforded product 3b (0.248 g, 99% yield) as a yellow solid. IR (Diamond-ATR) ν 3287, 1608, 1507, 1239, 1167, 1028, 809, 549 cm⁻¹; ¹H NMR (CDCl₃) δ 7.26 (d, J = 8.2 Hz, 4H), 6.86 (d, J = 9.0 Hz, 4H), 5.75 (s, 1H), 3.78 (s, 6H), 2.18 (s, 1H); ¹³C {¹H} NMR (CDCl₃) δ 158.9, 136.4, 127.7, 113.8, 75.4, 55.3.

(4-chlorophenyl)(4-methoxyphenyl)methanol (3c)
The title compound was derived from 4-chlorobenzaldehyde (0.1413 g, 1.01 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.850 g, 4.02 mmol, 4.0 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc (5:1) afforded product 3c (0.203 g, 81% yield) as an off-white solid. IR (Diamond-ATR) ν 3300, 1509, 1247, 1170, 1031, 1004, 802, 551, 516 cm⁻¹; ¹H NMR (CDCl₃) δ 7.30 (s, 4H), 7.24 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.77 (d, J = 3.1 Hz, 1H), 3.79 (s, 3H), 2.20 (d, J = 3.5 Hz, 1H); ¹³C {¹H} NMR (CDCl₃) δ 159.2, 142.4, 135.8, 133.1, 128.5, 127.9, 127.7, 114.0, 75.2, 55.3.
(4-(dimethylamino)phenyl)(4-methoxyphenyl)-methanol (3d)
The title compound was derived from 4-(dimethylamino)benzaldehyde (0.174 g, 1.17 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.271 g, 1.28 mmol, 1.1 equiv) in 3.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (5:1) afforded product 3d (0.174, 58% yield) as an off white solid. IR (Diamond-ATR) v 3299, 1612, 1510, 1244, 1169, 1031, 804, 550 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.29 (d, \(J = 8.6\) Hz, 2H), 7.20 (d, \(J = 8.2\) Hz, 2H), 6.85 (d, \(J = 8.6\) Hz, 2H), 6.69 (d, \(J = 9.0\) Hz, 2H), 5.73 (d, \(J = 3.5\) Hz, 1H), 3.78 (s, 3H), 2.92 (s, 6H), 2.07 (d, \(J = 3.9\) Hz, 1H); \(^{13}\)C \{\(^1\)H\} NMR (CDCl\(_3\)) \(\delta\) 158.7, 150.1, 136.6, 132.2, 127.6, 127.5, 113.7, 112.5, 75.5, 55.3, 40.6.

N-(4-(hydroxy(p-tolyl)methyl)phenyl)acetamide (3e)
The title compound was derived from 4-acetamidobenzaldehyde (0.192 g, 1.18 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.459 g, 2.35 mmol, 2.0 equiv) in 3.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (1:1) afforded product 3e (0.199 g, 66% yield) as a yellow solid. Mp 139–142 °C; IR (Diamond-ATR) v 3309, 1657, 1601, 1535, 1412, 1318, 1268, 1012, 819, 758, 552, 477 cm\(^{-1}\); \(^1\)H NMR (DMSO) \(\delta\) 9.85 (s, 1H), 7.48 (d, \(J = 8.6\) Hz, 2H), 7.21-7.25 (m, 4H), 7.09 (d, \(J = 7.8\) Hz, 2H), 5.72 (d, \(J = 4.3\) Hz, 1H), 5.60 (d, \(J = 3.9\) Hz, 1H), 2.25 (s, 3H), 2.01 (s, 1H); \(^{13}\)C \{\(^1\)H\} NMR (DMSO) \(\delta\) 168.0, 142.8, 140.5, 137.8, 135.5, 128.5, 126.5, 126.1, 118.7, 73.7, 23.9, 20.6; HRMS (ESI-TOF) \(m/z\) [M+H]+ calcd for C\(_{16}\)H\(_{18}\)NO\(_2\) 256.1332, found 256.1329.

tert-butyl (4-(hydroxy(p-tolyl)methyl)phenyl)-carbamate (3f)
The title compound was derived from 4-(Boc-amino)benzaldehyde (0.100 g, 0.45 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.239 g, 1.13 mmol, 2.5 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc (3:1)
afforded product 3f (0.111 g, 74% yield) as a yellow solid. Mp 106–109 °C; IR (Diamond-ATR) ν 3367, 1696, 1507, 1235, 1157, 1035, 824, 574 cm⁻¹; ¹H NMR (CDCl₃) δ 7.24–7.32 (m, 6H), 6.85 (d, J = 8.6 Hz, 2H), 6.47 (s, 1H), 5.75 (s, 1H), 3.78 (s, 3H), 2.16 (s, 1H), 1.50 (s, 9H); ¹³C {¹H} NMR (CDCl₃) δ 159.0, 152.7, 138.7, 137.6, 136.2, 127.8, 127.1, 118.5, 113.8, 80.5, 75.4, 55.3, 28.3; HRMS (ESI-TOF) m/z [M+Na]+ calcd for C₁₉H₂₃NO₄Na 352.1519, found 352.1520.

4-(hydroxy(4-methoxyphenyl)methyl)benzoic acid (3g)
The title compound was derived from 4-formylbenzoic acid (0.174 g, 1.16 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.737 g, 3.48 mmol, 3.0 equiv) in 5.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc/ACOH (1.5:1:0.01% v/v) afforded product 3g (0.208 g, 69% yield) as a white solid. Mp 158-160 °C; IR (Diamond-ATR) ν 3468, 2920, 1675, 1607, 1508, 1423, 1293, 1228, 1169, 1025, 742, 551 cm⁻¹; ¹H NMR (DMSO) δ 12.80 (s, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.92 (s, 1H), 5.71 (s, 1H), 3.71 (s, 3H); ¹³C {¹H} NMR (DMSO) δ 167.2, 158.2, 150.9, 137.2, 129.2, 129.1, 127.5, 126.1, 113.5, 73.4, 55.0; HRMS (ESI-TOF) m/z [M-H]- calcd for C₁₅H₁₃O₄ 257.0819, found 257.0817.

4-(hydroxy(4-methoxyphenyl)methyl)benzaldehyde (3h)
The title compound was derived from 4-(diethoxymethyl) benzaldehyde (0.258 g, 1.24 mmol, 1.0 equiv) and 4-methoxyphenylmagnesium bromide (0.419 g, 1.98 mmol, 1.6 equiv) in 3.0 mL of anhydrous THF. Purification by silica gel chromatography using hexanes/EtOAc (3:1) afforded product 3h (66.0 mg, 22% yield) as a yellow oil. IR (Diamond-ATR) ν 3421, 1690, 1605, 1509, 1244, 1169, 1027, 818, 785, 554 cm⁻¹; ¹H NMR (CDCl₃) δ 9.98 (s, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 5.86 (s, 1H), 3.79 (s, 3H), 2.34 (s, 1H); ¹³C {¹H} NMR (CDCl₃) δ 191.9, 159.4, 150.6, 135.5, 135.4, 129.9, 128.1, 126.8, 114.2, 75.5, 55.3;
HRMS (El) m/z [M+] calcd for C₁₅H₁₄O₃ 242.0943, found 242.0944.

(2-methoxyphenyl)(p-tolyl)methanol (3i)
The title compound was derived from 2-methoxybenzaldehyde (0.298 g, 2.19 mmol, 1.0 equiv) and p-tolylmagnesium bromide (0.642 g, 3.29 mmol, 1.5 equiv) in 5.0 mL of anhydrous THF. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (gradient: 49:1 → 12:1) afforded product 3i (0.396 g, 79% yield) as a white solid. IR (Diamond-ATR) ν 3298, 1598, 1486, 1280, 1240, 1186, 1029, 806, 749, 556 cm⁻¹; ¹H NMR (CDCl₃) δ 7.26-7.20 (m, 4H), 7.10 (d, J = 7.8 Hz, 2H), 6.92 (t of d, J = 0.8, 7.4 Hz, 1H), 6.85 (d of d, J = 0.8, 8.6 Hz, 1H), 6.00 (s, 1H), 3.76 (s, 3H), 3.05 (s, 1H), 2.31 (s, 3H); ¹³C {¹H} NMR (CDCl₃) δ 156.6, 140.3, 136.6, 132.1, 128.8, 128.5, 127.7, 126.4, 120.7, 110.6, 71.9, 55.3, 21.0.
prop-2-yne-1,1,3-triyltribenzene (4a)
The title compound was derived from diphenylmethanol (13.3 mg, 0.072 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (15.0 mg, 0.072 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (18.7 mg, 0.12 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by automated flash column chromatography on silica gel using hexanes and subsequent CH$_3$CN/hexanes extraction afforded product 4a (7.8 mg, 41% yield) as a yellow oil. IR (Diamond-ATR) ν 2922, 1595, 1488, 1451, 755, 689, 558 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.43–7.49 (m, 6H), 7.29–7.34 (m, 7H), 7.21–7.25 (m, 2H), 5.21 (s, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 141.7, 131.7, 128.6, 128.2, 128.0, 127.9, 126.9, 123.5, 90.2, 84.9, 43.8.

(3-($p$-tolyl)prop-1-yne-1,3-diyl)dibenzene (4b)
The title compound was derived from phenyl($p$-tolyl)methanol (21.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (22.1 mg, 0.11 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (27.5 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes afforded product 4b (20.2 mg, 67% yield) as a yellow oil. IR (Diamond-ATR) ν 2921, 1654, 1595, 1488, 1451, 755, 689, 558 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.43–7.49 (m, 6H), 7.29–7.34 (m, 7H), 7.21–7.25 (m, 2H), 5.21 (s, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 141.9, 138.8, 136.5, 131.7, 129.3, 128.6, 128.2, 127.9, 127.83, 127.75, 126.8, 123.6, 90.4, 84.7, 43.4, 21.0.

(3-($o$-tolyl)prop-1-yne-1,3-diyl)dibenzene (4c)
The title compound was derived from phenyl($o$-tolyl)methanol (21.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (22.1 mg, 0.11 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (27.5 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes afforded product 4c (15.2 mg, 51% yield) as a yellow oil. IR (Diamond-ATR) ν 2923, 1597, 1489, 1449, 1266, 1027, 754, 690 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.50 (dd, J = 1.6, 7.03 Hz, 1H), 7.44–7.46 (m, 2H), 7.37–7.39 (m, 2H), 7.27–7.32 (m, 5H), 7.14–7.25 (m, 4H), 5.38 (s, 1H), 2.33 (s, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ
The title compound was derived from (4-methoxyphenyl)phenylmethanol (21.5 mg, 0.10 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (20.9 mg, 0.10 mmol, 1.0 equiv), and HBF₄·OEt₂ (26.0 mg, 0.16 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by silica gel column chromatography using hexanes/diethyl ether (40:1) afforded product 4d (26.2 mg, 87% yield) as a yellow oil. IR (Diamond-ATR) ν 2930, 1598, 1507, 1247, 1173, 1029, 755, 691 cm⁻¹; ¹H NMR (CDCl₃) δ 7.41-7.48 (m, 4H), 7.28-7.36 (m, 7H), 7.20-7.24 (m, 1H), 6.85 (d, J = 9.0 Hz, 2H), 5.16 (s, 1H), 3.77 (s, 3H); ¹³C {¹H} NMR (CDCl₃) δ 158.5, 142.0, 133.9, 131.7, 128.9, 128.6, 128.2, 127.9, 127.8, 126.8, 123.5, 114.0, 90.5, 84.7, 55.3, 42.9.

The title compound was derived from bis(4-methoxyphenyl)methanol (3b) (22.3 mg, 0.091 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (19.0 mg, 0.091 mmol, 1.0 equiv), and HBF₄·OEt₂ (23.7 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Aqueous workup afforded product 4e (27.2 mg, 91% yield) as a yellow/orange oil. IR (Diamond-ATR) ν 2930, 1601, 1507, 1244, 1170, 1027, 756, 689 cm⁻¹; ¹H NMR (CDCl₃) δ 7.48-7.51 (m, 2H), 7.36 (d, J = 8.2 Hz, 4H), 7.31-7.33 (m, 3H), 6.88 (d, J = 8.6 Hz, 4H), 5.15 (s, 1H), 3.81 (s, 6H); ¹³C {¹H} NMR (CDCl₃) δ 158.4, 134.3, 131.6, 128.8, 128.2, 127.9, 123.6, 113.9, 90.8, 84.5, 55.3, 42.1.

The title compound was derived from (4-chlorophenyl)(phenyl)methanol (21.7 mg, 0.10 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (20.6 mg, 0.10 mmol, 1.0 equiv), and HBF₄·OEt₂ (25.7 mg, 0.16 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by automated flash column chromatography on silica gel using hexanes and subsequent CH₃CN/hexanes extraction afforded product 4f (5.7 mg, 19% yield) as a yellow oil. IR
1-chloro-4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)benzene (4g)
The title compound was derived from (4-chlorophenyl)(4-methoxyphenyl)methanol (3c) (22.4 mg, 0.090 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (18.7 mg, 0.090 mmol, 1.0 equiv), and HBF₄·OEt₂ (23.4 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by silica gel column chromatography using hexanes/EtOAc (10:1) afforded product 4g (25.3 mg, 84% yield) as a yellow oil. IR (Diamond-ATR) ν 2928, 1599, 1508, 1487, 1248, 1172, 1089, 1014, 755, 690, 552 cm⁻¹; ¹H NMR (CDCl₃) δ 7.41-7.48 (m, 4H), 7.28-7.33 (m, 7H), 7.22-7.24 (m, 1H), 6.77-6.79 (m, 2H), 5.14 (s, 1H); ¹³C {¹H} NMR (CDCl₃) δ 154.4, 142.0, 134.1, 131.7, 129.1, 128.6, 128.2, 127.9, 127.8, 126.8, 123.5, 115.4, 90.4, 84.7, 42.9.

4-(1,3-diphenylprop-2-yn-1-yl)phenol (4h)
The title compound was derived from 4-(hydroxy(phenyl)methyl)phenol (3a) (21.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (21.9 mg, 0.11 mmol, 1.0 equiv), and HBF₄·OEt₂ (27.3 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification was conducted by automated flash column chromatography on silica gel using hexanes/EtOAc (5:1) and subsequent CH₃CN/hexanes extraction afforded product 4h (19.9 mg, 66% yield) as a burgundy/brown oil. IR (Diamond-ATR) ν 3317, 3025, 1596, 1509, 1489, 1441, 1169, 754, 690, 552 cm⁻¹; ¹H NMR (CDCl₃) 7.41-7.48 (m, 4H), 7.28-7.33 (m, 7H), 7.22-7.24 (m, 1H), 6.77-6.79 (m, 2H), 5.14 (s, 1H); ¹³C {¹H} NMR (CDCl₃) δ 154.4, 142.0, 134.1, 131.7, 129.1, 128.6, 128.2, 127.9, 127.8, 126.8, 123.5, 115.4, 90.4, 84.7, 42.9.
N-(4-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)phenyl)acetamide (4i)
The title compound was derived from N-(4-hydroxy(p-tolyl)methyl)phenyl)acetamide (3e) (22.6 mg, 0.088 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (18.4 mg, 0.088 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (22.9 mg, 0.141 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc (1:2) and subsequent CH$_3$CN/hexanes extraction afforded product 4i (18.3 mg, 61% yield) as a yellow oil. IR (Diamond-ATR) ν 3301, 2922, 1662, 1599, 1508, 1407, 1314, 754, 689 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.45-7.49 (m, 4H), 7.38-7.40 (m, 3H), 7.30-7.33 (m, 4H), 7.14 (d, J = 7.8 Hz, 2H), 5.15 (s, 1H), 2.34 (s, 3H), 2.15 (s, 3H); $^{13}$C $^1$H NMR (CDCl$_3$) δ 168.3, 138.7, 137.9, 136.6, 136.5, 131.6, 129.3, 128.4, 128.2, 127.9, 127.7, 123.5, 120.1, 90.3, 84.7, 42.8, 24.5, 21.0; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{24}$H$_{22}$NO 340.1696, found 340.1693.

4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)benzoic acid (4j)
The title compound was derived from 4-(hydroxy(4-methoxyphenyl)methyl)benzoic acid (3g) (13.8 mg, 0.053 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl)borate (1a) (11.1 mg, 0.053 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (11.2 mg, 0.069 mmol, 1.3 equiv) in 0.3 mL of CH$_3$CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc/CH$_3$COH (2:1:0.01% v/v) and subsequent CH$_3$CN/hexanes extraction afforded product 4j (11.3 mg, 62% yield) as a yellow oil. IR (Diamond-ATR) ν 2919, 1691, 1607, 1508, 1297, 1246, 1173, 758, 740, 691, 554 cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 8.02 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.50 7.53 (m, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.37-7.38 (m, 3H), 6.92 (d, J = 8.6 Hz, 2H), 5.41 (s, 1H), 3.77 (s, 3H); $^{13}$C $^1$H NMR (acetone-$d_6$) δ 159.9, 148.3, 134.5, 132.5, 131.0, 129.8, 129.4, 129.2, 128.7, 124.3, 115.0, 91.0, 85.8, 55.6, 43.3 (the carbonyl carbon and one aromatic carbon were not resolved in this spectrum); HRMS (ESI-TOF) m/z [M+H]- calcd for C$_{23}$H$_{17}$O$_3$ 341.1183, found 341.1186.
1-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)-2-(trifluoromethyl)benzene (5a)
The title compound was derived from (4-methoxyphenyl) (phenyl)methanol (17.6 mg, 0.082 mmol, 1.0 equiv), potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl)borate (1h) (22.6 mg, 0.082 mmol, 1.0 equiv), and HBF₄·OEt₂ (21.2 mg, 0.13 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by silica gel column chromatography using hexanes/EtOAc (15:1) afforded product 5a (26.8 mg, 89% yield) as a yellow/orange oil. IR (Diamond-ATR) ν 2929, 1601, 1508, 1314, 1249, 1167, 1127, 1031, 764, 697 cm⁻¹; ¹H NMR (CDCl₃) δ 7.64 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 7.4 Hz, 1H), 7.42-7.47 (m, 3H), 7.30-7.38 (m, 5H), 7.21-7.24 (m, 1H), 6.85 (d, J = 8.6 Hz, 2H), 5.20 (s, 1H), 3.77 (s, 3H); ¹³C {¹H} NMR (CDCl₃) δ 158.5, 141.6, 134.1, 133.5, 131.6, 131.3, 128.9, 128.6, 127.8, 127.6, 126.9, 125.7 (q, J = 5.4 Hz), 123.6 (q, J = 273.7 Hz), 121.8, 114.0, 96.4, 80.7, 55.2, 43.2; ¹⁹F NMR (CDCl₃) δ -62.17 (s, 3F); HRMS (EI) m/z [M+] calcd for C₂₃H₁₇F₃O 366.1232, found 366.1231.

1-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)-3,5-bis(trifluoromethyl)benzene (5b)
The title compound was derived from (4-methoxyphenyl) (phenyl)methanol (14.8 mg, 0.069 mmol, 1.0 equiv), potassium trifluoro((3,5-bis(trifluoromethyl)phenyl)ethynyl)borate (1i) (23.8 mg, 0.069 mmol, 1.0 equiv), and HBF₄·OEt₂ (17.9 mg, 0.11 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by silica gel column chromatography using hexanes/EtOAc (14:1) afforded product 5b (25.6 mg, 85% yield) as a yellow/orange oil. IR (Diamond-ATR) ν 2928, 1600, 1509, 1381, 1275, 1171, 1129, 697, 681 cm⁻¹; ¹H NMR (CDCl₃) δ 7.88 (s, 2H), 7.78 (s, 1H), 7.25-7.41 (m, 7H), 6.88 (d, J = 9.0, 2H), 5.20 (s, 1H), 3.79 (s, 3H); ¹³C {¹H} NMR (CDCl₃) δ 158.8, 141.1, 132.9, 131.8 (q, J = 33.7 Hz), 131.6 (q, J = 4.6 Hz), 128.9, 128.8, 127.8, 127.2, 125.8, 123.0 (q, J = 273.0 Hz), 121.3 (q, J = 3.8 Hz), 114.2, 94.5, 81.8, 55.3, 42.9; ¹⁹F NMR (CDCl₃) δ -63.13 (s, 6F); HRMS (EI) m/z [M+] calcd for C₂₄H₁₆F₆O 434.1105, found 434.1100.
1-chloro-3-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)benzene (5c)
The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (19.3 mg, 0.090 mmol, 1.0 equiv), potassium trifluoro((3-chlorophenyl)ethynyl)borate (1f) (21.9 mg, 0.090 mmol, 1.0 equiv), and HBF₄·OEt₂ (23.4 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by silica gel column chromatography using hexanes/EtOAc (14:1) afforded product 5c (29.7 mg, 99% yield) as a yellow/orange oil. IR (Diamond-ATR) \(\nu\) 2930, 1592, 1507, 1247, 1173, 1030, 780, 696, 680 cm\(^{-1}\); \(^1\)H NMR (CDCl₃) \(\delta\) 7.45-7.46 (m, 1H), 7.39-7.41 (m, 2H), 7.30-7.35 (m, 5H), 7.19-7.28 (m, 3H), 6.86 (d, \(J = 9.0\) Hz, 2H), 5.16 (s, 1H), 3.77 (s, 3H); \(^{13}\)C \{\(^1\)H\} NMR (CDCl₃) \(\delta\) 158.6, 141.7, 134.0, 133.5, 131.6, 129.8, 129.4, 128.9, 128.6, 128.2, 127.8, 126.9, 125.2, 114.0, 91.9, 83.3, 55.3, 42.9; HRMS (EI) \(m/z\) [M+] calcd for C\(_{22}\)H\(_{17}\)ClO 332.0968, found 332.0962.

1,2-dichloro-4-(3-(4-chlorphenyl)-3-(4-methoxyphenyl)prop-1-yn-1-yl)benzene (5d)
The title compound was derived from (4-chlorophenyl)(4-methoxyphenyl)methanol (3c) (18.6 mg, 0.075 mmol, 1.0 equiv), potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (1e) (20.7 mg, 0.075 mmol, 1.0 equiv), and HBF₄·OEt₂ (19.3 mg, 0.12 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by silica gel column chromatography using hexanes/EtOAc (20:1) afforded product 5d (25.0 mg, 83% yield) as a yellow oil. IR (Diamond-ATR) \(\nu\) 2926, 1508, 1487, 1461, 1173, 1089, 1031, 817 cm\(^{-1}\); \(^1\)H NMR (CDCl₃) \(\delta\) 7.54 (d, \(J = 2.0\) Hz, 1H), 7.35-7.37 (m, 1H), 7.25-7.33 (m, 7H), 6.87 (d, \(J = 9.0\) Hz, 2H), 5.12 (s, 1H), 3.79 (s, 3H); \(^{13}\)C \{\(^1\)H\} NMR (CDCl₃) \(\delta\) 158.8, 140.0, 133.3, 132.9, 132.8, 132.48, 132.45, 130.8, 130.3, 129.1, 128.80, 128.79, 123.2, 114.2, 92.1, 82.8, 55.3, 42.3; HRMS (EI) \(m/z\) [M+] calcd for C\(_{22}\)H\(_{15}\)Cl\(_3\)O 400.0188, found 400.0186.
**4-(3-(3-fluorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-yl)benzaldehyde (5e)**

The title compound was derived from 4-(hydroxy(4-methoxyphenyl)methyl)benzaldehyde (3h) (21.1 mg, 0.087 mmol, 1.0 equiv), potassium trifluoro((3-fluorophenyl)-ethynyl)borate (1g) (19.7 mg, 0.087 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (22.6 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes/EtOAc (6:1) afforded product 5e (24.6 mg, 82% yield) as a yellow oil.

**IR (Diamond-ATR)** ν 2926, 1697, 1603, 1578, 1508, 1246, 1148, 1032, 783, 681 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 9.99 (s, 1H), 7.84 (d, $J$ = 8.2 Hz, 2H), 7.58 (d, $J$ = 8.2 Hz, 2H), 7.32 (d, $J$ = 8.6 Hz, 2H), 7.25-7.28 (m, 2H), 7.15-7.18 (m, 1H), 7.00-7.05 (m, 1H), 6.88 (d, $J$ = 9.0 Hz, 2H), 5.23 (s, 1H), 3.79 (s, 3H); $^{13}$C ($^1$H) NMR (CDCl$_3$) δ 191.7, 162.3 (d, $J$ = 246.14 Hz), 158.9, 148.5, 135.2, 132.4, 130.1, 129.8 (d, $J$ = 6.2 Hz), 128.9, 128.4, 127.5 (d, $J$ = 3.1 Hz), 124.9, 118.5 (d, $J$ = 23.0 Hz), 115.6 (d, $J$ = 21.5 Hz), 114.3, 90.3, 84.3, 55.3, 43.0; $^{19}$F NMR (CDCl$_3$) δ -112.97 (s, 1F); HRMS (EI) m/z [M+] calcd for C$_{23}$H$_{17}$FO$_2$ 344.1213, found 344.1217.

**4-(3-([1,1′-biphenyl]-4-yl)-1-phenylprop-2-yn-1-yl)phenol (5f)**

The title compound was derived from 4-(hydroxy(phenyl)methyl)phenol (3a) (16.7 mg, 0.083 mmol, 1.0 equiv), potassium trifluoro([1,1′-biphenyl]-4-ylethynyl)borate (1k) (23.6 mg, 0.083 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (21.6 mg, 0.13 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (5:1) afforded product 5f (21.3 mg, 71% yield) as an orange/pink oil.

**IR (Diamond-ATR)** ν 3331, 2922, 1597, 1508, 1485, 1447, 1170, 840, 761, 692, 560 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.57-7.59 (m, 2H), 7.53 (s, 4H), 7.41-7.45 (m, 4H), 7.29-7.36 (m, 5H), 7.21-7.25 (m, 1H), 6.78 (d, $J$ = 8.6 Hz, 2H), 5.17 (s, 1H), 4.84 (s, 1H); $^{13}$C ($^1$H) NMR (CDCl$_3$) δ 154.4, 142.0, 140.7, 140.4, 134.1, 132.1, 129.1, 128.8, 128.6, 127.8, 127.5, 127.0, 126.9, 126.8, 122.4, 115.4, 91.1, 84.6, 43.0; HRMS (EI) m/z [M+] calcd for C$_{27}$H$_{20}$O 360.1514, found 360.1509.
1-(3-(4-methoxyphenyl)-3-phenylprop-1-yn-1-yl)-naphthalene (5g)
The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (18.5 mg, 0.086 mmol, 1.0 equiv), potassium trifluoro(naphthalen-1-ylythynyl)borate (1j) (22.2 mg, 0.086 mmol, 1.0 equiv), and HBF₄·OEt₂ (22.3 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (20:1) afforded product 5g (21.0 mg, 70% yield) as a yellow oil. IR (Diamond-ATR) ν 2926, 1603, 1507, 1245, 1174, 1030, 797, 772, 696, 564 cm⁻¹; ¹H NMR (CDCl₃) δ 8.33 (d, J = 7.4 Hz, 1H), 7.78-7.84 (m, 2H), 7.70 (d, J = 7.4 Hz, 1H), 7.47-7.54 (m, 4H), 7.33-7.44 (m, 5H), 7.23-7.27 (m, 1H), 6.88 (d, J = 8.6 Hz, 2H), 5.33 (s, 1H), 3.78 (s, 3H); ¹³C {¹H} NMR (CDCl₃) δ 158.6, 142.1, 134.0, 133.5, 133.2, 130.4, 129.0, 128.7, 128.4, 128.2, 127.9, 126.9, 126.7, 126.3, 125.2, 121.2, 114.1, 95.5, 82.9, 55.3, 43.3 (one aromatic carbon was not resolved in this spectrum); HRMS (EI) m/z [M+] calcd for C₂₆H₂₀O₃ 348.1514, found 348.1508.

4-(1-(4-methoxyphenyl)-3-(naphthalen-1-yl)prop-2-yn-1-yl)-benzoic acid (5h)
The title compound was derived from (hydroxy(4-methoxyphenyl)methyl)benzoic acid (3g) (19.7 mg, 0.076 mmol, 1.0 equiv), potassium trifluoro(naphthalen-1-ylythynyl)borate (1j) (19.7 mg, 0.076 mmol, 1.0 equiv), and HBF₄·OEt₂ (19.8 mg, 0.12 mmol, 1.6 equiv) in 0.3 mL of CH₃CN. Purification by silica gel column chromatography using hexanes/EtOAc/AcOH (1.5:1:0.01% v/v) afforded product 5h (19.8 mg, 66% yield) as a yellow oil. IR (Diamond-ATR) ν 2922, 1689, 1606, 1507, 1245, 1174, 1032, 771 cm⁻¹; ¹H NMR (acetone-d₆) δ 8.33-8.36 (m, 1H), 8.06 (d, J = 8.2 Hz, 2H), 7.93-7.97 (m, 2H), 7.72-7.78 (m, 3H), 7.49-7.62 (m, 5H), 6.96 (d, J = 8.6 Hz, 2H), 5.61 (s, 1H), 3.79 (s, 3H); ¹³C {¹H} NMR (acetone-d₆) δ 159.9, 148.3, 134.5, 134.3, 131.4, 131.1, 129.9, 129.6, 129.4, 128.8, 127.9, 127.5, 126.8, 126.4, 121.8, 115.1, 96.2, 83.8, 55.6, 43.7 (the carbonyl carbon and one aromatic carbon were not resolved in this spectrum); HRMS (EI) m/z [M+] for C₂₇H₂₀O₃ 392.1412, found 392.1417.
4-(3-(3-chlorophenyl)-1-(4-methoxyphenyl)prop-2-yn-1-yl)-N,N-dimethylaniline (5i)
The title compound was derived from (4-(dimethylamino)phenyl)(4-methoxyphenyl)methanol (3d) (20.5 mg, 0.080 mmol, 1.0 equiv), potassium trifluoro(3-chlorophenyl)ethynyl)borate (1f) (19.4 mg, 0.080 mmol, 1.0 equiv), and HBF$_4$$\cdot$OEt$_2$ (33.6 mg, 0.21 mmol, 2.6 equiv) in 0.3 mL of CH$_3$CN. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (3:1) afforded product 5i (18.4 mg, 61% yield) as a brown oil. IR (Diamond-ATR) \(\nu\) 2926, 1607, 1507, 1246, 1172, 1033, 782, 680, 555 cm$^{-1}$; $^1$H NMR (CDCl$_3$) \(\delta\) 7.44–7.45 (m, 1H), 7.31–7.33 (m, 3H), 7.18–7.26 (m, 4H), 6.85 (d, $J$ = 8.6 Hz, 2H), 6.69 (d, $J$ = 9.0 Hz, 2H), 5.08 (s, 1H), 3.78 (s, 3H), 2.91 (s, 6H); $^{13}$C {^1}H NMR (CDCl$_3$) \(\delta\) 158.4, 149.6, 134.3, 134.0, 131.5, 129.8, 129.6, 129.4, 128.8, 128.4, 128.0, 125.5, 113.9, 112.7, 92.7, 82.8, 55.3, 41.9, 40.6; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{24}$H$_{23}$ClNO 376.1463, found 376.1458.

4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)aniline (5j)
The title compound was derived from tert-butyl (4-(hydroxy(p-tolyl)methyl)phenyl)carbamate (3f) (20.5 mg, 0.062 mmol, 1.0 equiv), potassium trifluoro(3,4-dichlorophenyl)ethynyl borate (1e) (17.3 mg, 0.062 mmol, 1.0 equiv), and HBF$_4$$\cdot$OEt$_2$ (26.2 mg, 0.16 mmol, 2.6 equiv) in 0.3 mL of CH$_3$CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc (1.3:1) followed by a pentane wash and subsequent CH$_3$CN/hexanes extraction to afford product 5j (15.3 mg, 51% yield) as a burgundy oil. IR (Diamond-ATR) \(\nu\) 3372, 2928, 1607, 1506, 1461, 1244, 1173, 1127, 1030, 817, 729, 569 cm$^{-1}$; $^1$H NMR (CDCl$_3$) \(\delta\) 7.53 (m, 1H), 7.34–7.36 (m, 1H), 7.24–7.30 (m, 3H), 7.15 (d, $J$ = 8.2 Hz, 2H), 6.85 (d, $J$ = 8.6 Hz, 2H), 6.64 (d, $J$ = 8.2 Hz, 2H), 5.05 (s, 1H), 3.78 (s, 3H); $^{13}$C {^1}H NMR (CDCl$_3$) \(\delta\) 158.5, 145.3, 133.9, 133.3, 132.3, 132.1, 131.5, 130.8, 130.2, 128.7, 128.6, 123.7, 115.3, 114.0, 93.3, 82.0, 55.3, 42.0; HRMS (ESI-TOF) m/z [M+H]$^+$ calcd for C$_{22}$H$_{18}$Cl$_2$NO 382.0760, found 382.0758.
1-methoxy-4-(1-phenylhept-2-yn-1-yl)benzene (5k)
The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (23.1 mg, 0.11 mmol, 1.0 equiv), potassium trifluoro(hex-1-yn-1-yl)borate (1d) (20.3 mg, 0.11 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (27.9 mg, 0.17 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes/EtOAc (15:1) afforded product 5k (21.9 mg, 73% yield) as a yellow oil.

$\text{IR (Diamond-ATR)} \nu 2929, 1653, 1598, 1248, 1172, 1029, 698 \text{ cm}^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.34–7.36 (m, 2H), 7.26–7.30 (m, 4H), 7.17–7.21 (m, 1H), 6.82 (d, $J = 9.0$ Hz, 2H), 4.92 (s, 1H), 3.76 (s, 3H), 2.28 (td, $J = 2.4$, 7.0 Hz, 2H), 1.51–1.56 (m, 2H), 1.41–1.46 (m, 2H), 0.92 (t, $J = 7.0$ Hz, 3H); $^{13}$C \{$^1$H\} NMR (CDCl$_3$) $\delta$ 158.3, 142.8, 134.7, 128.8, 128.4, 127.7, 126.5, 113.8, 84.9, 80.8, 55.2, 42.4, 31.1, 22.0, 18.6, 13.6.

$(E)$-(3-(4-methoxyphenyl)prop-1-ene-1,3-diyl)dibenzene (6a)
The title compound was derived from (4-methoxyphenyl)(phenyl)methanol (21.4 mg, 0.100 mmol, 1.0 equiv), potassium trifluoro(2-(3-fluorophenyl)vinyl)borate (21.0 mg, 0.100 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (25.9 mg, 0.16 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes/EtOAc (15:1) afforded product 6a (29.0 mg, 97% yield) as a pale yellow oil.

$\text{IR (Diamond-ATR)} \nu 2927, 1607, 1508, 1244, 1175, 1031, 966, 829, 744, 693, 549 \text{ cm}^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.35–7.37 (m, 2H), 7.19–7.32 (m, 8H), 7.14 (d, $J = 8.6$ Hz, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 6.65 (dd, $J = 7.4$, 15.6 Hz, 1H), 6.32 (d, $J = 15.6$ Hz, 1H), 4.84 (d, $J = 7.4$ Hz, 1H), 3.77 (s, 3H); $^{13}$C \{$^1$H\} NMR (CDCl$_3$) $\delta$ 158.1, 143.8, 137.3, 135.6, 132.9, 131.1, 129.6, 128.6, 128.5, 128.4, 127.2, 126.34, 126.26, 113.8, 55.2, 53.3.

$(E)$-4,4′- (3-(3-fluorophenyl)prop-2-ene-1,1-diyl)bismethoxybenzene (6b)
The title compound was derived from bis(4-methoxyphenyl)methanol (3b) (21.0 mg, 0.086 mmol, 1.0 equiv), potassium trifluoro(2-(3-fluorophenyl)vinyl)borate (19.6 mg, 0.086 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (22.3 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes/EtOAc (9:1) afforded product 6b (29.1 mg, 97% yield) as a pink oil. IR (Diamond-ATR) $\nu$ 2929, 1608, 1581, 1506, 1242, 1173,
(E)-N-(4-(3-phenyl-1-(p-tolyl)allyl)phenyl)acetamide (6c)
The title compound was derived from N-(4-hydroxy(p-tolyl)methyl)acetamide (3e) (22.4 mg, 0.088 mmol, 1.0 equiv), potassium trifluoro(E)-2-phenylethenylborate (18.5 mg, 0.088 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (22.8 mg, 0.14 mmol, 1.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes/EtOAc (1:2) and subsequent CH$_3$CN/hexanes extraction afforded product 6c (23.2 mg, 77% yield) as a pale white/yellow oil. IR (Diamond-ATR) $\nu$ 3294, 2922, 1662, 1599, 1509, 1407, 1369, 1315, 1262, 966, 816, 741, 691, 522 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.41–7.43 (m, 2H), 7.34–7.37 (m, 2H), 7.15–7.29 (m, 5H), 7.10 (s, 4H), 6.61 (dd, $J = 7.4, 16.0$ Hz, 1H), 6.31 (d, $J = 15.6$ Hz, 1H), 4.81 (d, $J = 7.4$ Hz, 1H), 2.32 (s, 3H), 2.13 (s, 3H); $^{13}$C ($^1$H) NMR (CDCl$_3$) $\delta$ 168.3, 140.4, 139.7, 137.2, 136.2, 136.0, 132.6, 131.2, 129.2, 129.1, 128.5, 128.4, 127.2, 126.3, 120.0, 53.2, 24.5, 21.0; HRMS (ESI-TOF) $m/z$ [M+H$^+$] calcd for C$_{24}$H$_{24}$NO 342.1852, found 342.1849.

(E)-4-(3-(3-fluorophenyl)-1-(4-methoxyphenyl)allyl)-N,N-dimethylaniline (6d)
The title compound was derived from (4-(dimethylamino)phenyl)(4-methoxyphenyl)methanol (3d) (21.4 mg, 0.083 mmol, 1.0 equiv), potassium trifluoro(2-(3-fluorophenyl)vinyl) borate (18.9 mg, 0.083 mmol, 1.0 equiv), and HBF$_4$·OEt$_2$ (34.9 mg, 0.2 mmol, 2.6 equiv) in 0.3 mL of CH$_3$CN. Purification by silica gel column chromatography using hexanes/EtOAc (6:1) afforded product 6d (25.1 mg, 84% yield) as a pale white/yellow oil. IR (Diamond-ATR) $\nu$ 2926, 1609, 1507, 1244, 1174, 1140, 1034, 813, 774, 552 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.19–7.25 (m, 1033, 964, 825, 553 cm$^{-1}$); $^{1}$H NMR (CDCl$_3$) $\delta$ 7.20–7.25 (m, 1H), 7.05–7.13 (m, 6H), 6.84–6.91 (m, 5H), 6.61–6.66 (m, 1H), 6.26 (d, $J = 15.6$ Hz, 1H), 4.79 (d, $J = 7.4$ Hz, 1H), 3.78 (s, 6H); $^{13}$C ($^1$H) NMR (CDCl$_3$) $\delta$ 163.1 (d, $J = 245.4$ Hz), 158.2, 139.7 (d, $J = 7.7$ Hz), 135.6, 134.7, 129.9 (d, $J = 3.1$ Hz), 129.8 (d, $J = 2.3$ Hz), 129.5, 122.1 (d, $J = 2.3$ Hz), 113.94 (d, $J = 21.5$ Hz), 113.87, 112.7 (d, $J = 22.2$ Hz), 55.2, 52.4; $^{19}$F NMR (CDCl$_3$) $\delta$ $-113.70$ (q, $J = 9.3$ Hz, 1F); HRMS (EI) $m/z$ [M]+ calcd for C$_{23}$H$_{21}$FO$_2$ 348.1526, found 348.1523.
1H), 7.04−7.15 (m, 6H), 6.83−6.90 (m, 3H), 6.62−6.71 (m, 3H), 6.27 (d, \(J = 16.0\) Hz, 1H), 4.75 (d, \(J = 7.4\) Hz, 1H), 3.78 (s, 3H), 2.91 (s, 6H); \(^{13}\)C \({^{1}H}\) NMR (CDCl\(_3\)) \(\delta\) 163.1 (d, \(J = 244.6\) Hz), 158.1, 149.3, 140.0 (d, \(J = 7.7\) Hz), 136.0, 135.1, 131.4, 129.9, 129.8, 129.5, 129.1, 122.1 (d, \(J = 3.1\) Hz), 113.79, 113.78 (d, \(J = 21.5\) Hz), 112.74, 112.65 (d, \(J = 22.2\) Hz), 55.2, 52.3, 40.7; \(^{19}\)F NMR (CDCl\(_3\)) \(\delta\) −113.82 (q, \(J = 9.3\) Hz, 1F); HRMS (ESI-TOF) \(m/z\) [M+H]+ calcd for C\(_{24}\)H\(_{25}\)FNO 362.1915, found 362.1912.

\((E)-4-(3-(3-fluorophenyl)-1-(4-methoxyphenyl)allyl)-benzoic acid (6e)\)

The title compound was derived from 4-(hydroxy(4-methoxyphenyl)methyl)benzoic acid (3g) (21.4 mg, 0.083 mmol, 1.0 equiv), potassium trifluoro(2-(3-fluorophenyl)vinyl) borate (18.9 mg, 0.083 mmol, 1.0 equiv), and HBF\(_4\)·OEt\(_2\) (17.4 mg, 0.12 mmol, 1.3 equiv) in 0.3 mL of CH\(_3\)CN. Purification was conducted by silica gel column chromatography using hexanes/EtOAc/AcOH (2:1:0.01% v/v) and subsequent CH\(_3\)CN/hexanes extraction afforded product 6e (23.0 mg, 77% yield) as a pale yellow oil. IR (Diamond-ATR) \(\nu\) 2922, 1685, 1607, 1508, 1245, 1176, 1033, 963, 778, 683, 548 cm\(^{-1}\); \(^{1}H\) NMR (acetone-d\(_6\)) \(\delta\) 8.01 (d, \(J = 8.2\) Hz, 2H), 7.44 (d, \(J = 8.2\) Hz, 2H), 7.22−7.37 (m, 5H), 6.89−7.01 (m, 4H), 6.49 (d, \(J = 16.0\) Hz, 1H), 5.01 (d, \(J = 8.2\) Hz, 1H), 3.77 (s, 3H); \(^{13}\)C \({^{1}H}\) NMR (acetone-d\(_6\)) \(\delta\) 164.1 (d, \(J = 243.1\) Hz), 159.5, 150.4, 141.0 (d, \(J = 7.7\) Hz), 136.0, 134.9, 131.3, 131.2, 131.1 (d, \(J = 3.1\) Hz), 130.8, 130.4, 129.4, 123.52, 123.50, 114.8 (d, \(J = 20.7\) Hz), 113.4 (d, \(J = 22.2\) Hz), 55.6, 54.2; \(^{19}\)F NMR (acetone-d\(_6\)) \(\delta\) −115.09 (q, \(J = 9.3\) Hz, 1F); HRMS (ESI-TOF) \(m/z\) [M+H]+ calcd for C\(_{23}\)H\(_{20}\)FO\(_3\) 363.1391, found 363.1388.

1-methoxy-2-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)-benzene (7)

The title compound was derived from (2-methoxyphenyl)(p-tolyl)methanol (3i) (65.8 mg, 0.288 mmol, 1.0 equiv), potassium trifluoro(phenylethynyl) borate (1a) (60.0 mg, 0.288 mmol, 1.0 equiv), and HBF\(_4\)·OEt\(_2\) (74.6 mg, 0.461 mmol, 1.6 equiv) in 1.0 mL of CH\(_3\)CN. Purification by automated flash column chromatography on silica gel using hexanes/diethyl ether (99:1) afforded product 7 (60.1 mg, 67% yield) as a yellow oil. IR (Diamond-ATR) \(\nu\) 1597, 1488, 1460, 1243, 1103, 1026, 803, 749, 690, 560, 524 cm\(^{-1}\).
$^1$H NMR (CDCl$_3$) δ 7.60–7.62 (m, 1H), 7.44–7.47 (m, 2H), 7.35 (d, $J = 8.2$ Hz, 2H), 7.25–7.29 (m, 3H), 7.19–7.23 (m, 1H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.95 (t of d, $J = 1.1$, 7.4 Hz, 1H), 6.84–6.86 (m, 1H), 5.65 (s, 1H), 3.82 (s, 3H), 2.29 (s, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 156.1, 138.8, 136.0, 131.7, 130.5, 129.0, 128.9, 128.13, 128.05, 127.71, 127.68, 123.8, 120.9, 110.7, 91.2, 83.3, 55.5, 36.2, 21.0; HRMS (DART-TOF+) m/z [M+H] calcd for C$_{23}$H$_{21}$O 313.1592, found 313.1600.

2-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)phenol (8)
The title compound was derived from 1-methoxy-2-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)benzene (7) (60.1 mg, 0.192 mmol, 1.0 equiv) and boron tribromide solution [1.0 M in methylene chloride] (0.145 g, 0.577 mmol, 3.0 equiv) in 2.0 mL of anhydrous DCM. Purification by automated flash column chromatography on silica gel using hexanes/EtOAc (gradient: 24:1 → 9:1) and subsequent CH$_3$CN/hexanes extraction afforded product 8 (42.0 mg, 73% yield) as a yellow oil. IR (Diamond-ATR) ν 3527, 1595, 1488, 1454, 1185, 1087, 822, 749, 689 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.48–7.52 (m, 2H), 7.41–7.44 (m, 1H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.31–7.35 (m, 3H), 7.19–7.22 (m, 1H), 7.17 (m, 2H), 6.96 (t of d, $J = 1.2$, 7.4 Hz, 1H), 6.85 (d of d, $J = 1.2$, 8.2 Hz, 1H), 5.50 (s, 1H), 5.44 (s, 1H), 2.35 (s, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 153.3, 137.2, 136.7, 131.7, 129.5, 129.4, 128.5, 128.23, 128.19, 127.6, 127.5, 123.0, 121.0, 116.6, 89.1, 85.3, 38.2, 21.0; HRMS (DART-TOF+) m/z [M+H] calcd for C$_{22}$H$_{19}$O 299.1436, found 299.1437.
2-benzyl-3-(p-tolyl)benzofuran (9)
The title compound was derived from 2-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)phenol (8) (42.0 mg, 0.141 mmol, 1.0 equiv) and t-BuOK (31.6 mg, 0.282 mmol, 2.0 equiv) in 1.13 mL of anhydrous dioxane. Purification by automated flash column chromatography on silica gel using hexanes/diethyl ether (gradient: 99:1 → 49:1) and subsequent CH$_3$CN/hexanes extraction afforded product 9 (19.7 mg, 47% yield) as a yellow solid. Mp 65–68 °C; IR (Diamond-ATR) ν 1512, 1492, 1453, 1159, 977, 820, 740, 719, 694, 492, 454 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.57–7.59 (m, 1H), 7.40–7.45 (m, 3H), 7.20–7.31 (m, 9H), 4.20 (s, 2H), 2.42 (s, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 154.3, 152.3, 138.0, 137.0, 129.5, 129.4, 128.9, 128.8, 128.6, 128.5, 126.5, 123.9, 122.6, 119.8, 118.1, 111.1, 32.9, 21.3; HRMS (DART-TOF+) m/z [M+H] calcd for C$_{22}$H$_{19}$O 299.1436, found 299.1440.
2-ALKENYL AND 2-ALKYNYL TETRAHYDROPYRANS

2-(phenylethynyl)tetrahydro-2H-pyran (10a)
The title compound was derived from 2-methoxytetrahydroxyran (18.7 mg, 0.161 mmol, 1.0 equiv.), potassium trifluoro(phenylethynyl)borate (1a) (50.3 mg, 0.242 mmol, 1.5 equiv.) and HBF₄·OEt₂ (32.9 μL, 0.242 mmol, 1.5 equiv.) in 1.61 mL of CH₃CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (49:1) and subsequent CH₃CN/hexanes extraction afforded product 10a (24.6 mg, 82% yield) as a yellow oil. ¹H NMR (CDCl₃) δ 7.44-7.46 (m, 2H), 7.28-7.31 (m, 3H), 4.49-4.52 (m, 1H), 4.02-4.07 (m, 1H), 3.56-3.62 (m, 1H), 1.89-1.94 (m, 1H), 1.75-1.82 (m, 1H), 1.55-1.65 (m, 3H); ¹³C {¹H} NMR (CDCl₃) δ 131.7, 128.23, 128.16, 122.7, 88.1, 85.15, 67.41, 66.59, 32.15, 25.64, 21.79.

(E)-2-styryltetrahydro-2H-pyran (10b)
The title compound was derived from 2-methoxytetrahydroxyran (11.6 mg, 0.100 mmol, 1.0 equiv.), potassium trifluoro(E)-2-phenylethynylborate (31.5 mg, 0.150 mmol, 1.5 equiv.) and HBF₄·OEt₂ (20.4 μL, 0.150 mmol, 1.5 equiv.) in 1.0 mL of CH₃CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 49:1) and subsequent CH₃CN/hexanes extraction afforded product 10b (6.7 mg, 36% yield) as a yellow oil. ¹H NMR (CDCl₃) δ 7.37-7.39 (m, 2H), 7.28-7.31 (m, 3H), 6.57-6.61 (m, 1H), 6.18-6.24 (m, 1H), 4.06-4.09 (m, 1H), 3.95-4.00 (m, 1H), 3.51-3.58 (m, 1H), 1.88-1.91 (m, 1H), 1.72-1.76 (m, 1H), 1.43-1.65 (m, 4H); ¹³C {¹H} NMR (CDCl₃) δ 137.0, 130.8, 129.7, 128.5, 127.4, 126.4, 78.0, 68.4, 32.2, 25.9, 23.4.

2-(hex-1-tn-1-yl)tetrahydro-2H-pyran (10c)
The title compound was derived from 2-methoxytetrahydroxyran (31.4 mg, 0.271 mmol, 1.0 equiv.), potassium trifluoro(hex-1-yn-1-yl)borate (1d) (76.3 mg, 0.406 mmol, 1.5 equiv.) and HBF₄·OEt₂ (55.2 μL, 0.406 mmol, 1.5 equiv.) in 2.71 mL of CH₃CN (C = 0.1 M). Aqueous work-up afforded product 10c (37.8 mg, 84% yield) as a yellow oil. ¹H NMR (CDCl₃) δ 4.21-4.24 (m, 1H), 3.95-
3.99 (m, 1H), 3.47-3.52 (m, 1H), 2.20-2.24 (m, 2H), 1.80-1.85 (m, 2H), 1.38-1.57 (m, 8H), 0.90 (t, J = 7.0 Hz, 3H); $^{13}$C $^{1}H$ NMR (CDCl$_3$) δ 85.7, 79.1, 67.3, 66.6, 32.5, 30.7, 25.7, 21.94, 21.90, 18.4, 13.5.

2-((3-fluorophenyl)ethynyl)tetrahydro-2H-pyran (10d)
The title compound was derived from 2-methoxytetrahydropyran (17.1 mg, 0.147 mmol, 1.0 equiv.), potassium trifluoro((3-fluorophenyl)ethynyl)borate (1g) (49.8 mg, 0.220 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (30.0 μL, 0.220 mmol, 1.5 equiv.) in 1.5 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (49:1) and subsequent CH$_3$CN/hexanes extraction afforded product 10d (14.3 mg, 48% yield) as a yellow oil. $^1H$ NMR (CDCl$_3$) δ 7.21-7.29 (m, 2H), 7.12-7.16 (m, 1H), 6.99-7.04 (m, 1H), 4.48-4.51 (m, 1H), 4.01-4.06 (m, 1H), 3.56-3.62 (m, 1H), 1.87-1.96 (m, 2H), 1.73-1.82 (m, 1H), 1.55-1.66 (m, 3H); $^{13}$C $^{1}H$ NMR (CDCl$_3$) δ 162.3 (d, J = 246.1 Hz), 129.8 (d, J = 9.2 Hz), 127.6 (d, J = 3.1 Hz), 124.6 (d, J = 9.2 Hz), 118.5 (d, J = 23.0 Hz), 115.6 (d, J = 21.5 Hz), 89.1, 83.9, 67.3, 66.7, 32.1, 25.6, 21.8. $^{19}$F NMR (CDCl$_3$) δ −113.12 (m, 1F);  

2-((4-methoxyphenyl)ethynyl)tetrahydro-2H-pyran (10e)
The title compound was derived from 2-methoxytetrahydropyran (16.1 mg, 0.139 mmol, 1.0 equiv.), potassium trifluoro((4-methoxyphenyl)ethynyl)borate (1b) (49.5 mg, 0.208 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (28.3 μL, 0.208 mmol, 1.5 equiv.) in 1.39 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 97:3) and subsequent CH$_3$CN/hexanes extraction afforded product 10e (10.2 mg, 34% yield) as a yellow oil. $^1H$ NMR (CDCl$_3$) δ 7.37-7.40 (m, 2H), 6.81-6.83 (m, 2H), 4.47-4.49 (m, 1H), 4.02-4.07 (m, 1H), 3.80 (s, 3H), 3.55-3.60 (m, 1H), 1.90 (m, 2H), 1.74-1.81 (m, 1H), 1.55-1.63 (m, 3H); $^{13}$C $^{1}H$ NMR (CDCl$_3$) δ 133.2, 114.9, 113.8, 86.7, 85.0, 67.6, 66.7, 55.2, 32.3, 25.7, 21.9.
2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS

2-(phenylethynyl)tetrahydrofuran (11a)
The title compound was derived from 2-ethoxytetrahydrofuran (20.2 mg, 0.174 mmol, 1.0 equiv.), potassium trifluoro(phenylethynyl)borate (1a) (54.4 mg, 0.261 mmol, 1.5 equiv.) and HBF₄·OEt₂ (35.6 μL, 0.261 mmol, 1.5 equiv.) in 1.74 mL of CH₃CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 50:1 → 17:1) and subsequent CH₃CN/hexanes extraction afforded product 11a (27.5 mg, 92% yield) as a yellow oil. ¹H NMR (CDCl₃) δ 7.42-7.44 (m, 2H), 7.28-7.30 (m, 3H), 4.79-4.83 (m, 1H), 3.98-4.04 (m, 1H), 3.83-3.88 (m, 1H), 2.04-2.12 (m, 2H), 1.90-1.98 (m, 1H); ¹³C {¹H} NMR (CDCl₃) δ 131.7, 128.19, 128.16, 122.78, 89.0, 84.4, 68.6, 67.9, 33.4, 25.5; IR (Diamond-ATR) ν 2979, 2950, 2870, 1489, 1333, 1047, 914, 754, 689 cm⁻¹.

2-(naphthalene-1-ylethynyl)tetrahydrofuran (11b)
The title compound was derived from 2-ethoxytetrahydrofuran (15.7 mg, 0.135 mmol, 1.0 equiv.), potassium trifluoro(naphthalene-1-ylethynyl)borate (1j) (52.2 mg, 0.202 mmol, 1.5 equiv.) and HBF₄·OEt₂ (27.5 μL, 0.202 mmol, 1.5 equiv.) in 1.35 mL of CH₃CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (99:1) and subsequent CH₃CN/hexanes extraction afforded product 11b (29.7 mg, 99% yield) as a yellow oil. ¹H NMR (CDCl₃) δ 8.30 (d, J = 8.2 Hz, 1H), 7.81 (t, J = 9.0 Hz, 2H), 7.66 (d, J = 7.0 Hz, 1H), 7.48-7.57 (m, 2H), 7.40 (t, J = 7.4 Hz, 1H), 4.95-4.98 (m, 1H), 4.05-4.11 (m, 1H), 3.89-3.94 (m, 1H), 2.25-2.35 (m, 1H), 2.11-2.23 (m, 2H), 1.93-2.04 (m, 1H); ¹³C {¹H} NMR (CDCl₃) δ 133.3, 133.1, 130.5, 128.7, 128.2, 126.7, 126.3, 126.1, 125.1, 120.4, 94.1, 82.5, 68.8, 67.9, 33.6, 25.5; IR (Diamond-ATR) ν 2979, 2948, 2868, 1394, 1331, 1045, 912, 798, 770, 567 cm⁻¹.

2-((4-butylphenyl)ethynyl)tetrahydrofuran (11c)
The title compound was derived from 2-ethoxytetrahydrofuran (15.3 mg, 0.131 mmol, 1.0 equiv.), potassium ((4-butylphenyl)ethynyl)trifluoroborate (1c) (52.1 mg, 0.197 mmol, 1.5 equiv.) and HBF₄·OEt₂ (26.8 μL, 0.197 mmol, 1.5 equiv.) in 1.31 mL of CH₃CN (C = 0.1 M).
Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) afforded product 11c (28.0 mg, 93% yield) as a yellow oil. $^1$H NMR (CDCl$_3$) δ 7.32-7.35 (m, 2H), 7.09-7.11 (m, 2H), 4.79-4.82 (m, 1H), 3.98-4.03 (m, 1H), 3.82-3.87 (m, 1H), 2.58 (t, $J = 7.8$ Hz, 2H), 2.18-2.27 (m, 1H), 2.02-2.14 (m, 2H), 1.88-1.98 (m, 1H), 1.53-1.61 (m, 2H), 1.28-1.38 (m, 1H), 0.91 (t, $J = 7.4$ Hz, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 143.3, 131.6, 128.3, 119.9, 88.3, 84.6, 86.6, 67.8, 35.5, 33.4, 33.3, 25.5, 22.3, 13.9; IR (Diamond-ATR) ν 2955, 2928, 2858, 1508, 1458, 1333, 1049, 914, 831, 561 cm$^{-1}$.

2-((3,4-dichlorophenyl)ethynyl)tetrahydrofuran (11e) The title compound was derived from 2-ethoxytetrahydrofuran (17.2 mg, 0.148 mmol, 1.0 equiv.), potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (1b) (53.0 mg, 0.223 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (30.3 μL, 0.223 mmol, 1.5 equiv.) in 1.48 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 12:1) afforded product 11d (23.3 mg, 78% yield) as a yellow oil. $^1$H NMR (CDCl$_3$) δ 7.35-7.38 (m, 2H), 6.80-6.83 (m, 2H), 4.78-4.81 (m, 1H), 3.98-4.03 (m, 1H), 3.82-3.87 (m, 1H), 3.79 (s, 3H), 2.18-2.25 (m, 1H), 2.02-2.14 (m, 2H), 1.89-1.98 (m, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 159.5, 133.1, 114.9, 113.8, 87.6, 84.3, 68.7, 67.8, 55.2, 33.4, 25.5; IR (Diamond-ATR) ν 2952, 2870, 2837, 1605, 1507, 1288, 1244, 1171, 1046, 1028, 830 cm$^{-1}$.

2-((3,4-dichlorophenyl)ethynyl)tetrahydrofuran (11e) The title compound was derived from 2-ethoxytetrahydrofuran (14.5 mg, 0.124 mmol, 1.0 equiv.), potassium trifluoro((3,4-dichlorophenyl)ethynyl)borate (1e) (51.7 mg, 0.187 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (25.4 μL, 0.187 mmol, 1.5 equiv.) in 1.24 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (99:1) and subsequent CH$_3$CN/hexanes extraction afforded product 11e (19.3 mg, 64% yield) as a yellow oil. $^1$H NMR (CDCl$_3$) δ 7.51-7.52 (m, 1H), 7.35-7.37 (m, 1H), 7.23-7.26 (m, 1H), 4.77-4.80 (m, 1H), 3.96-4.02 (m, 1H), 3.83-3.88 (m, 1H), 2.19-2.28 (m, 1H), 2.02-2.14 (m, 2H), 1.90-1.99 (m, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 133.3, 132.7, 132.4, 130.8, 130.3, 122.8, 91.2, 82.2, 68.4, 68.1, 33.3, 25.5; IR
2-((3-fluorophenyl)ethynyl)tetrahydrofuran (11f)
The title compound was derived from 2-ethoxytetrahydrofuran (18.3 mg, 0.158 mmol, 1.0 equiv.), potassium trifluoro((3-fluorophenyl)ethynyl)borate (1g) (53.5 mg, 0.237 mmol, 1.5 equiv.) and HBF₄·OEt₂ (32.2 μL, 0.237 mmol, 1.5 equiv.) in 1.58 mL of CH₃CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (50:1) and subsequent CH₃CN/hexanes extraction afforded product 11f (18.4 mg, 61% yield) as a yellow oil. 

1H NMR (CDCl₃) δ 7.19-7.28 (m, 2H), 7.11-7.14 (m, 1H), 6.98-7.03 (m, 1H), 4.79-4.82 (m, 1H), 3.98-4.03 (m, 1H), 3.84-3.89 (m, 1H), 2.20-2.29 (m, 1H), 2.03-2.13 (m, 2H), 1.90-1.99 (m, 1H); 13C {¹H} NMR (CDCl₃) δ 162.3 (d, J = 246.1 Hz), 129.8 (d, J = 9.2 Hz), 127.5 (d, J = 3.8 Hz), 124.6 (d, J = 9.2 Hz), 118.5 (d, J = 22.2 Hz), 115.6 (d, J = 21.5 Hz), 90.1, 83.2 (d, J = 3.8 Hz), 68.5, 68.0, 33.3, 25.5; 19F NMR (CDCl₃) δ -113.14 (q, J = 5.9 Hz, 1F); IR (Diamond-ATR) ν 2980, 2952, 2872, 1579, 1485, 1173, 1149, 1048, 869, 782, 681 cm⁻¹.

2-((2-(trifluoromethyl)phenyl)ethynyl)tetrahydrofuran (11g)
The title compound was derived from 2-ethoxytetrahydrofuran (14.5 mg, 0.123 mmol, 1.0 equiv.), potassium trifluoro((2-(trifluoromethyl)phenyl)ethynyl)borate (1h) (51.7 mg, 0.187 mmol, 1.5 equiv.) and HBF₄·OEt₂ (25.5 μL, 0.187 mmol, 1.5 equiv.) in 1.25 mL of CH₃CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) and subsequent CH₃CN/hexanes extraction afforded product 11g (24.7 mg, 82% yield) as a yellow oil. 

1H NMR (CDCl₃) δ 7.62-7.64 (m, 1H), 7.56-7.58 (m, 1H), 7.45-7.48 (m, 1H), 7.37-7.40 (m, 1H), 4.85-4.87 (m, 1H), 3.98-4.04 (m, 1H), 3.85-3.91 (m, 1H), 2.18-2.26 (m, 1H), 2.06-2.17 (m, 2H), 1.90-1.99 (m, 1H); 13C {¹H} NMR (CDCl₃) δ = 133.9, 131.8, 131.3, 128.0, 125.7 (q, J = 5.4 Hz), 123.5 (q, J = 273.8 Hz), 121.1 (q, J = 2.3 Hz), 95.0, 80.3, 68.5, 67.9, 33.1, 25.1; 19F NMR (CDCl₃) δ -62.48 (s, 3F); IR (Diamond-ATR) ν 2981, 2874, 1315, 1166, 1128, 1109, 1049, 1032, 764 cm⁻¹.
2-(hex-1-yn-1-yl)tetrahydrofuran (11h)
The title compound was derived from 2-ethoxytetrahydrofuran (22.9 mg, 0.197 mmol, 1.0 equiv.), potassium trifluoro(hex-1-yn-1-yl)borate (1d) (55.6 mg, 0.296 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (40.2 μL, 0.296 mmol, 1.5 equiv.) in 1.97 mL of CH$_3$CN (C = 0.1 M). Aqueous workup afforded product 11h (19.3 mg, 64% yield) as a yellow oil. A pure sample was obtained after the work-up. Attempts to run the crude product through a pad of silica gel resulted in the decomposition of 11h. $^1$H NMR (CDCl$_3$) δ 4.53-4.57 (m, 1H), 3.91-3.97 (m, 1H), 3.75-3.80 (m, 1H), 2.20 (td, $J = 2.0, 7.0$ Hz, 2H), 2.08-2.16 (m, 1H), 1.97-2.07 (m, 1H), 1.82-1.95 (m, 2H), 1.44-1.52 (m, 2H), 1.35-1.42 (m, 2H), 0.90 (t, $J = 7.4$ Hz, 3H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 85.2, 79.9, 68.4, 67.6, 33.5, 30.7, 25.4, 21.9, 18.4, 13.6; IR (Diamond-ATR) ν 2956, 2931, 2871, 1458, 1355, 1332, 1051, 907 cm$^{-1}$.

(E)-2-styryltetrahydrofuran (12a)
The title compound was derived from 2-ethoxytetrahydrofuran (20.0 mg, 0.172 mmol, 1.0 equiv.), potassium trans-styryltrifluoroborate (54.2 mg, 0.258 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (35.1 μL, 0.258 mmol, 1.5 equiv.) in 1.72 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 19:1) and subsequent CH$_3$CN/hexanes extraction afforded product 12a (22.3 mg, 74% yield) as a yellow oil. $^1$H NMR (CDCl$_3$) δ 7.37-7.39 (m, 2H), 7.28-7.32 (m, 2H), 7.20-7.25 (m, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.20 (dd, $J = 6.3, 15.6$ Hz, 1H), 4.44-4.50 (m, 1H), 3.94-4.00 (m, 1H), 3.81-3.86 (m, 1H), 2.08-2.16 (m, 1H), 1.88-2.04 (m, 2H), 1.67-1.75 (m, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 136.8, 130.5, 130.4, 128.5, 127.4, 126.4, 79.6, 68.1, 32.4, 25.9; IR (Diamond-ATR) ν 2971, 2867, 1493, 1448, 1049, 963, 745, 691 cm$^{-1}$.

(E)-2-(3-fluorostyryl)tetrahydrofuran (12b)
The title compound was derived from 2-ethoxytetrahydrofuran (18.1 mg, 0.156 mmol, 1.0 equiv.), potassium 2-(3-fluorophenyl)vinyltrifluoroborate (53.4 mg, 0.234 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (31.9 μL, 0.234 mmol, 1.5 equiv.) in 1.56 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 19:1) and subsequent CH$_3$CN/hexanes extraction afforded product
12b (23.4 mg, 78% yield) as a yellow oil. $^1$H NMR (CDCl$_3$) δ 7.23-7.28 (m, 1H), 7.06-7.14 (m, 2H), 6.89-6.94 (m, 1H), 6.55 (d, $J = 15.6$ Hz, 1H), 6.22 (dd, $J = 6.3$, 16.0 Hz, 1H), 4.45-4.50 (m, 1H), 3.94-4.00 (m, 1H), 3.82-3.87 (m, 1H), 2.09-2.17 (m, 1H), 1.89-2.04 (m, 2H), 1.65-1.75 (m, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 163.0 (d, $J = 245.4$ Hz), 139.2 (d, $J = 7.7$ Hz), 132.0, 129.9 (d, $J = 8.4$ Hz), 129.1 (d, $J = 3.1$ Hz), 122.3 (d, $J = 3.1$ Hz), 114.2 (d, $J = 21.5$ Hz), 112.8 (d, $J = 21.5$ Hz), 79.3, 68.2, 32.3, 25.9; $^{19}$F NMR (CDCl$_3$) δ -113.71 (q, $J = 6.3$ Hz, 1F); IR (Diamond-ATR) ν 2972, 2869, 1582, 1487, 1445, 1264, 1142, 1050, 962, 870, 776, 682 cm$^{-1}$.

(E)-2-(4-(trifluoromethyl)styryl)tetrahydrofuran (12c)

The title compound was derived from 2-ethoxytetrahydrofuran (14.4 mg, 0.124 mmol, 1.0 equiv.), potassium (E)-trifluoro(4-(trifluoromethyl)styryl)borate (51.7 mg, 0.186 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (25.3 μL, 0.186 mmol, 1.5 equiv.) in 1.24 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) and subsequent CH$_3$CN/hexanes extraction afforded product 12c (23.5 mg, 78% yield) as a yellow oil. $^1$H-NMR (CDCl$_3$) δ 7.55 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 6.62 (d, $J = 16.0$ Hz, 1H), 6.31 (dd, $J = 6.6$, 16.0 Hz, 1H), 4.50 (q, $J = 6.6$ Hz, 1H), 3.96–4.01 (m, 1H), 3.83–3.89 (m, 1H), 2.11–2.19 (m, 1H), 1.92–2.04 (m, 2H), 1.68–1.77 (m, 1H); $^{13}$C {$^1$H} NMR (CDCl$_3$) δ 140.3 (q, $J = 1.5$ Hz), 133.3, 129.4, 129.1, 128.8, 126.5, 125.4 (q, $J = 3.8$ Hz), 79.2, 68.3, 32.3, 25.9; $^{19}$F NMR (CDCl$_3$) δ -62.50 (s, 1F); IR (Diamond-ATR) ν 2977, 2869, 1612, 1322, 1162, 1103, 1066, 1047, 860, 813 cm$^{-1}$.

(E)-2-(4-methylstyryl)tetrahydrofuran (12d)

The title compound was derived from 2-ethoxytetrahydrofuran (18.5 mg, 0.159 mmol, 1.0 equiv.), potassium (E)-trifluoro(4-methylstyryl)borate (2) (53.6 mg, 0.239 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (32.5 μL, 0.239 mmol, 1.5 equiv.) in 1.59 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 16:1) afforded product 12d (16.1 mg, 54% yield) as a yellow oil. $^1$H NMR (CDCl$_3$) δ 7.26–7.28 (m, 2H), 7.10–7.11 (m, 2H), 6.55 (d, $J = 16.0$ Hz, 1H), 6.15 (dd, $J = 6.6$, 15.6 Hz, 1H),
4.45 (q, J = 6.7 Hz, 1H), 3.94-3.99 (m, 1H), 3.80-3.86 (m, 1H), 2.32 (s, 3H), 2.07-2.15 (m, 1H), 1.88-2.01 (m, 2H), 1.66-1.75 (m, 1H); $^{13}$C $^{1}$H NMR (CDCl$_3$) δ 137.3, 134.1, 130.4, 129.4, 129.2, 126.3, 79.77, 68.1, 32.4, 25.9, 21.2; IR (Diamond-ATR) ν 2970, 2922, 2864, 1513, 1050, 964, 795, 513 cm$^{-1}$.

$(E)$-2-(2-([1,1′-biphenyl]-4-yl)vinyl)tetrahydrofuran (12e)

The title compound was derived from 2-ethoxytetrahydrofuran (13.9 mg, 0.120 mmol, 1.0 equiv.), potassium $(E)$-2-([1,1′-biphenyl]-4-yl)trifluoroborate (51.4 mg, 0.180 mmol, 1.5 equiv.), and HBF$_4$·OEt$_2$ (24.5 μL, 0.180 mmol, 1.5 equiv.) in 1.20 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 13:1) and subsequent CH$_3$CN/hexanes extraction afforded product 12e (21.6 mg, 72% yield) as a white solid. $^1$H-NMR (CDCl$_3$) δ 7.53–7.60 (m, 4H), 7.40–7.46 (m, 4H), 7.31–7.35 (m, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.25 (dd, J = 6.6, 15.6 Hz, 1H), 4.49 (q, J = 6.6 Hz, 1H), 3.95–4.01 (m, 1H), 3.82–3.86 (m, 1H), 2.10–2.18 (m, 1H), 1.89–2.02 (m, 2H), 1.68–1.77 (m, 1H); $^{13}$C $^{1}$H NMR (CDCl$_3$) δ 140.7, 140.2, 135.9, 130.6, 129.9, 128.7, 127.2, 127.1, 126.9, 126.8, 79.7, 68.2, 32.4, 25.9; IR (Diamond-ATR) ν 2928, 2852, 1486, 1048, 971, 854, 758, 687, 489 cm$^{-1}$; HRMS (DART-TOF+) m/z [M + H] calcd for C$_{18}$H$_{19}$O 251.1436, found 251.1437.

2-(1H-inden-2-yl)tetrahydrofuran (12f)

The title compound was derived from 2-ethoxytetrahydrofuran (18.7 mg, 0.161 mmol, 1.0 equiv.), potassium trifluoro(1H-inden-2-yl)borate (53.6 mg, 0.242 mmol, 1.5 equiv.) and HBF$_4$·OEt$_2$ (32.9 μL, 0.242 mmol, 1.5 equiv.) in 1.61 mL of CH$_3$CN (C = 0.1 M). Purification by automated flash column chromatography on silica gel using hexanes/ethyl acetate (gradient: 99:1 → 13:1) and subsequent CH$_3$CN/hexanes extraction afforded product 12f (23.6 mg, 79% yield) as a yellow oil. $^1$H-NMR (CDCl$_3$) δ 7.40–7.42 (m, 1H), 7.30–7.32 (m, 1H), 7.11–7.15 (m, 1H), 4.82 (t, J = 7.0 Hz, 1H), 3.97–4.02 (m, 1H), 3.84–3.90 (m, 1H), 3.39 (s, 2H), 2.15–2.23 (m, 1H), 1.95–2.03 (m, 2H), 1.81–1.89 (m, 1H); $^{13}$C $^{1}$H NMR (CDCl$_3$) δ 150.4, 144.7, 143.2, 126.6, 126.3, 124.2, 123.6, 120.6, 77.7, 68.2, 38.1, 32.1, 26.0; IR (Diamond-ATR) ν 2971, 2868, 1459, 1390, 1050, 916, 850, 751, 716, 555 cm$^{-1}$. 83
APPENDIX II: NMR SPECTRA

POTASSIUM TRIFLUOROBORATE SALTS

1a
(DMSO-d$_6$, 400 MHz)

1a
(DMSO-d$_6$, 100 MHz)
MeO-\(\equiv\)BF\(_3\)K

1b
(DMSO-\(d_6\), 400 MHz)

MeO-\(\equiv\)BF\(_3\)K

1b
(DMSO-\(d_6\), 100 MHz)
Bu-\(\equiv\)BF\(_3\)K

1c
(DMSO-\(d_6\), 400 MHz)

Bu-\(\equiv\)BF\(_3\)K

1c
(DMSO-\(d_6\), 100 MHz)
$\equiv BF_3K$

1d
(DMSO-$d_6$, 400 MHz)

$\equiv BF_3K$

1d
(DMSO-$d_6$, 100 MHz)
Cl\text{-}\text{C}_6\text{H}_4\text{-}\equiv\text{BF}_3\text{K}

1e

(DMSO-\text{d}_6, 400 MHz)

Cl\text{-}\text{C}_6\text{H}_4\text{-}\equiv\text{BF}_3\text{K}

1e

(DMSO-\text{d}_6, 100 MHz)
Cl\[\text{C}_6\text{H}_4\\equiv\text{BF}_3\text{K}

1f
(DMSO-d$_6$, 400 MHz)

Cl\[\text{C}_6\text{H}_4\\equiv\text{BF}_3\text{K}

1f
(DMSO-d$_6$, 100 MHz)
$\text{Ph} - \equiv \text{BF}_3\text{K}$

1g

(DMSO-d$_6$, 400 MHz)

$\text{Ph} - \equiv \text{BF}_3\text{K}$

1g

(DMSO-d$_6$, 100 MHz)
$\text{F}_3\text{C} \equiv \text{BF}_3\text{K}$

(DMSO-$d_6$, 400 MHz)

$\text{F}_3\text{C} \equiv \text{BF}_3\text{K}$

(DMSO-$d_6$, 100 MHz)
1k
(DMSO-d$_6$, 400 MHz)

1k
(DMSO-d$_6$, 100 MHz)
$\text{BF}_3\text{K}$

**2b**

*(DMSO-$d_6$, 400 MHz)*

$\text{BF}_3\text{K}$

**2b**

*(DMSO-$d_6$, 100 MHz)*

96
BENZHYDRYL ALCOHOLS
INTERNAL ALKENES AND ALKYNES

4a
(CDCl₃, 400 MHz)

4a
(CDCl₃, 100 MHz)
4b
(CDCl₃, 400 MHz)

4b
(CDCl₃, 100 MHz)
4j
(acetone-$d_6$, 400 MHz)

(acetone-$d_6$, 100 MHz)
BENZOFURAN

(CDC\textsubscript{3}, 400 MHz)

(CDC\textsubscript{3}, 100 MHz)
2-ALKENYL AND 2-ALKYNYL TETRAHYDROPYRANS

10a
(CDCl₃, 400 MHz)

10a
(CDCl₃, 100 MHz)
$\textbf{10c}$
(CDC$_3$, 400 MHz)

$\textbf{10c}$
(CDC$_3$, 100 MHz)
2-ALKENYL AND 2-ALKYNYL TETRAHYDROFURANS

11a
(CDC$_3$, 400 MHz)

11a
(CDC$_3$, 100 MHz)
12d (CDCl₃, 400 MHz)

12d (CDCl₃, 100 MHz)
APPENDIX III: NMR STUDIES

NMR 1:
16 μL of HBF₄·OEt₂ in 0.6 mL of CD₃CN was transferred to a NMR tube and the following spectra were acquired immediately.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>¹H NMR</strong></td>
<td><img src="image" alt="1H NMR spectrum" /></td>
</tr>
<tr>
<td><strong>¹³C NMR</strong></td>
<td><img src="image" alt="13C NMR spectrum" /></td>
</tr>
<tr>
<td><strong>¹⁹F NMR</strong></td>
<td><img src="image" alt="19F NMR spectrum" /></td>
</tr>
</tbody>
</table>
NMR 2:
14.0 mg of 4-methylbenzhydryl alcohol in 0.6 mL of CD₃CN was transferred to a NMR tube and the following spectra were acquired immediately.

**¹H NMR**

**¹³C NMR**
**NMR 3:**
14.7 mg of potassium phenylacetylenetri fluoroborate 1a in 0.6 mL of CD₃CN was transferred to a NMR tube and the following spectra were acquired immediately.

**1H NMR**

**13C NMR**

**19F NMR**
**NMR 4:**
In a NMR tube containing 14.7 mg of potassium phenylacetylenetrifluoroborate 1a (1.0 equiv.) and 0.6 mL of CD$_3$CN, 16 µL of HBF$_4$·OEt$_2$ (1.6 equiv.) was added. The NMR tube was gently mixed and the following spectra were acquired immediately.

<table>
<thead>
<tr>
<th></th>
<th>$^{1}$H NMR</th>
<th>$^{13}$C NMR</th>
<th>$^{19}$F NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image1" alt="1H NMR spectrum" /></td>
<td><img src="image2" alt="13C NMR spectrum" /></td>
<td><img src="image3" alt="19F NMR spectrum" /></td>
</tr>
</tbody>
</table>

159
NMR 5:
In a NMR tube containing 14.0 mg of 4-methylbenzydryl alcohol (1.0 equiv.) and 0.6 mL of CD$_3$CN, 16 μL of HBF$_4$·OEt$_2$ (1.6 equiv.) was added. The NMR tube was gently mixed and the following spectra were acquired immediately.

<table>
<thead>
<tr>
<th></th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
<th>$^{19}$F NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$^1$H NMR</strong></td>
<td><img src="image1" alt="1H NMR spectrum" /></td>
<td><img src="image2" alt="13C NMR spectrum" /></td>
<td><img src="image3" alt="19F NMR spectrum" /></td>
</tr>
<tr>
<td><strong>$^{13}$C NMR</strong></td>
<td><img src="image2" alt="13C NMR spectrum" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>$^{19}$F NMR</strong></td>
<td></td>
<td></td>
<td><img src="image3" alt="19F NMR spectrum" /></td>
</tr>
</tbody>
</table>
7. REFERENCES


