Ring-Opening and Ring-Expansion Reactions of *Gem*-Difluorinated Cyclopropanes and Cyclopropenones

Vor der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

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I, Xingben Wang, declare that this thesis and the work presented in it are my own and have been generated by me as the result of my original research.

Hiermit erkläre ich an Eides statt / I do solemnly swear that:

1. This work was done wholly or mainly while in candidature for the doctoral degree at this faculty and university.

2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this university or any other institution, this has been clearly stated.

3. Where I have consulted the published work of others or myself, this is always clearly attributed.

4. Where I have quoted from the work of others or myself, the source is always given. This thesis is entirely my work, with the exception of such quotations.

5. I have acknowledged all major sources of assistance.

6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what others did and I contributed myself.

7. Parts of this work have been published before. See the of list references below.

8. ChatGPT and Grammarly were used for the language corrections of this thesis.

The work presented in this thesis was carried out from October 2020 until December 2023 at the Institute of Organic Chemistry, RWTH Aachen University, under the supervision of Professor Dr. Frédéric W. Patureau.

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X. B. Wang, C. Yu, I. L. Atodiresei, and F. W. Patureau*. Phosphine catalyzed dearomative [3+2] cycloaddition of benzoxazoles with a cyclopropenone, *Org. Lett.* **2022**, 24, 1127.

X. B. Wang, F. Xiao, and F. W. Patureau*. CO_2 and Palladium Enabled Highly Chemoselective Hydroxylation of gem-Difluorocyclopropanes, *Org. Chem. Front.* **2024**, 11, advance article.

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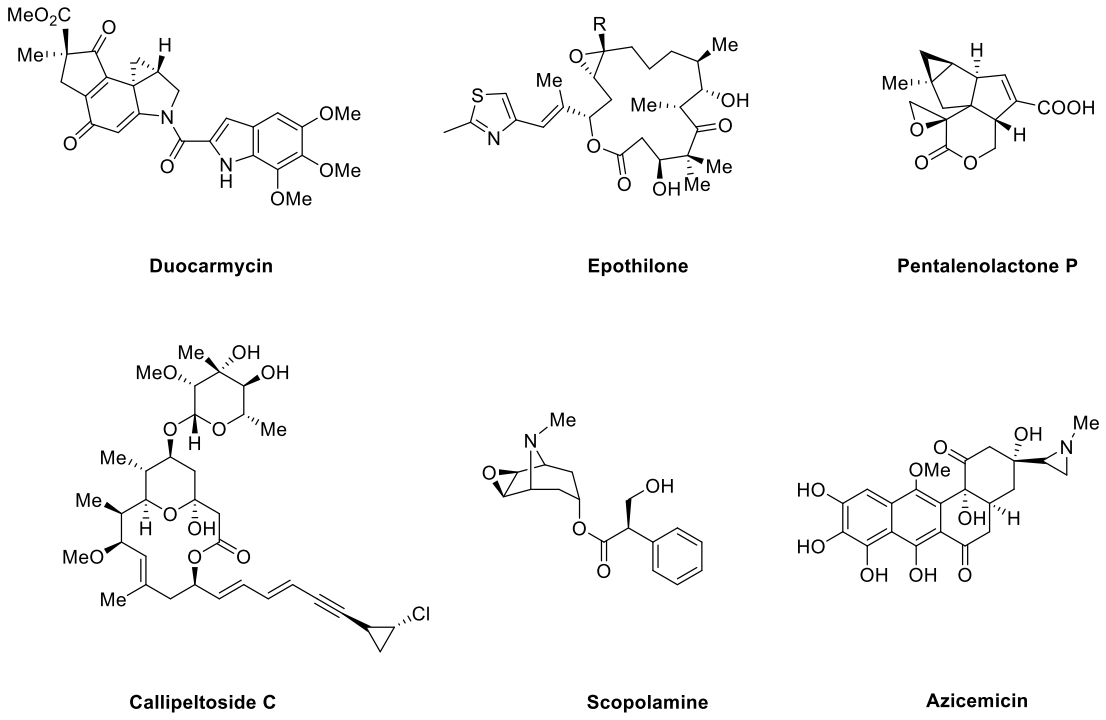
1 Introduction

1.1 Development of Three-Membered Rings

The development of numerous novel medications [1-3] is an ongoing process driven by scientific and technological advancements. However, the synthesis of diverse structural medicinal compounds requires continuous research and development efforts from organic chemists and pharmacologists. One highly efficient approach to synthesizing cyclic structures [4-5] involves the formation of new C-C and C-X bonds [6], which are essential for constructing a wide range of cyclic structures commonly found in medicinal compounds.

Nonetheless, establishing novel chemical bonds presents significant challenges due to the limited reactivity and inert nature of existing chemical bonds. Therefore, it is imperative to develop methodologies for such research that not only demonstrates high selectivity but also high reactivity. This pursuit of selective and active methodologies is crucial for the advancement of medicinal chemistry and the development of new therapeutic agents (**Scheme 1**).

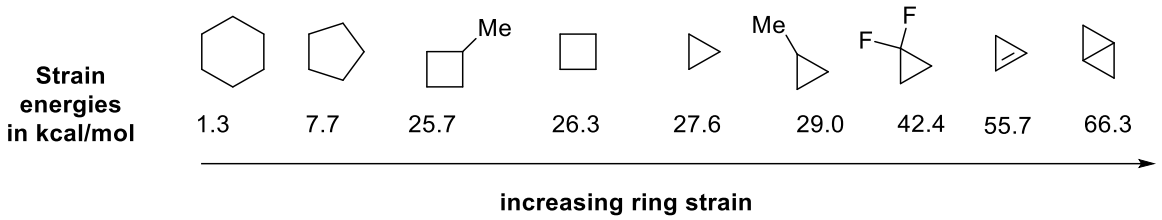


Scheme 1 Natural products and biological molecules

Over the past few decades, transition metal catalysts have proven highly advantageous in facilitating C-C or C-X bond cleavage of heterocyclic and cyclic compounds in cross coupling reactions (**Scheme 2**). Our literature investigation has revealed that small-ring compounds [7-9], particularly three- and four-membered rings, [10] play a pivotal role in activating of C-C bonds with transition metals. Among cyclic structures, the six-membered ring exhibit the highest stability, while the five-membered ring compounds are relatively similar, characterized by ring tensions mostly below 10 kcal/mol. Furthermore, ring strain intensifies when the ring is further condensed, as observed in three- or four-membered rings. While the addition of substituents can alleviate ring strain due to the

Thorpe-Ingold effect, the strain remains notably higher compared to the compounds with five- and six-membered rings. We also observed that ring tension increases with ring expansion, but synthesizing these macrocyclic molecules is challenging.

The choice of three-membered ring compounds as focal points in transition metal-catalyzed C-C bond activation to induce ring-opening and ring-expansion reactions holds considerable significance. Three-membered ring compounds are simple to make and handle, and their relatively high inherent ring strain promotes the formation of cyclic compounds. [11-14]

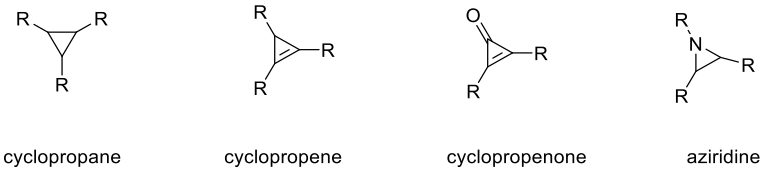


Scheme 2 Strain of various small ring compounds

1.2 Synthesis of Three-Membered Rings

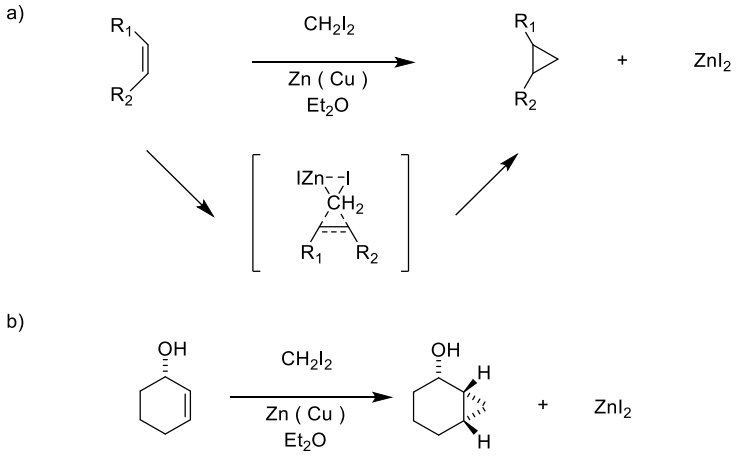
1.2.1 Synthesis of Cyclopropane Derivatives

Cyclopropane derivatives encompass cyclopropanes, cyclopropenes, cyclopropenones, and heteroatom-containing cyclopropanes, [15-19] which can be substituted with various functional groups. These differently structured cyclopropanes exhibit entirely diverse chemical properties and react in distinct ways. Therefore, it is worth research how to synthesize cyclopropane derivatives utilizing molecules with diverse structural architectures. This section mainly focuses on synthesizing cyclopropane derivatives with a range of structural variations, offering essential support for the continued utilization of cyclopropane in various reactions (**Scheme 3**).



Scheme 3 Three-membered rings with different structures

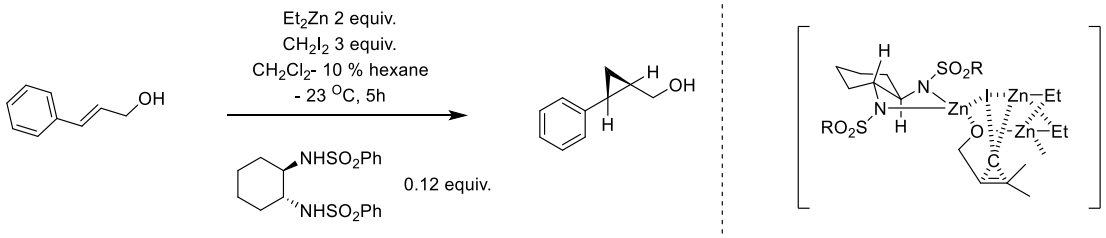
The most practical and effective method for synthesis of cyclopropanes involves the cycloaddition reaction between carbene reagents and alkenes. As early as 1958, Howard Ensign Simmons and R. D. Smith's team [20] discovered that 1,1-dihalides in conjunction with zinc-copper couples can produce carbene-like reagents in situ. Notably, diethyl zinc can substitute the zinc-copper couple, enhancing the practicality of this reaction significantly. This reaction demonstrates the high degree of stereospecificity and is particularly sensitive to steric hindrance. Moreover, targeting the side with lower steric hindrance for addition is relatively straightforward (**Scheme 4**).



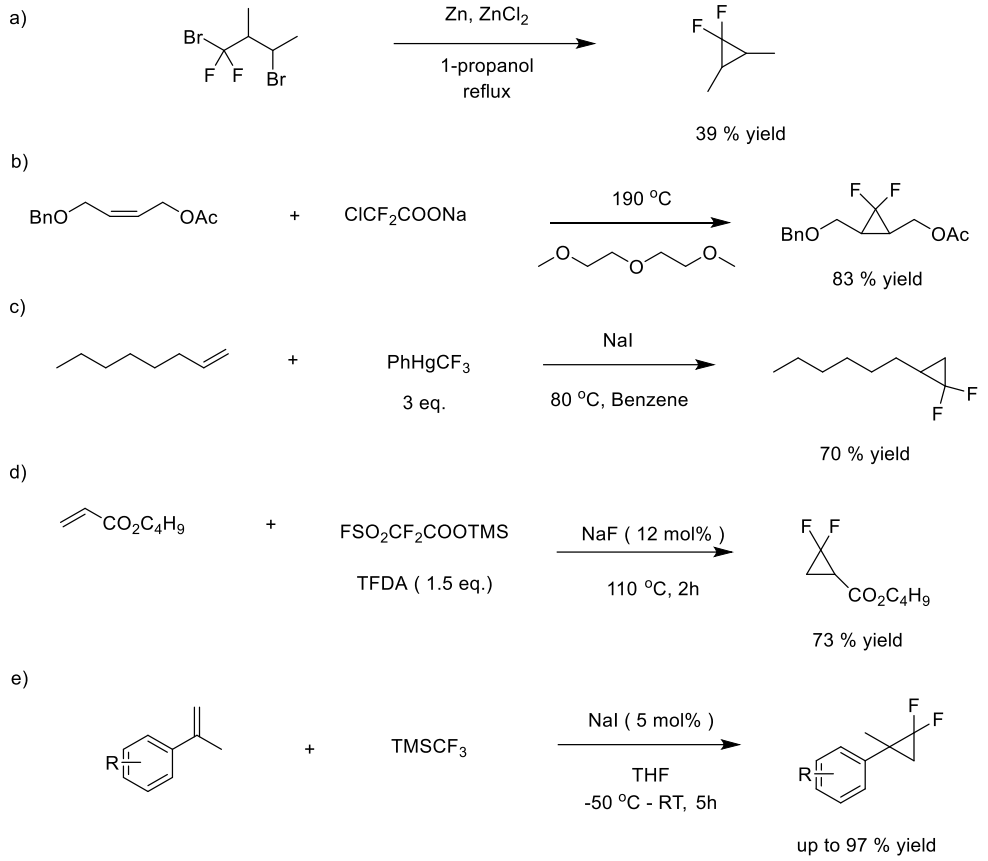
Scheme 4 Synthesis of cyclopropane via organozinc reagents

Although the Simmons–Smith reaction was discovered very early, its asymmetric synthesis was not reported until 1992. Kobayashi and colleagues [21] successfully achieved an asymmetric reaction for the cyclopropanation of cinnamyl alcohol by incorporating a chiral di-sulfonamide in this reaction. The presence of a hydroxyl group is crucial for this reaction as the zinc-copper couple can react with the hydroxyl group. Its further coordination with the chiral di-sulfonamide ligand allows for stereoselective control to be achieved, resulting in moderate enantioselectivity. Additionally, up

until 2008, Katsuki's research team [22] achieved high efficiency and enantioselectivity in the cyclopropanation reaction using other chiral ligands (**Scheme 5**).



Scheme 5 Synthesis of chiral cyclopropanes via organozinc regents



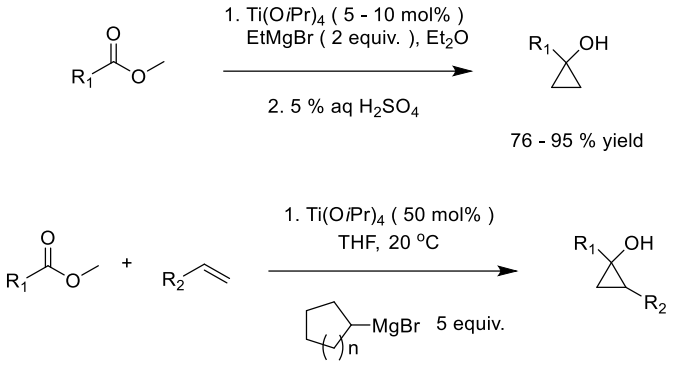
Scheme 6 Synthesis of difluorocyclopropanes

One significant class of cyclopropane compounds is difluorocyclopropane. The introduction of fluorine atoms substantially alters their chemical properties. As early as 1955, the Tarrant and Lilyquist groups [23] reported the zinc-mediated cyclopropanation of 1,3-dibromo-2,2-difluoro-2-methylbutane, synthesis 1,1-difluoro-2,3-dimethylcyclopropane in a 39% yield (**Scheme 6a**). However, there was considerable room for improvement due to limited reactants and low yields. The synthesis of difluorocyclopropane witnessed advancements upon the discovery of difluorocarbene in 1960, offering a new avenue for its synthesis. Nonetheless, the direct addition of difluorocarbene to olefins necessitated high temperatures, leading to challenges due to side reactions in olefins at elevated temperatures.

In 1960, the Haszeldine group [24] reported the pyrolysis of sodium chlorodifluoroacetate in refluxing diglyme, synthesis difluorocarbene and enabling its cyclopropanation reaction with

olefins. However, this reaction required a high temperature of up to 190 °C (**Scheme 6b**). Subsequently, in 1972, the Seyferth group [25] introduced a different method for synthesizing difluorocarbene using $PhHgCF_3$ and NaI. Nevertheless, the Seyferth reagent's high toxicity and challenges in industrialization limited its use for difluorocyclopropane synthesis (**Scheme 6c**).

Reports on the less active *n*-butyl acrylates reacting with difluorocarbenes were scarce until 2000. The Dolbier group [26] employed trimethylsilyl fluorosulfonyl difluoroacetic (TFDA) under NaF conditions to generate difluorocarbene, which under specific conditions, led to the corresponding product (**Scheme 6d**). In 2011, Prakash and Hu's team [27] introduced an handling and more practical method for synthesizing difluorocyclopropane. Using $TMSCF_3$ with a catalytic amount of NaI was required to generate difluorocarbene. The mild reaction conditions, versatile substrate, and excellent yields provide robust support for further exploration into the ring-opening and ring-expansion reactions of *gem*-difluorocyclopropanes (**Scheme 6e**).



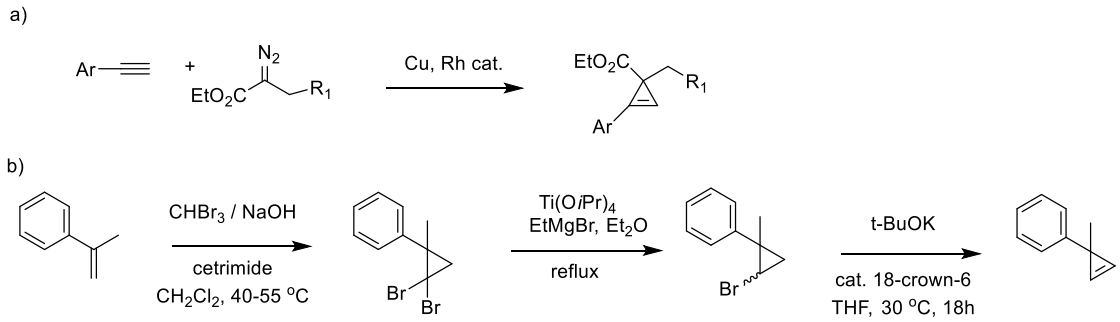
Scheme 7 Synthesis of cyclopropanol

Another significant category of cyclopropane derivatives comprises cyclopropanol compounds. The three-membered ring of cyclopropanol is exceptionally unstable due to its high strain, often resulting in the production of propionaldehyde upon ring breakage. Despite this instability, its high reactivity allows for straightforward addition of cyclopropyl groups to molecules, significantly enhancing the antiviral capabilities of medications. In 1989, O. Kulinkovich and colleagues [28-29] successfully executed a reaction involving the Grignard reagent with an ester to produce cyclopropanol using $Ti(OiPr)_4$ as a catalyst. This reaction exhibits a wide range of applications and accommodates functional groups such as ether, thioether, and imine. Through further investigation into the mechanism of reaction, Kulinkovich and associates [30] discovered that Ti-cyclopropane intermediates, analogous to alkenes, are formed by exchanging ligands with alkenes. This facilitates the utilization of all alkenes participating in the reaction, significantly expanding potential application of the reaction. Consequently, the provision of various alkenes enables the production of cyclopropanol with desired structures. For the asymmetric synthesis of cyclopropanol, Corey's research team [31] employed the chira taddol ligand to realize the asymmetric catalysis of this reaction (**Scheme 7**).

1.2.2 Synthesis of Cyclopropene Derivatives

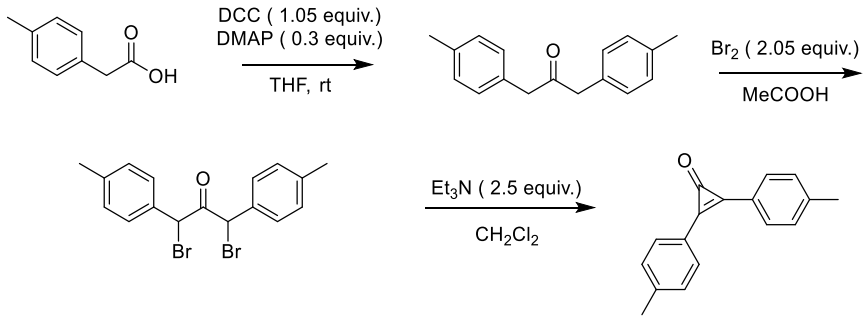
Cyclopropene derivatives [32-34] are compounds that not only exhibit the high tension of the three-membered ring but also contain the vinyl functional groups, which have garnered considerable attention in research. Althoughy the studies on cyclopropene derivatives began in the 19th century,

it wasn't until 1922 that Demjanov and colleagues achieved its effective synthesis and isolation. Following this milestone, researchers developed several novel methods for synthesizing cyclopropane derivatives. For cyclopropene compounds containing electron-withdrawing groups, a direct approach involves generating carbene intermediates from diazo compounds catalyzed by metals such as Cu and Rh. These carbene intermediates then undergo subsequent reactions with various alkynes, resulting in the formation of the corresponding cyclopropene compounds (**Scheme 8a**).[36] Synthesizing of cyclopropenes with an electron-donating group is more challenging. Initially, dibromocyclopropane is synthesized from alkenes and tribromomethane under NaOH. Subsequently, the removal of one bromine atom occurs under Ti catalyst and ethylmagnesium bromide. Finally, the elimination reaction in the presence of *t*-BuOH yields the final product (**Scheme 8b**).[37]



Scheme 8 Synthesis of ordinary cyclopropenes

In 1958, Breslow and his colleagues achieved the first synthesis of cyclopropenones. Subsequently, various synthetic methods were developed. [38-39] One of the most practical approaches for synthesizing cyclopropenone involves initiating the process with 4-Me phenylacetic acid, followed by a condensation reaction with DCC and DMAP to generate the corresponding ketone. Next, the addition of Br_2 in the presence of acetic acid as solvent, leads to the formation of a dibromo-substituted product. Finally, two molecules of HBr are removed with the assistance of triethylamine to obtain the desired product, cyclopropenone. (**Scheme 9**).

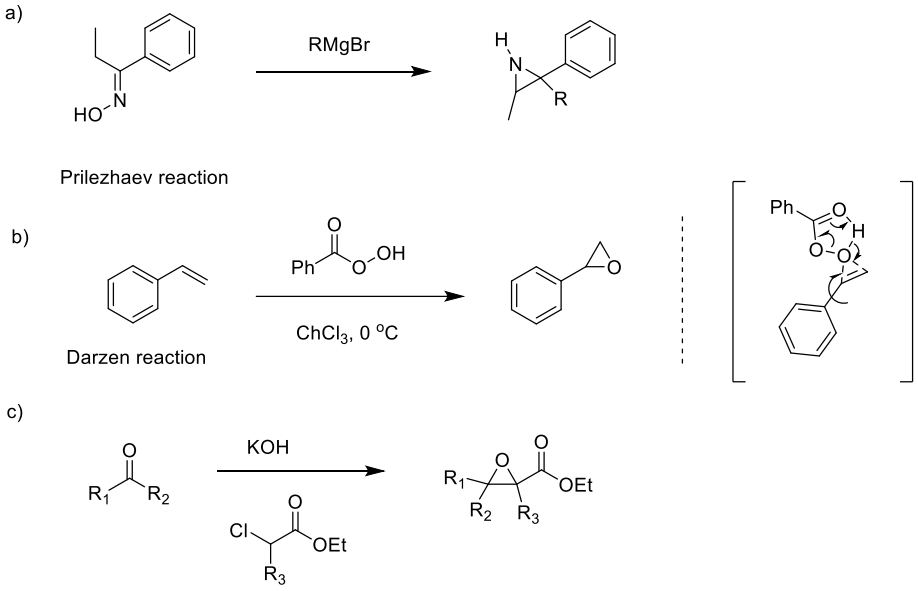


Scheme 9 Synthesis of ordinary cyclopropenones

1.2.3 Synthesis of Heteroatom-Containing Cyclopropanes

Heteroatom-containing cyclopropanes are another important type of cyclic compounds. Its characteristics have changed dramatically owing to the inclusion of heteroatoms. The reaction of oximes with Grignard reagents is widely used in the formation of nitrogen-containing cyclopropanes. The advantage of this reaction is that the corresponding aziridine can be obtained by changing different types of Grignard reagents (**Scheme 10a**).[40-41] Another heteroatom cyclopropane is

propylene oxide.[42] Epoxides are mainly formed primarily by the reaction of olefins with peroxy acids. The reactant is stable, compatible with a wide range of organic solvents, and is extensively employed in various applications. (**Scheme 10b**). The Darzen's group [43] published a more effective method of synthesizing propylene oxide. Aldehydes or ketones react with -halogenated carboxylates in the presence of a strong base (KOH) to produce the corresponding propylene oxide (**Scheme 10c**).



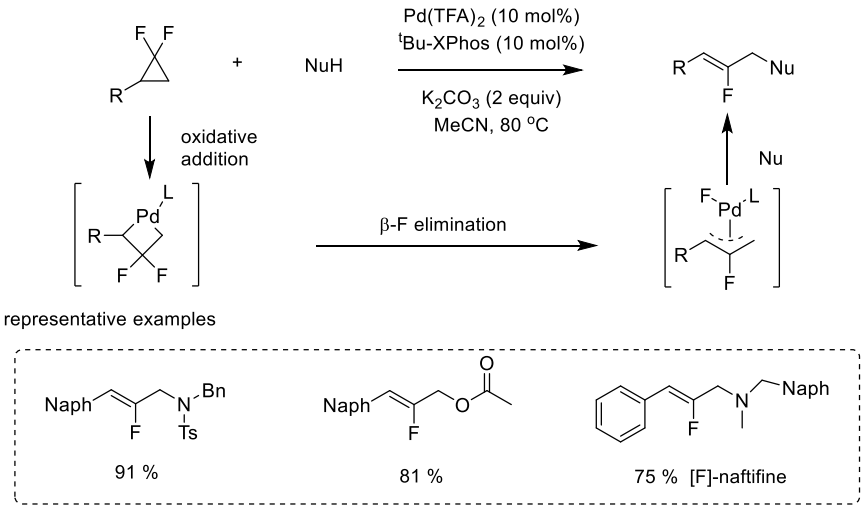
Scheme 10 Synthesis of heteroatom-containing cyclopropenes with different structures

1.3 The Ring-Opening and Expansion Reactions of Three-Membered Rings

As we know, cyclopropanes containing different substitution groups have different chemical properties. Moreover, over the past two decades, more than half of all newly developed medications have been linked to the research and development of drugs containing fluorine. [80-84] The addition of fluorine atoms to pharmaceuticals can confer remarkable electrical, physical, biological, and reactivity properties. This section mainly introduces the research on the ring-opening and expansion reaction of *gem*-difluorinated cyclopropanes and cyclopropenones.

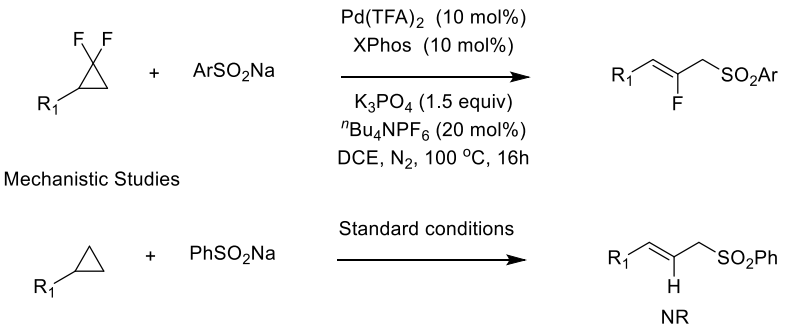
1.3.1 The Ring Opening and Expansion Reaction of *Gem*-Difluorinated Cyclopropanes

The synthesis of *gem*-difluorinated cyclopropanes [44-47] has been reported as early as 1960, yet advancements in their transformation and application were limited in subsequent years. In 1983, Isogai group explored Palladium-catalyzed hydrogenolysis of difluorocyclopropanes. [48] However, it was'n not until 2015 that Fu and collaborators demonstrated the feasibility of palladium metal for ring opening of *gem*-difluorinated cyclopropanes, garnering considerable attention from organic chemists and resulting in significant contributions to the field in the last decade. Over the past ten years, transition metal palladium has been widely employed, particularly in cross-coupling reactions, serving as a versatile tool. Fu's group [49] reported cross-coupling reactions of *gem*-difluorinated cyclopropanes with various nucleophiles employing commercial palladium catalysts. The reaction showcased a broad array of nucleophilic reagents, including amines, alcohols, carboxylic acids, and specific carbon nucleophiles. The authors proposed a fluoroallylic palladium species as the mechanism, resulting in a range of highly *cis*-selective fluoroallylic amines, ethers, esters. This groundbreaking discovery provide a new path for transition-metal-catalyzed ring-opening and ring-expansion reactions of *gem*-difluorinated cyclopropanes (**Scheme 11**).



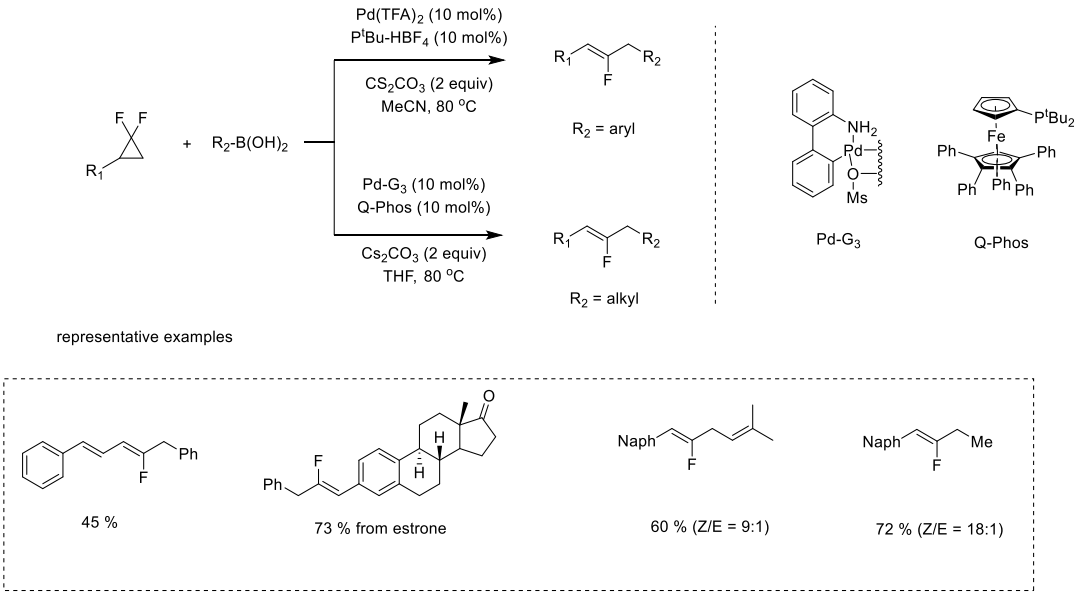
Scheme 11 Palladium-catalyzed *gem*-difluorinated cyclopropanes cross coupling with some nucleophilic reagents

Based on Fu's study, Zhang research group [50] successfully developed $Pd(TFA)_2$/X-Phos as a catalytic system for the ring-opening sulfonylation of geminal difluorinated cyclopropanes in 2019. In this reaction, aryl ammonium sulfites were employed as a nucleophile, which coupled with fluoroallylic palladium species, efficiently synthesis fluorinated allyl sulfone product. The addition of *n*-Bu_4NPF_6 (20 mol%) as a phase transfer catalyst played a crucial role in improving the reaction yield, addressing the poor solubility of aryl ammonium sulfite in DCE. In the control experiment, the author also used normal cyclopropane and indicated that the presence of an F atom was critical to the ring-opening reaction (**Scheme 12**).

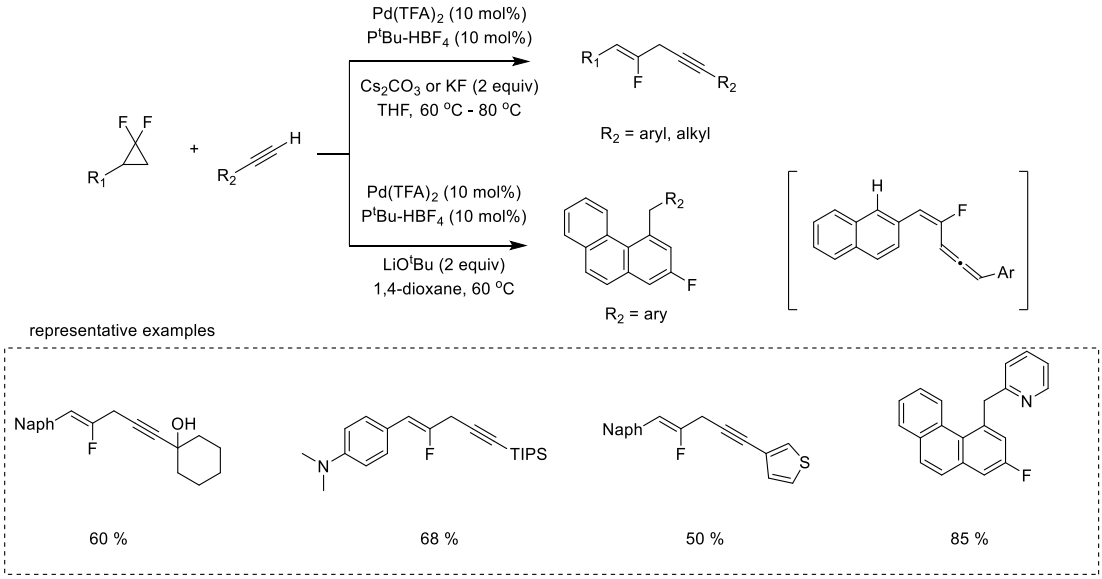


Scheme 12 Palladium-catalyzed sulfonylation of *gem*-difluorinated cyclopropanes

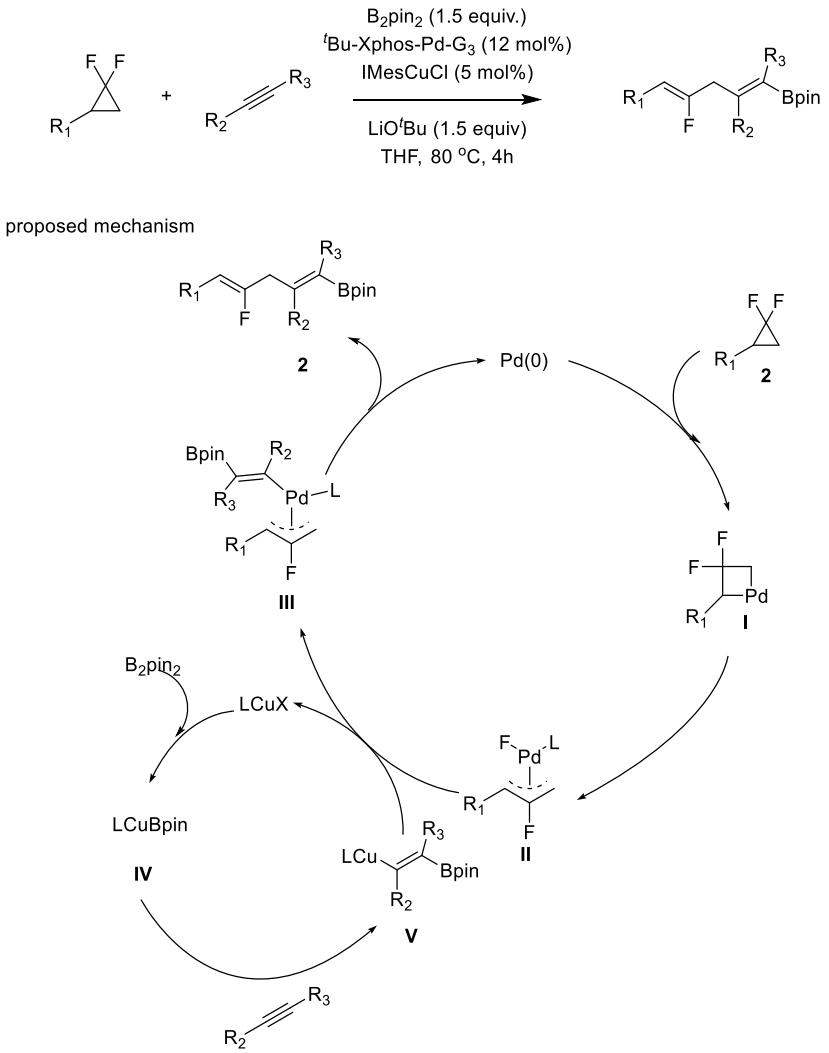
In the same year, the Fu's team [51] continued their exploration by developing the Suzuki-type reaction between *gem*-difluorinated cyclopropanes and organoboronic acid. Fluoroallyl palladium species and aryl boronic acids were able to undergo the transmetallation step well in the presence of Cs_2CO_3 to obtain the desired product in good yield. The reaction demonstrated good functional tolerance of *gem*-difluorinated cyclopropanes and aryl-boronic acids. Furthermore, the authors also confirmed that Pd-G3 and Q-Phos worked best for the catalytic system in the case of alkyl-boronic acids (**Scheme 13**).



Scheme 13 Palladium-catalyzed arylation/alkenylation/alkylation of *gem*-difluorinated cyclopropanes



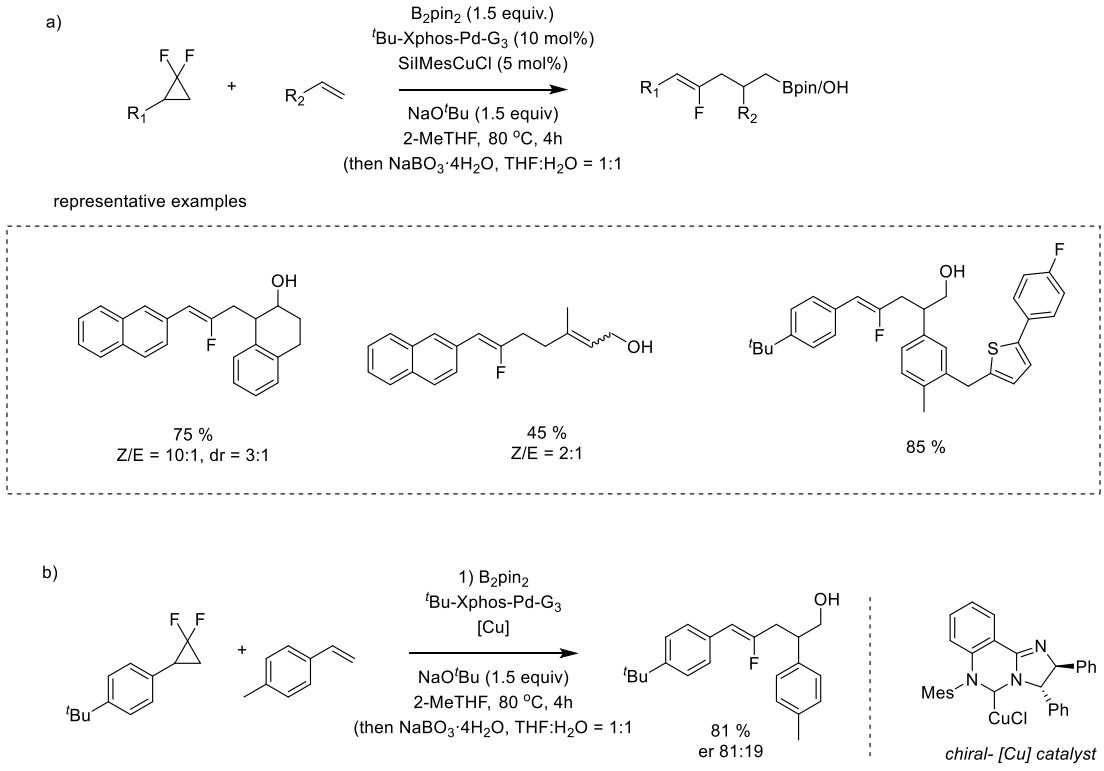
Scheme 14 Palladium-catalyzed alkynylation of *gem*-difluorinated cyclopropanes



Scheme 15 Cu/Pd-catalyzed for the synthesis of boryl-substituted monofluoroalkenes

Fu's group not only explored the reactions of *gem*-difluorinated cyclopropanes with common nucleophiles but also investigated its reactivity with unsaturated alkenes and alkynes. [52] In 2020, they published a paper detailing the Sonogashira reaction of *gem*-difluorinated cyclopropanes with terminal alkynes to produce alkynyl compounds. The reaction showcased a broad substrate scope, exhibiting high reactivity with both alkyl and aryl alkynes. Interestingly, when employing aromatic alkynes, the formation of fluorinated phenanthrene products was achieved selectively by implementing a ring closure step, altering the base and solvent used in the reaction. (**Scheme 14**).

For the reaction of alkynes, Fu's research group also explored difunctionalization reactions.[53] They developed a Pd/Cu co-catalyst system to catalyze the reaction of *gem*-difluorinated cyclopropanes with alkyne, and B_2Pin_2, to produce boron- and allyl fluoride-containing cis-olefins. In terms of the reaction process, the Cu catalyst initially activates B_2pin_2 and alkynes to generate the boryl alkenyl copper intermediate **V**, which then reacts with the fluoroallylic palladium species formed by Pd catalysis to produce the target product. It is worth mentioning that terminal alkynes were also well tolerated under standard reaction conditions, suggesting that the Cu catalyst had a strong control effect in reaction selectivity (**Scheme 15**).

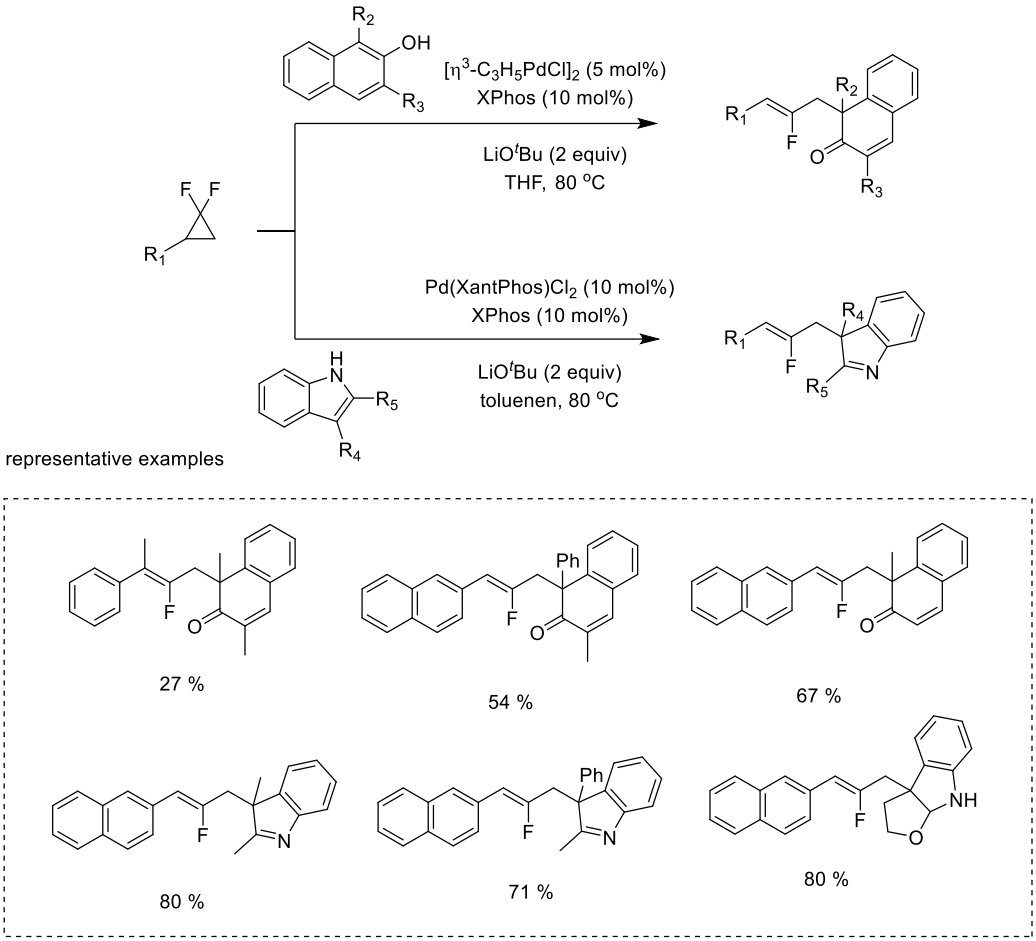


Scheme 16 opper/palladium dual-catalyzed three-component reaction of *gem*-difluorinated cyclopropanes, alkenes, and B_2pin_2

They also reported the difunctionalization of *gem*-difluorinated cyclopropanes with alkenes at the same time.[54] The catalytic mechanism of this reaction is fundamentally similar to that of alkynes, Through the partial oxidation of boric acid ester, alcohol products can be obtained in good yields. It is worth noting that chiral Cu-NHC complexes were used to achieve asymmetric catalysis of this reaction, and the product was also formed with good yield and enantioselectivity (81:19 er, 81%

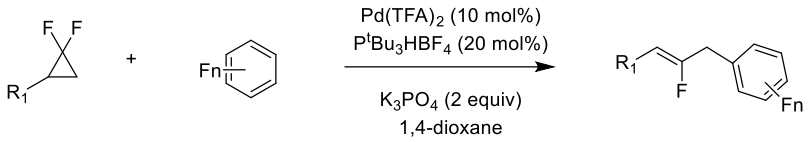
yield). The reaction involving cyclopropane difluoride has not only been reported by the Fu's group but also by other research groups (**Scheme 16**).

In addition to Fu group, other groups also have significant contributed to the area of gem-difluorinated cyclopropanes. In 2020, Lin's group [55] published the dearomative allylation reaction of naphthol and indole with *gem*-difluorinated cyclopropanes. The author employed two different palladium catalysts to facilitate the reaction for different substrates. This reaction demonstrates a wide substrate applicability, with the capability to synthesize good results for naphthols of diverse structures, including large and sterically hindered starting materials. For the indole, the reaction occured at the third position. Furthermore, the author achieved the synthesis of a polycyclic compound through thoughtful substrate design (**Scheme 17**).



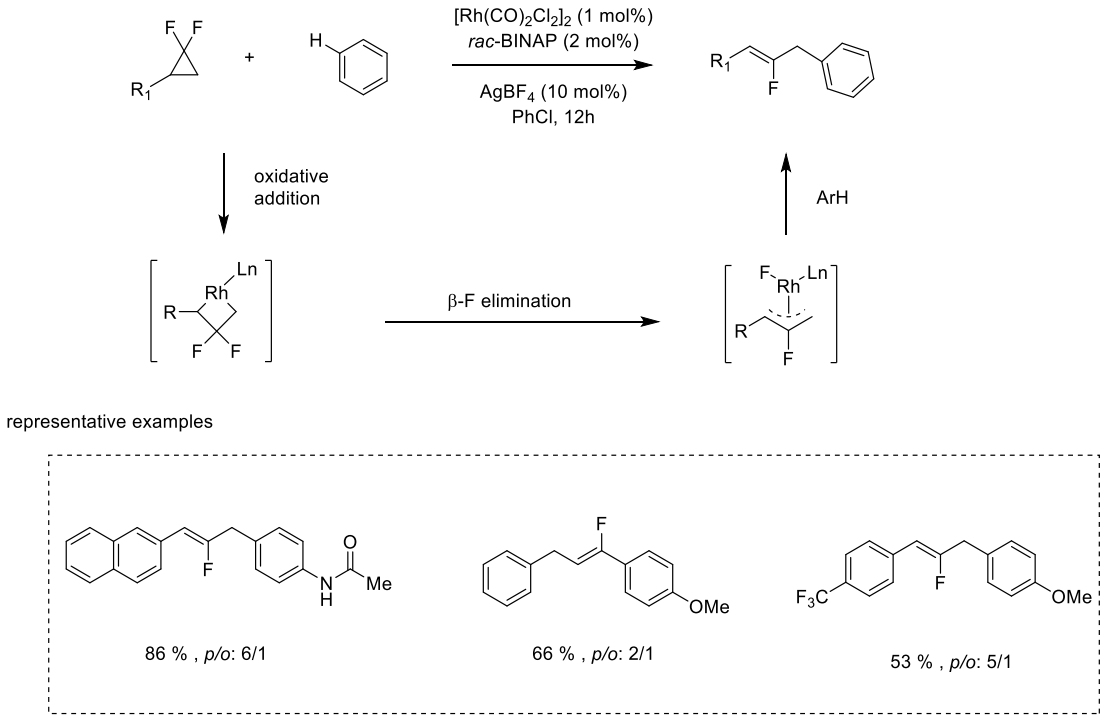
Scheme 17 Palladium-catalyzed allylic alkylation dearomatization of b-naphthols and indoles with *gem*-difluorinated cyclopropanes

In addition to dearomative allylation reactions for aryl compounds, Zhang's research group [56] also reported aromatic ring C-H bond functionalization. Initially, the group achieved this reaction with electron-deficient polyfluoroaromatic hydrocarbons using $Pd(TFA)_2$ and $PtBu_3$•HBF_4 catalytic system. The reaction involves the generation of polyfluorinated aromatic anions under basic conditions, which subsequently undergoes nucleophilic addition reactions with fluoroallylic palladium species. However, it is important to note that the reaction is limited to polyfluoroarenes, and 1,3-difluorobenzene was not a compatible substrate (**Scheme 18**).



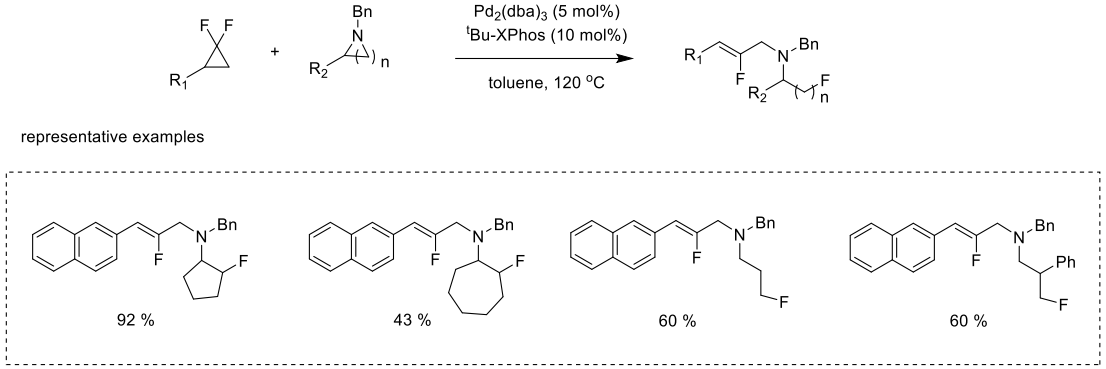
Scheme 18 Palladium-catalyzed C−H allylation of electron-deficient polyfluoroarenes

Yin's research group [57] developed an effcient strategy for common aromatic compounds, through a rhodium-catalyzed system to successfully accomplish the cross-coupling reaction between common aromatics and *gem*-difluorinated cyclopropanes. The C-H allylation reaction proceeds smoothly, resulting in the desired products with high yields and excellent regioselectivity. Mechanistically, the transition metal rhodium can form fluoroallylic rhodium species when reacting with gem-difluorinated cyclopropanes, which can undergo C-H activation of simple arenes through an electrophilic metallation process. Finally, a reductive elimination process occurs to obtain the desired product and the Rh-catalyst participate the next catalytic next cycle. However, the selectivity of this reaction is not very well for some aryl substitutions, therefore further efforts are still worth trying to improve chemoselectivity (**Scheme 19**).



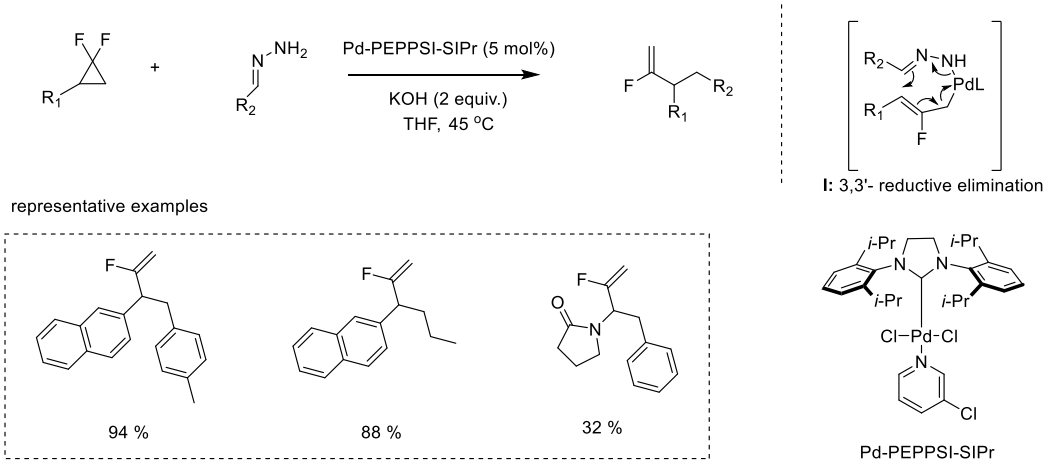
Scheme 19 Rhodium catalyzed regioselective C-H allylation of arenes with *gem*-difluorinated cyclopropanes

To Investigate the fate of fluoride ions in *gem*-difluorinated cyclopropanes after ring-opening, Liu's research group [58] achieved a breakthrough in 2023 by capturing the departing fluorine atom through strategic substrate design. The Pd-catalyzed *gem*-difluorinated cyclopropanes and aziridine difunctionalization synthesis were successfully achieved in this reaction. This is the first time to achieve the 100% atom-economical reaction of fluorine atoms in *gem*- difluorinated cyclopropanes. The process involves an amine attack on fluoroallylic palladium species, generating coordinated *N*-allyl aziridines, which are subsequently transformed into the final fluorinated amine (**Scheme 20**).



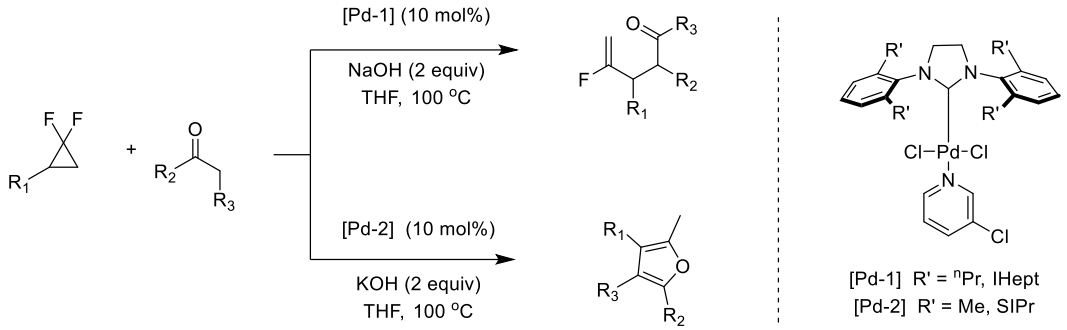
Scheme 20 Palladium-catalyzed fluorinative difunctionalization of aziridines and azetidines

The cross-coupling reaction of *gem*- difluorinated cyclopropanes under transition metal catalysis primarily yields fluoroalkenes. This predominance arises from the high reactivity of the produced fluoroallylic metal species with nucleophiles in the terminal position, while reactions at the benzylic position are more challenging. In 2021, a breakthrough work was developed by Li research group,[59] through palladium-catalyzed cross-coupling of *gem*- difluorinated cyclopropanes and hydrazones, resulting in benzylic substituted products. The hydrazones allow them to undergo similar inner-sphere 3,3'-reductive elimination reactions driven by denitrogenation, and the auxiliary role of sterically NHC ligands is also crucial for regioselectivity. This reaction has a wide range of substrates, which provides an alternative pathway for the synthesis of novel products from *gem*-difluorinated compounds (**Scheme 21**).



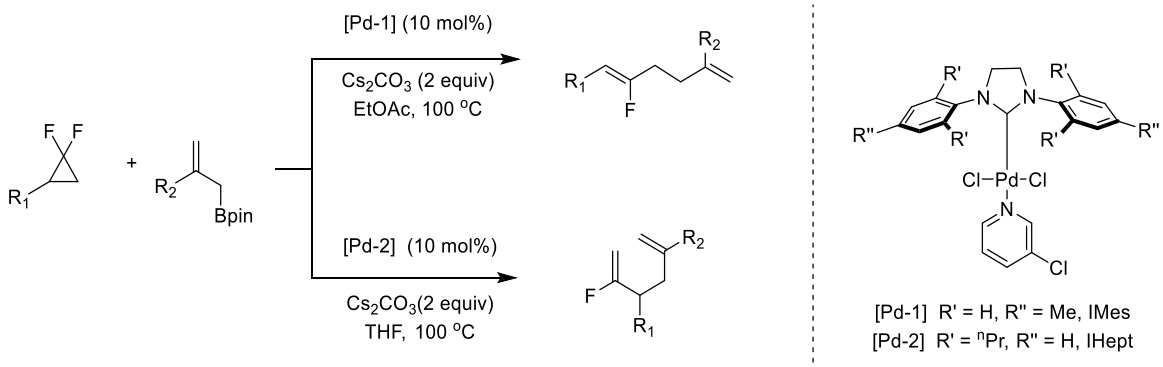
Scheme 21 Palladium-catalyzed defluorinative alkylation of gem-difluorocyclopropanes

Then, the Lv and Li groups [60] applied this method to achieve the selective cross-coupling reaction of *gem*-difluorinated cyclopropanes with common ketones. By employing various NHC ligand structures, the researchers were able to generate both ß-fluoroalkene and benzylic-substituted fluoroalkene products, highlighting the crucial role of NHC ligands in this reaction. Additionally, they observed that when the steric hindrance of the NHC ligand is minimal, the starting material can undergo further intramolecular cyclization reactions, synthesis furan products with diverse structures. This reaction demonstrates wide applicability to a variety of *gem*-difluorinated cyclopropanes and ketones with different structures, serving as an exemplary instance of ligand control in a chemical process (**Scheme 22**).



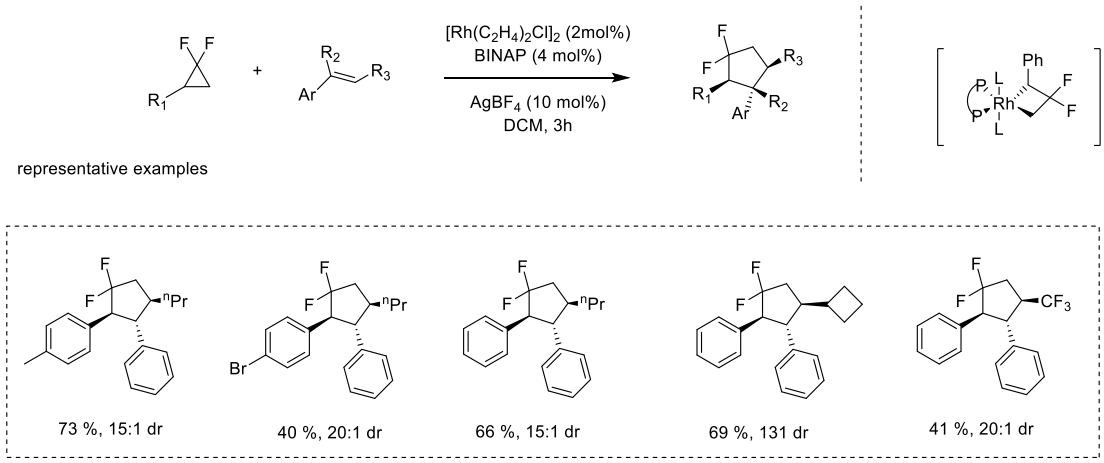
Scheme 22 Ligand-controlled regioselective and chemodivergent defluorinative functionalization of *gem*-difluorocyclopropanes

In 2022, researchers [61] further extended their work on the selective cross-coupling reaction of *gem*-difluorinated cyclopropanes with all-carbon allyl nucleophiles. The reaction's outcome is modulated by NHC ligands of different structures. Specifically, the NHC ligand with the least steric hindrance (IMES) promotes the formation of linear products, while the NHC ligand with greater steric hindrance (IHept) encourages the production of branched-chain products. Additionally, the authors employed DFT calculations to support the role of NHC ligand sterics. This comprehensive theoretical and experimental investigation provided a solid foundation for understanding the site selectivity in *gem*-difluorinated cyclopropane reactions (**Scheme 23**).



Scheme 23 Pd/NHC-controlled regiodivergent defluorinative allylation of *gem*-difluorocyclopropanes

The application of *gem*-difluorinated cyclopropanes has primarily been documented in the context of ring-opening reactions, with no prior reports of their utilization in ring-expansion reactions. However, in 2023, the Xia group [62] reported a breakthrough by using the Rh and BINAP reaction system to achieve the [3+2] cycloaddition reaction of *gem*-difluorinated cyclopropanes with commonly available alkenes. This reaction showed remarkable compatibility with various functional groups and exceptional regioselectivity. It represents a novel pathway for the synthesis of fluorinated cyclopentanes (**Scheme 24**).

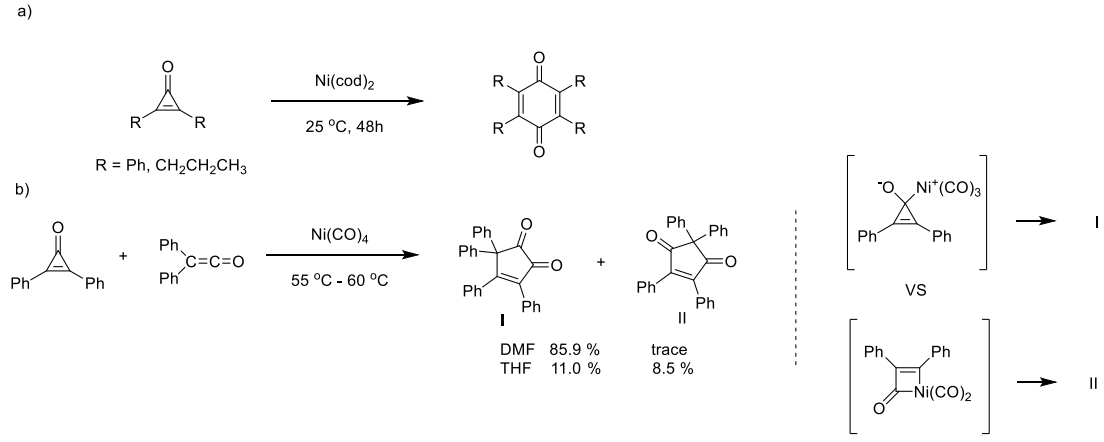


Scheme 24 Rhodium-catalyzed [3+2] cycloaddition of *gem*-difluorinated cyclopropanes with internal olefins

1.3.2 Cyclopropenones Ring Opening and Expansion Reactions

Cyclopropenones are an essential part of cyclopropane derivatives. It has a high reactivity due to the C=C, C=O, and tension ring properties. However, owing to its high reactivity, its reaction selectivity is not easy to control, leading to a series of side product in most case. Because of its complexity and challenge, it has attracted a great attention from organic chemists.

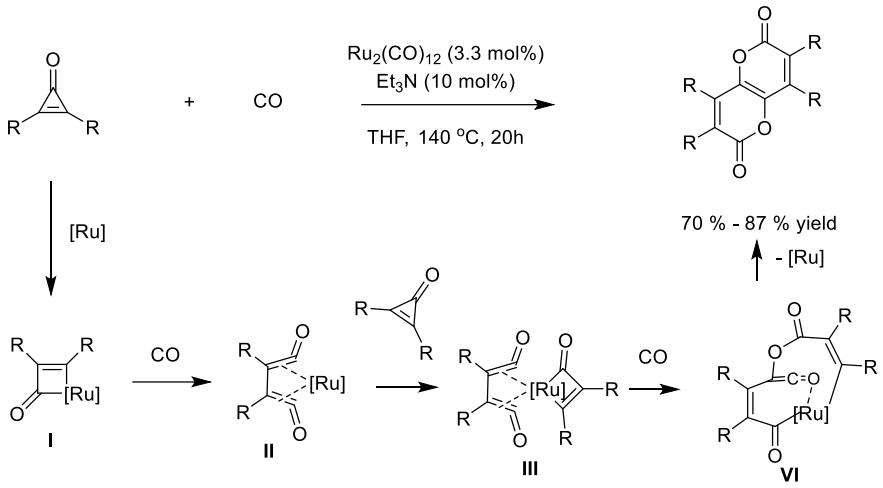
The first synthesis of cyclopropenones was reported in 1959, but the transition metal-catalyzed ring-opening and ring-expansion reaction of cyclopropenones was not reported until 1972. Takaya and colleagues [63] discovered that $Ni(cod)_2$ catalyzed dimerization of cyclopropenone at room temperature, synthesis a benzoquinone product. This reaction has epoch-making significance for the cyclopropenone reaction. This discovery has provided valuable guidance for subsequent researchers exploring transition metal-catalyzed reactions involving cyclopropenone (**Scheme 25a**).



Scheme 25 Ni-catalyzed ring expansion reaction of cyclopropenone

Then, in 1976, Akio Baba's team [64] utilized $Ni(CO)_4$ to realize the ring expansion reaction of cyclopropenones with ketenes. The authors obtained two products with different reaction positions from the reaction. Surprisingly, the scientists found that merely altering solvents was sufficient to exert control over the generation of these two compounds. When employing DMF as the solvent, only product **I** was formed. When the solvent was changed to THF, the proportion of product **II** significantly increased. Additionally, the authors proposed their theory regarding the mechanism behind the formation of these two products. They suggested that product **I** arised when the metal Ni

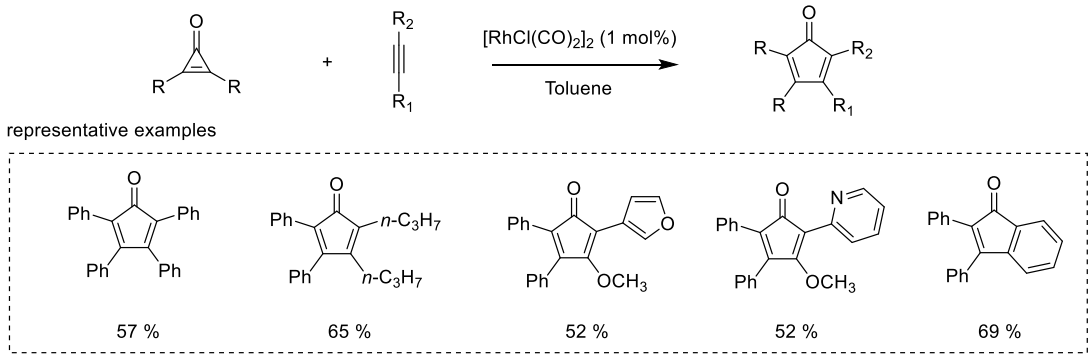
activated the C=O bond in cyclopropenone. Conversely, when Ni activated the C-C bond of cyclopropenone, the reaction tended toward producing product **II**. This sequence of discoveries has consistently broadened the application scope of cyclopropenone (**Scheme 25b**).



Scheme 26 Ruthenium-catalyzed synthesis of pyranopyrandiones

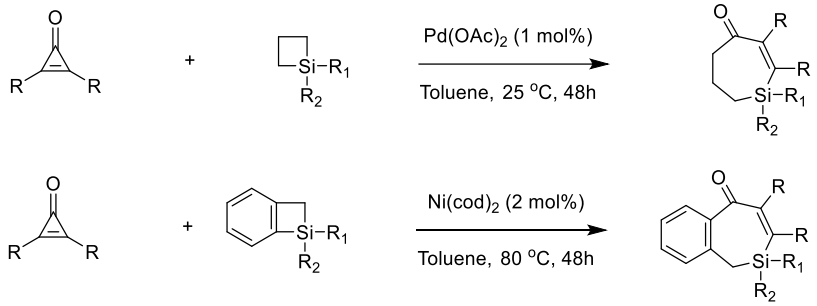
In addition to nickel catalysts, researchers have experimented with other types of metal catalysts. In 2002, Mitsudo's team[65] reported that $Ru_3(CO)_{12}$ catalyzed the reaction of cyclopropenone with CO. This reaction involves two molecules of cyclopropenone and CO to synthesize pyranopyrandiones in high yields. Regarding the reaction mechanism, the authors proposed that metal Ru first activated the C–C bond of cyclopropenone, and then inserted a molecule of CO to generate intermediate **II**. However, intermediate **II** was not reduced and eliminated immediately. Instead, it continued to react with a molecule of cyclopropenone, where it inserted another molecule of CO. Through two reduction and elimination stages, the final product was obtained (**Scheme 26**).

Transition metal Rh-catalyzed ring-opening and ring-expansion reactions in small ring molecules were reported as early as the 1980s, indicating its high reactivity in C-C bond activation. In 2006, Wender and co-workers[66] reported that Rh catalyzed ring-opening reaction of cyclopropenone with phenylacetylenes, lesding to product in excellent yield. Alkynes bearing diverse substituents, such as alkyl, aryl, heterocyclic groups, and others, were tolerated to this reaction. Surprisingly, even benzynes also showed good reactivity with cyclopropenones. These findings demonstrated the wide applicability of Rh catalysis in the ring-opening and ring-expansion processes of small ring molecules (**Scheme 27**).



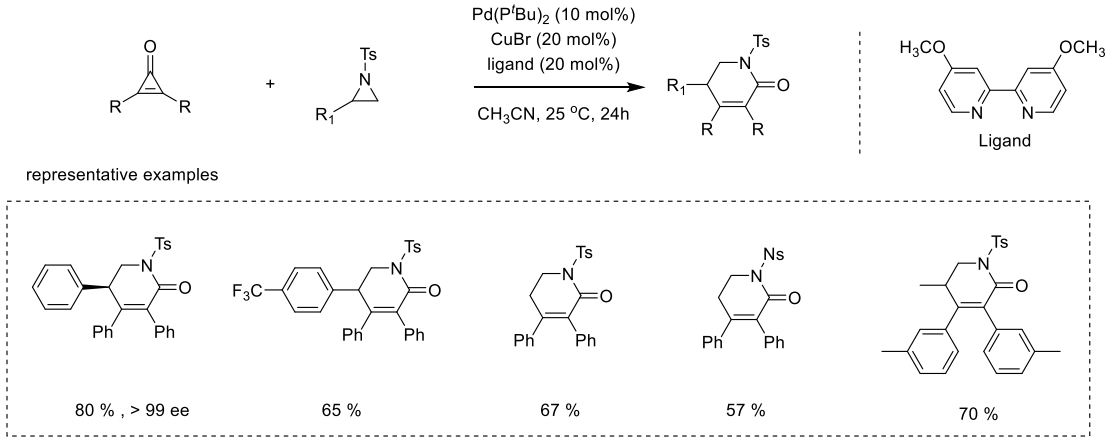
Scheme 27 Cyclopentadienone synthesis by rhodium-catalyzed [3 + 2] cycloaddition reactions of cyclopropenones and alkynes

Besides rhodium catalysts, palladium catalysts are also widely employed. In 2021, Zhao's research[67] group reported the bond exchange reaction between the C-C bond of the cyclopropenone molecule and the Si-C bond of silacyclobutanes. The author successfully achieved this reaction at room temperature with 1 mol% palladium catalyst, leading to the desired products in good yields. Furthermore, no reaction occurred when ligands were added to the reaction system, possibly because ligands were more likely to coordinate with the metal, potentially resulting in transition metal poisoning. For benzosilacyclobutanes, the original palladium catalytic system was unsuitable. The author solved this problem perfectly by using 2 mol% $Ni(cod)_2$ instead of palladium, which provided us with another way to construct a new type of silicon-containing macrocycle (**Scheme 28**).



Scheme 28 Intermolecular bond cross-exchange reaction between cyclopropenones and silacyclobutanes

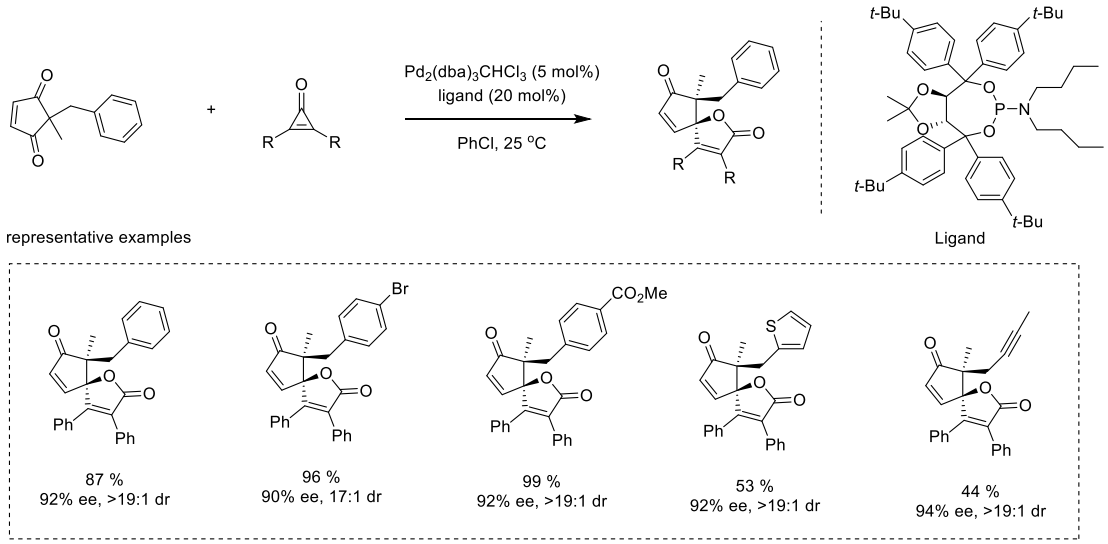
Then in 2021, The researchers[68] published a highly selective ring expansion reaction involving cyclopropenone and cyclopropylamine using a palladium-copper co-catalysis system. This reaction is applies to a wide scope of substrates. For chiral cyclopropylamine, the resulting product also showed good reactivity and the ee value remained. For cyclopropenone and cyclopropylamine with different structures, the corresponding products can be obtained in moderate to excellent yields (**Scheme 29**).



Scheme 29 A ring expansion strategy towards diverse azaheterocycles

There are relatively few reports on the asymmetric catalysis of cyclopropenones. In 2021, Xu and co-workers[69] reported the (3+2) cycloaddition of cyclopropenones and cyclic 1,3-diketones catalyzed by $pd_2(dba)_3{\cdot}CH_3Cl$ with a chiral taddol phosphoramidite ligand. This reaction yields a multi-chiral center product with a spiro ring structure. Notably, the reaction exhibits the attributes of broad substrate applicability, outstanding yield, and remarkable enantioselectivity. The resulting

chiral oxaspiro cyclopentenone–lactone scaffolds hold significant importance in molecular structures, emphasizing the significance of synthesizing such chiral structures (**Scheme 30**).



Scheme 30 Enantioselective palladium-catalyzed of cyclopropenones with cyclic 1,3-diketones

1.4 Conclusion

According to the summary and analysis of the preceding literature, the transition metal species that can effectively catalyze the ring-opening and ring-expansion reaction of the three-membered ring are relatively rare. Among them, the majority of reactions are catalyzed by palladium. Despite numerous efforts in recent years to develop ring-opening and ring-expansion reaction systems catalyzed by various metal, there remains a relatively limited range of catalytic systems that can efficiently drive these reactions. Activating C-C bonds or C-X bonds [70-72] within three-membered ring compounds using diverse catalysts is a crucial step in establishing new catalytic systems. Developing efficient catalytic systems to facilitate ring-opening and ring-expanding reactions in a wide variety of small organic molecules, which is highly desirable objective in organic synthesis. Especially, developing various catalytic methods to activate the C-C bond or C-X bond of three-membered ring. This approach serves as guidance in the development of novel molecular precursors for potential therapeutic applications. This section mainly discusses the selective ring-opening and ring-expansion reactions utilizing transition metal catalysts between a series of three-membered ring compounds and other small organic molecules.

Based on the literature, we aim to develop new catalyst systems to enable the reactivity of less active compounds with *gem*-difluorinated cyclopropane or cyclopropenone. Our objective is to achieve highly chemoselective ring-opening and ring-expansion reactions using new transition metal catalysis or other catalystsis. This endeavor aims to generate a range of novel molecules with unique C-C bond structures, providing innovative prospects for drug discovery.

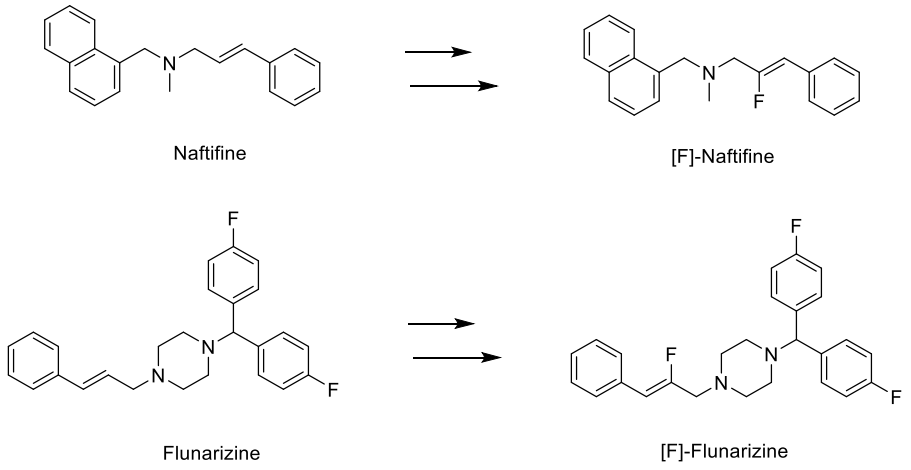
2 Results and Discussion

2.1 Pd-Catalyzed Access to Mono- and Di-fluoroallylic Amines from Primary Anilines with *Gem*-Difluorocyclopropane

Author contributions: X. W. performed the corresponding experiments and drafted the manuscript. Prof. Dr. Patureau supervised the project and edited the draft.
This work has been published: *Chem. Commun.* **2023**, 59, 486.

2.1.1 Background and Motivation

Allylamine is an important form of nitrogen-containing compound found in both natural products and biological molecules,[73-75] such as Naftifine[76-77], an antifungal medication, and Flunarizine[78-79], a calcium blocker. At the same time, fluorine-containing drug[80-84] research and development accounted for more than half of all new pharmaceuticals developed in the last 20 years. This is because fluorine incorporation can give organic compounds remarkable electronic, physical, biological properties and reactivity. As a result, we anticipated that establishing simple synthetic methods for gaining access to fluorinated allyl-amines would be a critical goal in order to generate new strong medications or fluorine-derivatize current ones (**Scheme 31**). it is crucial not only for the development of new drugs, but also for the development of existing drugs.

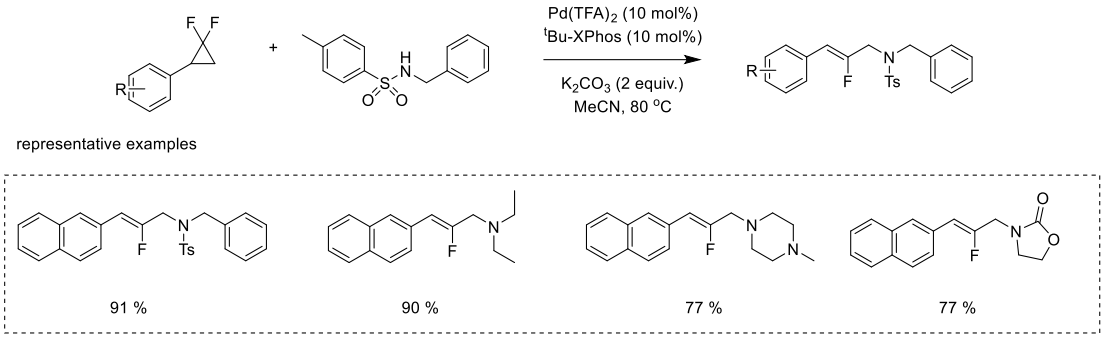


Scheme 31 Bioactive allylamine examples

The synthesis of allylamine structures with transition metal catalysts[85-94] is a frequent and efficient approach. However, in the synthesis of allylamines with different structures, the synthesis of allyl and amino sources with various structures has always been a major challenge. *gem*-difluorocyclopropanes is a fluorine-containing three-membered ring structure which can be easily synthesized under simple conditions. Meanwhile, it can activate the C-C and C-F bonds under the catalysis of transition metals such as Pd, Rh, and others to synthesize fluorinated alkenes propyl metal compounds. Moreover, it can be used to make fluorine-containing allylamine compounds when combined with other amino groups. In 2015, Fu and co-worker report the cross-coupling reaction of *gem*-difluorocyclopropane with amines. The reaction has a wide range of substrate

universality, and good yields can be obtained for amine compounds with different structures (**Scheme 32**).

However, most amines are pre-functionalized, and disfluorinated allyl amination has never been reported by using normal amines. The development of reaction conditions for the selective mono- or di- allyl amination of cheap and readily available amine sources (such as anilines) necessitates not only good catalytic system control under monofunctionalization, but also high catalytic activity under difunctionalization. It has extremely promising application prospects in the synthesis of fluorine-containing allylamine compounds of various structures.

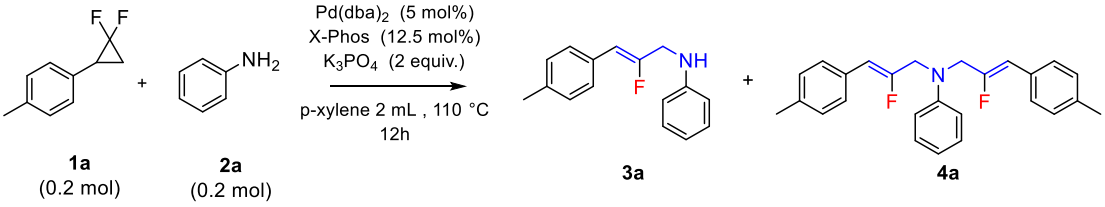


Scheme 32 Palladium-catalyzed *gem*-difluorinated cyclopropanes coupling with highly active amines

2.1.2 Condition Optimizations

At first, we chose the 4-Methyl *gem*-Difluorocyclopropanes (**1a**) and simple aniline (**2a**) as the model substrates. When I did not add metal catalyst Pd or ligand in the reaction system, the reaction cannot occur (entry 1). Next we chose the ratio of **1a**:**2a** is 1:1, under the $Pd(dba)_2$ (5 mmol %) ,

Table 1. Screening of Conditions for synthesis of mono- or di- 2-fluoroallylic amines[a]



Entry	variations from standard conditions	Yield (3a)[c]	Yield (4a)[c]	3a:4a[c]
1	Without Pd $(dba)_2$ or X-Phos	NR	-	-
2	1a:2a=1:1	29 %	4 %	7.25:1
3	1a:2a =1:2	54 %	2 %	> 20:1
4	1a:2a =1:3	90 %(89 %)[b]	2 %	> 20:1
5	1a:2a =2:1	1%	75 %	< 1:20
6	1a:2a =3:1	1%	90 %(90 %)[b]	< 1:20

[a]Reaction conditions: **1a** (0.20 mmol),**2a** (0.20 mmol), catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Isolated yields. [c]Determined by ^1H NMR.

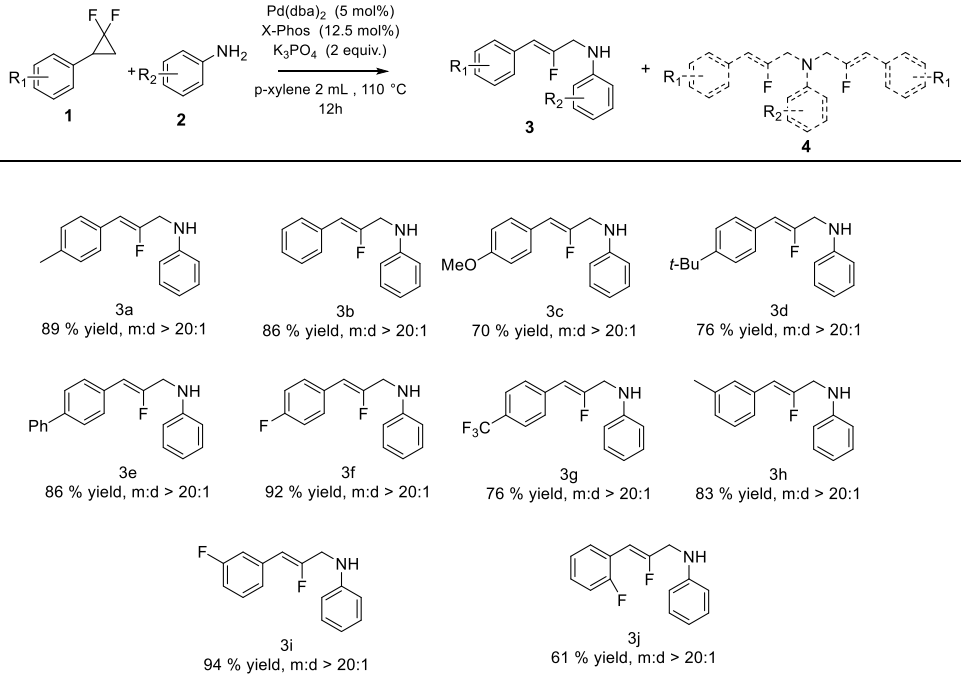
X-phos (12.5 mmol %) and K_3PO_4 (2 eq.) in the p-xylene at 110 °C for 12h. This afforded the Monofunctional product **3a** in 29% yield, and the difunctional product **4a** yield only 4%.

Next we increased the amount of the **2a**. This afforded the monofunctional 2-fluoroallylic amines product **1a** in impressive 90% isolated yield, and the chemical selectivity was as high as 20:1 (entry 4-5). By increasing the amount of **2a** we can easily control the chemoselective of the **1a** and **2a** , the di-functionalization reaction was well inhibited. This reaction phenomenon indicates that Pd-catalyzed mono-functionalization of anilines with *gem*-Difluorocyclopropanes has high reactivity, and di-functionalization reactions occur with great difficulty. However, we were surprised to find that only **4a** was observed in the reaction we tried to change the ratio of **1a**:**2a** to 2:1. Then we study by continuously add **1a** (the ratio of **1a:2a** to 3:1). This afforded a new di-2-fluoroallylic amines substance **4a** in impressive 90% isolated yield, and the chemical selectivity was as high as 20:1 (entry 6-7) (**Table 1**).

2.1.3 Substrate Scope Studies of Monofunctional Products

With these optimized reaction conditions in hand, we investigated the reaction scope with various *gem*-difluorocyclopropanes and anilines. First, we tested *gem*-difluorocyclopropanes with different functional groups on the Para aromatic ring. Electron-neutral (**3b**), electron-donating (**3a, 3c,** and **3d**), and electron-withdrawing (**3f**, and **3g**) functional groups afforded the corresponding monofunctional 2-fluoroallylic amines products in excellent yields (70 - 92 %) with excellent chemoselective (m:d > 20:1). For meta or ortho aromatic ring substituted *gem*-difluorocyclopropanes (**3h, 3i,** and **3j**) we also tried, and get excellent yields (61 - 94 %) with excellent chemoselectivity (m:d > 20:1) (**Table 2**).

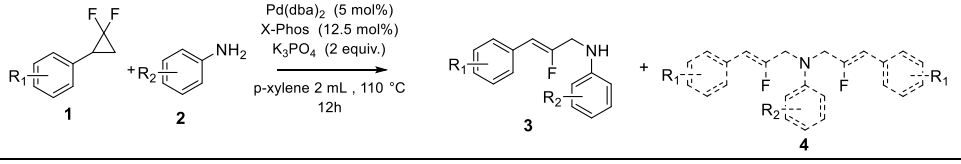
Table 2 monofunctional products scope of *gem*-Difluorocyclopropanes[ab]

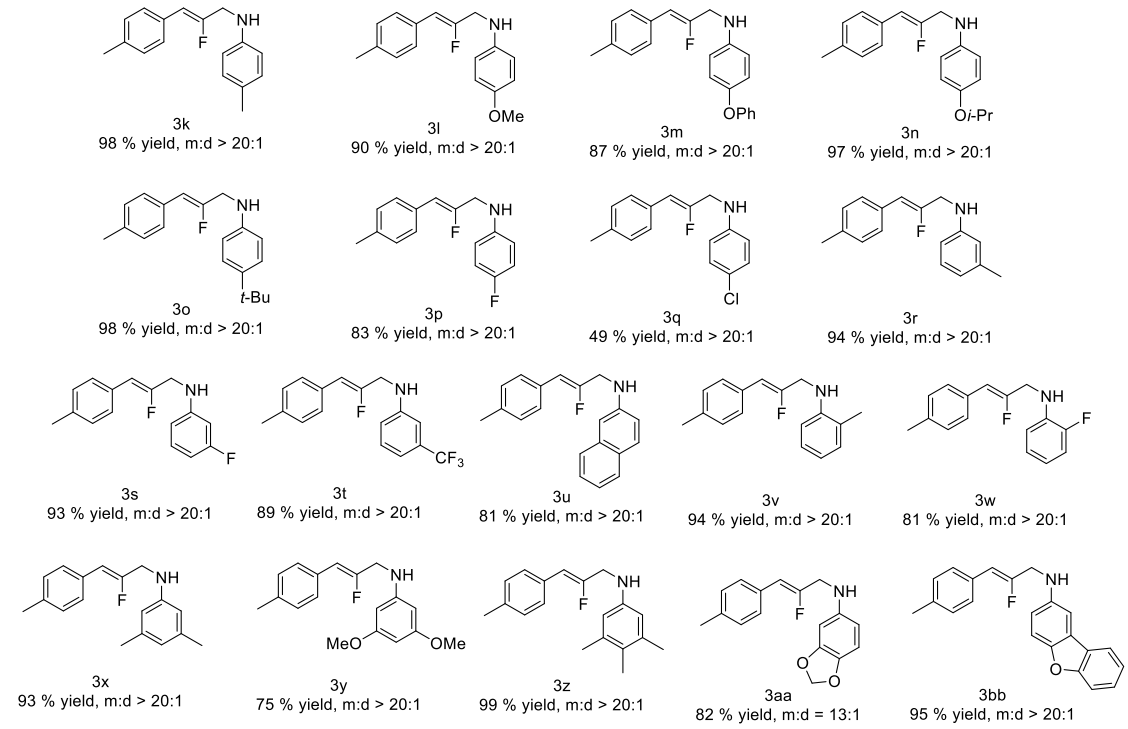


[a]Reaction conditions: **1** (0.20 mmol), **2** (0.60 mmol), Pd catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Determined by ^1H NMR.

Moreover, substitutions at the para, meta or ortho position of anilines could be achieved. A wide range of functional groups anilnes proved to be tolerated, including methyl (**3k** and **3r**), Methoxy (**3l**), Methoxyphenyl (**3m**), Methoxyisopropyl (**3n**), tert-butyl (**3o**), fluoro (**3p** and **3s**), chloro (**3q**) and trifluoromethyl (**3t**). This afforded corresponding mono-2-fluoroallylic structure product in 49% - 98% isolated yield, with excellent chemoselective (m:d > 20:1).In particular, we were surprised to find that 2-Me or 2-F anilines were reactive, withrespectively 94 and 81% yields , m:d > 20:1. In addition, difunctional or trifunctional anilines (**3x, 3y** and **3z**) were still achieved. Interestingly, we observed that aniline-containing heterocyclic structures were applicable in the experiment, yielding corresponding mono-2-fluoroallylic structure products (**3aa**, and **3bb**) in yields ranging from 82% - 95%, with m:d ratios of 13:1 and greater than 20:1 (**Table 3**).

Table 3 monofunctional products scope of anilines[ab]



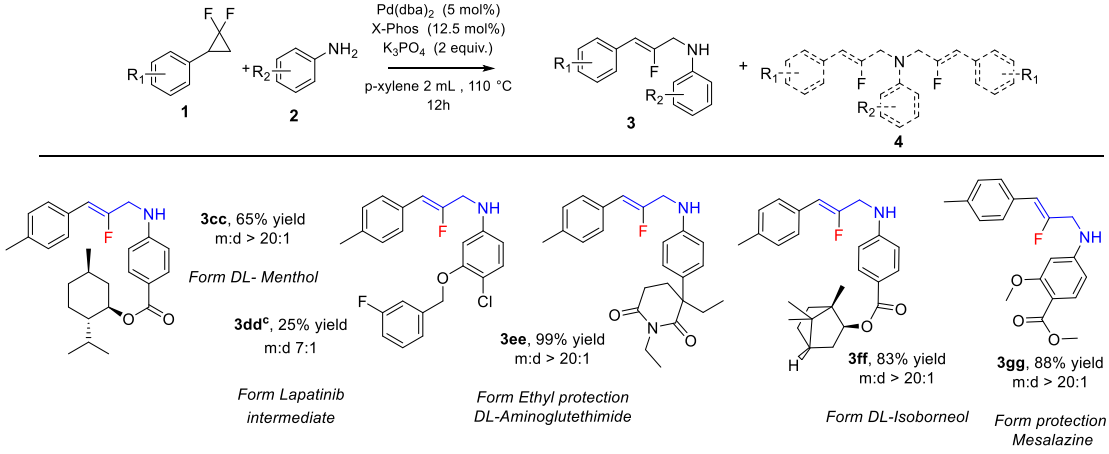


[a]Reaction conditions: **1** (0.20 mmol), **2** (0.60 mmol), Pd catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Determined by ^1H NMR.

In addition, we also focus on the application of biologically or naturally relevant small molecules. As shown in **Table 4,** a series of biologically molecules, such as Lapatinib intermediate (**3dd**), Ethyl protection DL-Aminoglutethimide (**3ee**) and protection Mesalazine (**3gg**) could be tolerated, with high isolated yield (25% - 99%) and excellent chemoselectivity (m:d 7:1->20:1). Certainly, naturally molecules, including DL- Menthol and DL-Isoborneol also could be tolerated, and the yield is 65 - 83% with excellent chemoselectivity (m:d > 20:1). Certainly, naturally molecules , including DL-

Menthol and DL-Isoborneol also could be tolerated, and the yield is 65 - 83% with excellent chemoselectivity (m:d > 20:1).

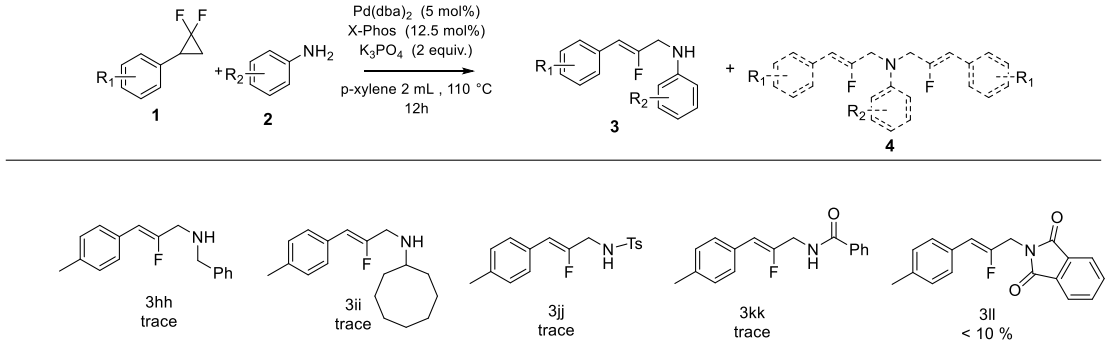
Table 4 monofunctional products scope of biologically molecules[ab]



[a]Reaction conditions: **1** (0.20 mmol), **2** (0.60 mmol), Pd catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Determined by ^1H NMR. [c]1a:2dd = 1:1.

The above results can demonstrate the high relevance of the synthetic method described here, despite some other substrate limitations, such as amides or aliphatic amine nucleophiles (**3hh-3jj**) (**table 5**).

Table 5 Monofunctional products scope of special amines[ab]

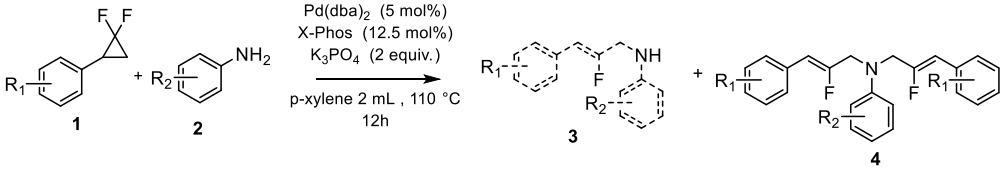


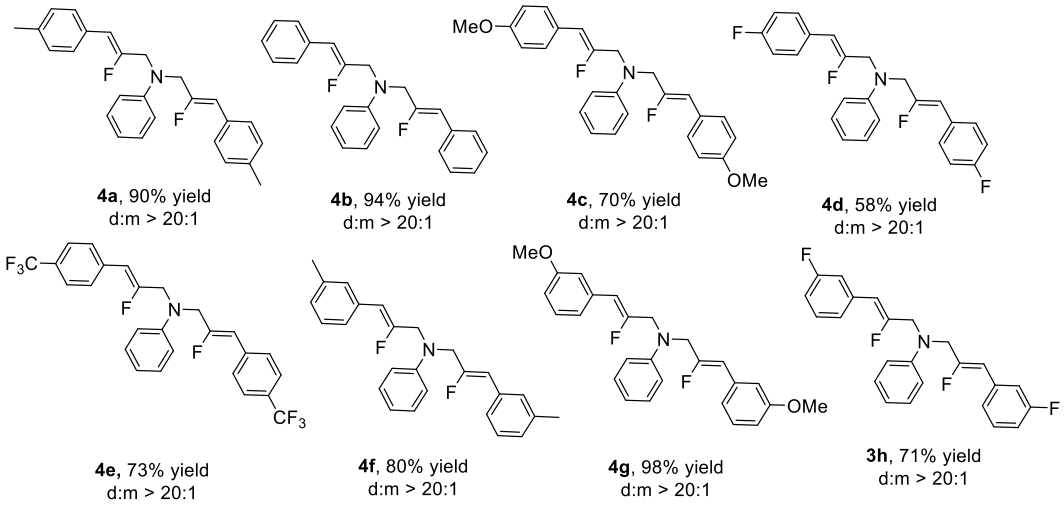
[a]Reaction conditions:**1** (0.20 mmol), **2** (0.60 mmol), Pd catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Determined by ^1H NMR.

2.1.4 Substrate Scope Studies of Difunctional Products

We then turned our attention to the new di-2-fluoroallylic amines and their synthesis. A series of *gem*-difluorocyclopropanes proved to be tolerated, including substituents such as methyl (**4a,** and **4f**), methoxy (**4c** and **4g**), fluoro (**4d** and **4h**) and trifluoromethyl (**4e**), yielding the corresponding di-2-fluoroallylic structures in excellent yields considering that two distinct C─N bonds are formed in the process (58-98%), with moreover excellent di-selectivity (d:m > 20:1) (**Table 6**).

Table 6 difunctional products scope of *gem*-Difluorocyclopropanes[ab]

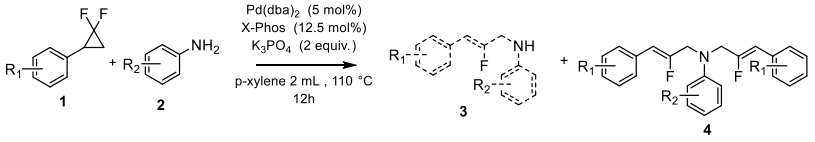


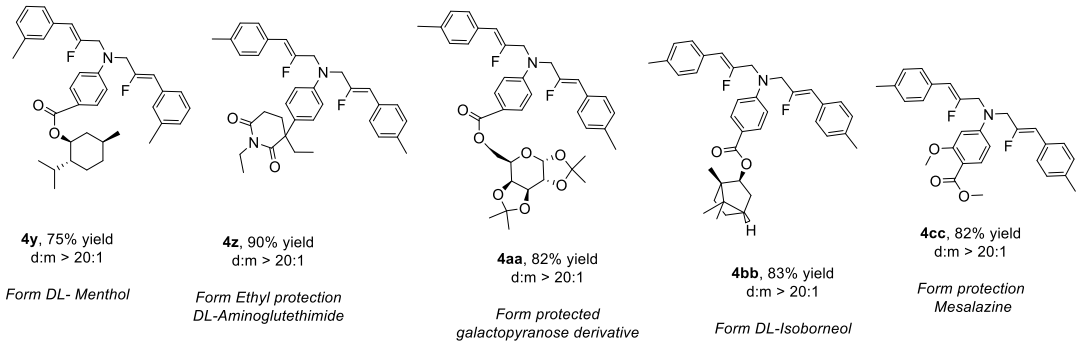


[a]Reaction conditions: **1** (0.60 mmol), **2** (0.20 mmol), Pd catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Determined by ^1H NMR.

In addition, substituents at para, meta or ortho positions of the aniline were well accommodated. These include methyl (**4i** and **4o**), methoxy (**4j**), phenoxy (**4m**), isopropyloxy (**4n**), tert-butyl (**4k**), fluoro (**4l** and **4p**) and trifluoromethyl groups (**4q**). Interestingly, even sterically hindered 2-methyl aniline converted to the di-functionalized product (**4r**), although with a reaction time extended to 24 h, affording 82% yield and an encouraging di-selectivity (d:m = 9:1). In addition, multifunctional and heterocyclic anilines were also found competent (**4s, 4t, 4u, 4v, 4w** and **4x**), with good to excellent yields (52 - 94%) and excellent di-selectivity (d:m >20:1) (**Table 8**).

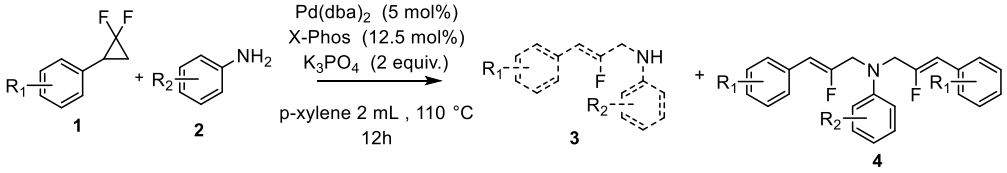
Table 7 diofunctional products scope of biocative molecules[ab]

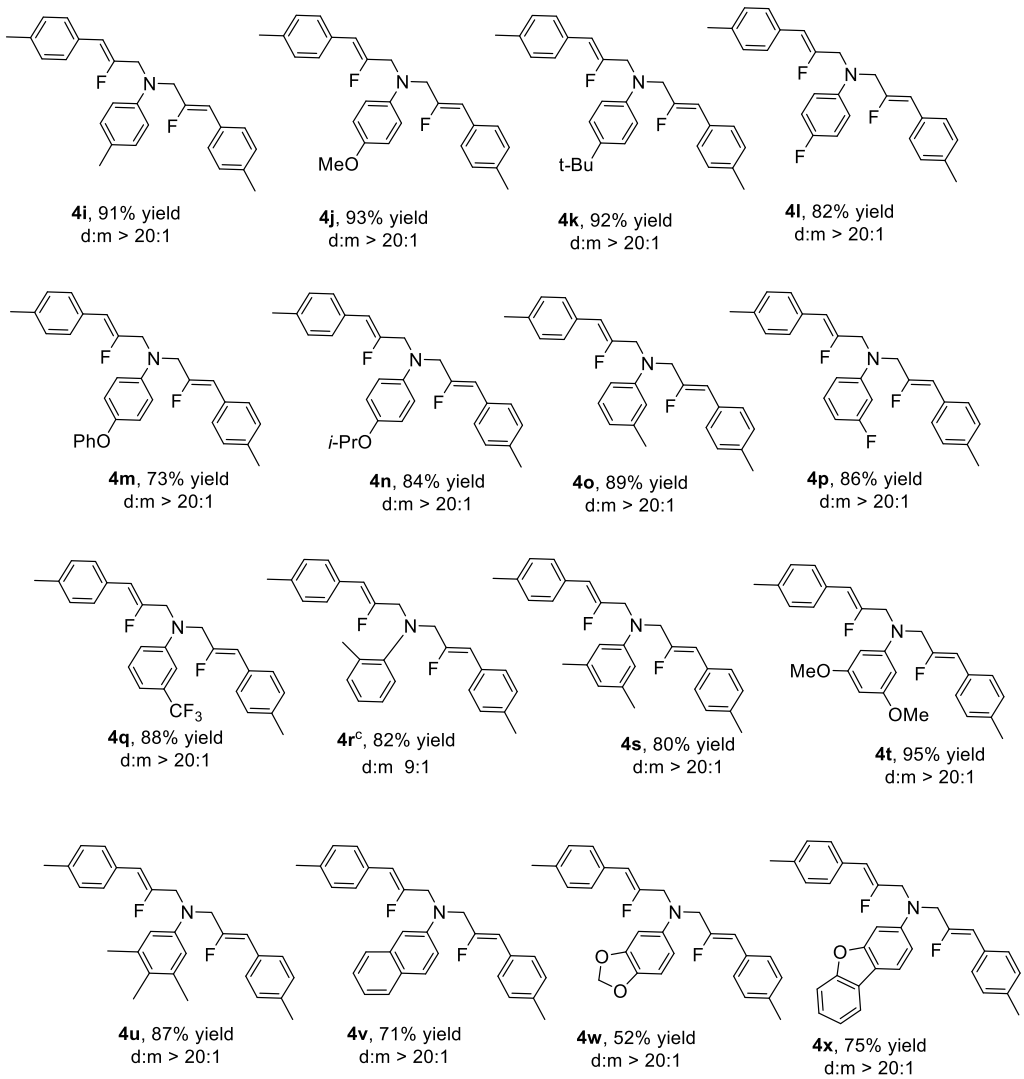




[a]Reaction conditions: **1** (0.60 mmol), **2** (0.20 mmol), Pd catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Determined by ^1H NMR.

Table 8 difunctional products scope of anilines[ab]



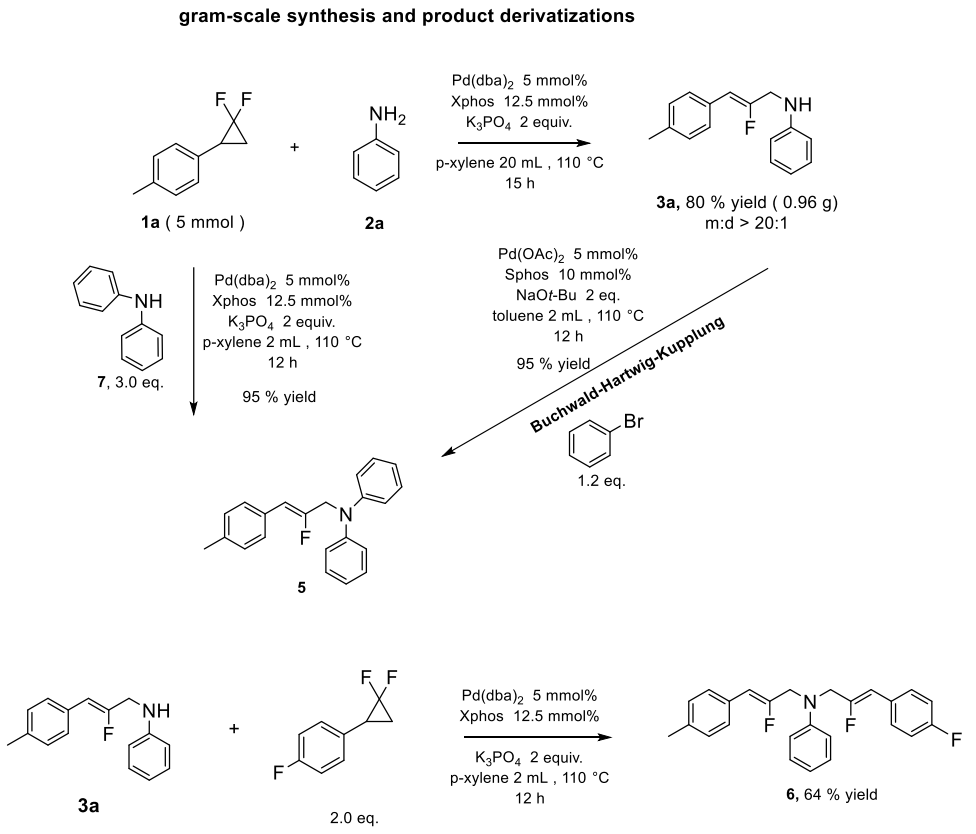


[a]Reaction conditions: **1** (0.60 mmol), **2** (0.20 mmol), Pd catalyst (5 mol %) with ligand (12.5mol %), K_3PO_4 (2 eq.) in p-xylene (2.0 mL) at 110 °C for 12 h. [b]Determined by ^1H NMR.

Next, bioactive and natural fragments such as ethyl protected DL-aminoglutethimide (**4z**), protected mesalazine (**4cc**), a protected galactopyranose derivative (**4aa**), DL- menthol (**4y**) and DL-isoborneol (**4bb**), were all tolerated in this synthetic method, typically associated to excellent yields (75-90%) and di-selectivities (d:m > 20:1, Table 3) (**Table 7**).

2.1.5 Synthetic Utility

In order to explore the synthetic utility of the method, a gramscale reaction was conducted for mono-functionalized product **3a**. This target was thus obtained in remarkably preserved 80% isolated yield (0.96 g), with high mono-selectivity (m:d > 20:1).

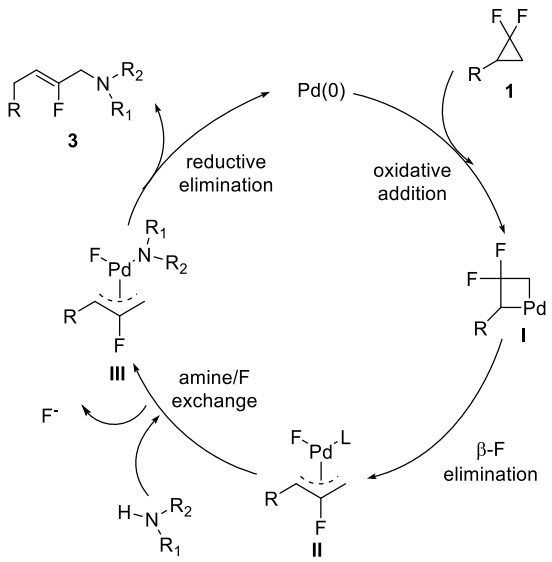


Scheme 33 Synthetic utility and further developments

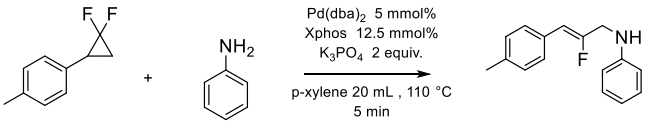
Furthermore, we verified that diphenylamine reacts in a similar fashion to the primary anilines described in this study, with **1a**, affording indeed 95% isolated yield (**5**). Moreover, product **3a** could also be obtained from **5** in likewise excellent 95% yield with a classical Buchwald-Hartwig coupling reaction. [39] Finally, unsymmetrical di-2-fluoroallylic product **6**, with two different allylic arms, could be accessed from **6** reacting with a different *gem*-difluorocyclopropane, under otherwise similar reaction conditions (64%, **Scheme 33**). This demonstrates the feasibility of attaching two different fluoroallyl functional groups on primary anilines in a sequential fashion (**Scheme 33**). [95]

2.1.6 Mechanism Studies

Based on some previous reports, we assume a possible mechanism that the formation of mono or di 2-fluoroallylic amines were out-lined in. First, the palladium (0) could quickly activate the C-C bond of the *gem*-difluorocyclopropanes to form intermediate **I**, followed by β-F elimination to give π-allylpalladium species **II**. Then the reaction intermediate II is attacked by other nucleophile amines to give product **III**. Finally, mo-di 2-fluoroallylic amines were obtained by C-C bond elimination, and palladium (0) continues the next reaction cycle (**Scheme 34**).



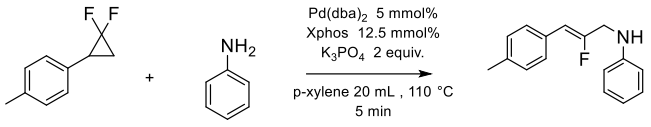
Scheme 34 Proposed mechanism



0.1 mmol
0.2 mmol
0.4 mmol
0.8 mmol

0.036 mmol
0.058 mmol
0.144 mmol
0.144 mmol

(determined by ^{1}H NMR analysis, 1,2,3-trimethoxybenzene as an internal standard)



0.1 mmol
0.2 mmol
0.4 mmol
0.8 mmol

0.064 mmol
0.074 mmol
0.076mmol
0.072 mmol

(determined by ^{1}H NMR analysis, 1,2,3-trimethoxybenzene as an internal standard)

Scheme 35 Kinetic order in *gem*-difluorocyclopropane a1,b1

Experimentally, we observed first order kinetics with respect to the *gem*-difluorocyclopropane building block **1a** in the 0.05 to 0.40 M concentration range. In aniline substrate **2a**, however, the reaction has an approximate zeroth order. These findings point to an early rate limiting phase, such as the activation of strained C-C bonds or the subsequent β-F elimination step towards intermediate **II** (**Scheme 35**).

2.1.7 Conclusion

In summary, we have developed a Pd-catalyzed highly selective synthesis of mono- and di- 2-fluoroallylic amines from primary anilines and *gem*-difluorocyclopropanes. Through simple alteration of the substrate ratios, excellent mono- and di-selectivities could be achieved, above 20:1 in general. High functional group compatibility was moreover demonstrated with 64 different

examples, including natural and bioactive fragments. In addition to the newly opened chemical space in terms of potentially interesting fluorinated drug candidates, these results should encourage the further development of cross coupling methods based on the very versatile *gem*-difluorocyclopropane and related strained building blocks.

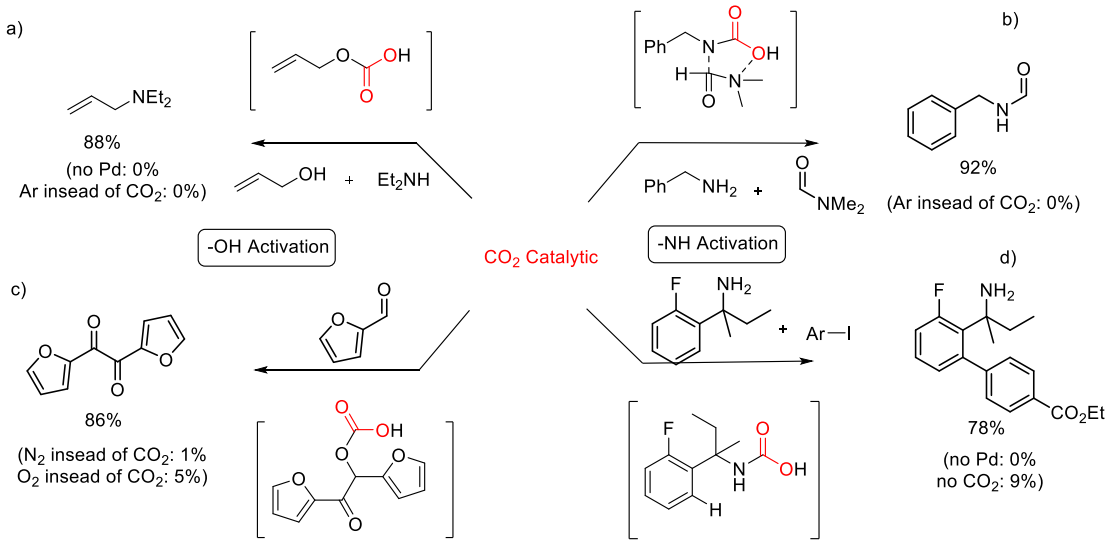
2.2 CO_2 and Palladium co-Catalyzed Synthesis of Fluorinated Cinnamyl Alcohol

Author contributions: X. W. performed the corresponding experiments and drafted the manuscript. X.F. contributed to preparing a number of starting materials. Prof. Dr. Patureau supervised the project and edited the draft.

This work has been published: *Org. Chem. Front.* **2024**, 11, advance article.

2.2.1 Introduction

Cinnamyl alcohol is a crucial chemical industry intermediate for the synthesis of drug molecules, flavors, and fungicides[96-100]. Its primary method of synthesis concentrates on the hydrogenation reduction reaction of cinnamaldehyde or ester, which has clear limitations in terms of its synthesis[100-101]. Additionally, more than half of all new medications created in the past 20 years were related to the research and development of fluorine-containing drugs. Organic compounds can acquire amazing electrical, physical, biological, and reactivity features when fluorine atoms are added to pharmaceuticals. Building a powerful synthesis of fluorine-containing cinnamyl alcohol is therefore extremely important.



Scheme 36 CO_2 catalytically activates N-H or O-H bonds

Carbon dioxide (CO_2) holds an increasingly vital position in the atmosphere and is readily available, cost-effective, non-toxic, chemically stable, and recyclable.[102-106] In numerous studies, it is predominantly employed as a convenient source of C1.However, its catalytic activity, in particular in cooperation with transition metal co-catalysts, has received relatively sparse attention.[107-108] In the literature, some of the most notable CO_2 catalyzed synthetic methods are Yamamoto's 1996 amination of allylic alcohols (**Scheme 36a**),[109] Xu and Wang's 2015 formylation of amines (**Scheme 36c**),[110] Das's 2017 dehydrogenative synthesis of -diketones (**Scheme 36b**),[111] and Young's 2019 C─H arylation of benzylamines (**Scheme 36d**),[112] among others.[113-117] In most of these methods, CO_2 transiently activates a nucleophilic position in the substrate, leading to CO_2

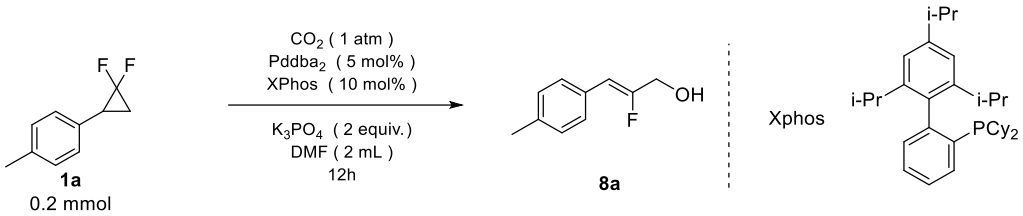
adduct intermediates with starkly altered reactivity. Nevertheless, the use of CO_2 as a catalyst is still underappreciated for the development of innovative synthetic methods, overshadowed by its many other uses. In the present study, we utilized CO_2 catalysis in order to activate one of the weakest and most important nucleophiles in organic synthesis: water. In particular, the use of H_2O as a nucleophile in Pd-catalyzed cross coupling chemistry remains a daunting challenge, in spite of elegant seminal works on the topic.[118-121] Another challenge arises from the tendency of most C─OH coupling products to exhibit higher reactivity and nucleophilicity compared to H_2O. Consequently, this often leads to undesired side reactions involving the formation of multiple bonds, particularly in the absence of bulky substituents that shield the reaction site. To address this issue, we hypothesized that CO_2 catalysis could serve to enhance the nucleophilicity of water while reducing that of the valuable C─OH coupling products. As a result, we developed a method for the hydroxylation of *gem*-difluorocyclopropanes,[122] which are increasingly recognized as versatile building blocks in cross-coupling chemistry. This was achieved under the co-catalysis of CO_2 and Pd(0), enabling the synthesis of a broad range of significant fluorinated cinnamyl alcohols. [123-127]

2.3.2 Condition Optimizations

Based on the previous introduction, We chose the 4-Methyl *gem*-Difluorocyclopropanes (**1a**) as the model substrates, and screened different catalysts, ligands, temperature, solvents and other conditions.

First, we investigated the effect of different temperatures on the reaction. At different temperatures, the reaction can occur, but when the temperature is lower than 30 °C, the reaction basically stops. The yield increases as the temperature continues to rise, so does the yield. When the temperature reached 80 °C, the target product was obtained in 40% yield (**Table 9**).

Table 9 Screening of Conditions for synthesis of fluorinated cinnamyl alcohol about about temperature[ab]



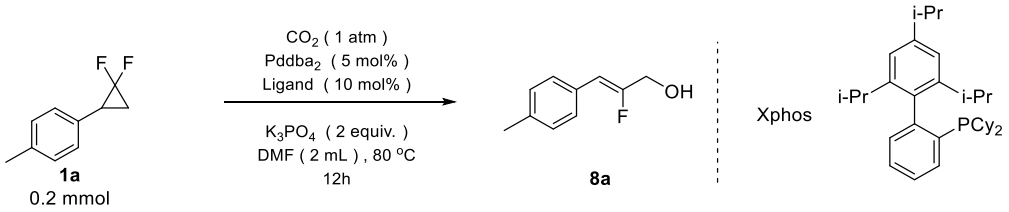
Entry	Temperature	Yield (c1)[c]
1	30 °C	< 10 %
2	50 °C	15 %
3	60 °C	38 %
4	70 °C	36 %
5	80 °C	40 %
6	90 °C	20 %

[a] Unless otherwise noted, the standard reaction conditions were as follows: **1a** (0.2 mmol) , solvent (2 mL), $Pddba_2$ (5 mol%), XPhos (10 mol%), K_3PO_4 (2 eq.) . [b] The yield was determined by ^1H NMR analysis of the crude reaction

mixture using 1,3,5-trimethoxybenzene as an internal standard.

Next, we continued to investigate the effect of different phosphine ligands in the reaction. First, neither the bisphosphine ligand or the triphenylphosphine can obtain the target product. Although RuPhos can obtain product **8a** with a yield of 20%, it is not better than XPhos. Therefore, we chose XPhos as the optimal ligand for the next step of condition screening (**table 10**).

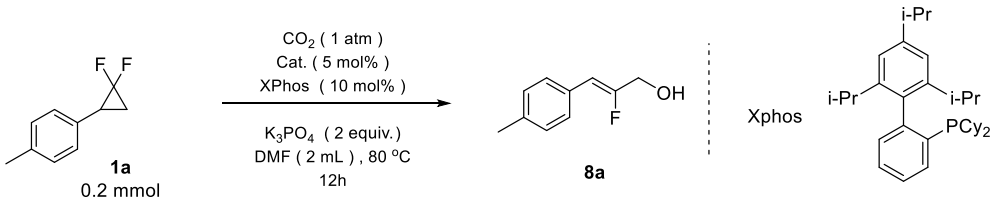
Table 10 Screening of Conditions for synthesis of fluorinated cinnamyl alcohol about about ligand[ab]



Entry	Ligand	Yield (c1)[c]
1	XPhos	40 %
2	RuPhos	20 %
3	*t*-BuXphos	< 5 %
4	dppb	< 5 %
5	PPh_3	< 5 %

[a] Unless otherwise noted, the standard reaction conditions were as follows: **1a** (0.2 mmol) , solvent (2 mL), $Pddba_2$ (5 mol%), K_3PO_4 (2 eq.) . [b] The yield was determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Tbale 11 Screening of Conditions for synthesis of fluorinated cinnamyl alcohol about about Palladium catalyst[ab]



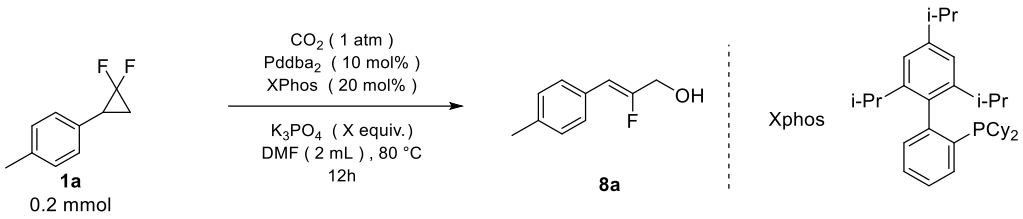
Entry	Cat.	Yield (c1)[c]
1	$Pddba_2$	40 %
2	$Pd_2(dba)_3$	36 %
3	$Pd_2(dba)_3{\cdot}CHCl_3$	28 %
4	$Pd(OAc)_2$	NR
5	$Pddba_2$ (10 mol%), Xphos (20 mol%)	64 %

[a] Unless otherwise noted, the standard reaction conditions were as follows: **1a** (0.2 mmol) , solvent (2 mL), [Pd] (5 mol%), XPhos (10 mol%), K_3PO_4 (2 eq.) . [b] The yield was determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Following that, we also investigated the effect of different palladium catalysts on the reaction. The target product **8a** cannot be obtained using divalent palladium catalysts (such as $Pd(OAc)_2$, $PdCl_2$). And other types of zero-valent palladium are not as effective as $Pddba_2$. When the amount of catalyst palladium increased to 10 mol%, the yield rises to 64% (**Table 11**).

Next, we investigated the amount of different bases. We found that the reaction could proceed without bases, but the yield decreases. As the amount of base continuously increased, the yield also continuously increased. When the amount of base increased to 3eq, the highest yield was 80%. When we add 10eq of water to the reaction system, we can achieve the desired product **8a** with an excellent 98% yield. As we predicted, when CO_2 in the reaction system is replaced with N_2, the reaction does not occur. Finally, we obtain the reaction's optimal conditions (**Table 12**).

Tbale 12 Screening of Conditions for synthesis of fluorinated cinnamyl alcohol about about additives[ab]



Entry	variations from standard conditions	Yield (c1)[c]
1	K_3PO_4 (0 eq.)	30 %
2	K_3PO_4 (2 eq.)	64 %
3	K_3PO_4 (3 eq.)	80 %
4	K_3PO_4 (5 eq.)	60%
5	H_2O instead of DMF	8 %
6	H_2O (10 equiv.) instead of K_3PO_4	46 %
7	Add H_2O (10 eq.)	98 %
8	N_2 instead of CO_2	6 %

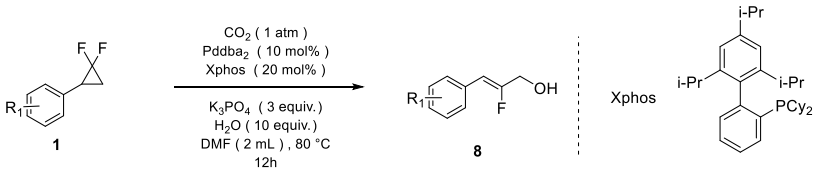
[a] Unless otherwise noted, the standard reaction conditions were as follows: **1a** (0.2 mmol) , solvent (2 mL), $Pddba_2$ (5 mol%), XPhos (10 mol%), K_3PO_4 (2 eq.) . [b] The yield was determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

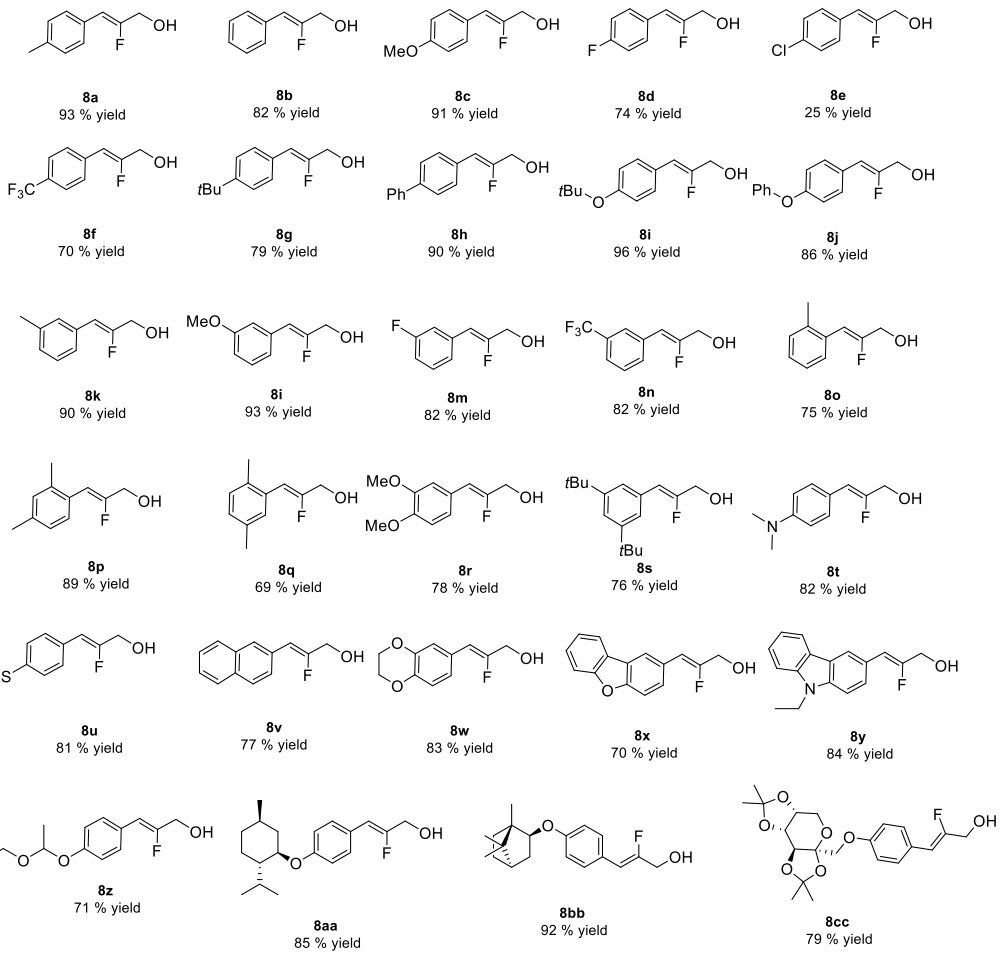
2.3.3 Substrate Scope Studies

With these optimized reaction conditions in hand, we investigated the reaction scope with various *gem*-difluorocyclopropanes. First, we tested the para-position of *gem*-difluorocyclopropanes with different functional groups, Electron-neutral (**8b**), electron-donating (**8a, 8c, 8h, 8i, 8j** and **8g**), and electron-withdrawing (**8d, 8e** and **8f**) functional groups afforded the corresponding monofunctional 2-fluoroallylic amines products in excellent yields (27 - 96 %). Particularly **8e** chlorine-substituted

compounds can also get medium yields under optimal conditions. Next meta or ortho aromatic ring substituted of *gem*-difluorocyclopropanes were alsoexplored (**8k – 8o**) with promisingto excellent yields (75 - 93 %). In addition, Di-substituted *gem*-difluorocyclopropanes structures (**8p, 8q, 8r**) as well as bulky 3,5-substitutents were likewise well tolerated (**8s**), with 69 – 89 % yields, respectively. Furthermore, Para-heteroatom substitution (**8t, 8u**) also gave excellent yields. Notably, the heterocycle-containing *gem*-difluorocyclopropanes, such as Naphthalene, Benzofuran, Carbazole and Benzodioxane, the products were obtained in good yields. The long-chain branched compound **8z** also showed good universality. Finally, we focus on the application of biologically or naturally relevant small molecules. As shown in **Table 13**, a series of biologically molecules, such as Dl - Menthol (**8aa**) , DL-Isoborneol (**8bb**) and protected galactopyranose derivative (**8cc**) could be tolerated, with high isolated yield (79% - 92%).

Table 13 Products scope[a]

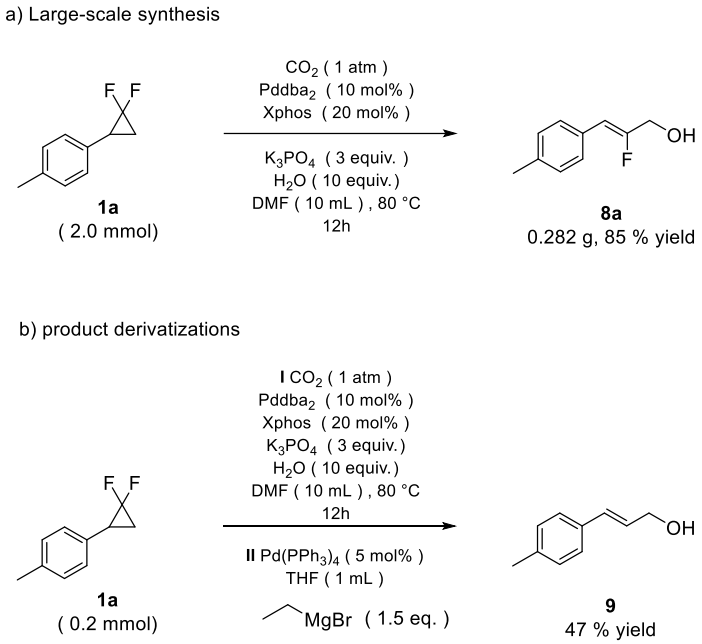




[a]Substrate scope, isolated yields. Reaction conditions: 1a (0.20 mmol), catalyst (10 mol%), Xphos ligand (20 mol %), K_3PO_4 (3 equiv.), H_2O (10 equiv.),in DMF (2.0 mL) at 80 °C for 12h.

2.3.4 Synthetic Utility

In order to explore the synthetic utilities of our reaction, a largescale reaction was conducted for product **8a**. This product was thus obtained in remarkably preserved 85% (0.282 g) isolated yield. Next, to explore the value, follow up transformations on **1a** were conducted. Starting directly from starting material **1a**, a two-step reaction takes place. This directly led to the removal of fluorine from product **9**, resulting in a moderate yield (47%) of the normal cinnamyl alcohol (**Scheme 37**). [36]

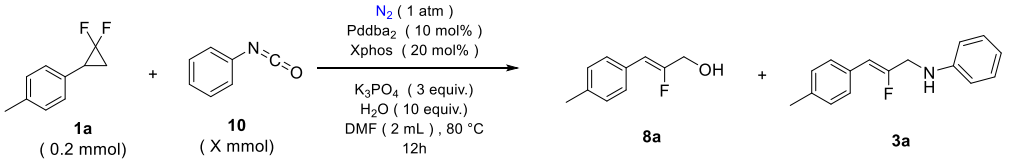


Scheme 37 Synthetic utility and further developments

2.2.5 CO_2 control Experiment

In order to investigate the impact of the amount of CO_2 on the reaction, we employed the hydrolysis reaction of isocyanatobenzene to produce an equivalent amount of CO_2 in situ[25]. We discovered that the reaction could take place and that **8a** could be produced in a 42% yield when we added an equivalent amount of isocyanatobenzene. However, the by-product **3a** is also generated in the reaction. According to our previous report, the reaction of *gem*-difluorocyclopropanes[26-35] with aniline is easy to occur under this condition. Then, as we further decreased the amount of **10**, we were astonished to discover that adding a catalytic amount (20 mol%) of **10** was sufficient to achieve a good yield of **8a** (58% yield). This demonstrates once more how important CO_2 is to this process (**Scheme 38**).

control experiment

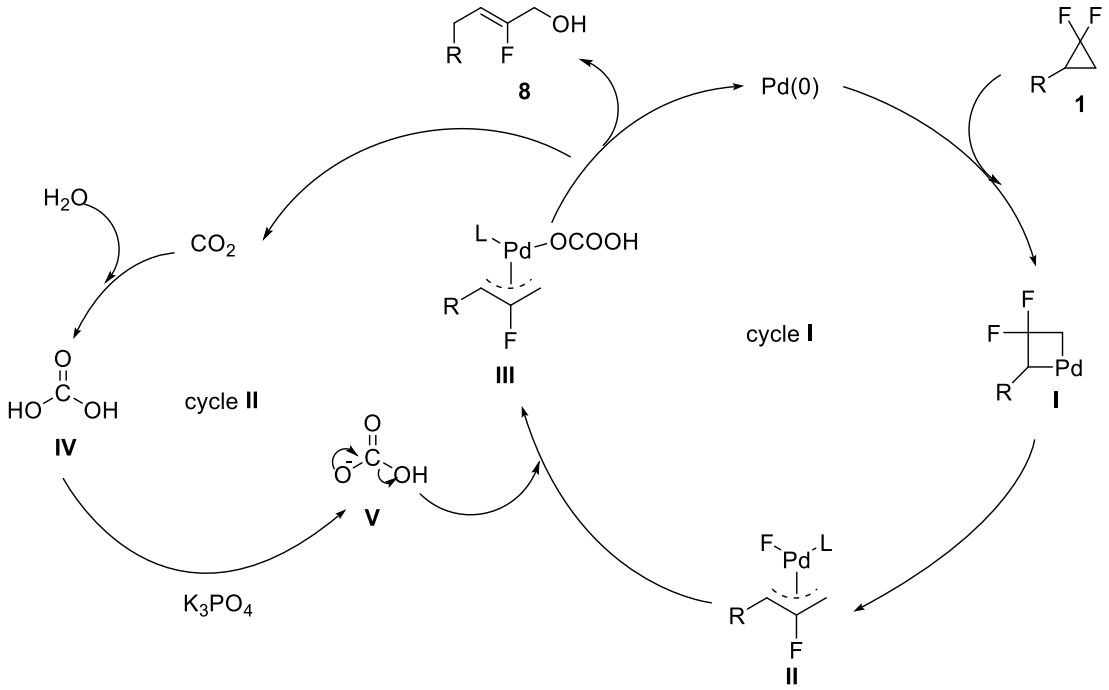


Entry	Deviation from standard conditions	**8a** Yield	**3a** Yield
1	0.2 mmol of **10**	42 %	20 %
2	0.1 mmol of **10**	47 %	12 %
3	0.04 mmol of **10**	58 %	< 5 %

Scheme 38 Controlled experiment

2.2.6 Mechanism Studies

Based on some previous reports[37-38], we envisioned a possible mechanism that the synthesis of fluorinated cinnamyl alcohol (**Scheme 39**). The C-C bond of the *gem*-difluorocyclopropanes may be promptly activated by palladium (0) in the first mechanism cycle to form intermediate **I**, which was then followed by -F elimination to produce -allylpalladium species **II**. At the same time, CO_2 first activates water molecules to obtain intermediate **IV** in the second mechanism cycle, and then deprotonates under the action of base to obtain intermediate **V.** Intermediate **II** would then be attacked by the OH-nucleophile to give species **III**, Thus CO_2 will enter the next cycle. Finally, the product would be obtained by C–O bond reductive elimination, thus regenerating the Pd(0) active catalyst.

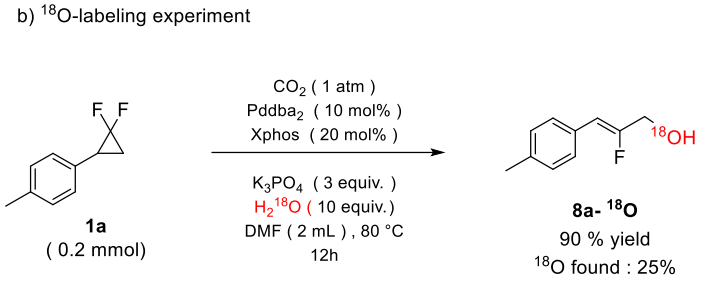


Scheme 39 Proposed experimental mechanism

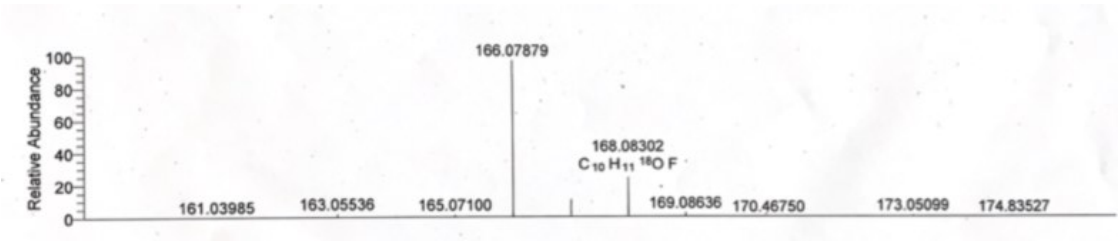
2.2.7 Experiment Reaction

X-Phos (19.1 mg, 0.04 mmol) and $Pd(dba)_2$ (11.4 mg, 0.02 mmol), *gem*-difluorocyclopropanes **1a** (0.2 mmol), $H_2{}^{18}O$ (10.0 eq., 36 mg), K_3PO_4 (3.0 eq., 127.2 mg) were dissolved in 2 mL DMF and

CO_2 was bubbled through the solution for about two minutes. then the mixture was stirred at 80 ºC for about 12 h until the starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. The crude was purified by column chromatography to give the products **2a-^{18}O** and ^{18}O was detected in HRMS. This indicates that the source of the hydroxyl groups in the product comes from water. However, the ^{18}O incorporation is slightly less than one-third of that from the labeled $H_2(^{18}O)$ reagent, indicating a degree of label scrambling. The most plausible explanation for this scrambling is the generation of pivotal carbonate intermediate(s) from water and CO_2. In this scenario, each of the three resultant oxygen atoms possesses an equal likelihood of forming the C─O bond during the reductive elimination event at the Pd (II) center. (**Scheme 40**)



EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_{11}{}^{18}OF$ [M]+ 168.08364, measured 168.08302



Scheme 40 Mechanistic experiments

2.2.8 Conclusion

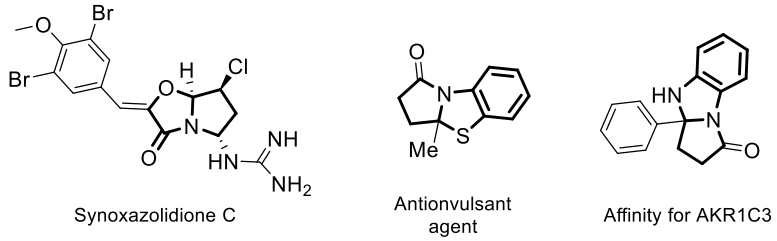
In summary, we have developed the hydroxylation of *gem*-Difluorocyclopropanes under the co-catalysis conditions of metal palladium and CO_2, and a series of fluorine-containing cinnamyl alcohol products with different structures were obtained. The reaction conditions are mild, and the yield is excellent. Moreover, the reaction had good substrate universality and was also applicable to some natural products and drug molecules. In addition, By controlling certain conditions, the F atom in the product can be removed, and a series of normal structure cinnamyl alcohols can be obtained. This provided a good way for cinnamyl alcohol in medicinal chemistry and organic synthesis.

2.3 Phosphine-catalyzed Dearomative [3+2] Cycloaddition of Benzoxazoles with a Cyclopropenone

Author contributions: X. W. performed the corresponding experiments and drafted the manuscript. C.Y. contributed to preparing a number of starting materials. The X-Ray data was analyzed by Dr. I. L. Atodiresei. Prof. Dr. Patureau supervised the project and edited the draft.
This work has been published: *Org. Lett.* **2022**, *24*, 1127.

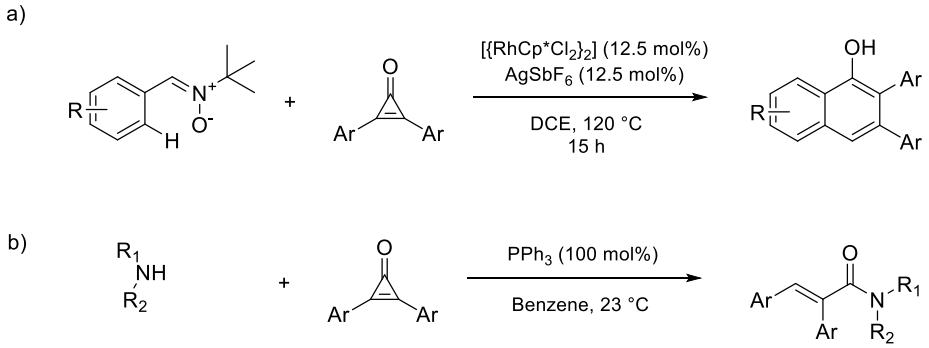
2.3.1 Introduction

Hydropyrrolo-Benzoxazole heterocycles[128-134] are a very important type of nitrogen-containing heterocycles, in natural products and biological molecules, it is also prevalent. For example, in antiepileptic, anticancer antibacterial, and antifungal activities, hydropyrrolo-benzazole heterocycles play an important role. Thus, the synthesize of these molecules has become the focus and hotspot of research (**Scheme 41**).



Scheme 41 Examples of natural products and bioactive compounds based on the benzopyrrolo-oxazolone or similar scaffold

"The cyclopropenone system must have strong resonance stabilization indeed to compensate for its high angle strain". Breslow and his colleagues were also surprised by the surprising relative stability of 1,2-diphenyl cyclopropenone. [135-136]



Scheme 42 Ring-opening and ring-expansion reaction of cyclopropenone

The activation of C-C bonds is an important concept for the re-organization or coupling of organic scaffolds, but due to their intrinsic stability.[137] It is a very difficult process to achieve in the context of synthetic methods. To enable such approaches, C-C strained, frequently cyclic building blocks can be used, which are then spring loaded for C-C bond activation.[138-156] In this regard, 1,2-diphenyl cyclopropenone, a very strained cyclic molecule which is known since the late 1950s, is currently experiencing a renaissance in the context of synthetic technique advancements based on

C-C bond activation. Even though its highly strained structure makes it an ideal building block for C─C bond activation, it usually still requires a precious metal salt as catalyst.[157-185] The most frequent are based on rhodium, palladium, ruthenium, silver, and even nickel for the catalytic opening of 1,2-diphenyl cyclopropenone.

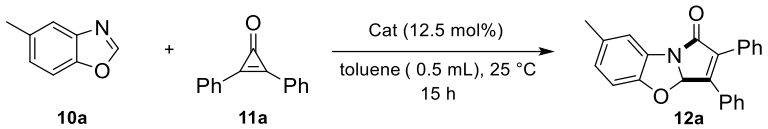
In 2016, Li's group[158] reported that Rh catalyzed nitrogen DGs to activate aryl C-H bonds realize the aromatization reaction of cyclopropenone. The reaction exhibits high chemoselectivity and a wide range of substrate application. A number of naphthol structure compounds were synthesized (**Scheme 42a**).

In 2015, the Presche group[186] used simple phosphine catalysts to achieve the coupling of cyclopropenone with amine nucleophiles to produce a series of enone molecules. The authors linked such compounds into biopolymers to study their biological activity (**Scheme 42b**). And with this study, the cyclopropenone ligation is poised to join the ranks of chemicals with utility in living systems. As a result, there is significant benefit in inventing an efficient and convenient method for realizing cyclopropenone conversion.

2.3.2 Condition Optimizations

Based on previous reports, we propose herein such a method, with the simple triphenyl phosphine catalyzed dearomative [3+2] cycloaddition of benzoxazoles with 1,2-diphenyl cyclopropenone. We chose the 5-Methylbenzoxazole (**10a**) and 1,2-Diphenylcyclopropen-3-one (**11a**) as the model substrates.

Table 14 Screening of Conditions for synthesis about catalysts[ab]



10a (0.2 mmol) **11a** (0.2 mmol) **12a**

Entry	variations from standard conditions	Yield (c1)
1	PPh_3	37 %
2	Binap	NR
3	*p*-Me-PPh_3	22 %
4	dppb	15 %

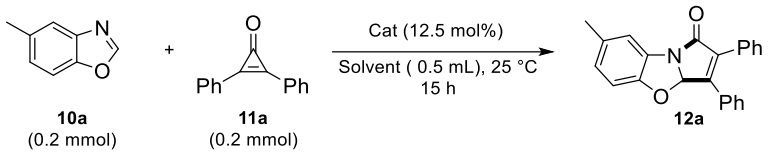
[a] Unless otherwise noted, the standard reaction conditions were as follows: 10a (0.2 mmol), 11a (0.2 mmol), solvent (0.5 mL). [b] The yield was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

First, we tried different kinds of phosphine catalysts. We found that the bisphosphine catalyst is not suitable for this reaction (entry2,4), But the product can be obtained in the yield of 37% with the simple triphenylphosphine (entry1), and we also tried triphenylphosphine with other structures, and it was not better than before (entry3) (**Table 14**).

Next, we investigated the effect of different kinds of solvents on the reaction. We discovered that the intended product could be produced in the majority of the solvents except acetonitrile and

methanol (entry2,4). However, in common solvents, we obtained only moderate yields of the product (22% - 37%). Surprisingly, we discovered that the desired product can be produced in chloroform get 67% yield (entry7) (**Table 15**).

Table 15 Screening of Conditions for synthesis about solvent[ab]

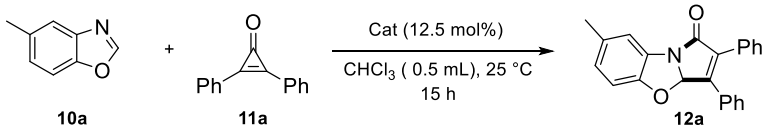


10a (0.2 mmol) **11a** (0.2 mmol) **12a**

Entry	variations from standard conditions	Yield (c1)[c]
1	Toluene	37 %
2	CH_3CN instead of toluene	NR
3	EA instead of toluene	22 %
4	CH_3OH instead of toluene	< 10 %
5	DCM instead of toluene	27 %
6	Et_2O instead of toluene	27 %
7	$CHCl_3$ instead of toluene	67 %

[a] Unless otherwise noted, the standard reaction conditions were as follows: 10a (0.2 mmol), 11a (0.2 mmol), solvent (0.5 mL). [b] The yield was determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Tabel 16 Screening of Conditions for synthesis about Amount of reactants[ab]



10a **11a** **12a**

Entry	variations from standard conditions	Yield (c1)[c]
1	a1:b1=1:1	67%
2	a1:b1=1:1.25	34 %
3	a1:b1=1.25:1	51 %
4	a1:b1=1.5:1	67 %
5	a1:b1=2:1	88 %
6	a1:b1=3:1	97 %

[a] Unless otherwise noted, the standard reaction conditions were as follows: 10a (0.2 mmol), 11a (0.2 mmol), solvent (0.5 mL). [b] The yield was determined by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

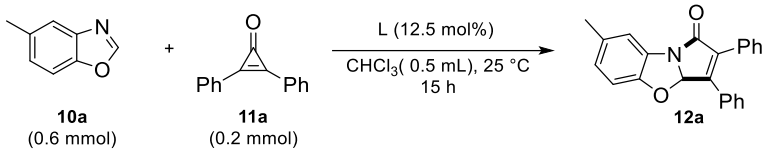
Finally, we investigated the effect of different mass ratios on the reaction. We found that increasing the amount of cyclopropenone decreased the reaction yield, resulting in only a 34% yield (entry 2).

The yield of the reaction rose as the amount of benzoxazole increased. We produced the desired product in up to 97% yield by increasing the amount of benzoxazole to 3 eq (Table 16).

2.3.3 Asymmetric Catalysis Research

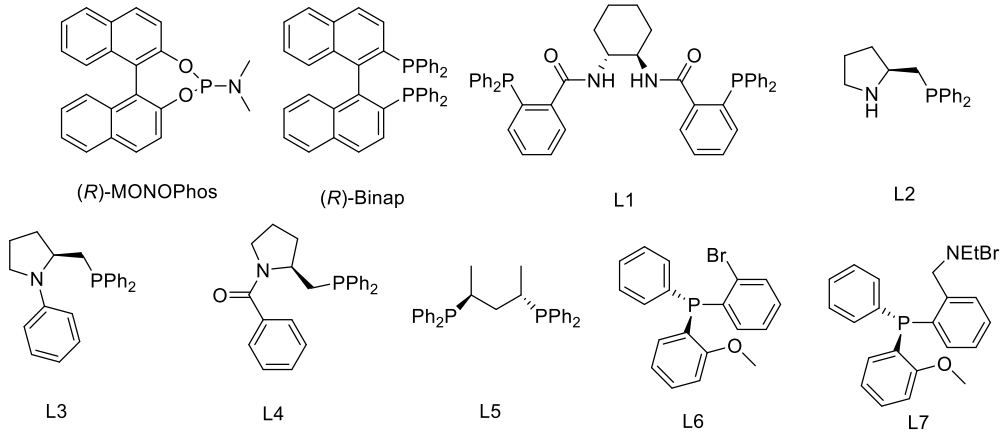
The asymmetric catalysis of this reaction has also been investigated. First, we investigated standard commercial chiral phosphine catalysts such as MONOPhos, Binap, and others, and tried different reaction temperatures, but failed to obtain the target products (entry2, 3, 8, 12, 13). It's gratifying to know that diarylphosphine with an alkane structure can catalyze this reaction. L4 phosphine catalyst has the highest yield (42%), but the ee value is just 4%. We achieved the target product with a yield of 21% and an ee value of 46% using the commercial phosphine catalyst L5, which is the best result we have obtained thus far (**Table 17**).

Table 17 Screening of Conditions for synthesis about chiral catalysts[ab]



10a (0.6 mmol) **11a** (0.2 mmol) **12a**

entry	Cat.	Temp	Yield
1	L1(5 mol%)	25	NR
2	(R)-MONOPhos (10 mol%)	25	NR
3	(R)-Binap (5 mol%)	25	NR
4	L2 (10 mol%)	25	25% / 38 *ee*
5	L3 (10 mol%)	25	NR
6	L4 (10 mol%)	25	42% / 4 *ee*
7	L5 (5 mol%)	25	21% / 46 *ee*
8	(*R,R*)DIOP (5 mol%)	25	12% / 39 *ee*
9	L6 (10 mol%)	25	NR
10	L7 (10 mol%)	25	NR
11	L1 (5 mol%)	70	NR
12	(R)-MONOPhos (10 mol%)	70	NR
13	(R)-Binap (5 mol%)	70	NR

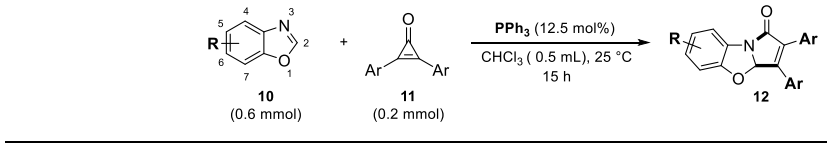


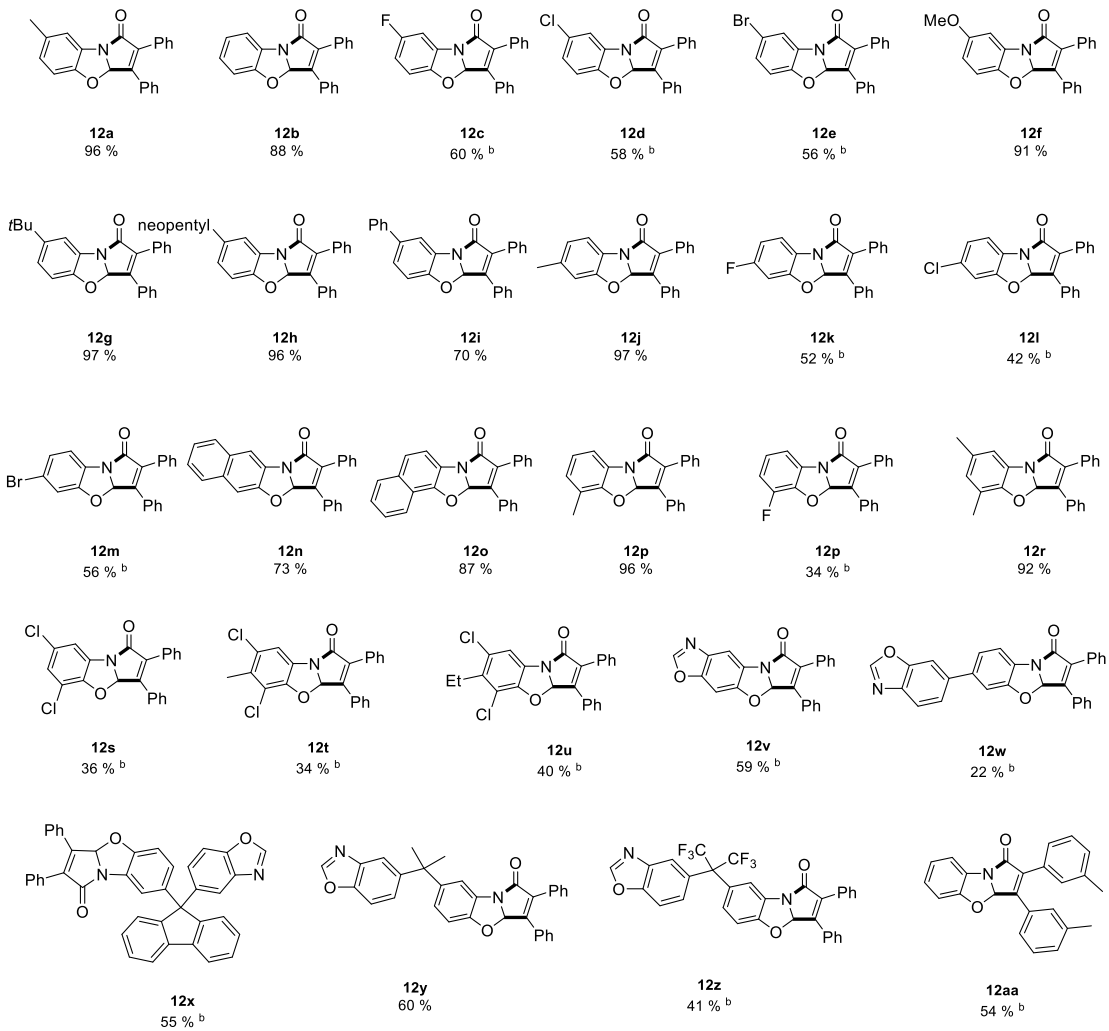
[a] Unless otherwise noted, the standard reaction conditions were as follows: **10a** (0.6 mmol), **11a** (0.2 mmol), solvent (0.5 mL). [b] The yield was determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

2.3.4 Substrate Scope Studies

Next, with these best reaction conditions in hand, we then investigated the reaction scope with various benzoxazoles. First, we tested C5-substituted benzoxazole substrates. Electron-neutral (**12b**), and electron-donating (**12a, 12f, 12g, 12h**) afforded the corresponding benzopyrrolo-oxazolone coupling products in excellent yields (88 - 97%). Although electron-withdrawing groups performed somewhat less well at 25 °C (**12c - 12e**), increasing the reaction temperature to 70 °C afforded promising yields, in the 56% - 60% range. Next, C6-substitution was also explored (**12j – 12m**), as well as C7 (**12p, 12q**) with promising to excellent yields. di- and tri-substituted benzoxazole structures (**12n, 12o, 12r – 12u**) also can get good yields. Bulky C4-substitutents were likewise well tolerated (**12g**, **12h** with respectively 97 and 96% yields).

Table 18 products scope[a]





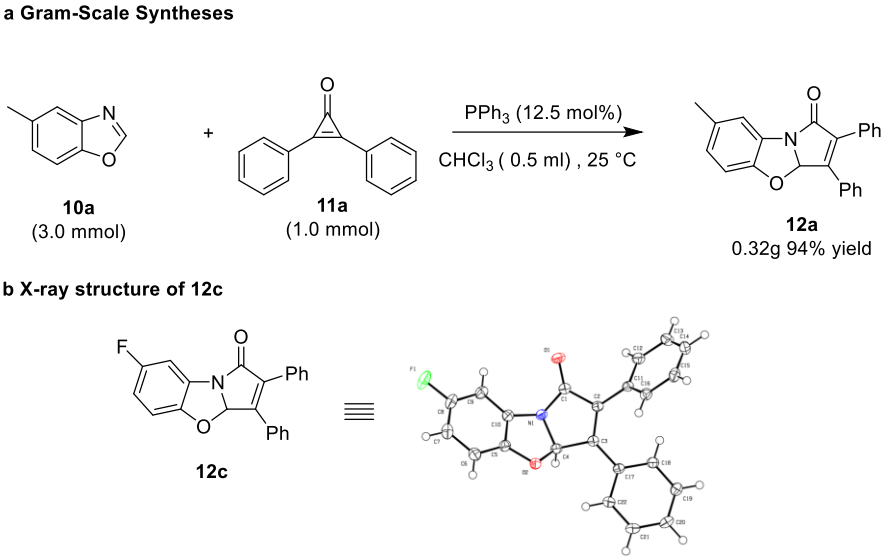
[a] Scope, isolated yields. All reactions were carried out on a 0.2 mmol scale for 15 h under the standard conditions.

[b] The reaction was carried out at 70 °C.

Interestingly even fused and alternatively tethered dibenzoxazole substrates were found applicable, yielding the corresponding single coupling cycloaddition products (**12v** – **12z**) in 22-60% yields. Moreover, the 1,2-Diphenylcyclopropen-3-one **11a** could be replaced with a different cyclopropenone **11aa** (product **12aa**) (**Table 18**).

2.3.5 Synthetic Utility and X-ray Data

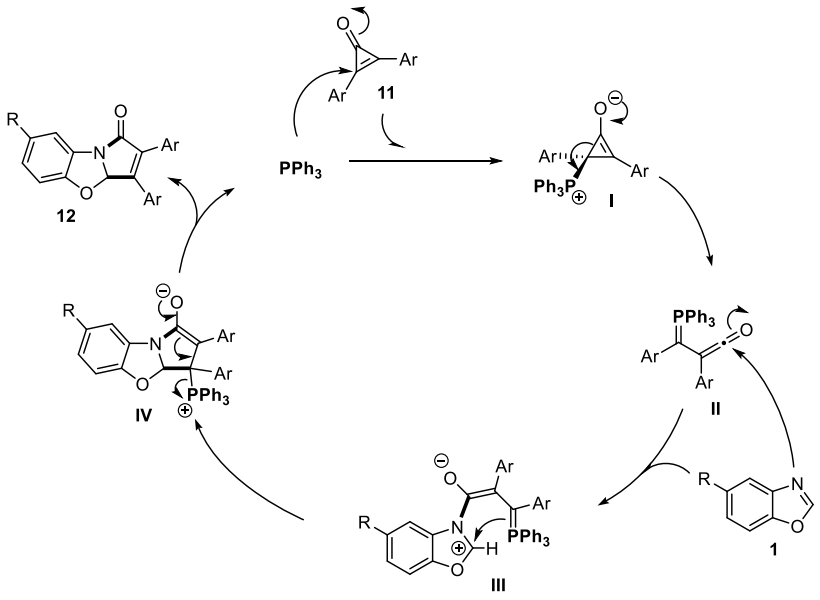
To demonstrate the practicability of our reaction, a 1 mmol scale batch was conducted for product **12a**. This product was thus obtained in remarkably preserved 94% isolated yield (320 mg) in moreover only 1 mL chloroform. In addition, the X-ray diffraction analysis of product **12a** confirmed the structural interpretation (**Scheme 43**).



Scheme 43 Gram-Scale Syntheses and X-ray structure of product **12c** (space group : P 21/n (14))

2.3.6 Mechanism Studies

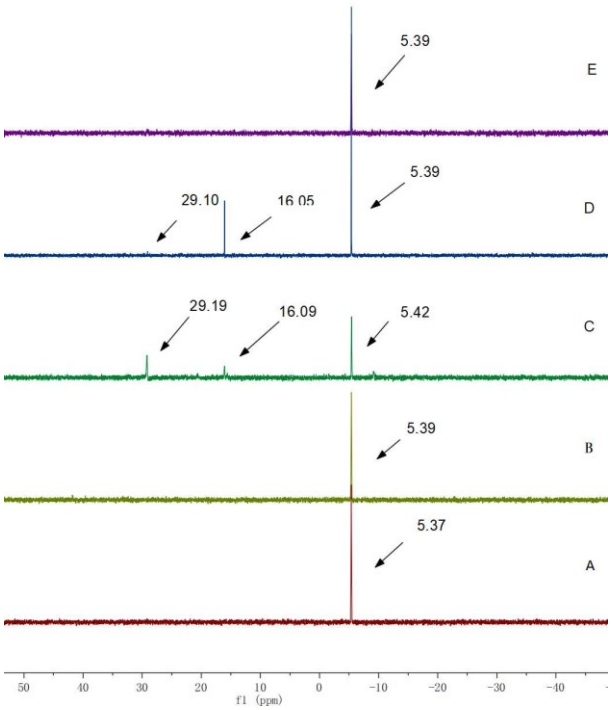
Based on some literature precedents, we assume that the phosphine organocatalyst activates the



Scheme 44 Proposed mechanism

strained and electrophilic cyclopropenone to form zwitterionic intermediate **I**, which would then progress to ketene ylide intermediate **II** (**Scheme 44**). The latter species would then undergo a nucleophilic dearomative attack from the benzoxazole coupling partner to generate intermediate **III**. This would rapidly cyclize to form the second C─C bond towards intermediate **IV**. Phosphine elimination would then regenerate the organocatalyst, releasing coupling product **12**.

Figure 1 Mechanistic experiments[a]



[a]Comparison of the ^{31}P NMR spectra of A): only PPh_3 in $CDCl_3$; B): PPh_3 and 1a (1:24); C): PPh_3 and 2a (1:8); D): PPh_3, 1a and 2a (1:24:8); E): PPh_3, 1a and 2a (1:24:8) after stirring the mixture for 15 h.

To further investigate this mechanism, we conducted crucial ^{31}P NMR experiments (**Figure 1**). Experiment A revealed that the ^{31}P NMR signal of PPh_3 shifts at -5.4 ppm in $CDCl_3$, a solvent known to accommodate the reaction well. The addition of Benzoxazole **10a** did not alter this signal, even in substantial excess (24 equiv., experiment B). However, upon adding strained electrophilic cyclopropenone **11a** (8 equiv.), two new signals appeared at +16.1 and +29.2 ppm, likely corresponding to new species (experiment C). One or both might correspond to intermediates I and/or II, as the observed chemical shifts are compatible. Furthermore, when 24 equiv. of Benzoxazole **10a** were added, the signal at +29.1 ppm disappeared (experiment D), indicating that this particular species is likely a productive intermediate in the reaction. Subsequently, upon stirring this mixture for an additional 15 hours, only the PPh_3 signal remained (-5.4 ppm, experiment E), thereby confirming the intermediacy of the noted signals in experiments C and D, as well as the catalytic role of the phosphine.

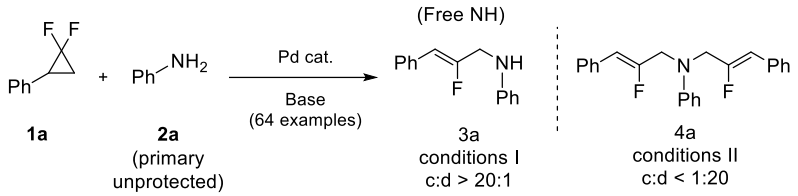
2.3.7 Conclusion

In summary, we have developed a triphenyl phosphine organo-catalyzed dearomative [3+2] cycloaddition of benzoxazoles with 1,2-diphenyl cyclopropenone. The cyclic and fused nature of the coupling product was confirmed by X-ray crystallography. Moreover, a mechanistic investigation was conducted with ^{31}P NMR, leading to important insights regarding the existence of phosphorus based catalytic intermediates. This contribution should encourage the further development of organo-catalyzed C─C bond activation coupling methods.

3 Summary and Outlook

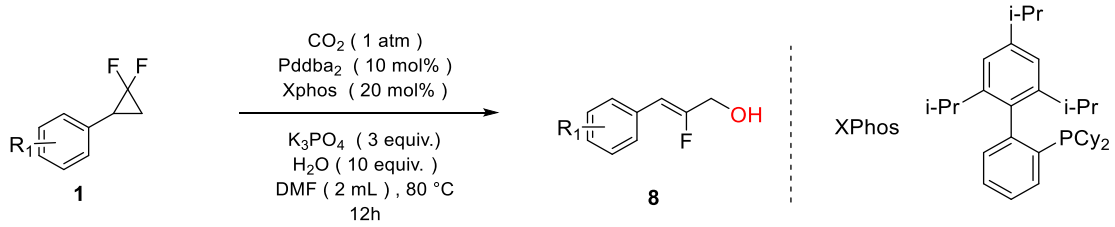
Small ring molecules are important structures in drug molecules and an important part of building molecular structures. Here we utilize the unique reactivity of three-membered rings to activate their C-X bonds and C-C bonds, to construct a series of new structural cyclic or chain compounds.

First, we reported the Pd-catalyzed highly selective synthesis of mono- and di- 2-fluoroallylic amines from simple anilines and *gem*-difluorocyclopropanes. Palladium catalysis allowed *gem*-difluorinated cyclopropanes to yield highly reactive allyl surrogates when reacted with anilines, providing mono or di 2-fluoroallylic amines derivatives in good yields with high chemoselective under mild conditions. Under certain conditions, the palladium catalyst could efficiently control the single and double chemoselectivity of the reaction products. This provided a high chemical selectivity way for allyl amination and fluorination in medicinal chemistry and organic synthesis (**Scheme 45**).



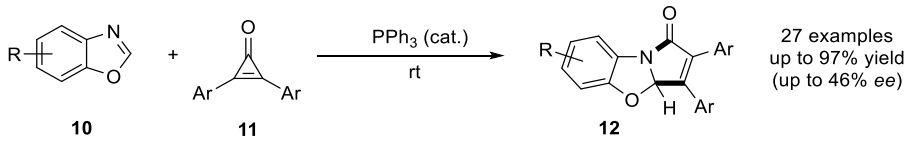
Scheme 45 Pd-catalyzed access to mono- and di-fluoroallylic amines from primary anilines with *gem*-difluorocyclopropane

Next, we reported the hydroxylation of *gem*-Difluorocyclopropanes under the co-catalysis conditions of palladium and CO_2, and a series of fluorine-containing cinnamyl alcohol products with different structures were obtained. This reaction occurred through metal palladium activates C-C, C-F bonds, CO_2 activates water molecules. An array of fluorinated cinnamyl alcohols were produced in good yields under mild reaction conditions, demonstrating high substrate applicability. Due to these favorable conditions and high yields, this provides an effective method for synthesizing fluorinated cinnamyl alcohols in the fields of medicinal chemistry and organic synthesis (**Scheme 46**).



Scheme 46 CO_2 and Palladium co-catalyzed Synthesis of Fluorinated Cinnamyl Alcohol

Finally, we reported the triphenyl phosphine organo-catalyzed dearomative [3+2] cycloaddition of benzoxazoles with 1,2-diphenyl cyclopropenone. While cyclopropenone was a highly versatile building block for coupling reactions due to its unique strain and functionality, it's activation without precious metal catalysis is rare. The reaction scope, mechanism and possible future applications of this organocatalyzed cycloaddition were herein discussed (**Scheme 47**).



Scheme 47 Phosphine-Catalyzed Dearomative [3+2] Cycloaddition of Benzoxazoles with a Cyclopropenone

Focus on activating C-C bonds or C-X bonds within three-membered ring compounds using diverse catalysts to establish new catalytic systems is highly useful. These systems enable the achievement of ring-opening and ring-expanding reactions in other small organic molecules. The unique features of three-membered ring reactions are instrumental in realizing the conversion of C-C bonds or C-X bonds and constructing cyclic (heteroatom-containing) organic compounds with specific structures. This approach plays a significant guiding role in the development of novel molecular precursors for potential therapeutic applications.

In the future, I hope to utilize a range of non-metal catalysts like PPh_3 and CO_2 to activate C-C bonds or C-X bonds, facilitating the construction of various cyclic molecules. This approach aligns with the principles of green chemistry and offers a solution to the dependency on non-renewable metal catalysts.

4 Experiment and Data

4.1 General Information

NMR spectroscopy

NMR spectra were obtained on an Agilent VNMRS 400 or a Bruker Av 600 using $CDCl_3$ as solvents. Chemical shifts are given in ppm and coupling constants (*J*) in Hz. ^1H spectra were calibrated in relation to the reference measurement of TMS (0.00 ppm). ^{13}C spectra were calibrated in relation to the deuterated solvent, namely $CDCl_3$ (77.16 ppm). The following abbreviations were used for ^1H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them.

Reagents

Flash chromatography was performed on silica gel (60 M, 0.04-0.063 mm) by standard technique. All the chemicals used for synthesis were purchased from Sigma Aldrich, abcr, Alfa Aesar, TCI, Fisher, or chemPUR.

IR spectra

IR spectra were meansured on a PerkinElmer 100 FT-IR spectrometer with an UATR Diamond KRS-5 unit

Mass apectra

High resolution mass spectra (HRMS) were obtained on a Thermo Scientific LTQ Orbitrap XL spectrometer.

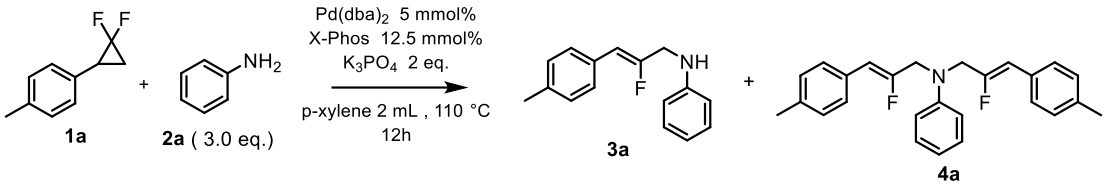
X-ray measurement

Crystallographic data were collected on a Bruker Kappa APEX II CCD-diffractometer with monochromatic Mo–Kα radiation (λ=0.71073 Å) and a CCD detector.

4.2 Experimental Data and Methods

4.2.1 Pd-catalyzed Access to Mono- and Di-fluoroallylic Amines from Primary Anilines

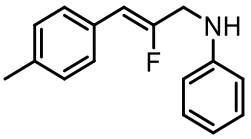
General procedure of mono-fluoroallylic amines



1a 2a (3.0 eq.) 3a 4a

Under N_2 atmosphere, X-Phos (11.9 mg, 0.025 mmol) and $Pd(dba)_2$ (5.7 mg, 0.01 mmol), *gem*-difluorocyclopropanes **1a** (0.2 mmol), aniline[3] **2a** (0.6 mmol), K_3PO_4 (2.0 eq., 84.8 mg) were dissolved in 2 mL p-xylene, then the mixture was stirred at 110 °C for about 12 h to the starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. A portion of the residue was analyzed with ^1H NMR to determine selectivity and recovered. The crude was purified by column chromatography to give the products **3**.

Preparation of the product



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)aniline

3a: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 43 mg product was obtained by 90% isolated yield as yellow solid.

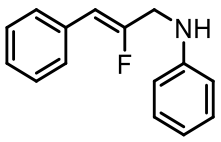
1H NMR (600 MHz, Chloroform-d) δ 7.43 (d, J = 7.9 Hz, 2H), 7.25 (t, J = 7.9 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 6.81 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 7.9 Hz, 2H), 5.77 (d, J = 39.6 Hz, 1H), 4.04 (d, J = 9.8 Hz, 3H), 2.38 (s, 3H).

19F NMR (565 MHz, Chloroform-d) δ -110.41 – -110.61 (m).

13C NMR (151 MHz, Chloroform-d) δ 156.6 (d, J = 266.5 Hz), 147.3, 137.1 (d, J = 2.4 Hz), 130.1 (d, J = 2.7 Hz), 129.3, 129.2, 128.5 (d, J = 6.9 Hz), 118.3, 113.2, 106.8 (d, J = 6.7 Hz), 45.6 (d, J = 33.4 Hz), 21.3.

IR (neat, cm-1): ṽ: 3416, 2918, 1694, 1599, 1501, 1433, 1312, 1249, 1153, 1103, 989, 862, 744.

ESI-HRMS: mass spectrometry: m/z calcd for C16H16NF [M+H]+ 242.13395, measured 242.13329.



(*Z*)-*N*-(2-fluoro-3-phenylallyl)aniline

3b: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 39 mg product was obtained by 86% isolated yield as yellow oil.

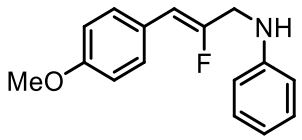
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 6.9 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.09 (m, 3H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 3H), 5.67 (d, *J* = 39.5 Hz, 1H), 3.91 (d, *J* = 10.3 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.45 – -109.60 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2 (d, *J* = 267.7 Hz), 147.2, 133.0 (d, *J* = 2.8 Hz), 129.4, 128.6 (d, *J* = 7.0 Hz), 128.5, 127.3 (d, *J* = 1.8 Hz), 118.3, 113.2, 106.8 (d, *J* = 6.6 Hz), 45.5 (d, *J* = 33.8 Hz).

IR (neat, cm^{-1}): ṽ: 3418, 2920, 1694, 1601, 1504, 1439, 1315, 1263, 1105, 870, 749.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{15}H_{14}NF$ $[M+H]^+$ 228.11830, measured 228.11794.



(*Z*)-*N*-(2-fluoro-3-(4-methoxyphenyl)allyl)aniline

3c: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 36 mg product was obtained by 70% isolated yield as brown solid.

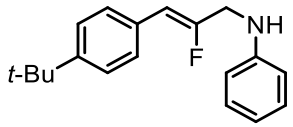
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.7 Hz, 2H), 7.15 – 7.07 (m, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 5.62 (d, *J* = 39.7 Hz, 1H), 3.94 (br, 1H), 3.91 (d, *J* = 10.6 Hz, 2H), 3.72 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -112.32 – -112.49 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.7 (d, *J* = 2.7 Hz), 155.8 (d, *J* = 265.1 Hz), 147.3, 129.8 (d, *J* = 7.2 Hz), 129.3, 125.7 (d, *J* = 2.8 Hz), 118.2, 113.9, 113.2, 106.4 (d, *J* = 6.8 Hz), 55.3, 45.6 (d, *J* = 33.4 Hz).

IR (neat, cm^{-1}): ṽ: 3416, 2929, 1692, 1601, 1504, 1434, 1305, 1248, 1154, 1105, 1033, 854, 742.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{16}H_{16}ONF$ $[M-H]^-$ 256.11322, measured 256.11249.



(*Z*)-*N*-(3-(4-(*tert*-butyl)phenyl)-2-fluoroallyl)aniline

3d: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 43 mg product was obtained by 76% isolated yield as yellow oil.

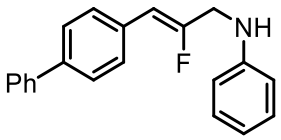
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 – 7.08 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.4 Hz, 2H), 5.65 (d, *J* = 39.7 Hz, 1H), 3.95 – 3.88 (m, 3H), 1.23 (s, 9H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.40 – -110.59 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.7 (d, *J* = 266.7 Hz), 150.3 (d, *J* = 2.1 Hz), 147.3, 130.2 (d, *J* = 2.4 Hz), 129.3, 128.3 (d, *J* = 7.1 Hz), 125.4, 118.3, 113.2, 106.7 (d, *J* = 6.7 Hz), 45.6 (d, *J* = 33.7 Hz), 34.6, 31.3.

IR (neat, cm^{-1}): ṽ: 3420, 2960, 1694, 1602, 1506, 1437, 1364, 1264, 1105, 986, 863, 747.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{19}H_{22}NF$ $[M+H]^+$ 284.18090, measured 284.18045.



(*Z*)-*N*-(3-([1,1'-biphenyl]-4-yl)-2-fluoroallyl)aniline

3e: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 52 mg product was obtained by 86% isolated yield as brown solid.

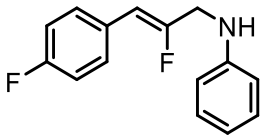
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 6H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 5.73 (d, *J* = 39.4 Hz, 1H), 3.95 (d, *J* = 9.7 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -108.96 – -109.13 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.4 (d, *J* = 268.1 Hz), 147.2, 140.7, 139.9 (d, *J* = 2.5 Hz), 132.1 (d, *J* = 2.4 Hz), 129.4, 129.0 (d, *J* = 7.2 Hz), 128.8, 127.3, 127.1, 127.0, 118.4, 113.2, 106.5 (d, *J* = 6.6 Hz), 45.6 (d, *J* = 33.7 Hz).

IR (neat, cm^{-1}): ṽ: 3399, 2920, 1596, 1503, 1311, 1157, 1067, 982, 908, 867, 751, 688.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{21}H_{18}NF$ $[M+Na]^+$ 326.13155, measured 326.13123.



(*Z*)-*N*-(2-fluoro-3-(4-fluorophenyl)allyl)aniline

3f: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 45 mg product was obtained by 92% isolated yield as yellow oil.

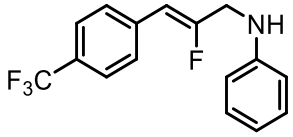
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 5.64 (d, *J* = 39.1 Hz, 1H), 3.94 (br, 1H), 3.91 (d, *J* = 9.7 Hz, 2H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.74 (dt, *J* = 39.1, 9.8 Hz), -114.13 – -114.32 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.8 (dd, *J* = 247.1, 3.2 Hz), 156.9 (dd, *J* = 267.5, 2.3 Hz), 147.1, 130.2 (t, *J* = 7.6 Hz), 129.4, 129.1 (t, *J* = 3.0 Hz), 118.4, 115.5, 115.3, 113.2, 105.7 (d, *J* = 6.7 Hz), 45.4 (d, *J* = 33.8 Hz).

IR (neat, cm^{-1}): ṽ: 3418, 2920, 1695, 1601, 1504, 1436, 1378, 1228, 1157, 1106, 985, 749.

APCI-HRMS: mass spectrometry: m/z calcd for $C_{15}H_{14}NF_2$ $[M+H]^+$ 246.10888, measured 246.10889.



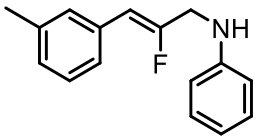
(*Z*)-*N*-(2-fluoro-3-(4-(trifluoromethyl)phenyl)allyl)aniline

3g: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 45 mg product was obtained by 76% isolated yield as brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (s, 4H), 7.15 – 7.11 (m, 2H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 2H), 5.73 (d, *J* = 38.7 Hz, 1H), 3.95 (d, *J* = 8.5 Hz, 3H).

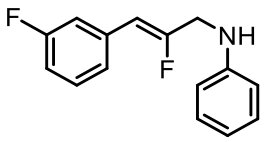
^{19}F NMR (564 MHz, Chloroform-*d*) δ -62.60, -106.26 – -106.42 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.1 (d, *J* = 271.2 Hz), 147.0, 136.5, 129.4, 129.1 (d, *J* = 2.5 Hz), 128.7 (d, *J* = 7.4 Hz), 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 271.8 Hz), 118.5, 113.1, 105.5 (d, *J* = 6.0 Hz), 45.3 (d, *J* = 34.1 Hz).
IR (neat, cm^{-1}): ṽ: 3418, 2922, 1694, 1603, 1506, 1415, 1322, 1263, 1163, 1066, 1017, 865, 750.
EI-HRMS: mass spectrometry: m/z calcd for $C_{16}H_{13}NF_4$ $[M]^+$ 295.09786, measured 295.09788.



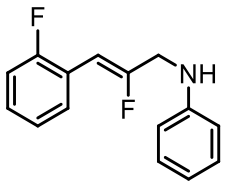
(*Z*)-*N*-(2-fluoro-3-(*m*-tolyl)allyl)aniline

3h: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 40 mg product was obtained by 83% isolated yield as brown oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (s, 2H), 7.15 – 7.09 (m, 3H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 2H), 5.64 (d, *J* = 39.6 Hz, 1H), 3.94 (br, 1H), 3.91 (d, *J* = 9.9 Hz, 2H), 2.25 (s, 3H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.54 – -109.70 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.0 (d, *J* = 267.4 Hz), 147.2, 138.0, 132.9 (d, *J* = 2.8 Hz), 129.3, 129.3 (d, *J* = 6.7 Hz), 128.4, 128.0 (d, *J* = 2.3 Hz), 125.7 (d, *J* = 7.3 Hz), 118.3, 113.2, 106.9 (d, *J* = 6.3 Hz), 45.5 (d, *J* = 33.6 Hz), 21.4.
IR (neat, cm^{-1}): ṽ: 3446, 2922, 1693, 1603, 1504, 1436, 1277, 1243, 1102, 984, 847, 740, 688.
APCI-HRMS: mass spectrometry: m/z calcd for $C_{16}H_{16}NF$ $[M+H]^+$ 242.13395, measured 242.13414.



(*Z*)-*N*-(2-fluoro-3-(3-fluorophenyl)allyl)aniline

3i: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 46 mg product was obtained by 94% isolated yield as yellow oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.20 – 7.08 (m, 6H), 6.87 – 6.81 (m, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.4 Hz, 2H), 5.67 (d, *J* = 38.6 Hz, 1H), 3.93 (d, *J* = 9.3 Hz, 3H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -107.35 – -107.60 (m), -113.18 – -113.41 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.8 (d, *J* = 244.6 Hz), 158.2 (d, *J* = 269.7 Hz), 147.0, 135.0 (dd, *J* = 8.5, 2.4 Hz), 129.8 (d, *J* = 8.4 Hz), 129.4, 124.3 (dd, *J* = 6.4, 2.8 Hz), 118.4, 115.2 (dd, *J* = 22.7, 8.6 Hz), 114.0 (d, *J* = 2.2 Hz), 113.1, 105.8 (dd, *J* = 6.2, 2.7 Hz), 45.4 (d, *J* = 33.9 Hz).
IR (neat, cm^{-1}): ṽ: 3418, 2921, 2326, 1692, 1602, 1505, 1438, 1310, 1246, 1152, 963, 875, 750.
APCI-HRMS: mass spectrometry: m/z calcd for $C_{15}H_{13}NF_2$ $[M+H]^+$ 246.10888, measured 246.10929.



(*Z*)-*N*-(2-fluoro-3-(2-fluorophenyl)allyl)aniline

3j: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 30 mg product was obtained by 61% isolated yield as yellow oil.

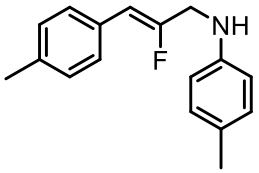
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.65 (m, 1H), 7.16 – 7.09 (m, 3H), 7.05 – 7.00 (m, 1H), 6.97 – 6.91 (m, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 2H), 5.96 (d, *J* = 39.1 Hz, 1H), 3.96 (d, *J* = 10.4 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -107.73 – -108.21 (m), -116.75 – -117.02 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.4 (d, *J* = 249.3 Hz), 158.5 (dd, *J* = 269.6, 2.2 Hz), 147.1, 130.1 (dd, *J* = 12.2, 2.9 Hz), 129.4, 128.7 (d, *J* = 8.5 Hz), 124.1 (d, *J* = 3.6 Hz), 120.8 (dd, *J* = 12.1, 2.6 Hz), 118.4, 115.2 (d, *J* = 22.2 Hz), 113.2, 98.6 (t, *J* = 6.6 Hz), 45.6 (d, *J* = 32.8 Hz).

IR (neat, cm^{-1}): ṽ: 3418, 2921, 1695, 1602, 1503, 1452, 1313, 1253, 1152, 1112, 985, 824, 750.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{15}H_{13}NF_2$ $[M+H]^+$ 246.10888, measured 246.10830.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-4-methylaniline

3k: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 50 mg product was obtained by 98% isolated yield as brown oil.

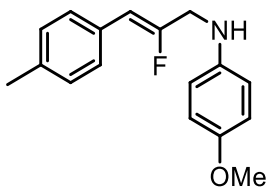
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 8.4 Hz, 2H), 5.62 (d, *J* = 39.7 Hz, 1H), 3.87 (d, *J* = 10.3 Hz, 2H), 3.84 – 3.69 (br, 1H), 2.24 (s, 3H), 2.16 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.32 – -110.47 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.8 (d, *J* = 266.8 Hz), 145.0, 137.0 (d, *J* = 2.3 Hz), 130.2 (d, *J* = 2.4 Hz), 129.8, 129.2, 128.5 (d, *J* = 7.2 Hz), 127.5, 113.4, 106.7 (d, *J* = 6.7 Hz), 45.9 (d, *J* = 33.3 Hz), 21.3, 20.4.

IR (neat, cm^{-1}): ṽ: 3400, 2913, 1691, 1613, 1515, 1449, 1340, 1245, 1156, 1091, 987, 878, 808.

APCI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{18}NF$ $[M+H]^+$ 256.14960, measured 256.14968.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-4-methoxyaniline

3l: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 49 mg product was obtained by 91% isolated yield as black solid.

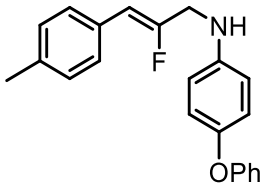
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.74 – 6.68 (m, 2H), 6.60 – 6.53 (m, 2H), 5.62 (d, *J* = 39.8 Hz, 1H), 3.85 (d, *J* = 10.8 Hz, 2H), 3.71 (br, 1H), 3.66 (s, 3H), 2.24 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.32 – -110.50 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9 (d, *J* = 266.4 Hz), 152.7, 141.4, 137.0 (d, *J* = 2.6 Hz), 130.2 (d, *J* = 2.4 Hz), 129.2, 128.5 (d, *J* = 7.0 Hz), 114.9, 114.7, 106.8 (d, *J* = 6.8 Hz), 55.8, 46.6 (d, *J* = 33.0 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3398, 2919, 1691, 1613, 1507, 1462, 1343, 1233, 1154, 1035, 873, 816, 761.

EI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{18}ONF$ $[M]^+$ 271.13669, measured 271.13661.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-4-phenoxyaniline

3m: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 58 mg product was obtained by 87% isolated yield as yellow oil.

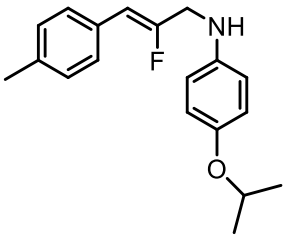
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.08 – 7.03 (m, 1H), 6.97 (t, *J* = 8.8 Hz, 4H), 6.72 (d, *J* = 8.6 Hz, 2H), 5.77 (d, *J* = 39.6 Hz, 1H), 4.02 (d, *J* = 11.0 Hz, 2H), 4.00 (br, 1H), 2.38 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.43 – -110.64 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.9, 156.5 (d, *J* = 266.5 Hz), 148.4, 143.8, 137.1 (d, *J* = 2.3 Hz), 130.1 (d, *J* = 2.4 Hz), 129.5, 129.2, 128.5 (d, *J* = 7.0 Hz), 122.1, 121.2, 117.3, 114.3, 107.0 (d, *J* = 6.8 Hz), 46.1 (d, *J* = 33.1 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3424, 2915, 1691, 1589, 1508, 1407, 1333, 1229, 1151, 1074, 989, 869, 747.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{22}H_{20}ONF$ $[M+K]^+$ 372.11605, measured 372.11599.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-4-isopropoxyaniline

3n: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 58 mg product was obtained by 97% isolated yield as brown oil.

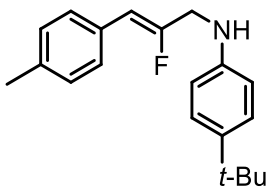
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 5.63 (d, *J* = 39.7 Hz, 1H), 4.33 – 4.23 (m, 1H), 3.85 (d, *J* = 10.6 Hz, 2H), 3.69 (br, 1H), 2.24 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.22 – -110.42 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9 (d, *J* = 266.6 Hz), 150.7, 141.6, 137.0 (d, *J* = 2.3 Hz), 130.2 (d, *J* = 2.5 Hz), 129.2, 128.5 (d, *J* = 7.0 Hz), 117.9, 114.5, 106.8 (d, *J* = 6.8 Hz), 71.1, 46.5 (d, *J* = 33.0 Hz), 22.2, 21.2.

IR (neat, cm^{-1}): ṽ: 3418, 2978, 1693, 1507, 1454, 1374, 1337, 1227, 1116, 946, 860, 814.

EI-HRMS: mass spectrometry: m/z calcd for $C_{19}H_{22}ONF$ $[M]^+$ 299.16799, measured 299.16793.



(*Z*)-4-(*tert*-butyl)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)aniline

3o: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 58 mg product was obtained by 98% isolated yield as yellow oil.

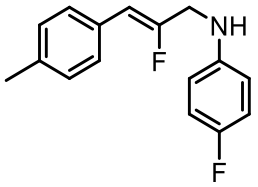
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 5.65 (d, *J* = 39.7 Hz, 1H), 3.88 (d, *J* = 10.3 Hz, 2H), 3.83 (br, 1H), 2.24 (s, 3H), 1.20 (s, 9H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.20 – -110.42 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9 (d, *J* = 266.4 Hz), 144.9, 141.0, 137.0 (d, *J* = 2.3 Hz), 130.2 (d, *J* = 2.5 Hz), 129.2, 128.5 (d, *J* = 6.9 Hz), 126.1, 112.9, 106.6 (d, *J* = 6.7 Hz), 45.8 (d, *J* = 33.4 Hz), 33.9, 31. 6, 21.3.

IR (neat, cm^{-1}): ṽ: 3383, 2956, 1695, 1614, 1516, 1455, 1360, 1300, 1191, 1158, 1079, 992, 816.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{20}H_{24}NF$ $[M+Na]^+$ 320.17850, measured 320.17773.



(*Z*)-4-fluoro-*N*-(2-fluoro-3-(*p*-tolyl)allyl)aniline

3p: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 43 mg product was obtained by 83% isolated yield as brown solid.

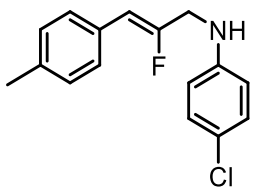
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.85 – 6.79 (m, 2H), 6.56 – 6.50 (m, 2H), 5.62 (d, *J* = 39.6 Hz, 1H), 3.86 (d, *J* = 10.7 Hz, 3H), 2.25 (s, 3H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -110.72 (dt, *J* = 39.7, 10.7 Hz), -127.01 – -127.12 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2 (d, *J* = 30.5 Hz), 155.5, 143.5 (d, *J* = 1.9 Hz), 137.2 (d, *J* = 2.3 Hz), 130.0 (d, *J* = 2.5 Hz), 129.2, 128.5 (d, *J* = 7.2 Hz), 115.8 (d, *J* = 22.3 Hz), 114.2 (d, *J* = 7.4 Hz), 107.0 (d, *J* = 6.7 Hz), 46.2 (d, *J* = 32.9 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3391, 2920, 1691, 1610, 1510, 1343, 1221, 1155, 1111, 989, 874, 785.

EI-HRMS: mass spectrometry: m/z calcd for $C_{16}H_{15}NF_2$ $[M]^+$ 259.11671, measured 59.11663.



(*Z*)-4-chloro-*N*-(2-fluoro-3-(*p*-tolyl)allyl)aniline

3q: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 27 mg product was obtained by 49% isolated yield as brown solid.

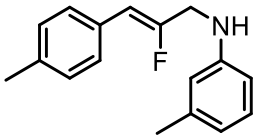
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.9 Hz, 2H), 7.11 – 7.02 (m, 4H), 6.52 (d, *J* = 8.8 Hz, 2H), 5.61 (d, *J* = 39.5 Hz, 1H), 3.98 (br, 1H), 3.88 (d, *J* = 10.5 Hz, 2H), 2.25 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.77 – -110.91 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.0 (d, *J* = 266.5 Hz), 145.8, 137.2 (d, *J* = 2.3 Hz), 129.9 (d, *J* = 2.5 Hz), 129.2 (d, *J* = 5.9 Hz), 128.5 (d, *J* = 7.0 Hz), 122.9, 114.3, 107.1 (d, *J* = 6.8 Hz), 45.6 (d, *J* = 33.4 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3390, 2917, 1691, 1599, 1495, 1340, 1239, 1156, 1083, 993, 874, 814, 711.

EI-HRMS: mass spectrometry: m/z calcd for $C_{16}H_{15}NClF$ $[M]^+$ 275.08716, measured 275.08730.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-3-methylaniline

3r: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 48 mg product was obtained by 94% isolated yield as brown solid.

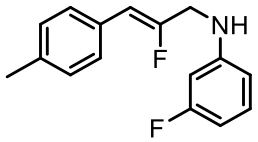
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.02 – 6.97 (m, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 6.5 Hz, 2H), 5.63 (d, *J* = 39.8 Hz, 1H), 3.88 (d, *J* = 10.1 Hz, 2H), 3.86 (br, 1H), 2.24 (s, 3H), 2.20 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.32 – -110.47 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.8(d, *J* = 266.8 Hz), 147.3, 139.2, 137.0 (d, *J* = 2.3 Hz), 130.2 (d, *J* = 2.5 Hz), 129.22, 129.18, 128.5 (d, *J* = 7.0 Hz), 119.2, 114.0, 110.3, 106.7 (d, *J* = 6.7 Hz), 45.6 (d, *J* = 33.5 Hz), 21.7, 21.3.

IR (neat, cm^{-1}): ṽ: 3415, 2919, 1694, 1603, 1510, 1443, 1325, 1269, 1178, 1104, 988, 857, 769.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{18}NF$ $[M+Na]^+$ 278.13155, measured 278.13071.



(*Z*)-3-fluoro-*N*-(2-fluoro-3-(*p*-tolyl)allyl)aniline

3s: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 48 mg product was obtained by 93% isolated yield as yellow oil.

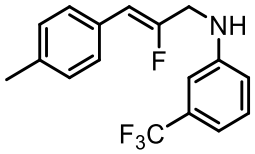
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.99 (m, 3H), 6.37 – 6.32 (m, 2H), 6.28 (d, *J* = 11.4 Hz, 1H), 5.62 (d, *J* = 39.5 Hz, 1H), 4.04 (br, 1H), 3.88 (dd, *J* = 10.7, 5.3 Hz, 2H), 2.25 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.75 – -110.95 (m), -112.51 – -112.66 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.1 (d, *J* = 243.3 Hz), 155.9 (d, *J* = 266.5 Hz), 149.0 (d, *J* = 10.5 Hz), 137.2 (d, *J* = 2.4 Hz), 130.4 (d, *J* = 10.2 Hz), 129.9 (d, *J* = 2.7 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 109.0 (d, *J* = 2.4 Hz), 107.1 (d, *J* = 6.8 Hz), 104.7 (d, *J* = 21.7 Hz), 100.0 (d, *J* = 25.5 Hz), 45.4 (d, *J* = 33.4 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3429, 2926, 1694, 1592, 1506, 1438, 1336, 1285, 1144, 1102, 967, 863, 757.

EI-HRMS: mass spectrometry: m/z calcd for $C_{16}H_{15}NF_2$ $[M]^+$ 259.11671, measured 259.11645.



(Z)-N-(2-fluoro-3-(p-tolyl)allyl)-3-(trifluoromethyl)aniline

3t: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 55 mg product was obtained by 90% isolated yield as yellow oil.

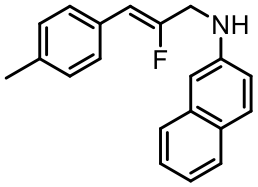
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.79 (s, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 5.66 (s, 1H), 4.11 (br, 1H), 3.92 (dd, *J* = 11.1, 6.0 Hz, 2H), 2.24 (s, 3H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -62.87, -110.98 – -111.14 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.7 (d, *J* = 266.4 Hz), 147.4, 137.3 (d, *J* = 2.5 Hz), 131.7 (q, *J* = 31.8 Hz), 129.8 (d, *J* = 2.8 Hz), 129.8, 129.2, 128.5 (d, *J* = 6.9 Hz), 124.3 (q, *J* = 272.4 Hz), 116.0, 114.7 (q, *J* = 3.8 Hz), 109.5 (q, *J* = 4.1 Hz), 107.4 (d, *J* = 6.7 Hz), 45.3 (d, *J* = 33.2 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3425, 2924, 1694, 1614, 1513, 1444, 1335, 1256, 1160, 1068, 993, 861, 696.

EI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{15}NF_4$ $[M]^+$ 309.11351, measured 309.11331.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)naphthalen-2-amine

3u: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 47 mg product was obtained by 81% isolated yield as black solid.

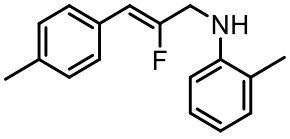
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 – 7.51 (m, 3H), 7.32 – 7.24 (m, 3H), 7.14 (d, *J* = 6.6 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.87 – 6.78 (m, 2H), 5.67 (d, *J* = 39.6 Hz, 1H), 4.07 (br, 1H), 3.99 (d, *J* = 10.3 Hz, 2H), 2.23 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.35 – -110.50 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.3 (d, *J* = 266.5 Hz), 144.9, 137.1 (d, *J* = 2.3 Hz), 135.0, 130.1 (d, *J* = 2.6 Hz), 129.2, 129.1, 128.5 (d, *J* = 7.1 Hz), 127.9, 127.7, 126.5, 126.1, 122.4, 117.7, 107.0 (d, *J* = 6.7 Hz), 105.4, 45.6 (d, *J* = 33.4 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3400, 2916, 1685, 1625, 1503, 1428, 1306, 1220, 1148, 953, 806, 705.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{20}H_{18}NF$ $[M+H]^+$ 292.14960, measured 292.14928.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-2-methylaniline

3v: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 48 mg product was obtained by 94% isolated yield as yellow oil.

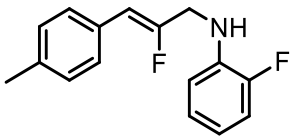
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 3H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.78 – 6.71 (m, 2H), 5.78 (d, *J* = 39.6 Hz, 1H), 4.09 (d, *J* = 10.4 Hz, 2H), 3.94 (br, 1H), 2.38 (s, 3H), 2.25 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.42 – -110.55 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6 (d, *J* = 266.3 Hz), 145.2, 137.1 (d, *J* = 2.4 Hz), 130.3, 130.1 (d, *J* = 2.5 Hz), 129.2, 128.5 (d, *J* = 6.9 Hz), 127.2, 122.3, 117.9, 110.3, 106.8 (d, *J* = 6.7 Hz), 45.6 (d, *J* = 33.3 Hz), 21.3, 17.5.

IR (neat, cm^{-1}): ṽ: 3440, 2919, 1694, 1604, 1510, 1448, 1312, 1262, 1125, 1051, 983, 860, 746.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{18}NF$ $[M+H]^+$ 256.14960, measured 256.14956.



(*Z*)-2-fluoro-*N*-(2-fluoro-3-(*p*-tolyl)allyl)aniline

3w: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 42 mg product was obtained by 81% isolated yield as yellow oil.

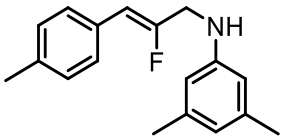
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.95 – 6.88 (m, 2H), 6.69 (t, *J* = 8.3 Hz, 1H), 6.62 – 6.56 (m, 1H), 5.64 (d, *J* = 39.5 Hz, 1H), 4.22 (br, 1H), 3.94 (d, *J* = 10.2 Hz, 2H), 2.25 (s, 3H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -110.65 – -110.88 (m), -136.19 – -136.35 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.1 (d, *J* = 266.4 Hz), 151.7 (d, *J* = 238.6 Hz), 137.2 (d, *J* = 2.4 Hz), 135.7 (d, *J* = 11.5 Hz), 130.0 (d, *J* = 2.8 Hz), 129.2, 128.5 (d, *J* = 7.2 Hz), 124.6 (d, *J* = 3.6 Hz), 117.6 (d, *J* = 7.1 Hz), 114.6 (d, *J* = 18.6 Hz), 112.6 (d, *J* = 3.0 Hz), 106.9 (d, *J* = 6.7 Hz), 45.1 (d, *J* = 34.0 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3434, 2921, 1694, 1620, 1515, 1450, 1336, 1256, 1189, 1112, 1036, 860, 740.

EI-HRMS: mass spectrometry: m/z calcd for $C_{16}H_{15}NF_2$ $[M]^+$ 259.11671, measured 259.11664.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-3,5-dimethylaniline

3x: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 50 mg product was obtained by 93% isolated yield as yellow oil.

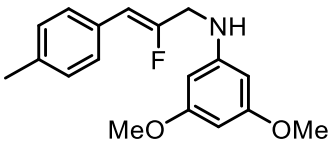
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.34 (s, 1H), 6.24 (s, 2H), 5.64 (d, *J* = 39.8 Hz, 1H), 3.88 (d, *J* = 9.9 Hz, 2H), 3.81 (br, 1H), 2.25 (s, 3H), 2.16 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.23 – -110.38 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.9 (d, *J* = 266.8 Hz), 147.4, 139.0, 137.0 (d, *J* = 2.3 Hz), 130.2 (d, *J* = 2.7 Hz), 129.2, 128.5 (d, *J* = 6.9 Hz), 120.3, 111.1, 106.5 (d, *J* = 6.9 Hz), 45.6 (d, *J* = 33.8 Hz), 21.5, 21.2.

IR (neat, cm^{-1}): ṽ: 3412, 2918, 1694, 1601, 1512, 1474, 1334, 1189, 1034, 858, 820, 689.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{18}H_{20}NF$ $[M+K]^+$ 308.12114, measured 308.12103.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-3,5-dimethoxyaniline

3y: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 45 mg product was obtained by 75% isolated yield as yellow oil.

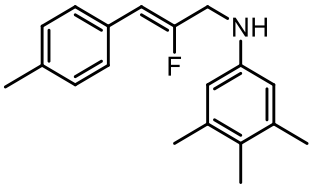
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 5.96 (s, 1H), 5.91 (s, 2H), 5.75 (d, *J* = 39.5 Hz, 1H), 4.08 (br, 1H), 3.99 (d, *J* = 10.6 Hz, 2H), 3.78 (s, 6H), 2.37 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.44 – -110.62 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.8, 156.4 (d, *J* = 266.5 Hz), 149.2, 137.1 (d, *J* = 2.4 Hz), 130.1 (d, *J* = 2.6 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 106.9 (d, *J* = 6.8 Hz), 92.1, 90.5, 55.2, 45.5 (d, *J* = 33.3 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3410, 2933, 1693, 1598, 1514, 1456, 1338, 1201, 1149, 1065, 861, 808, 681.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{18}H_{20}O_2NF$ $[M+Na]^+$ 324.13703, measured 324.13641.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-3,4,5-trimethylaniline

3z: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 56 mg product was obtained by 99% isolated yield as yellow oil.

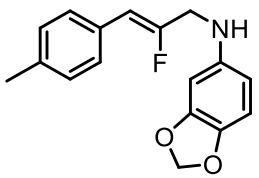
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.30 (s, 2H), 5.63 (d, *J* = 39.8 Hz, 1H), 3.85 (d, *J* = 9.8 Hz, 2H), 3.67 (br, 1H), 2.24 (s, 3H), 2.13 (s, 6H), 1.98 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.10 – -110.24 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2 (d, *J* = 266.5 Hz), 144.8, 137.4, 136.9 (d, *J* = 2.3 Hz), 130.3 (d, *J* = 2.4 Hz), 129.2, 128.5 (d, *J* = 7.0 Hz), 124.9, 112.8, 106.4 (d, *J* = 6.6 Hz), 45.9 (d, *J* = 33.7 Hz), 21.3, 20.9, 14.5.

IR (neat, cm^{-1}): ṽ: 3408, 2918, 1907, 1694, 1609, 1500, 1443, 1328, 1216, 1136, 991, 837, 702.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{19}H_{22}NF$ $[M+H]^+$ 284.18090, measured 284.18088.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)benzo[*d*][1,3]dioxol-5-amine

3aa: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 47 mg product was obtained by 82% isolated yield as brown oil.

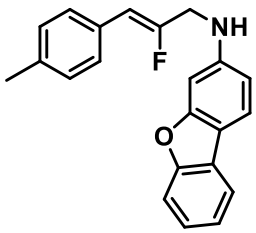
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 8.3 Hz, 1H), 6.24 (d, *J* = 2.3 Hz, 1H), 6.05 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.79 (s, 2H), 5.63 (d, *J* = 39.6 Hz, 1H), 3.85 (d, *J* = 10.9 Hz, 2H), 3.75 (br, 1H), 2.26 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.49 – -110.67 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.5 (d, *J* = 266.5 Hz), 148.4, 142.8, 140.3, 137.1, 130.1 (d, *J* = 1.5 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 108.6, 107.0 (d, *J* = 6.8 Hz), 105.1, 100.7, 96.5, 46.6 (d, *J* = 33.1 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3417, 2884, 1693, 1624, 1493, 1292, 1202, 1106, 1037, 934, 809, 730.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{16}NF$ $[M+H]^+$ 286.12378, measured 286.12306.



(*Z*)-*N*-(2-fluoro-3-(*p*-tolyl)allyl)dibenzo[*b*,*d*]furan-3-amine

3bb: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 40:1). 63 mg product was obtained by 95% isolated yield as yellow solid.

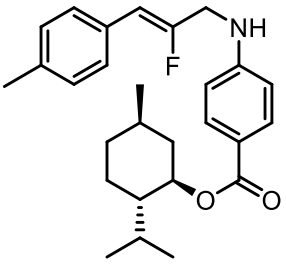
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.19 – 7.14 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 2.0 Hz, 1H), 6.59 (dd, *J* = 8.4, 2.1 Hz, 1H), 5.66 (d, *J* = 39.5 Hz, 1H), 4.19 (br, 1H), 3.96 (d, *J* = 10.7 Hz, 2H), 2.23 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.60 – -110.74 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.2, 156.1 (d, *J* = 266.5 Hz), 155.9, 147.7, 137.2 (d, *J* = 2.4 Hz), 130.0 (d, *J* = 2.6 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 125.1, 124.9, 122.6, 121.2, 119.3, 115.3, 111.2, 110.2, 107.2 (d, *J* = 6.7 Hz), 45.8 (d, *J* = 33.2 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3417, 2917, 1693, 1636, 1499, 1424, 1339, 1257, 1159, 1011, 872, 747.

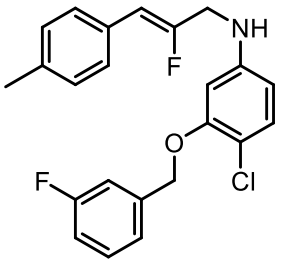
EI-HRMS: mass spectrometry: m/z calcd for $C_{22}H_{18}ONF$ $[M]^+$ 331.13669, measured 331.13666.



(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)amino)benzoate

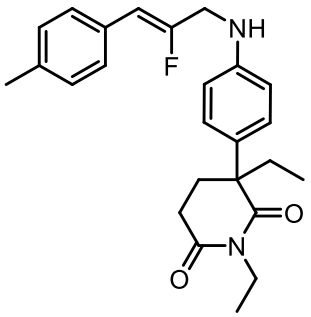
3cc The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 55 mg product was obtained by 65% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 5.60 (d, *J* = 39.4 Hz, 1H), 4.82 – 4.74 (m, 1H), 4.43 (br, 1H), 3.93 (d, *J* = 10.1 Hz, 2H), 2.23 (s, 3H), 2.05 – 1.98 (m, 1H), 1.92 – 1.83 (m, 1H), 1.66 – 1.58 (m, 2H), 1.50 – 1.38 (m, 2H), 1.09 – 0.93 (m, 2H), 0.87 – 0.77 (m, 7H), 0.70 (d, *J* = 7.0 Hz, 3H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.81 – -110.96 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 155.6 (d, *J* = 266.8 Hz), 150.9, 137.3 (d, *J* = 2.3 Hz), 131.5, 129.9(d, *J* = 2.5 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 120.1, 111.9, 107.2 (d, *J* = 6.7 Hz), 74.1, 47.4, 44.9 (d, *J* = 33.9 Hz), 41.2, 34.4, 31.5, 26.5, 23.8, 22.1, 21.3, 20.8, 16.6.
IR (neat, cm^{-1}): ṽ: 3363, 2952, 1672, 1599, 1527, 1338, 1267, 1172, 1112, 965, 903, 838, 727.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{34}O_2NF$ $[M+Na]^+$ 446.24658, measured 446.24504.



(*Z*)-4-chloro-*N*-(2-fluoro-3-(*p*-tolyl)allyl)-3-((3-fluorobenzyl)oxy)aniline

3dd: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 21 mg product was obtained by 26% isolated yield as brown oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.21 (m, 1H), 7.13 – 7.08 (m, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.94 – 6.88 (m, 1H), 6.73 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 2.9 Hz, 1H), 6.41 (dd, *J* = 8.9, 2.8 Hz, 1H), 5.61 (d, *J* = 39.5 Hz, 1H), 4.94 (s, 2H), 3.84 (d, *J* = 10.9 Hz, 2H), 3.78 (br, 1H), 2.25 (s, 3H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.75 (dt, *J* = 39.3, 10.9 Hz), -112.87 – -112.99 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.0 (d, *J* = 245.9 Hz), 156.1 (d, *J* = 266.7 Hz), 146.7, 142.7, 139.7 (d, *J* = 7.3 Hz), 137.2 (d, *J* = 2.3 Hz), 130.0 (d, *J* = 8.4 Hz), 130.0 (d, *J* = 2.5 Hz), 129.2, 128.5 (d, *J* = 7.0 Hz), 124.8, 122.7 (d, *J* = 2.9 Hz), 117.0, 115.3, 114.7 (d, *J* = 21.2 Hz), 114.2 (d, *J* = 22.2 Hz), 112.3, 107.1 (d, *J* = 6.8 Hz), 71.5 (d, *J* = 1.9 Hz), 46.0 (d, *J* = 33.1 Hz), 21.2.
IR (neat, cm^{-1}): ṽ: 3419, 2922, 2329, 1693, 1592, 1503, 1225, 1140, 1056, 907, 860, 783.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{23}H_{20}ONClF_2$ $[M+Na]^+$ 422.10937, measured 422.10796.



(*Z*)-1,3-diethyl-3-(4-((2-fluoro-3-(*p*-tolyl)allyl)amino)phenyl)piperidine-2,6-dione

4ee: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from

5:1). 81 mg product was obtained by 99% isolated yield as brown oil.[4]

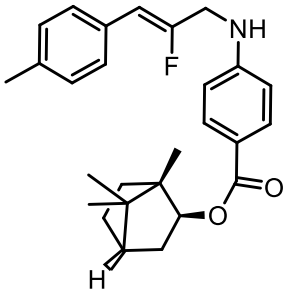
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 5.62 (d, *J* = 39.5 Hz, 1H), 4.03 (br, 1H), 3.88 (d, *J* = 10.4 Hz, 2H), 3.85 – 3.72 (m, 2H), 2.55 – 2.47 (m, 1H), 2.44 – 2.35 (m, 1H), 2.24 (s, 3H), 2.17 – 2.11 (m, 1H), 2.06 – 1.98 (m, 1H), 1.96 – 1.88 (m, 1H), 1.80 – 1.72 (m, 1H), 1.05 (t, *J* = 7.0 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.46 – -110.66 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.4, 172.2, 156.3 (d, *J* = 266.5 Hz), 146.4, 137.1 (d, *J* = 2.3 Hz), 130.0 (d, *J* = 2.4 Hz), 129.2, 128.7, 128.5 (d, *J* = 6.9 Hz), 127.1, 113.3, 106.9 (d, *J* = 6.6 Hz), 50.5, 45.4 (d, *J* = 33.3 Hz), 35.2, 33.8, 30.0, 25.9, 21.3, 13.3, 9.1.

IR (neat, cm^{-1}): ṽ: 3396, 2972, 1910, 1666, 1529, 1455, 1355, 1214, 1122, 1045, 908, 861, 730.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{25}H_{29}O_2N_2F$ $[M+Na]^+$ 431.21053, measured 431.20950.



(1*S*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)amino)benzoate

3ff: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 10:1). 70 mg product was obtained by 83% isolated yield as yellow solid.

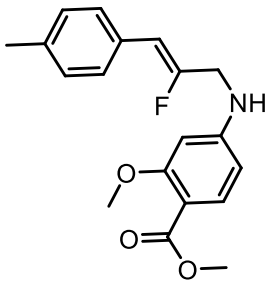
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 2H), 5.61 (d, *J* = 39.4 Hz, 1H), 4.99 (d, *J* = 9.9 Hz, 1H), 4.42 (br, 1H), 3.95 (dd, *J* = 10.4, 5.8 Hz, 2H), 2.41 – 2.32 (m, 1H), 2.24 (s, 3H), 2.08 – 2.00 (m, 1H), 1.75 – 1.66 (m, 1H), 1.63 (t, *J* = 4.6 Hz, 1H), 1.36 – 1.25 (m, 1H), 1.24 – 1.18 (m, 1H), 1.01 (dd, *J* = 13.8, 3.4 Hz, 1H), 0.87 (s, 3H), 0.81 (d, *J* = 5.4 Hz, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.88 – -111.04 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.9, 155.6 (d, *J* = 266.8 Hz), 150.9, 137.3 (d, *J* = 2.1 Hz), 131.5, 129.8 (d, *J* = 2.5 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 120.2, 112.0, 107.3 (d, *J* = 6.6 Hz), 79.7, 49.1, 47.8, 45.1, 44.9 (d, *J* = 33.7 Hz), 37.0, 28.1, 27.5, 21.3, 19.8, 19.0, 13.6.

IR (neat, cm^{-1}): ṽ: 3360, 2953, 1907, 1671, 1530, 1450, 1341, 1285, 1230, 1170, 1114, 984, 770.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{32}O_2NF$ $[M+Na]^+$ 444.23093, measured 444.22995.



methyl (*Z*)-4-((2-fluoro-3-(*p*-tolyl)allyl)amino)-2-methoxybenzoate

3gg: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 10:1). 58 mg product was obtained by 88% isolated yield as yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 3.0 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.74 (dd, *J* = 8.9, 3.0 Hz, 1H), 5.63 (d, *J* = 39.6 Hz, 1H), 3.89 (d, *J* = 11.1 Hz, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 2.25 (s, 3H).

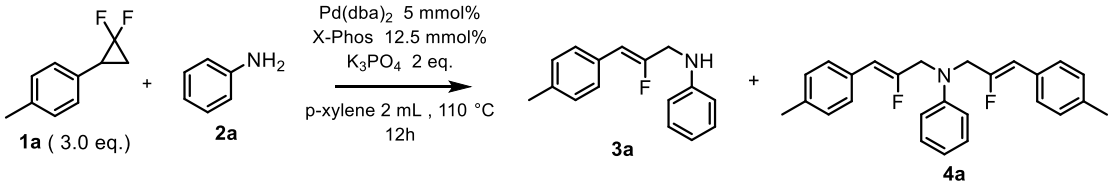
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.64 – -110.80 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 156.4 (d, *J* = 266.5 Hz), 152.2, 140.8, 137.1 (d, *J* = 2.3 Hz), 130.0 (d, *J* = 2.6 Hz), 129.2, 128.5 (d, *J* = 7.2 Hz), 120.8, 118.4, 116.4, 114.3, 107.1 (d, *J* = 6.9 Hz), 56.9, 52.1, 46.2 (d, *J* = 32.8 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3373, 2925, 1799, 1687, 1617, 1500, 1436, 1298, 1225, 1180, 1088, 1021, 877, 733.

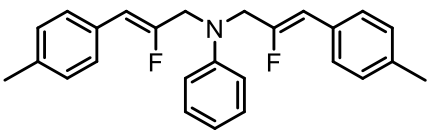
ESI-HRMS: mass spectrometry: m/z calcd for $C_{19}H_{20}O_3NF$ $[M+Na]^+$ 352.13194, measured 352.13203.

General procedure of di-fluoroallylic amines



Under N_2 atmosphere, X-Phos (11.9 mg, 0.025 mmol) and $Pd(dba)_2$ (5.7 mg, 0.01 mmol), *gem*-difluorocyclopropanes **1a** (0.6 mmol), aniline **2a** (0.2 mmol) , K_3PO_4 (2.0 eq., 84.8 mg) were dissolved in 2 mL p-xylene, then the mixture was stirred at 110 °C for about 12 h to the starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. A portion of the residue was analyzed with ^{1}H NMR to determine selectivity and recovered. The crude was purified by column chromatography to give the products **4**.

Preparation of the product



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)aniline**

4a: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 70 mg product was obtained by 90% isolated yield as yellow oil.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.28 (d, J = 8.0 Hz, 4H), 7.20 – 7.14 (m, 2H), 7.03 (d, J = 7.9 Hz, 4H), 6.81 (d, J = 8.2 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 5.55 (d, J = 39.7 Hz, 1H), 4.12 (d, J = 7.8 Hz, 2H),

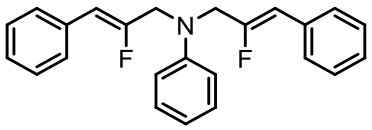
2.24 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-d) δ -110.38 – -110.62 (m).

^{13}C NMR (151 MHz, Chloroform-d) δ 155.4 (d, J = 269.2 Hz), 148.0, 137.2 (d, J = 2.2 Hz), 130.0 (d, J = 2.3 Hz), 129.4, 129.2, 128.6 (d, J = 7.1 Hz), 118.2, 113.2, 107.1 (d, J = 6.2 Hz), 51.5 (d, J = 34.2 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3409, 2920, 1909, 1691, 1589, 1504, 1378, 1218, 1129, 951, 906, 733.

ESI-HRMS: mass spectrometry: m/z calcd for C26H25NF2 [M+Na]+ 412.18473, measured 412.18445.



***N*,*N*-bis((*Z*)-2-fluoro-3-phenylallyl)aniline**

4b: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 68 mg product was obtained by 94% isolated yield as brown solid.

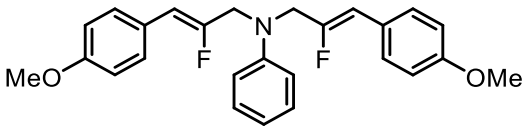
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 4H), 7.24 (t, *J* = 7.7 Hz, 4H), 7.21 – 7.17 (m, 2H), 7.17 – 7.14 (m, 2H), 6.85 – 6.81 (m, 2H), 6.76 – 6.71 (m, 1H), 5.60 (d, *J* = 39.5 Hz, 2H), 4.16 (d, *J* = 7.5 Hz, 4H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.51 – -109.64 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9 (d, *J* = 270.2 Hz), 147.8, 132.8 (d, *J* = 2.3 Hz), 129.4, 128.6 (d, *J* = 7.2 Hz), 128.5, 127.4 (d, *J* = 2.1 Hz), 118.3, 113.2, 107.1 (d, *J* = 6.0 Hz), 51.5 (d, *J* = 34.3 Hz).

IR (neat, cm^{-1}): ṽ:3028, 2923, 1910, 1690, 1598, 1499, 1263, 1276, 1178, 1126, 959, 861, 747.

EI-HRMS: mass spectrometry: m/z calcd for $C_{24}H_{21}NF_2$ $[M]^+$ 361.16366, measured 361.16350.



***N*,*N*-bis((*Z*)-2-fluoro-3-(4-methoxyphenyl)allyl)aniline**

4c: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 50:1). 59 mg product was obtained by 70% isolated yield as yellow solid.

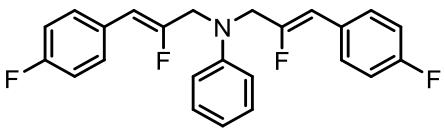
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.6 Hz, 4H), 7.20 – 7.14 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 4H), 6.72 (t, *J* = 7.3 Hz, 1H), 5.53 (d, *J* = 39.8 Hz, 2H), 4.13 (d, *J* = 8.0 Hz, 4H), 3.71 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -112.29 – -112.46 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.8 (d, *J* = 2.5 Hz), 154.5 (d, *J* = 267.8 Hz), 148.0, 129.9 (d, *J* = 7.2 Hz), 129.3, 125.6 (d, *J* = 2.2 Hz), 118.1, 113.9, 113.2, 106.7 (d, *J* = 6.4 Hz), 55.3, 51.4 (d, *J* = 34.1 Hz).

IR (neat, cm^{-1}): ṽ: 3046, 2930, 1900, 1692, 1601, 1504, 1350, 1247, 1175, 1030, 951, 858, 745.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{26}H_{25}O_2NF_2$ $[M+Na]^+$ 444.17456, measured 444.17416.



***N*,*N*-bis((*Z*)-2-fluoro-3-(4-fluorophenyl)allyl)aniline**

4d: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 46 mg product was obtained by 58% isolated yield as yellow solid.

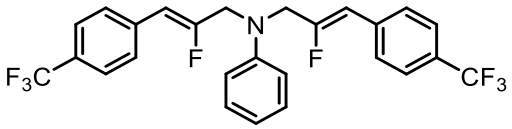
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 4H), 7.22 – 7.17 (m, 2H), 6.92 (t, *J* = 8.7 Hz, 4H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 5.56 (d, *J* = 39.1 Hz, 2H), 4.14 (d, *J* = 7.5 Hz, 4H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.68 – -110.83 (m), -113.84 – -113.94 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.8 (dd, *J* = 247.5, 3.2 Hz), 155.5 (dd, *J* = 269.7, 2.5 Hz), 147.7, 130.3 (t, *J* = 7.6 Hz), 129.4, 128.9 (t, *J* = 3.0 Hz), 118.4, 115.4 (d, *J* = 21.3 Hz), 113.1, 106.1 (d, *J* = 6.2 Hz), 51.5 (d, *J* = 34.1 Hz).

IR (neat, cm^{-1}): ṽ: 3382, 2922, 1895, 1692, 1598, 1504, 1379, 1225, 1129, 1017, 956, 857, 744.

APCI-HRMS: mass spectrometry: m/z calcd for $C_{24}H_{19}NF_4$ $[M+H]^+$ 398.15264, measured 398.15215.



***N*,*N*-bis((*Z*)-2-fluoro-3-(4-(trifluoromethyl)phenyl)allyl)aniline**

4e: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 50:1). 73 mg product was obtained by 73% isolated yield as brown solid.

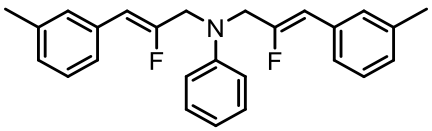
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (s, 8H), 7.22 – 7.18 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 5.65 (d, *J* = 38.6 Hz, 2H), 4.18 (d, *J* = 6.9 Hz, 4H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -62.63, -106.40 – -106.52 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.6 (d, *J* = 273.6 Hz), 147.4, 136.2, 129.5, 129.3, 129.1 (d, *J* = 2.3 Hz), 128.7 (d, *J* = 7.3 Hz), 125.4 (q, *J* = 3.7 Hz), 124.1 (q, J = 271.9 Hz), 118.8, 113.2, 106.1 (d, *J* = 5.6 Hz), 51.7 (d, *J* = 34.2 Hz).

IR (neat, cm^{-1}): ṽ: 2924, 1932, 1691, 1599, 1502, 1415, 1381, 1322, 1215, 1114, 1016, 946, 862, 752.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{26}H_{19}NF_8$ $[M+H]^+$ 498.14625, measured 498.14532.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*m*-tolyl)allyl)aniline**

4f: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 62 mg product was obtained by 80% isolated yield as brown oil.

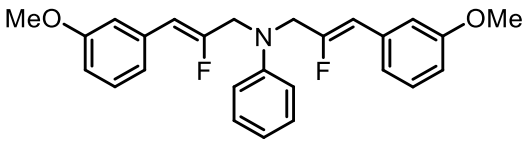
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.20 (m, 4H), 7.20 – 7.16 (m, 2H), 7.15 – 7.11 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 5.57 (d, *J* = 39.7 Hz, 2H), 4.15 (d, *J* = 7.6 Hz, 4H), 2.25 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.56 – -109.70 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.7 (d, *J* = 270.2 Hz), 147.9, 138.1, 132.7 (d, *J* = 2.4 Hz), 129.4, 129.3, 128.4, 128.1 (d, *J* = 2.0 Hz), 125.7 (d, *J* = 7.4 Hz), 118.3, 113.2, 107.2 (d, *J* = 6.0 Hz), 51.5 (d, *J* = 34.2 Hz), 21.4.

IR (neat, cm^{-1}): ṽ: 3384, 2921, 1925, 1690, 1598, 1501, 1379, 1302, 1219, 1129, 991, 949, 780.

APCI-HRMS: mass spectrometry: m/z calcd for $C_{26}H_{26}NF_2$ $[M+H]^+$ 390.20278, measured 390.20290.



***N*,*N*-bis((*Z*)-2-fluoro-3-(3-methoxyphenyl)allyl)aniline**

4g: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 50:1). 82 mg product was obtained by 98% isolated yield as yellow solid.

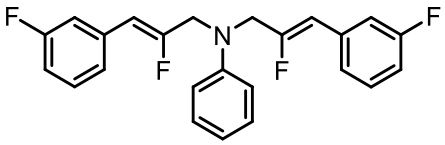
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.20 – 7.16 (m, 2H), 7.14 (t, *J* = 7.9 Hz, 2H), 6.99 – 6.94 (m, 4H), 6.84 – 6.80 (m, 2H), 6.75 – 6.69 (m, 3H), 5.57 (d, *J* = 39.2 Hz, 2H), 4.13 (d, *J* = 7.5 Hz, 1H), 3.69 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -108.67 – -108.82 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.7, 156.1 (d, *J* = 270.9 Hz), 147.8, 134.1 (d, *J* = 2.3 Hz), 129.5, 129.4, 121.3 (d, *J* = 6.9 Hz), 118.4, 113.8 (d, *J* = 7.6 Hz), 113.4, 113.2, 107.1 (d, *J* = 5.5 Hz), 55.2, 51.5 (d, *J* = 34.1 Hz).

IR (neat, cm^{-1}): ṽ: 3003, 2936, 1921, 1690, 1596, 1498, 1432, 1380, 1293, 1221, 1162, 1045, 907, 778.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{26}H_{25}O_2NF_2$ $[M+H]^+$ 422.19261, measured 422.19217.



***N*,*N*-bis((*Z*)-2-fluoro-3-(3-fluorophenyl)allyl)aniline**

4h: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 56 mg product was obtained by 71% isolated yield as brown oil.

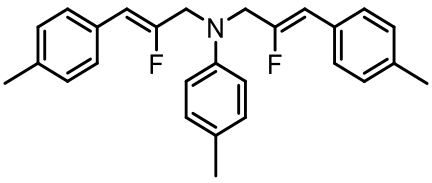
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 6H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.87 – 6.82 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 5.58 (d, *J* = 38.6 Hz, 2H), 4.15 (d, *J* = 7.2 Hz, 4H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -107.41 – -107.73 (m), -113.03 – -113.20 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.8 (d, *J* = 244.8 Hz), 156.8 (d, *J* = 272.1 Hz), 147.5, 134.8 (dd, *J* = 8.5, 2.1 Hz), 129.9 (d, *J* = 8.4 Hz), 129.5, 124.4 (dd, *J* = 6.5, 2.9 Hz), 118.6, 115.3 (dd, *J* = 22.7, 8.6 Hz), 114.3 (d, *J* = 20.9 Hz), 113.2, 106.3 (dd, *J* = 5.7, 2.6 Hz), 51.6 (d, *J* = 34.2 Hz).

IR (neat, cm^{-1}): ṽ: 3383, 2922, 1923, 1691, 1584, 1441, 1380, 1281, 1221, 1151, 1079, 966, 779.

APCI-HRMS: mass spectrometry: m/z calcd for $C_{24}H_{19}NF_4$ $[M+H]^+$ 398.15264, measured 398.15290.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-4-methylaniline**

4i: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 73 mg product was obtained by 91% isolated yield as brown oil.

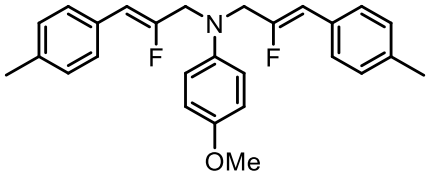
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 4H), 7.03 (d, *J* = 7.9 Hz, 4H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 5.54 (d, *J* = 39.8 Hz, 2H), 4.09 (d, *J* = 7.9 Hz, 4H), 2.24 (s, 6H), 2.17 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.20 – -110.42 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.6 (d, *J* = 269.4 Hz), 145.8, 137.1 (d, *J* = 2.2 Hz), 130.1 (d, *J* = 2.0 Hz), 129.9, 129.2, 128.5 (d, *J* = 6.9 Hz), 127.5, 113.5, 107.0 (d, *J* = 6.1 Hz), 51.7 (d, *J* = 34.0 Hz), 21.3, 20.3.

IR (neat, cm^{-1}): ṽ: 3385, 2920, 1906, 1692, 1615, 1515, 1377, 1214, 1131, 949, 906, 804, 730.

APCI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{27}NF_2$ $[M+H]^+$ 404.21843, measured 404.21861.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-4-methoxyaniline**

4j: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 80:1). 78 mg product was obtained by 93% isolated yield as brown solid.

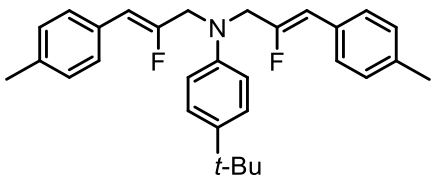
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.1 Hz, 4H), 7.03 (d, *J* = 7.9 Hz, 4H), 6.80 – 6.72 (m, 4H), 5.54 (d, *J* = 39.8 Hz, 2H), 4.05 (d, *J* = 9.0 Hz, 4H), 3.65 (s, 3H), 2.23 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.81 – -110.01 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9 (d, *J* = 269.5 Hz), 152.7, 142.5, 137.1 (d, *J* = 2.0 Hz), 130.1 (d, *J* = 2.2 Hz), 129.2, 128.5 (d, *J* = 7.0 Hz), 115.4, 114.8, 107.3 (d, *J* = 6.2 Hz), 55.7, 52.3 (d, *J* = 33.2 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3374, 2914, 1912, 1690, 1611, 1508, 1377, 1286, 1243, 1153, 1030, 909, 814.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{27}ONF_2$ $[M+H]^+$ 420.21335, measured 420.21279.



4-(*tert*-butyl)-*N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)aniline

4k: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 82 mg product was obtained by 92% isolated yield as brown oil.

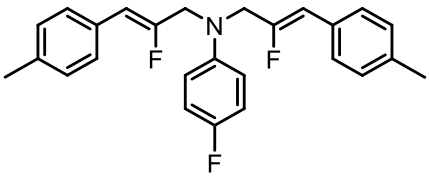
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.2 Hz, 4H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 4H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.57 (d, *J* = 39.8 Hz, 2H), 4.10 (d, *J* = 7.9 Hz, 4H), 2.24 (s, 6H), 1.20 (s, 9H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.20 – -110.36 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.6 (d, *J* = 269.4 Hz), 145.7, 140.8, 137.1 (d, *J* = 1.9 Hz), 130.1 (d, *J* = 2.0 Hz), 129.2, 128.6 (d, *J* = 7.0 Hz), 126.2, 112.9, 107.0 (d, *J* = 6.0 Hz), 51.6 (d, *J* = 34.1 Hz), 33.9, 31.5, 21.3.

IR (neat, cm^{-1}): ṽ: 3390, 2958, 1907, 1692, 1612, 1516, 1452, 1367, 1208, 1130, 954, 906, 810.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{30}H_{33}NF_2$ $[M+Na]^+$ 468.24733, measured 468.24661.



4-fluoro-*N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)aniline

4l: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 67 mg product was obtained by 82% isolated yield as brown oil.

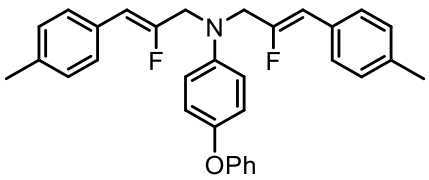
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.86 (t, *J* = 8.7 Hz, 2H), 6.78 – 6.73 (m, 2H), 5.54 (d, *J* = 39.6 Hz, 2H), 4.08 (d, *J* = 8.9 Hz, 4H), 2.25 (s, 6H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -110.36 – -110.51 (m), -126.94 – -126.99 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.27 (d, *J* = 237.2 Hz), 155.26 (d, *J* = 269.3 Hz), 144.6 (d, *J* = 2.2 Hz), 137.3 (d, *J* = 2.3 Hz), 129.9 (d, *J* = 2.3 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 115.7 (d, *J* = 22.2 Hz), 114.8 (d, *J* = 7.5 Hz), 107.4 (d, *J* = 6.3 Hz), 52.1 (d, *J* = 33.3 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3380, 2019, 1906, 1687, 1611, 1508, 1438, 1367, 1218, 1142, 937, 811, 734.

EI-HRMS: mass spectrometry: m/z calcd for $C_{26}H_{24}NF_3$ $[M]^+$ 407.18554, measured 407.18525.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-4-phenoxyaniline**

4m: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 80:1). 70 mg product was obtained by 73% isolated yield as brown oil.

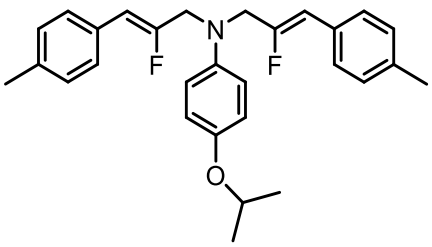
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.0 Hz, 4H), 7.37 – 7.32 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 4H), 7.10 – 7.06 (m, 1H), 7.04 – 6.99 (m, 4H), 6.97 – 6.92 (m, 2H), 5.72 (d, *J* = 39.6 Hz, 2H), 4.25 (d, *J* = 8.9 Hz, 4H), 2.40 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.18 – -110.36 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.7, 155.4 (d, *J* = 269.2 Hz), 148.6, 144.6, 137.3 (d, *J* = 2.1 Hz), 130.0 (d, *J* = 2.1 Hz), 129.6, 129.3, 128.6 (d, *J* = 7.2 Hz), 122.3, 120.8, 117.6, 114.8, 107.4 (d, *J* = 6.2 Hz), 52.0 (d, *J* = 33.3 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3030, 2921, 1906, 1691, 1591, 1508, 1378, 1287, 1234, 1131, 1023, 952, 731.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{32}H_{29}ONF_2$ $[M+H]^+$ 482.22900, measured 482.22859.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-4-isopropoxyaniline**

4n: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 80:1). 75 mg product was obtained by 84% isolated yield as brown oil.

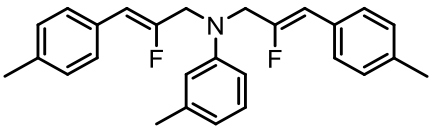
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.1 Hz, 4H), 7.04 (d, *J* = 7.9 Hz, 4H), 6.77 – 6.70 (m, 4H), 5.55 (d, *J* = 39.7 Hz, 2H), 4.34 – 4.26 (m, 1H), 4.05 (d, *J* = 8.8 Hz, 4H), 2.24 (s, 6H), 1.21 (s, 3H), 1.20 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.86 – -110.00 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.8 (d, *J* = 269.5 Hz), 150.8, 142.6, 137.1 (d, *J* = 2.2 Hz), 130.1 (d, *J* = 2.1 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 117.5, 115.2, 107.2 (d, *J* = 6.1 Hz), 70.8, 52.2 (d, *J* = 33.3 Hz), 22.25, 21.26.

IR (neat, cm^{-1}): ṽ: 3384, 2975, 1908, 1691, 1612, 1509, 1449, 1375, 1238, 1126, 1040, 953, 860, 731.

EI-HRMS: mass spectrometry: m/z calcd for $C_{29}H_{31}ONF_2$ $[M]^+$ 447.23682, measured 447.23659.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-3-methylaniline**

4o: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 72 mg product was obtained by 89% isolated yield as brown oil.

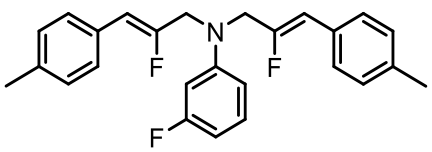
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.9 Hz, 4H), 7.23 – 7.17 (m, 5H), 6.81 – 6.77 (m, 2H), 6.70 (d, *J* = 7.5 Hz, 1H), 5.71 (d, *J* = 39.8 Hz, 2H), 4.27 (d, *J* = 7.5 Hz, 4H), 2.40 (s, 6H), 2.39 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.31 – -110.47 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5 (d, *J* = 269.2 Hz), 148.1, 139.1, 137.2 (d, *J* = 2.1 Hz), 130.1 (d, *J* = 2.5 Hz), 129.2, 128.6 (d, *J* = 7.1 Hz), 119.2, 113.9, 110.5, 107.0 (d, *J* = 6.1 Hz), 51.4 (d, *J* = 34.4 Hz), 22.0, 21.3.

IR (neat, cm^{-1}): ṽ: 3388, 2920, 1907, 1691, 1602, 1497, 1374, 1241, 1179, 1129, 952, 858, 730.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{27}NF_2$ $[M+Na]^+$ 426.20038, measured 426.19959.



3-fluoro-*N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)aniline

4p: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 70 mg product was obtained by 86% isolated yield as brown oil.

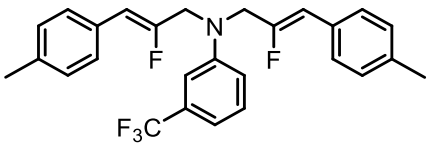
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.57 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 12.4 Hz, 1H), 6.44 – 6.38 (m, 1H), 5.55 (d, *J* = 39.5 Hz, 2H), 4.12 (d, *J* = 8.5 Hz, 4H), 2.25 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.72 – -110.90 (m), -111.87 – -111.97 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.0 (d, *J* = 243.2 Hz), 154.8 (d, *J* = 268.9 Hz), 149.7 (d, *J* = 10.4 Hz), 137.3 (d, *J* = 2.2 Hz), 130.4 (d, *J* = 10.2 Hz), 129.8 (d, *J* = 2.3 Hz), 129.4, 129.2, 128.5 (d, *J* = 7.1 Hz), 108.8 (d, *J* = 2.3 Hz), 107.4 (d, *J* = 6.3 Hz), 104.7 (d, *J* = 21.3 Hz), 100.5 (d, *J* = 26.2 Hz), 51.5 (d, *J* = 33.9 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3027, 2922, 1906, 1691, 1615, 1498, 1376, 1249, 1131, 1042, 994, 906, 860.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{26}H_{24}NF_3$ $[M+Na]^+$ 430.17531, measured 430.17443.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-3-(trifluoromethyl)aniline**

4q: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 80:1). 80 mg product was obtained by 88% isolated yield as brown oil.

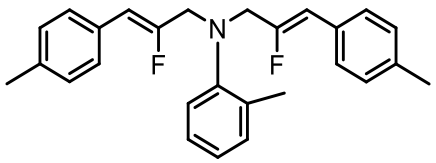
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 4H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 5H), 6.95 (d, *J* = 8.2 Hz, 2H), 5.56 (d, *J* = 39.3 Hz, 2H), 4.15 (d, *J* = 9.3 Hz, 4H), 2.24 (s, 6H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -62.73, -110.85 – -110.98 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.6 (d, *J* = 268.8 Hz), 148.2, 137.5 (d, *J* = 2.2 Hz), 131.7 (q, *J* = 31.7 Hz), 129.8, 129.7 (d, *J* = 2.4 Hz), 129.3, 128.6 (d, *J* = 7.1 Hz), 124.3 (q, *J* = 272.8 Hz), 116.3, 114.7 (d, *J* = 4.0 Hz), 109.6 (d, *J* = 3.8 Hz), 107.8 (d, *J* = 6.4 Hz), 51.5 (d, *J* = 33.3 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 3418, 2923, 1914, 1686, 1611, 1505, 1433, 1323, 1223, 1161, 1040, 949, 863, 775.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{24}NF_5$ $[M+Na]^+$ 480.17211, measured 480.17195.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-2-methylaniline**

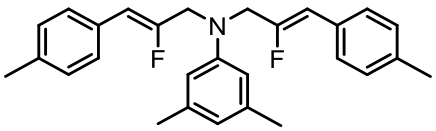
4r: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 66 mg product was obtained by 82% isolated yield as yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.8 Hz, 4H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.07 – 7.02 (m, 6H), 6.96 – 6.90 (m, 1H), 5.51 (d, *J* = 38.9 Hz, 2H), 3.82 (d, *J* = 16.1 Hz, 4H), 2.31 (s, 3H), 2.24 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -106.71 – -106.89 (m).

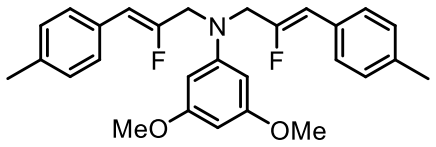
^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6 (d, *J* = 269.0 Hz), 149.1, 137.1 (d, *J* = 2.1 Hz), 134.4, 131.2, 130.3 (d, *J* = 2.3 Hz), 129.2, 128.5 (d, *J* = 7.3 Hz), 126.4, 124.5, 123.2, 108.9 (d, *J* = 6.8 Hz), 54.6 (d, *J* = 28.0 Hz), 21.3, 18.2.

IR (neat, cm^{-1}): ṽ: 3381, 2921, 1905, 1688, 1600, 1493, 1372, 1213, 1154, 1035, 939, 858, 766.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{27}NF_2$ $[M+H]^+$ 404.21843, measured 404.21841.



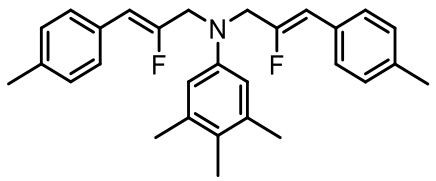
***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-3,5-dimethylaniline**

4s: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 67 mg product was obtained by 80% isolated yield as brown oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.9 Hz, 4H), 7.19 (d, *J* = 7.9 Hz, 4H), 6.59 (s, 2H), 6.54 (s, 1H), 5.69 (d, *J* = 39.8 Hz, 2H), 4.25 (d, *J* = 7.2 Hz, 4H), 2.39 (s, 6H), 2.33 (s, 6H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.27 – -110.42 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5 (d, *J* = 269.4 Hz), 148.2, 139.0, 137.1 (d, *J* = 2.1 Hz), 130.1 (d, *J* = 2.2 Hz), 129.2, 128.5 (d, *J* = 7.2 Hz), 120.3, 111.2, 106.8 (d, *J* = 6.1 Hz), 51.3 (d, *J* = 34.6 Hz), 21.8, 21.3.
IR (neat, cm^{-1}): ṽ: 3414, 2019, 1904, 1691, 1597, 1511, 1372, 1185, 1129, 1036, 954, 906, 730.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{28}H_{29}NF_2$ $[M+Na]^+$ 440.21603, measured 440.21506.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-3,5-dimethoxyaniline**

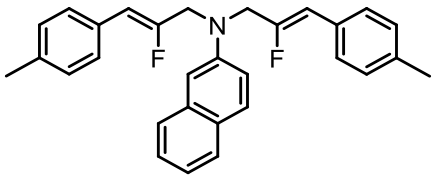
4t: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 85 mg product was obtained by 95% isolated yield as brown solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.0 Hz, 4H), 7.04 (d, *J* = 8.0 Hz, 4H), 6.01 (d, *J* = 2.0 Hz, 2H), 5.90 (s, 1H), 5.56 (d, *J* = 39.6 Hz, 2H), 4.11 (d, *J* = 8.0 Hz, 4H), 3.67 (s, 6H), 2.25 (s, 6H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.40 – -110.58 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.7, 155.2 (d, *J* = 269.0 Hz), 145.0, 137.2 (d, *J* = 2.2 Hz), 123.0 (d, *J* = 2.3 Hz), 129.2, 128.5 (d, *J* = 7.0 Hz), 107.2 (d, *J* = 6.2 Hz), 92.7, 90.2, 55.2, 51.5 (d, *J* = 34.2 Hz), 21.3.
IR (neat, cm^{-1}): ṽ: 3005, 2929, 1911, 1693, 1593, 1485, 1370, 1293, 1198, 1070, 969, 903, 804.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{28}H_{29}NF_2$ $[M+Na]^+$ 472.20586, measured 420.20497.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)-3,4,5-trimethylaniline**

4u: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 75 mg product was obtained by 87% isolated yield as brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.8 Hz, 4H), 7.03 (d, *J* = 7.8 Hz, 4H), 6.50 (s, 2H), 5.55 (d, *J* = 39.9 Hz, 2H), 4.08 (d, *J* = 7.2 Hz, 4H), 2.24 (s, 6H), 2.16 (s, 6H), 2.00 (s, 3H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.05 – -110.20 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.8 (d, *J* = 269.5 Hz), 145.7, 137.4, 137.1 (d, *J* = 2.0 Hz), 130.2 (d, *J* = 2.2 Hz), 129.2, 128.6 (d, *J* = 7.1 Hz), 125.0, 112.9, 106.8 (d, *J* = 6.2 Hz), 51.4 (d, *J* = 34.4 Hz), 21.3, 21.2, 14.5.
IR (neat, cm^{-1}): ṽ: 2918, 1906, 1688, 1605, 1496, 1366, 1222, 1179, 1153, 999, 906, 861, 729.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{29}H_{31}NF_2$ $[M+H]^+$ 432.24973, measured 432.24983.

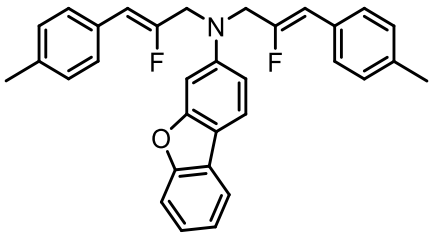


***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)naphthalen-2-amine**

4v: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 62 mg product was obtained by 71% isolated yield as brown oil.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 5H), 7.17 – 7.14 (m, 2H), 7.08 – 7.02 (m, 5H), 5.60 (d, *J* = 39.7 Hz, 2H), 4.24 (d, *J* = 7.9 Hz, 3H), 2.24 (s, 6H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.26 – -110.45 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.3 (d, *J* = 269.2 Hz), 145.8, 137.2 (d, *J* = 2.2 Hz), 134.7, 123.0 (d, *J* = 2.3 Hz), 129.22, 129.16, 128.6 (d, *J* = 7.1 Hz), 127.6, 127.4, 126.5 (d, *J* = 2.2 Hz), 122.8, 116.1, 107.7, 107.3 (d, *J* = 6.2 Hz), 51.6 (d, *J* = 34.1 Hz), 21.3.
IR (neat, cm^{-1}): ṽ: 3857, 2922, 1908, 1691, 1628, 1510, 1382, 1213, 1184, 1129, 1040, 955, 831.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{30}H_{27}NF_2$ $[M+Na]^+$ 462.20038, measured 462.19924.

***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)benzo[*d*][1,3]dioxol-5-amine**

4w: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 45 mg product was obtained by 52% isolated yield as brown solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.62 (d, *J* = 8.5 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 6.26 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.79 (s, 2H), 5.55 (d, *J* = 39.7 Hz, 2H), 4.05 (d, *J* = 9.0 Hz, 4H), 2.25 (s, 6H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.00 – -110.16 (m).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5 (d, *J* = 269.3 Hz), 148.5, 144.1, 140.4, 137.2 (d, *J* = 2.1 Hz), 130.0 (d, *J* = 2.3 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 108.5, 107.4 (d, *J* = 6.1 Hz), 106.3, 100.9, 97.3, 52.5 (d, *J* = 33.2 Hz), 21.3.
IR (neat, cm^{-1}): ṽ: 2921, 1911, 1695, 1631, 1502, 1431, 1371, 1274, 1204, 1127, 1034, 965, 807, 731.
ESI-HRMS: mass spectrometry: m/z calcd for $C_{27}H_{25}O_2NF_2$ $[M+H]^+$ 434.19261, measured 434.19126.



***N*,*N*-bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)dibenzo[*b*,*d*]furan-3-amine**

4x: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 72 mg product was obtained by 75% isolated yield as brown solid.

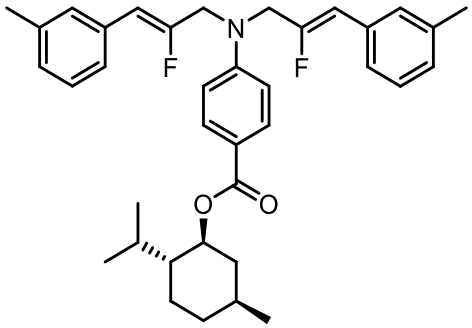
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 4H), 7.27 – 7.22 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 4H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.61 (d, *J* = 39.6 Hz, 2H), 4.24 (d, *J* = 8.3 Hz, 4H), 2.25 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.57 – -110.71 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.1, 156.1, 155.0 (d, *J* = 269.2 Hz), 148.4, 137.3, 129.8 (d, *J* = 2.4 Hz), 129.2, 128.6 (d, *J* = 7.1 Hz), 125.3, 124.6, 122.6, 121.1, 119.5, 115.3, 111.2, 109.5, 107.5 (d, *J* = 6.3 Hz), 96.2, 52.0 (d, *J* = 33.9 Hz), 21.2.

IR (neat, cm^{-1}): ṽ: 3021, 2920, 1916, 1690, 1601, 1503, 1456, 1377, 1239, 1156, 1010, 943, 811, 721.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{32}H_{27}ONF_2$ $[M+H]^+$ 480.21335, measured 480.21187.



(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-(bis((*Z*)-2-fluoro-3-(*m*-tolyl)allyl)amino)benzoate

4y: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 50:1). 86 mg product was obtained by 75% isolated yield as yellow oil.

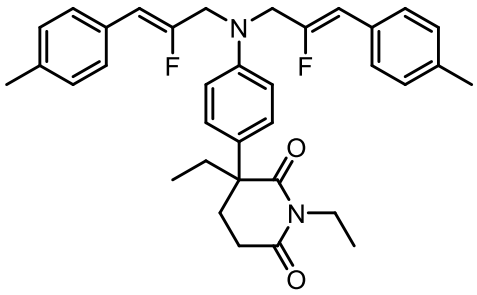
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 4H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.54 (d, *J* = 39.3 Hz, 2H), 4.82 – 4.77 (m, 1H), 4.19 (d, *J* = 7.9 Hz, 4H), 2.24 (s, 6H), 2.06 – 2.00 (m, 1H), 1.92 – 1.83 (m, 1H), 1.66 – 1.58 (m, 2H), 1.48 – 1.40 (m, 2H), 1.06 – 0.93 (m, 2H), 0.84 – 0.80 (m, 7H), 0.70 (d, *J* = 6.9 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.01 – -110.20 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.1, 154.8 (d, *J* = 269.8 Hz), 151.1, 138.1, 132.4 (d, *J* = 2.3 Hz), 131.4, 129.4 (d, *J* = 6.7 Hz), 128.5, 128.4, 125.8 (d, *J* = 7.2 Hz), 120.3, 112.0, 107.8 (d, *J* = 5.9 Hz), 74.1, 51.4 (d, *J* = 34.1 Hz), 47.4, 41.2, 34.4, 31.5, 26.5, 23.8, 22.1, 21.4, 20.8, 16.6.

IR (neat, cm^{-1}): ṽ: 3380, 2926, 1937, 1693, 1604, 1519, 1453, 1378, 1279, 1185, 1115, 1039, 961, 732.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{37}H_{43}O_2NF_2$ $[M+Na]^+$ 594.31541, measured 594.31439.



3-(4-(bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)amino)phenyl)-1,3-diethylpiperidine-2,6-dione

4z: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 10:1). 101 mg product was obtained by 90% isolated yield as brown oil.

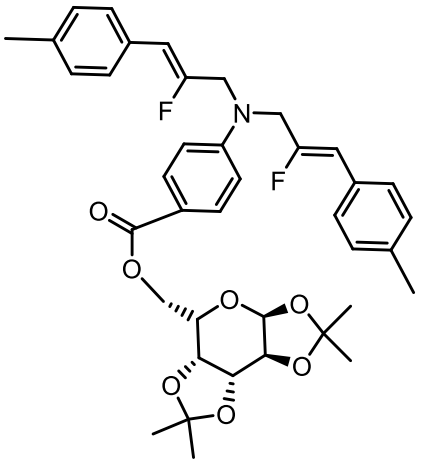
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 4H), 7.04 (d, *J* = 7.8 Hz, 4H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 5.54 (d, *J* = 39.6 Hz, 2H), 4.11 (d, *J* = 8.2 Hz, 4H), 3.86 – 3.70 (m, 2H), 2.55 – 2.48 (m, 1H), 2.44 – 2.36 (m, 1H), 2.24 (s, 6H), 2.17 – 2.10 (m, 1H), 2.06 – 1.98 (m, 1H), 1.98 – 1.90 (m, 1H), 1.80 – 1.71 (m, 1H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.51 – -110.66 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.3, 172.2, 155.1 (d, *J* = 269.1 Hz), 147.0, 137.3, 129.9 (d, *J* = 2.2 Hz), 129.2, 128.7, 128.6 (d, *J* = 6.9 Hz), 127.2, 113.3, 107.3 (d, *J* = 6.3 Hz), 51.4 (d, *J* = 33.9 Hz), 50.5, 35.3, 33.8, 30.0, 25.9, 21.3, 13.3, 9.2.

IR (neat, cm^{-1}): ṽ: 3374, 2972, 1904, 1669, 1516, 1453, 1357, 1212, 1123, 1045, 908, 862, 809, 730.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{35}H_{38}O_2N_2F_2$ $[M+Na]^+$ 579.27936, measured 579.27783.



((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(bis((Z)-2-fluoro-3-(p-tolyl)allyl)amino)benzoate

4aa: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 5:1). 111 mg product was obtained by 82% isolated yield as brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 4H), 7.04 (d, *J* = 7.9 Hz, 4H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.53 (d, *J* = 39.4 Hz, 2H), 5.47 (d, *J* = 4.9 Hz, 1H), 4.55 (dd, *J* =

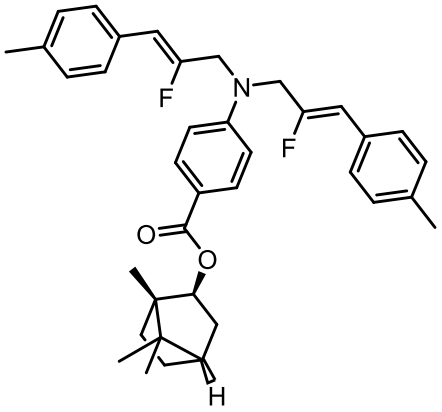
7.9, 2.4 Hz, 1H), 4.42 – 4.37 (m, 1H), 4.33 – 4.28 (m, 1H), 4.27 – 4.21 (m, 2H), 4.18 (d, *J* = 8.2 Hz, 4H), 4.10 – 4.05 (m, 1H), 2.24 (s, 6H), 1.43 (s, 3H), 1.39 (s, 3H), 1.27 (s, 3H), 1.24 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.95 – -111.14 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.3, 154.3 (d, *J* = 268.4 Hz), 151.4, 137.4, 131.6, 129.6 (d, *J* = 2.2 Hz), 129.3, 128.6 (d, *J* = 7.0 Hz), 119.3, 112.0, 109.6, 108.8, 107.6 (d, *J* = 6.2 Hz), 96.4, 71.2, 70.8, 70.6, 66.2, 63.3, 51.2 (d, *J* = 34.1 Hz), 26.1, 26.0, 25.0, 24.5, 21.3.

IR (neat, cm^{-1}): ṽ: 2986, 1908, 1703, 1604, 1518, 1378, 1323, 1278, 1185, 1105, 1069, 906, 767.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{39}H_{43}O_7N_1F_2$ $[M+Na]^+$ 698.28998, measured 698.28961.



(1*S*,2*S*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)amino)benzoate

4bb: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 10:1). 95 mg product was obtained by 83% isolated yield as brown oil.

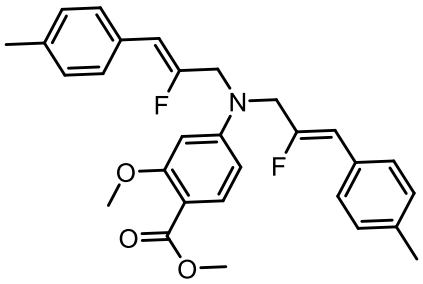
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 7.8 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.54 (d, *J* = 39.5 Hz, 2H), 4.99 (d, *J* = 9.4 Hz, 1H), 4.19 (d, *J* = 8.1 Hz, 4H), 2.40 – 2.33 (m, 1H), 2.25 (s, 6H), 2.09 – 2.01 (m, 1H), 1.74 – 1.65 (m, 1H), 1.65 – 1.61 (m, 1H), 1.33 – 1.26 (m, 1H), 1.24 – 1.15 (m, 1H), 1.01 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.87 (s, 3H), 0.82 (s, 3H), 0.81 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.99 – -111.15 (m).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 154.4 (d, *J* = 268.7 Hz), 151.2, 137.4 (d, *J* = 2.1 Hz), 131.4, 129.7 (d, *J* = 2.2 Hz), 129.3, 128.6 (d, *J* = 7.0 Hz), 120.2, 112.0, 107.6 (d, *J* = 6.2 Hz), 79.8, 51.3 (d, *J* = 34.1 Hz), 49.1, 47.9, 45.1, 37.0, 28.1, 27.4, 21.3, 19.8, 19.0, 13.6.

IR (neat, cm^{-1}): ṽ: 2954, 1907, 1696, 1604, 1517, 1450, 1377, 1281, 1224, 1185, 1117, 908, 834, 731.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{37}H_{41}O_2N_1F_2$ $[M+H]^+$ 570.31781, measured 570.31685.



methyl 4-(bis((*Z*)-2-fluoro-3-(*p*-tolyl)allyl)amino)-2-methoxybenzoate

4cc: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 10:1). 78 mg product was obtained by 82% isolated yield as brown oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 5H), 7.04 (d, *J* = 7.9 Hz, 4H), 6.94 (dd, *J* = 9.1, 3.3 Hz, 1H), 6.81 (d, *J* = 9.1 Hz, 1H), 5.55 (d, *J* = 39.5 Hz, 2H), 4.08 (d, *J* = 9.7 Hz, 4H), 3.79 (s, 3H), 3.74 (s, 3H), 2.24 (s, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -110.02 – -110.18 (m).

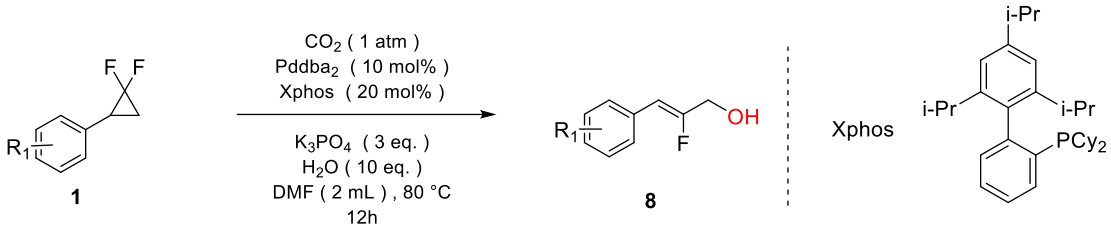
^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.9, 155.3 (d, *J* = 269.0 Hz), 152.2, 141.9, 137.3 (d, *J* = 2.0 Hz), 129.9 (d, *J* = 2.3 Hz), 129.2, 128.5 (d, *J* = 7.1 Hz), 120.7, 119.3, 117.1, 114.0, 107.7 (d, *J* = 6.2 Hz), 56.8, 52.13, 52.10 (d, *J* = 32.8 Hz), 21.3.

IR (neat, cm^{-1}): ṽ: 2948, 1909, 1724, 1613, 1504, 1436, 1294, 1242, 1182, 1082, 1022, 861, 807.

ESI-HRMS: mass spectrometry: m/z calcd for $C_{29}H_{29}O_3N_1F_2$ $[M+H]^+$ 478.21883, measured 478.21875.

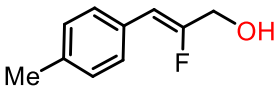
4.2.2 CO_2 and Palladium co-Catalyzed Synthesis of Fluorinated Cinnamyl Alcohol

General procedure for the reaction



X-Phos (19.1 mg, 0.04 mmol) and $Pd(dba)_2$ (11.4 mg, 0.02 mmol), *gem*-difluorocyclopropanes **1** (0.2 mmol), H_2O (10.0 eq., 36 mg), K_3PO_4 (3.0 eq., 127.2 mg) were dissolved in 2 mL DMF and CO_2 was bubbled through the solution for about two minutes., then the mixture was stirred at 80 °C for about 12 h to the starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. The crude was purified by column chromatography to give the products **8**.

Preparation of the product



(*Z*)-2-fluoro-3-(*p*-tolyl)prop-2-en-1-ol

8a: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 31 mg product was obtained by 93% isolated yield as yellow liquid.

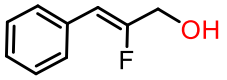
^{1}H NMR (600 MHz, Chloroform-d) δ 7.41 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.75 (d, J = 38.9 Hz, 1H), 4.27 (d, J = 14.8 Hz, 2H), 2.35 (s, 3H), 1.96 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-d) δ -114.35 (dt, J = 38.8, 14.9 Hz).

^{13}C NMR (151 MHz, Chloroform-d) δ 157.7 (d, J = 265.4 Hz), 137.5 (d, J = 2.4 Hz), 129.9 (d, J = 2.6 Hz), 129.3, 128.8 (d, J = 7.2 Hz), 107.7 (d, J = 6.8 Hz), 62.2 (d, J = 32.2 Hz), 21.4.

EI-HRMS: mass spectrometry: m/z calcd for C10H11OF [M]+ 166.07939, measured 166.07877

IR (neat, cm-1): ṽ: 3313, 2920, 2856, 1916, 1690, 1511, 1445, 1341, 1220, 1157, 1072, 865, 696.



(*Z*)-2-fluoro-3-phenylprop-2-en-1-ol

8b: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 25 mg product was obtained by 82% isolated yield as yellow liquid.

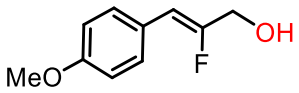
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 6.9 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.20 – 7.16 (m, 1H), 5.71 (d, *J* = 38.7 Hz, 1H), 4.21 (d, *J* = 14.3 Hz, 2H), 1.78 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.42 (dt, *J* = 39.0, 14.5 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.26 (d, *J* = 266.8 Hz), 132.82 (d, *J* = 3.6 Hz), 128.85 (d, *J* = 7.3 Hz), 128.65, 127.65 (d, *J* = 2.6 Hz), 107.65 (d, *J* = 6.8 Hz), 62.07 (d, *J* = 32.9 Hz).

EI-HRMS: mass spectrometry: m/z calcd for C_9H_9OF $[M]^+$ 152.06374, measured 152.06316

IR (neat, cm^{-1}): ṽ: 3310, 2922, 2854, 2085, 1663, 1536, 1455, 1346, 1281, 1160, 1074, 974, 752.



(*Z*)-2-fluoro-3-(4-methoxyphenyl)prop-2-en-1-ol

8c: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 33 mg product was obtained by 91% isolated yield as yellow solid.

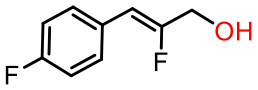
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.72 (d, *J* = 38.9 Hz, 1H), 4.27 (d, *J* = 15.4 Hz, 2H), 3.81 (s, 3H), 1.85 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.18 (dt, *J* = 39.0, 15.3 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.0 (d, *J* = 2.9 Hz), 157.0 (d, *J* = 264.1 Hz), 130.2 (d, *J* = 7.3 Hz), 125.5 (d, *J* = 2.9 Hz), 114.1, 107.4 (d, *J* = 7.2 Hz), 62.2 (d, *J* = 32.1 Hz), 55.4.

EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_{11}O_2F$ $[M]^+$ 182.07431, measured 182.07370

IR (neat, cm^{-1}): ṽ: 3369, 2928, 2850, 1899, 1695, 1606, 1509, 1345, 1297, 1159, 1009, 859, 695.



(*Z*)-2-fluoro-3-(4-fluorophenyl)prop-2-en-1-ol

8d: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 25 mg product was obtained by 74% isolated yield as yellow solid.

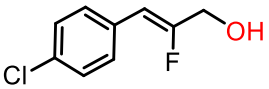
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 5.75 (d, *J* = 38.4 Hz, 1H), 4.28 (d, *J* = 14.4 Hz, 2H), 1.92 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.68 – -113.77 (m), -114.55 (dt, *J* = 38.6, 14.3 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.1 (dd, *J* = 247.6, 3.1 Hz), 158.0 (dd, *J* = 265.9, 2.4 Hz), 130.5 (t, *J* = 7.8 Hz), 128.9 (t, *J* = 3.0 Hz), 115.6 (d, *J* = 21.7 Hz), 106.6 (d, *J* = 6.8 Hz), 62.0 (d, *J* = 32.7 Hz).

EI-HRMS: mass spectrometry: m/z calcd for $C_9H_8OF_2$ $[M]^+$ 170.05432, measured 170.05381

IR (neat, cm^{-1}): ṽ: 3355, 2922, 2853, 1908, 1691, 1602, 1506, 1342, 1236, 1159, 1013, 861, 782.



(Z)-3-(4-chlorophenyl)-2-fluoroprop-2-en-1-ol

8e: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 10 mg product was obtained by 27% isolated yield as yellow solid.

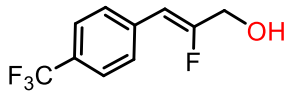
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 5.73 (d, *J* = 38.2 Hz, 1H), 4.25 (d, *J* = 13.7 Hz, 2H), 1.87 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -112.51 (dt, *J* = 38.3, 13.4 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.7 (d, *J* = 267.5 Hz), 133.3 (d, *J* = 3.4 Hz), 131.3 (d, *J* = 2.5 Hz), 130.1 (d, *J* = 7.6 Hz), 128.8, 106.5 (d, *J* = 6.5 Hz), 61.9 (d, *J* = 32.7 Hz).

EI-HRMS: mass spectrometry: m/z calcd for C_9H_8OClF [M]+ 186.02477, measured 186.02418

IR (neat, cm-1): ṽ: 3406, 2921, 2854, 1687, 1591, 1489, 1407, 1339, 1204, 1159, 1089, 1018, 865.



(*Z*)-2-fluoro-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol

8f: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 31 mg product was obtained by 70% isolated yield as yellow liquid.

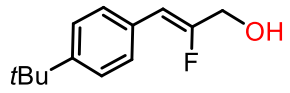
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 – 7.55 (m, 4H), 5.85 (d, *J* = 38.1 Hz, 1H), 4.32 (d, *J* = 12.7 Hz, 2H), 1.94 (b, 1H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -62.67, -110.29 (dt, *J* = 38.1, 12.7 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.0 (d, *J* = 269.7 Hz), 136.4, 129.4 (dd, *J* = 32.3, 2.3 Hz), 128.9 (d, *J* = 7.6 Hz), 125.6 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 271.9 Hz), 106.2 (d, *J* = 6.1 Hz), 61.7 (d, *J* = 33.3 Hz).

EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_8OF_4$ [M]+ 220.05113, measured 220.05093

IR (neat, cm-1): ṽ: 3286, 2927, 2860, 1693, 1617, 1449, 1413, 1321, 1168, 1066, 1017, 864.



(Z)-3-(4-(tert-butyl)phenyl)-2-fluoroprop-2-en-1-ol

8g: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 33 mg product was obtained by 79% isolated yield as yellow liquid.

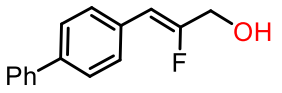
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 5.77 (d, *J* = 38.9 Hz, 1H), 4.28 (d, *J* = 14.4 Hz, 2H), 1.94 (b, 1H), 1.33 (s, 9H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.32 (dt, *J* = 39.0, 14.8 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.9 (d, *J* = 265.7 Hz), 150.7 (d, *J* = 2.2 Hz), 130.0 (d, *J* = 2.8 Hz), 128.6 (d, *J* = 7.1 Hz), 125.6, 107.5 (d, *J* = 6.8 Hz), 62.1 (d, *J* = 32.5 Hz), 34.7, 31.4.

EI-HRMS: mass spectrometry: m/z calcd for $C_{13}H_{17}OF$ [M]+ 208.12634, measured 208.12620

IR (neat, cm-1): ṽ: 3344, 2961, 2869, 1695, 1512, 1462, 1364, 1270, 1159, 1072, 1022, 866, 671.



(*Z*)-3-([1,1'-biphenyl]-4-yl)-2-fluoroprop-2-en-1-ol

8h: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 41 mg product was obtained by 90% isolated yield as yellow solid.

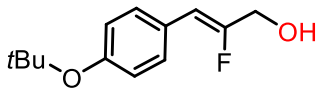
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 – 7.57 (m, 6H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.33 (m, 1H), 5.84 (d, *J* = 38.7 Hz, 1H), 4.32 (d, *J* = 14.2 Hz, 2H), 1.88 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -112.92 (dt, *J* = 38.8, 14.4 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.5 (d, *J* = 267.0 Hz), 140.7, 140.3 (d, *J* = 2.5 Hz), 131.9 (d, *J* = 2.6 Hz), 129.3 (d, *J* = 7.2 Hz), 128.9, 127.5, 127.3, 127.1, 107.3 (d, *J* = 6.6 Hz), 62.1 (d, *J* = 32.7 Hz).

EI-HRMS: mass spectrometry: m/z calcd for $C_{15}H_{13}OF$ $[M]^+$ 228.09504, measured 228.09430

IR (neat, cm^{-1}): ṽ: 3308, 2923, 2854, 2094, 1682, 1633, 1480, 1335, 1161, 1027, 968, 757.



(*Z*)-3-(4-(*tert*-butoxy)phenyl)-2-fluoroprop-2-en-1-ol

8i: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 43 mg product was obtained by 96% isolated yield as yellow liquid.

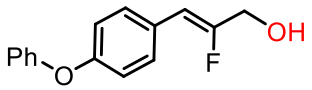
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 5.72 (d, *J* = 38.8 Hz, 1H), 4.26 (d, *J* = 14.9 Hz, 2H), 1.90 (b, 1H), 1.35 (s, 9H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.16 (dt, *J* = 39.0, 15.0 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.5 (d, *J* = 265.1 Hz), 154.9 (d, *J* = 3.0 Hz), 129.5 (d, *J* = 7.3 Hz), 128.0 (d, *J* = 2.9 Hz), 124.2, 107.3 (d, *J* = 7.1 Hz), 79.0, 62.1 (d, *J* = 32.5 Hz), 29.0.

EI-HRMS: mass spectrometry: m/z calcd for $C_{13}H_{14}O_2F$ $[M]^+$ 224.12126, measured 224.12078

IR (neat, cm^{-1}): ṽ: 3378, 2976, 2860, 1604, 1569, 1505, 1390, 1366, 1241, 1157, 1021, 890.



(*Z*)-2-fluoro-3-(4-phenoxyphenyl)prop-2-en-1-ol

8j: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 42 mg product was obtained by 86% isolated yield as yellow liquid.

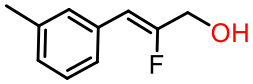
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.46 (m, 2H), 7.38 – 7.32 (m, 2H), 7.15 – 7.10 (m, 1H), 7.05 – 7.01 (m, 2H), 6.99 – 6.96 (m, 2H), 5.76 (d, *J* = 38.6 Hz, 1H), 4.28 (d, *J* = 14.7 Hz, 2H), 1.90 (b, 1H).

^{19}F NMR (564 MHz, Chloroform-*d*) δ -114.94 (dt, *J* = 38.6, 14.8 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.6 (d, *J* = 265.4 Hz), 157.0, 156.8 (d, *J* = 3.1 Hz), 130.3 (d, *J* = 7.4 Hz), 129.9, 127.9 (d, *J* = 2.9 Hz), 123.6, 119.3, 118.8, 107.1 (d, *J* = 7.2 Hz), 62.1 (d, *J* = 32.4 Hz).

EI-HRMS: mass spectrometry: m/z calcd for $C_{15}H_{13}O_2F$ $[M]^+$ 244.08996 measured 224.08931

IR (neat, cm^{-1}): ṽ: 3357, 2921, 2853, 1692, 1633, 1589, 1419, 1342, 1284, 1158, 1070, 864, 693.

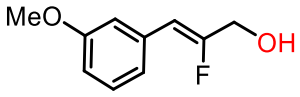


(*Z*)-2-fluoro-3-(*m*-tolyl)prop-2-en-1-ol

8k: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 30 mg product was obtained by 90% isolated yield as yellow liquid.

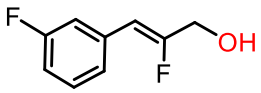
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.22 (m, 2H), 7.18 – 7.13 (m, 1H), 7.01 – 6.98 (m, 1H), 5.67 (d, *J* = 38.8 Hz, 1H), 4.19 (d, *J* = 14.5 Hz, 2H), 2.27 (s, 3H), 1.88 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.47 (dt, *J* = 38.5, 14.2 Hz).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.1 (d, *J* = 266.4 Hz), 138.2, 132.7 (d, *J* = 3.1 Hz), 129.5 (d, *J* = 7.3 Hz), 128.5, 128.5 (d, *J* = 2.8 Hz), 126.0 (d, *J* = 7.7 Hz), 107.7 (d, *J* = 6.8 Hz), 62.1 (d, *J* = 32.7 Hz), 21.6.
EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_{11}OF$ $[M]^+$ 166.07939, measured 166.07884
IR (neat, cm^{-1}): ṽ: 3307, 2922, 2853, 2161, 1662, 1547, 1461, 1276, 1159, 1076, 855, 696.



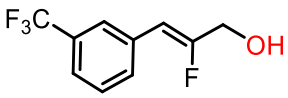
(*Z*)-2-fluoro-3-(3-methoxyphenyl)prop-2-en-1-ol

8l: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 34 mg product was obtained by 93% isolated yield as yellow liquid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.72 (d, *J* = 38.9 Hz, 1H), 4.27 (d, *J* = 15.4 Hz, 2H), 3.81 (s, 3H), 1.85 (b, 1H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.18 (dt, *J* = 39.0, 15.3 Hz).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.0 (d, *J* = 2.9 Hz), 157.0 (d, *J* = 264.1 Hz), 130.2 (d, *J* = 7.3 Hz), 125.5 (d, *J* = 2.9 Hz), 114.1, 107.4 (d, *J* = 7.2 Hz), 62.2 (d, *J* = 32.1 Hz), 55.4.
EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_{11}O_2F$ $[M]^+$ 182.07431, measured 182.07370
IR (neat, cm^{-1}): ṽ: 3371, 2928, 2855, 2086, 1694, 1581, 1458, 1294, 1161, 1041, 866, 778.



(*Z*)-2-fluoro-3-(3-fluorophenyl)prop-2-en-1-ol

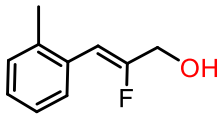
8m: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 28 mg product was obtained by 82% isolated yield as yellow liquid.
^{1}H NMR (600 MHz, Chloroform-d) δ 7.24 – 7.13 (m, 4H), 6.91 – 6.85 (m, 1H), 5.71 (d, J = 37.9 Hz, 1H), 4.22 (d, J = 13.4 Hz, 2H), 1.81 (b, 1H).
19F NMR (565 MHz, Chloroform-d) δ -111.41 (dt, J = 38.0, 13.4 Hz), -113.17 – -113.26 (m).
13C NMR (151 MHz, Chloroform-d) δ 163.01 (d, J = 244.7 Hz), 159.2 (d, J = 268.3 Hz), 134.9 (dd, J = 8.4, 2.5 Hz), 130.0 (d, J = 8.5 Hz), 124.6 (dd, J = 6.5, 2.9 Hz), 115.5 (dd, J = 22.5, 8.4 Hz), 114.6 (dd, J = 21.3, 2.2 Hz), 106.6 (dd, J = 6.3, 2.7 Hz), 61.8 (d, J = 33.2 Hz).
EI-HRMS: mass spectrometry: m/z calcd for C9H8OF2 [M]+ 170.05432, measured 170.05404
IR (neat, cm-1): ṽ: 3348, 2927, 2861, 1694, 1583, 1486, 1344, 1252, 1158, 1026, 951, 877, 782.



(*Z*)-2-fluoro-3-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol

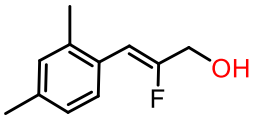
8n: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 36 mg product was obtained by 82% isolated yield as yellow liquid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.43 (m, 1H), 5.85 (d, *J* = 37.9 Hz, 1H), 4.32 (d, *J* = 13.0 Hz, 2H), 1.85 (b, 1H).
^{19}F NMR (564 MHz, Chloroform-*d*) δ -62.85, -111.15 (dt, *J* = 38.0, 13.1 Hz).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 159.6 (d, *J* = 268.8 Hz), 133.6 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 7.1 Hz), 131.1 (d, *J* = 32.4 Hz), 129.1, 125.6 – 125.3 (m), 124.2 (q, *J* = 270.0 Hz), 124.5 – 123.9 (m), 106.2 (d, *J* = 6.1 Hz), 61.7 (d, *J* = 33.0 Hz).
EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_8OF_4$ $[M]^+$ 220.05113, measured 220.05057
IR (neat, cm^{-1}): ṽ: 3379, 2930, 2858, 1697, 1447, 1327, 1163, 1124, 1037, 904, 798, 697.



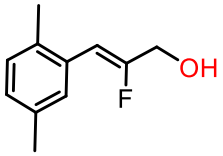
(*Z*)-2-fluoro-3-(*o*-tolyl)prop-2-en-1-ol

8o: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 25 mg product was obtained by 75% isolated yield as yellow liquid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.14 (m, 3H), 5.93 (d, *J* = 37.9 Hz, 1H), 4.32 (d, *J* = 14.0 Hz, 2H), 2.32 (s, 3H), 1.82 (b, 1H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.47 (dt, *J* = 38.0, 14.0 Hz).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.1 (d, *J* = 265.5 Hz), 136.0, 131.3 (d, *J* = 1.9 Hz), 130.2, 129.4 (d, *J* = 9.5 Hz), 127.7, 126.07, 105.0 (d, *J* = 7.8 Hz), 62.1 (d, *J* = 33.2 Hz), 20.3.
EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_{11}OF$ [M]+ 166.07939, measured 166.07916
IR (neat, cm-1): ṽ: 3355, 2925, 2862, 1692, 1454, 1383, 1198. 1161, 1070, 1025, 876, 752.



(*Z*)-3-(2,4-dimethylphenyl)-2-fluoroprop-2-en-1-ol

8p: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 32 mg product was obtained by 89% isolated yield as yellow liquid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.05 – 6.97 (m, 2H), 5.89 (d, *J* = 38.0 Hz, 1H), 4.30 (d, *J* = 14.5 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H), 1.87 (b, 1H).
^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.08 (dt, *J* = 38.1, 14.4 Hz).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.7 (d, *J* = 264.7 Hz), 137.5, 135.9, 131.0, 129.3 (d, *J* = 9.7 Hz), 128.3 (d, *J* = 2.3 Hz), 126.8, 105.0 (d, *J* = 7.7 Hz), 62.2 (d, *J* = 32.8 Hz), 21.3, 20.2.
EI-HRMS: mass spectrometry: m/z calcd for $C_{11}H_{13}OF$ [M]+ 180.09504, measured 180.09453
IR (neat, cm-1): ṽ: 3358, 2923, 2860, 1691, 1614, 1499, 1448, 1343, 1219, 1165, 1071, 1024, 854.



(*Z*)-3-(2,5-dimethylphenyl)-2-fluoroprop-2-en-1-ol

8q: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 25 mg product was obtained by 69% isolated yield as yellow liquid.

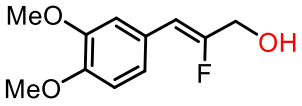
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.00 – 6.96 (m, 1H), 5.90 (d, *J* = 38.0 Hz, 1H), 4.31 (d, *J* = 14.2 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 3H), 1.88 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.60 (dt, *J* = 38.1, 14.1 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.9 (d, *J* = 265.3 Hz), 135.4, 132.9, 131.0, 130.1, 130.0 (d, *J* = 9.5 Hz), 128.5, 105.2 (d, *J* = 7.7 Hz), 62.2 (d, *J* = 33.2 Hz), 21.2, 19.8.

EI-HRMS: mass spectrometry: m/z calcd for $C_{11}H_{13}OF$ [M]+ 180.09504, measured 180.09482

IR (neat, cm-1): ṽ: 3347, 2924, 2863, 1692, 1613, 1497, 1451, 1345, 1282, 1166, 1071, 1026, 873.



(*Z*)-3-(3,4-dimethoxyphenyl)-2-fluoroprop-2-en-1-ol

8r: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 33 mg product was obtained by 79% isolated yield as yellow liquid.

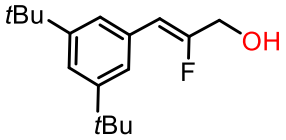
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 2.0 Hz, 1H), 7.02 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.71 (d, *J* = 38.6 Hz, 1H), 4.27 (d, *J* = 15.2 Hz, 2H), 3.88 (s, 6H), 1.99 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.78 (dt, *J* = 38.8, 15.4 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.1 (d, *J* = 264.2 Hz), 148.9, 148.7 (d, *J* = 2.6 Hz), 125.8 (d, *J* = 2.9 Hz), 121.9 (d, *J* = 6.3 Hz), 111.8 (d, *J* = 8.7 Hz), 111.1, 107.6 (d, *J* = 6.7 Hz), 62.2 (d, *J* = 32.2 Hz), 56.0, 55.9.

EI-HRMS: mass spectrometry: m/z calcd for $C_{11}H_{13}O_3F$ $[M]^+$ 212.08487, measured 212.08423

IR (neat, cm^{-1}): ṽ: 3461, 2927, 2843, 1689, 1602, 1513, 1416, 1263, 1148, 1022, 866, 766.



(*Z*)-3-(3,5-di-*tert*-butylphenyl)-2-fluoroprop-2-en-1-ol

8s: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 40 mg product was obtained by 76% isolated yield as yellow liquid.

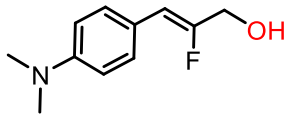
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 1.8 Hz, 2H), 7.35 (t, *J* = 1.8 Hz, 1H), 5.81 (d, *J* = 38.8 Hz, 1H), 4.29 (d, *J* = 14.8 Hz, 2H), 1.89 (b, 1H), 1.34 (s, 18H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.29 (dt, *J* = 39.0, 15.0 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.7 (d, *J* = 265.7 Hz), 151.0, 131.9 (d, *J* = 3.0 Hz), 123.2 (d, *J* = 7.2 Hz), 121.9 (d, *J* = 2.2 Hz), 108.6 (d, *J* = 6.6 Hz), 62.3 (d, *J* = 32.3 Hz), 35.0, 31.6.

EI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{25}OF$ $[M]^+$ 26418894, measured 264.18828

IR (neat, cm^{-1}): ṽ: 3350, 2958, 2867, 2156, 1692, 1694, 1461, 1362, 1248, 1162, 1072, 1024, 863.



(*Z*)-3-(4-(dimethylamino)phenyl)-2-fluoroprop-2-en-1-ol

8t: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 32 mg product was obtained by 82% isolated yield as yellow solid.

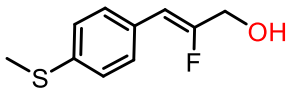
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.66 (d, *J* = 39.4 Hz, 1H), 4.25 (d, *J* = 16.4 Hz, 2H), 2.97 (s, 6H), 1.91 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.94 (dt, *J* = 39.9, 16.5 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9 (d, *J* = 261.8 Hz), 149.9 (d, *J* = 2.4 Hz), 129.9 (d, *J* = 7.2 Hz), 121.1 (d, *J* = 2.8 Hz), 112.4, 108.1 (d, *J* = 7.4 Hz), 62.5 (d, *J* = 31.6 Hz), 40.5.

EI-HRMS: mass spectrometry: m/z calcd for $C_{11}H_{14}ONF$ [M]+ 195.10594, measured 195.10523

IR (neat, cm-1): ṽ: 3382, 2920, 2853, 1690, 1607, 1522, 1441, 1355, 1230, 1197, 1156, 1067, 1008.



(*Z*)-2-fluoro-3-(4-(methylthio)phenyl)prop-2-en-1-ol

8u: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 32 mg product was obtained by 81% isolated yield as yellow solid.

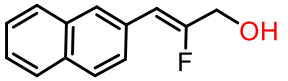
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 5.73 (d, *J* = 38.7 Hz, 1H), 4.27 (d, *J* = 14.5 Hz, 2H), 2.49 (s, 3H), 1.92 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.38 (dt, *J* = 38.6, 14.4 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.1 (d, *J* = 266.4 Hz), 138.0 (d, *J* = 2.8 Hz), 129.6 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 7.3 Hz), 126.5, 107.2 (d, *J* = 6.8 Hz), 62.1 (d, *J* = 32.6 Hz), 15.8.

EI-HRMS: mass spectrometry: m/z calcd for $C_{10}H_{11}OFS$ [M]+ 198.05146, measured 198.05086

IR (neat, cm-1): ṽ: 3365, 2920, 2854, 1690, 1593, 1492, 1408, 1345, 1208, 1159, 1095, 1006, 866.



(*Z*)-2-fluoro-3-(naphthalen-2-yl)prop-2-en-1-ol

8v: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 31 mg product was obtained by 77% isolated yield as yellow solid.

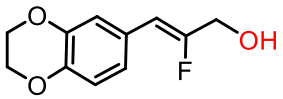
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.85 – 7.78 (m, 3H), 7.71 – 7.66 (m, 1H), 7.50 – 7.44 (m, 2H), 5.94 (d, *J* = 38.7 Hz, 1H), 4.34 (d, *J* = 14.2 Hz, 2H), 1.98 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -112.93 (dt, *J* = 39.0, 14.2 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.4 (d, *J* = 267.0 Hz), 133.4, 132.6 (d, *J* = 2.0 Hz), 130.3 (d, *J* = 3.1 Hz), 128.1, 128.1, 127.9 (d, *J* = 7.4 Hz), 127.5, 126.5 (d, *J* = 7.7 Hz), 126.2, 126.1, 107.7 (d, *J* = 6.7 Hz), 62.0 (d, *J* = 32.7 Hz).

EI-HRMS: mass spectrometry: m/z calcd for $C_{13}H_{11}OF$ $[M]^+$ 202.07939, measured 202.07884

IR (neat, cm^{-1}): ṽ: 3311, 2922, 3854, 1687, 1503, 1458, 1355, 1279, 1160, 1015, 952, 831.



(*Z*)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-fluoroprop-2-en-1-ol

8w: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 35 mg product was obtained by 83% isolated yield as yellow liquid.

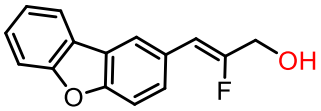
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 2.1 Hz, 1H), 6.97 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.65 (d, *J* = 38.5 Hz, 1H), 4.27 – 4.23 (m, 6H), 1.93 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.27 (dt, *J* = 38.5, 15.0 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.3 (d, *J* = 265.0 Hz), 143.4, 143.2 (d, *J* = 2.6 Hz), 126.4 (d, *J* = 2.8 Hz), 122.4 (d, *J* = 6.9 Hz), 117.6 (d, *J* = 7.9 Hz), 117.4, 107.3 (d, *J* = 6.8 Hz), 64.6, 64.5, 62.1 (d, *J* = 32.1 Hz).

EI-HRMS: mass spectrometry: m/z calcd for $C_{11}H_{11}O_3F$ [M]+ 210.06922, measured 210.06862

IR (neat, cm-1): ṽ: 3315, 2924, 2857, 1689, 1581, 1505, 1428, 1339, 1287, 1158, 1022, 881.



(*Z*)-3-(dibenzo[*b*,*d*]furan-2-yl)-2-fluoroprop-2-en-1-ol

8x: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 34 mg product was obtained by 70% isolated yield as yellow solid.

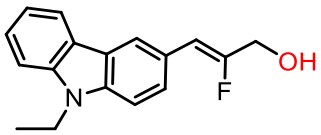
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 1.7 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.32 – 7.26 (m, 1H), 5.87 (d, *J* = 38.5 Hz, 1H), 4.28 (d, *J* = 15.2 Hz, 2H), 1.92 (b, 1H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.95 (dt, *J* = 38.6, 14.9 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.6 (d, *J* = 265.3 Hz), 156.7, 155.5 (d, *J* = 2.8 Hz), 128.3 (d, *J* = 6.6 Hz), 127.7 (d, *J* = 2.6 Hz), 127.5, 124.7, 124.2, 123.0, 120.9 (d, *J* = 8.2 Hz), 120.9, 111.9, 111.7, 107.7 (d, *J* = 6.8 Hz), 62.2 (d, *J* = 32.5 Hz).

EI-HRMS: mass spectrometry: m/z calcd for $C_{15}H_{11}O_2F$ [M]+ 242.07431, measured 242.07353

IR (neat, cm-1): ṽ: 3353, 2921, 2853, 1685, 1536, 1450, 1343, 1287, 1200, 1153, 1016, 897, 740.



(*Z*)-3-(9-ethyl-9*H*-carbazol-3-yl)-2-fluoroprop-2-en-1-ol

8y: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 45 mg product was obtained by 84% isolated yield as yellow solid.

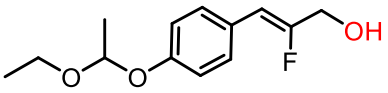
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.55 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.33 – 7.28 (m, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.13 (m, 1H), 5.86 (d, *J* = 39.0 Hz, 1H), 4.30 – 4.21 (m, 4H), 1.89 (b, 1H), 1.34 (t, *J* = 7.3 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.78 (dt, *J* = 39.1, 16.0 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.6 (d, *J* = 263.0 Hz), 140.4, 139.4 (d, *J* = 2.2 Hz), 126.9 (d, *J* = 6.8 Hz), 126.0, 123.7 (d, *J* = 2.6 Hz), 123.2, 123.1, 121.0 (d, *J* = 7.5 Hz), 120.6, 119.2, 108.6 (d, *J* = 30.1 Hz), 62.5 (d, *J* = 32.0 Hz), 37.7, 13.9.

EI-HRMS: mass spectrometry: m/z calcd for $C_{17}H_{16}ONF$ $[M]^+$ 269.12159, measured 269.12101

IR (neat, cm^{-1}): ṽ: 3277, 2923, 2854, 1678, 1596, 1468, 1377, 1336, 1229, 1155, 1008, 894, 749.



(*Z*)-3-(4-(1-ethoxyethoxy)phenyl)-2-fluoroprop-2-en-1-ol

8z: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 34 mg product was obtained by 71% isolated yield as yellow solid.

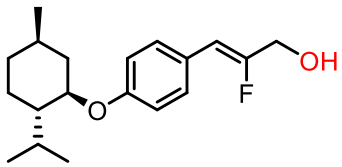
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.71 (d, *J* = 38.8 Hz, 1H), 5.39 (q, *J* = 5.3 Hz, 1H), 4.26 (d, *J* = 15.1 Hz, 2H), 3.78 (dq, *J* = 9.3, 7.1 Hz, 1H), 3.54 (dq, *J* = 9.3, 7.0 Hz, 1H), 2.03 (b, 1H), 1.50 (d, *J* = 5.3 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.66 (dt, *J* = 39.0, 15.3 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.3 (d, *J* = 259.7 Hz), 156.4 (d, *J* = 8.5 Hz), 130.1 (d, *J* = 7.7 Hz), 126.5 (d, *J* = 3.1 Hz), 117.4, 107.3 (d, *J* = 7.4 Hz), 99.6, 62.1 (d, *J* = 32.5 Hz), 61.6, 20.4, 15.3.

EI-HRMS: mass spectrometry: m/z calcd for $C_9H_9O_2F$ [M]+ 168.05866, measured 168.05853

IR (neat, cm-1): ṽ: 3155, 2927, 2857, 1693, 1608, 1511, 1439, 1342, 1222, 1163, 1020, 828.



(*Z*)-2-fluoro-3-(4-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)prop-2-en-1-ol

8aa: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 52 mg product was obtained by 85% isolated yield as yellow liquid.

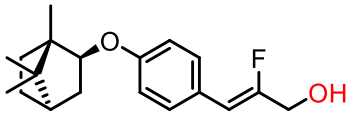
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.70 (d, *J* = 38.9 Hz, 1H), 4.26 (d, *J* = 15.4 Hz, 2H), 4.07 – 4.01 (m, 1H), 2.23 – 2.18 (m, 1H), 2.18 – 2.13 (m, 1H), 1.95 (s, 1H), 1.77 – 1.68 (m, 2H), 1.55 – 1.48 (m, 1H), 1.15 – 1.05 (m, 1H), 1.05 – 0.98 (m, 1H), 0.97 – 0.89 (m, 7H), 0.77 (d, *J* = 7.0 Hz, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.41 (dt, *J* = 38.9, 15.4 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.9 (d, *J* = 2.9 Hz), 156.8 (d, *J* = 263.9 Hz), 130.2 (d, *J* = 7.2 Hz), 125.2 (d, *J* = 2.9 Hz), 115.8, 107.5 (d, *J* = 7.2 Hz), 77.7, 62.2 (d, *J* = 32.2 Hz), 48.2, 40.4, 34.6, 31.6, 26.24, 23.9, 22.3, 20.9, 16.7.

EI-HRMS: mass spectrometry: m/z calcd for $C_{19}H_{27}O_2F$ [M]+ 306.19952, measured 306.19885

IR (neat, cm-1): ṽ: 3361, 2925, 2866, 1693, 1607, 1507, 1455, 1291, 1245, 1157, 1014, 858, 733.



(*Z*)-2-fluoro-3-(4-(((1*S*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)phenyl)prop-2-en-1-ol

8bb: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 15:1). 56 mg product was obtained by 92% isolated yield as yellow liquid.

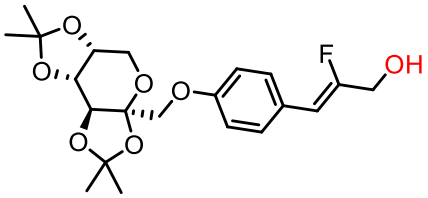
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.70 (d, *J* = 38.9 Hz, 1H), 4.36 – 4.30 (m, 1H), 4.26 (d, *J* = 15.5 Hz, 2H), 2.41 – 2.32 (m, 1H), 2.26 – 2.20 (m, 1H), 1.93 (s, 1H), 1.79 – 1.72 (m, 2H), 1.38 – 1.30 (m, 1H), 1.29 – 1.24 (m, 1H), 1.11 (dd, *J* = 13.3, 3.4 Hz, 1H), 0.95 (s, 3H), 0.92 (d, *J* = 4.0 Hz, 6H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -116.54 (dt, *J* = 39.1, 15.7 Hz).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.7 (d, *J* = 2.9 Hz), 156.7 (d, *J* = 263.5 Hz), 130.1 (d, *J* = 7.2 Hz), 124.9 (d, *J* = 2.9 Hz), 115.6, 107.6 (d, *J* = 7.2 Hz), 83.0, 62.3 (d, *J* = 32.0 Hz), 49.6, 47.7, 45.3, 37.0, 28.1, 26.9, 19.9, 19.1, 13.9.

EI-HRMS: mass spectrometry: m/z calcd for $C_{19}H_{25}O_2F$ [M]+ 304.18386, measured 304.18317

IR (neat, cm-1): ṽ: 3352, 2948, 2876, 1694, 1607, 1508, 1454, 1366, 1296, 1248, 1157, 1024, 858.



(*Z*)-2-fluoro-3-(4-(((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methoxy)phenyl)prop-2-en-1-ol

8cc: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 8:1). 65 mg product was obtained by 79% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.70 (d, *J* = 38.9 Hz, 1H), 4.64 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.54 (d, *J* = 2.6 Hz, 1H), 4.29 – 4.22 (m, 3H), 4.16 (d, *J* = 10.1 Hz, 1H), 4.04 (d, *J* = 10.1 Hz, 1H), 3.97 (dd, *J* = 13.0, 1.9 Hz, 1H), 3.79 (d, *J* = 13.0 Hz, 1H), 2.04 (b, 1H), 1.56 (s, 3H), 1.48 (d, *J* = 2.7 Hz, 6H), 1.34 (s, 3H).

^{19}F NMR (565 MHz, Chloroform-*d*) δ -115.84 (dt, *J* = 38.7, 15.1 Hz).

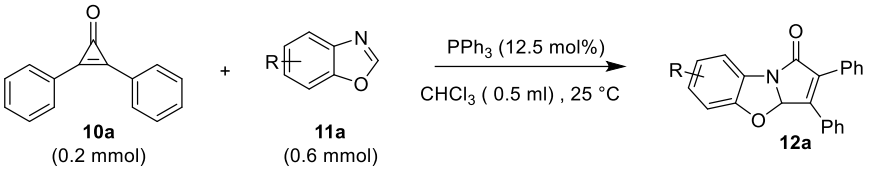
^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.9 (d, *J* = 2.7 Hz), 157.1 (d, *J* = 264.2 Hz), 130.1 (d, *J* = 7.2 Hz), 126.0 (d, *J* = 2.7 Hz), 114.8, 109.1 (d, *J* = 11.2 Hz), 107.2 (d, *J* = 7.1 Hz), 102.3, 71.1, 70.3, 70.1, 68.9, 62.1 (d, *J* = 32.3 Hz), 61.3, 26.7, 26.1, 25.5, 24.1.

EI-HRMS: mass spectrometry: m/z calcd for $C_{21}H_{27}O_7F$ [M]+ 410.17408, measured 410.17298

IR (neat, cm-1): ṽ: 3315, 2922, 2853, 2158, 1659, 1632, 1510, 1458, 1377, 1295, 1162, 1066, 1019, 863.

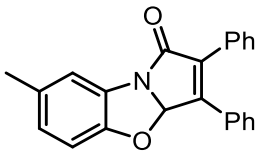
4.2.3 Phosphine Catalyzed Dearomative [3+2] Cycloaddition of Benzoxazoles with a Cyclopropenone

General procedure for the reaction



Triphenylphosphine (6.55 mg, 0.025 mmol) and cyclopropenone 10a (0.2 mmol),[3] Benzoxazole 11a (0.6 mmol) was added sequentially, then the mixture was stirred at 25 ºC for about 15 h to the starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. A portion of the residue was analyzed with 1H NMR to determine the diastereomeric ratio and recovered. The crude was purified by column chromatography to give the products 12a.

Preparation of the product



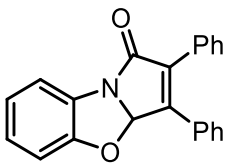
7-methyl-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12a: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 65 mg product was obtained by 96% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 - 7.54 (m, 2H), 7.46 - 7.42 (m, 2H), 7.41 - 7.34 (m, 7H), 6.87 - 6.84 (m, 2H), 6.78 (d, J = 7.8 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.92, 153.20, 150.86, 134.86, 131.77, 131.34, 130.54, 130.49, 130.27, 129.59, 129.20, 128.99, 128.78, 128.72, 125.85, 117.77, 109.21, 97.16, 21.19.ESI-HRMS: mass spectrometry: m/z calc. 362.11515 $[C_{23}H_{17}O_2NNa]^+$, measured 362.11467.

IR (neat, cm^{-1}): ṽ: 3426, 3054, 2915, 1722, 1601, 1485, 1346, 1250, 1192, 1128, 1081, 1030, 959, 898, 776, 690.

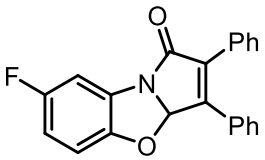


2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12b: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 57 mg product was obtained by 88% isolated yield as yellow solid.

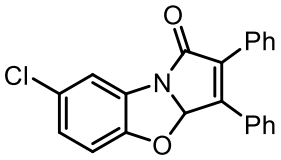
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 - 7.56 (m, 2H), 7.55 - 7.51 (m, 1H), 7.47 - 7.43 (m, 2H), 7.42 - 7.35 (m, 6H), 7.10 - 7.05 (m, 1H), 7.02 - 6.97 (m, 1H), 6.93 - 6.89 (m, 1H), 6.88 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 175.00, 155.27, 150.78, 134.84, 131.31, 130.53, 130.45, 130.38, 129.58, 129.24, 129.00, 128.79, 128.72, 125.82, 122.00, 117.10, 109.75, 97.08.
ESI-HRMS: mass spectrometry: m/z calc. 348.09950 $[C_{22}H_{15}O_2NNa]^+$, measured 348.09938.
IR (neat, cm^{-1}): ṽ: 3429, 3062, 2920, 1724, 1599, 1473, 1364, 1243, 1192, 1141, 1105, 1001, 948, 848, 752, 688.



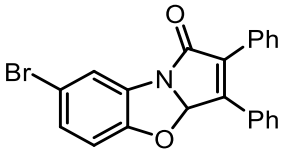
7-fluoro-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12c: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 41 mg product was obtained by 60% isolated yield as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 - 7.50 (m, 2H), 7.44 - 7.32 (m, 8H), 7.27 - 7.22 (m, 1H), 6.89 (s, 1H), 6.80 - 6.75 (m, 1H), 6.75 - 6.70 (m, 1H).
^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.65, 158.78, 157.19, 151.28 (d, J = 2.3 Hz), 151.03, 134.74, 131.13 (d, J = 12.0 Hz), 130.71, 130.70 (d, J = 130.5 Hz), 129.57, 129.38, 129.06, 128.87, 128.74, 111.35 (d, J = 24.2 Hz), 109.44 (d, J = 9.2 Hz), 105.76 (d, J = 28.6 Hz), 97.89.
^{19}F NMR (564 MHz, Chloroform-*d*) δ -120.59 – -120.70 (m).
ESI-HRMS: mass spectrometry: m/z calc. 366.09008 $[C_{22}H_{14}O_2NFNa]^+$, measured 366.08986.
IR (neat, cm^{-1}): ṽ: 3425, 3062, 2922, 1716, 1617, 1480, 1351, 1252, 1172, 1122, 1075, 946, 804, 761, 692.



7-chloro-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12d: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 42 mg product was obtained by 58% isolated yield as yellow solid.
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 - 7.52 (m, 2H), 7.49 (d, J = 2.4 Hz, 1H), 7.45 - 7.33 (m, 8H), 7.02 (dd, J = 8.4, 2.4 Hz, 1H), 6.89 (s, 1H), 6.79 (d, J = 9.0 Hz, 1H).
^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.65, 153.96, 150.95, 134.70, 131.47, 131.06, 130.73, 130.19, 129.55, 129.39, 129.06, 128.85, 128.71, 126.78, 125.49, 117.58, 110.25, 97.77.
ESI-HRMS: mass spectrometry: m/z calc. 382.06053 $[C_{22}H_{14}O_2NClNa]^+$, measured 382.06010.
IR (neat, cm^{-1}): ṽ: 3424, 2049, 2919, 1716, 1602, 1473, 1344, 1302, 1241, 1192, 1145, 1088, 958, 868, 776, 696.



7-bromo-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

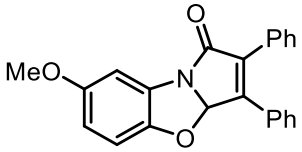
12e: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 45 mg product was obtained by 56% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, J = 2.4 Hz, 1H), 7.56 - 7.51 (m, 2H), 7.44 - 7.33 (m, 8H), 7.17 (dd, J = 8.4, 1.8 Hz, 1H), 6.89 (s, 1H), 6.75 (d, J = 8.4 Hz, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.68, 154.51, 150.95, 134.73, 131.82, 131.07, 130.75, 130.20, 129.57, 129.41, 129.08, 128.87, 128.72, 128.50, 120.29, 113.68, 110.90, 97.70.

ESI-HRMS: mass spectrometry: m/z calc. 426.01001 $[C_{22}H_{14}O_2NBrNa]^+$, measured 426.00942.

IR (neat, cm^{-1}): ṽ: 3419, 3050, 2910, 1712, 1599, 1471, 1343, 1303, 1242, 1190, 1143, 1086, 956, 869, 774, 690.



7-methoxy-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

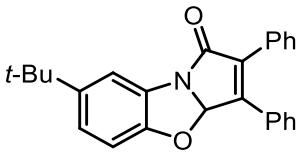
12f: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 65 mg product was obtained by 92% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 - 7.54 (m, 1H), 7.46 - 7.34 (m, 4H), 7.16 (d, J = 3.0 Hz, 0H), 6.87 (s, 0H), 6.61 - 6.55 (m, 0H), 3.81 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.67, 155.16, 150.95, 149.22, 134.76, 131.26, 130.97, 130.52, 130.47, 129.56, 129.21, 128.98, 128.78, 128.71, 110.13, 109.48, 104.29, 97.44, 56.20.

ESI-HRMS: mass spectrometry: m/z calc. 378.11006 $[C_{23}H_{17}O_3NNa]^+$, measured 378.10956.

IR (neat, cm^{-1}): ṽ: 3425, 3062, 2920, 1720, 1619, 1481, 1369, 1308, 1256, 1185, 1028, 958, 871, 777, 690.



7-(*tert*-butyl)-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

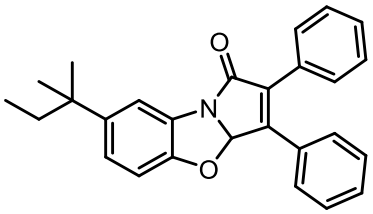
12g: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 74 mg product was obtained by 97% isolated yield as yellow liquid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 - 7.56 (m, 3H), 7.47 -7.43 (m, 2H), 7.41 - 7.34 (m, 6H), 7.08 (dd, J = 8.4, 2.4 Hz, 1H), 6.86 (s, 1H), 6.83 (d, J = 8.4 Hz, 1H), 1.36 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 175.04, 153.04, 150.83, 145.53, 134.83, 131.40, 130.53, 130.48, 130.22, 129.61, 129.20, 128.99, 128.75, 128.74, 122.23, 114.54, 108.84, 97.35, 34.80, 31.74.

ESI-HRMS: mass spectrometry: m/z calc. 382.18016 $[C_{26}H_{24}O_2N]^+$, measured 382,18022.

IR (neat, cm^{-1}): ṽ: 3434, 3058, 2961, 1720, 1608, 1485, 1341, 1233, 1196, 1140, 1060, 954, 779, 735, 693.



7-(*tert*-pentyl)-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

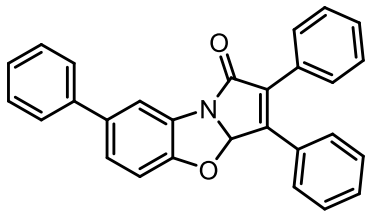
12h: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 76 mg product was obtained by 96% isolated yield as yellow liquid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 - 7.57 (m, 2H), 7.53 (d, J = 1.8 Hz, 1H), 7.48 - 7.44 (m, 2H), 7.43 - 7.35 (m, 6H), 7.03 (dd, J = 8.4, 1.8 Hz, 1H), 6.86 (s, 1H), 6.84 (d, J = 8.4 Hz, 1H), 1.68 (q, J = 7.2 Hz, 2H), 1.32 (s, 6H), 0.74 (t, J = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.93, 152.88, 150.67, 143.72, 134.73, 131.33, 130.42, 130.36, 130.15, 129.52, 129.10, 128.88, 128.64, 122.88, 115.00, 108.64, 97.25, 37.92, 37.01, 28.85, 28.72, 9.19.

ESI-HRMS: mass spectrometry: m/z calc. 418.17775 $[C_{27}H_{25}O_2NNa]^+$, measured 418.17641.

IR (neat, cm^{-1}): ṽ: 3327, 3062, 2962, 1716, 1609, 1487, 1439, 1340, 1246, 1139, 1100, 1064, 959, 907, 807, 692.



2,3,7-triphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

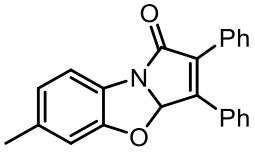
12i: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 56 mg product was obtained by 70% isolated yield as yellow liquid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, J = 1.8 Hz, 1H), 7.63 - 7.57 (m, 4H), 7.48 - 7.37 (m, 10H), 7.36 - 7.33 (m, 1H), 7.31 (dd, J = 8.4, 1.8 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.94 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.84, 154.73, 150.77, 140.62, 135.74, 134.78, 131.17, 130.91, 130.47, 130.31, 129.49, 129.17, 128.92, 128.76, 128.70, 128.63, 127.02, 127.01, 124.57, 115.81, 109.65, 97.44.

ESI-HRMS: mass spectrometry: m/z calc. 424.13080 $[C_{28}H_{19}O_2NNa]^+$, measured 424.12939.

IR (neat, cm^{-1}): ṽ: 3438, 3065, 2908, 1721, 1600, 1475, 1434, 1347, 1233, 1141, 1079, 1029, 944, 807, 754, 686.



6-methyl-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12j: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from

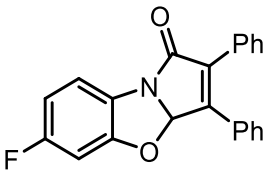
60:1). 66 mg product was obtained by 97% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 - 7.54 (m, 2H), 7.45 - 7.34 (m, 8H), 6.84 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.73 (s, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 175.12, 155.44, 150.67, 136.06, 134.90, 131.39, 130.54, 130.46, 129.58, 129.19, 128.99, 128.78, 128.72, 127.99, 122.20, 116.59, 110.60, 97.26, 21.66.

ESI-HRMS: mass spectrometry: m/z calc. 362.11515 $[C_{23}H_{17}O_2NNa]^+$, measured 362.11459.

IR (neat, cm^{-1}): ṽ: 3417, 1060, 2924, 1713, 1599, 1493, 1440, 1344, 1243, 1137, 1081, 954, 882, 809, 779, 692.



6-fluoro-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12k: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 36 mg product was obtained by 52% isolated yield as yellow solid.

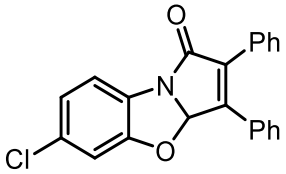
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 - 7.51 (m, 2H), 7.44 - 7.33 (m, 9H), 6.89 (s, 1H), 6.70 - 6.62 (m, 2H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 175.29, 161.80, 160.18, 156.09 (d, *J* = 13.7 Hz), 150.59, 130.73 (d, *J* = 132.0 Hz), 130.69, 129.58, 129.38, 129.08, 128.85, 128.69, 126.70 (d, *J* = 3.0 Hz), 117.08 (d, *J* = 10.3 Hz), 107.85 (d, *J* = 23.7 Hz), 99.13 (d, *J* = 28.8 Hz), 98.27.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -115.09 - -115.16 (m).

ESI-HRMS: mass spectrometry: m/z calc. 366.09008 $[C_{22}H_{14}O_2NFNa]^+$, measured 366.09027.

IR (neat, cm^{-1}): ṽ: 3274, 3083, 2920, 1724, 1617, 1481, 1445, 1345, 1314, 1233, 1118, 1080, 945, 844, 809, 690.



6-chloro-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

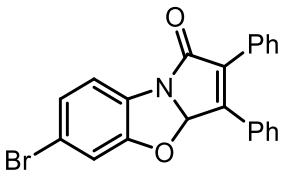
12l: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 30 mg product was obtained by 42% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 - 7.52 (m, 2H), 7.44 - 7.34 (m, 9H), 6.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.89 (d, *J* = 1.8 Hz, 1H), 6.89 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.94, 155.92, 150.73, 134.85, 131.12, 130.99, 130.73, 130.23, 129.57, 129.41, 129.36, 129.09, 128.87, 128.72, 121.92, 117.40, 110.72, 97.95.

ESI-HRMS: mass spectrometry: m/z calc. 382.06053 $[C_{22}H_{14}O_2NClNa]^+$, measured 382.06057.

IR (neat, cm^{-1}): ṽ: 3415, 1056, 2923, 1710, 1604, 1478, 1441, 1356, 1314, 1243, 1133, 1053, 940, 894, 801, 691.



6-bromo-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

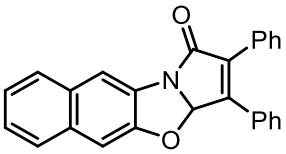
12m: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 45 mg product was obtained by 56% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 -7.52 (m, 2H), 7.44 - 7.34 (m, 9H), 7.11 (dd, J = 7.8, 1.8 Hz, 1H), 7.04 (d, J = 1.8 Hz, 1H), 6.88 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.82, 156.04, 150.74, 134.82, 131.09, 130.73, 130.20, 129.86, 129.56, 129.41, 129.08, 128.86, 128.71, 124.88, 118.22, 117.91, 113.44, 97.84.

ESI-HRMS: mass spectrometry: m/z calc. 426.01001 $[C_{22}H_{14}O_2BrNa]^+$, measured 426.00989.

IR (neat, cm^{-1}): ṽ: 3415, 3054, 2923, 1709, 1600, 1476, 1354, 1243, 1195, 1134, 1041, 942, 874, 799, 761, 690.



2,3-diphenylnaphtho[2,3-*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

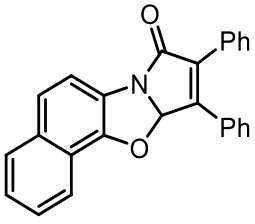
12n: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 55 mg product was obtained by 73% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.61 - 7.57 (m, 2H), 7.48 - 7.36 (m, 10H), 7.19 (s, 1H), 6.93 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.09, 154.41, 150.81, 134.94, 132.41, 131.24, 130.66, 130.43, 130.39, 130.23, 129.62, 129.35, 129.08, 128.85, 128.79, 128.03, 127.19, 125.86, 124.60, 114.15, 105.02, 97.00.

ESI-HRMS: mass spectrometry: m/z calc. 398.11515 $[C_{26}H_{17}O_2NNa]^+$, measured 398.11517.

IR (neat, cm^{-1}): ṽ: 3447, 3055, 2921, 1723, 1607, 1464, 1347, 1312, 1253, 1146, 1068, 953, 898, 837, 747, 691.



9,10-diphenylnaphtho[2,1-*d*]pyrrolo[2,1-*b*]oxazol-8(10a*H*)-one

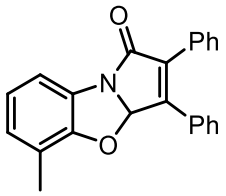
12o: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 65 mg product was obtained by 87% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 - 7.93 (m, 1H), 7.86 - 7.82 (m, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.68-7.63 (m, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.48 - 7.37 (m, 13H), 7.09 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 175.94, 150.92, 150.06, 135.08, 132.49, 131.51, 130.57, 130.55, 129.63, 129.26, 129.04, 128.87, 128.83, 128.47, 126.13, 125.71, 125.45, 121.85, 120.73, 120.29, 116.39, 98.37.

ESI-HRMS: mass spectrometry: m/z calc. 398.11515 $[C_{26}H_{17}O_2NNa]^+$, measured 398.11515.

IR (neat, cm^{-1}): ṽ: 3413, 3054, 2919, 1714, 1636, 1595, 1462, 1397, 1341, 1280, 1191, 1131, 1052, 962, 865, 747, 690.



5-methyl-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

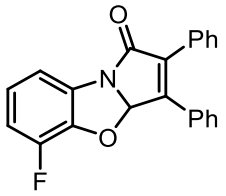
12p: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 65 mg product was obtained by 96% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 - 7.57 (m, 2H), 7.46 - 7.34 (m, 9H), 6.93 - 6.88 (m, 2H), 6.85 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.91, 153.53, 150.62, 134.84, 131.38, 130.48, 130.33, 129.67, 129.48, 129.07, 128.84, 128.69, 128.66, 127.36, 121.55, 120.00, 114.41, 96.84, 14.82.

ESI-HRMS: mass spectrometry: m/z calc. 362.11515 $[C_{23}H_{17}O_2NNa]^+$, measured 362,11516.

IR (neat, cm^{-1}): ṽ: 3424, 3056, 2920, 1720, 1636, 1598, 1444, 1339, 1250, 1138, 1115, 1035, 966, 903, 776, 686.



5-fluoro-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12q: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 23 mg product was obtained by 34% isolated yield as yellow solid.

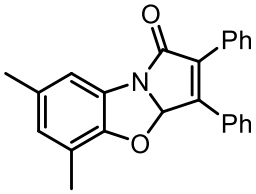
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 - 7.55 (m, 2H), 7.47 - 7.34 (m, 8H), 7.33 - 7.29 (m, 1H), 6.94 (s, 1H), 6.93 – 6.86 (m, 2H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.64, 150.36, 147.44, 145.80, 141.64 (d, J = 12.3 Hz), 134.65, 132.96 (d, J = 4.3 Hz), 130.91, 130.60, 130.11, 129.45, 129.27, 128.93, 128.71 (d, J = 5.4 Hz), 122.27 (d, J = 6.5 Hz), 113.88 (d, J = 17.4 Hz), 112.82 (d, J = 3.4 Hz), 98.35.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -137.38 - -137.43 (m).

ESI-HRMS: mass spectrometry: m/z calc. 366.09008 $[C_{22}H_{14}O_2NFNa]^+$, measured 366.08966.

IR (neat, cm^{-1}): ṽ: 3433, 3058, 2922, 1722, 1624, 1465, 1335, 1250, 1170, 1136, 1070, 960, 880, 777.



5,7-dimethyl-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

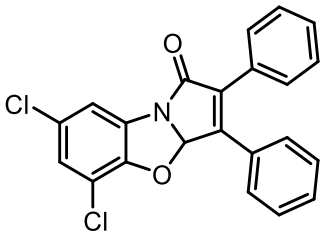
12r: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 65 mg product was obtained by 92% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60- 7.56 (m, 2H), 7.46 - 7.34 (m, 8H), 7.20 - 7.17 (m, 1H), 6.83 (s, 1H), 6.73 - 6.69 (m, 1H), 2.33 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.79, 151.45, 150.66, 134.84, 131.40, 131.24, 130.55, 130.27, 129.56, 129.48, 129.01, 128.81, 128.68, 128.64, 127.61, 119.36, 115.03, 96.89, 21.01, 14.77.

ESI-HRMS: mass spectrometry: m/z calc. 376.13080 $[C_{24}H_{19}O_2NNa]^+$, measured 376.13132.

IR (neat, cm^{-1}): $\tilde{\nu}$: 3416, 3058, 2917, 1717, 1630, 1482, 1361, 1306, 1197, 1130, 1030, 982, 905, 813, 774, 692.



5,7-dichloro-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

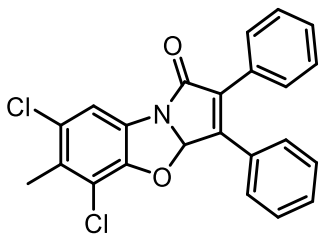
12s: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 28 mg product was obtained by 36% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 - 7.52 (m, 2H), 7.45 - 7.33 (m, 9H), 7.08 (d, J = 3.0 Hz, 1H), 6.94 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.36, 150.66, 150.35, 134.65, 132.22, 130.79, 130.73, 130.61, 129.88, 129.42, 129.00, 128.80, 128.72, 127.09, 125.77, 116.02, 114.97, 98.23.

ESI-HRMS: mass spectrometry: m/z calc. 416.02156 $[C_{22}H_{13}O_2NCl_2Na]^+$, measured 416.02126.

IR (neat, cm^{-1}): $\tilde{\nu}$: 3441, 1086, 2923, 1725, 1600, 1460, 1340, 1247, 1198, 1146, 1106, 1063, 961, 899, 770, 687.



5,7-dichloro-6-methyl-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

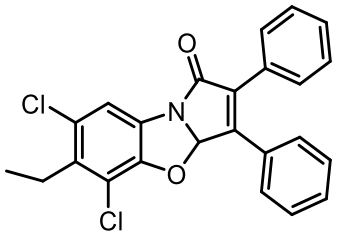
12t: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 28 mg product was obtained by 34% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.58 - 7.54 (m, 2H), 7.44 (s, 1H), 7.43 - 7.35 (m, 8H), 6.91 (s, 1H), 2.42 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.61, 150.68, 150.56, 134.68, 131.50, 130.83, 130.66, 129.97, 129.39, 129.32, 129.18, 128.94, 128.74, 128.69, 127.01, 115.91, 115.81, 97.99, 16.95.

ESI-HRMS: mass spectrometry: m/z calc. 430.03721 $[C_{23}H_{15}O_2NCl_2Na]^+$, measured 430.03625.

IR (neat, cm^{-1}): ṽ: 3442, 3056, 2921, 1725, 1614, 1457, 1405, 1342, 1301, 1238, 1144, 1094, 962, 866, 784, 692.



5,7-dichloro-6-ethyl-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

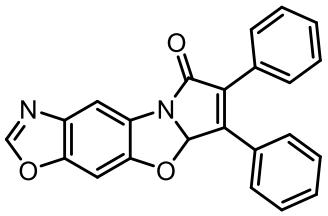
12u: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 100:1). 34 mg product was obtained by 40% isolated yield as white solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 - 7.53 (m, 2H), 7.46 - 7.33 (m, 9H), 6.91 (s, 1H), 2.96 - 2.86 (m, 2H), 1.16 (t, J = 7.8 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.62, 150.83, 150.59, 137.02, 134.69, 130.82, 130.67, 129.97, 129.39, 129.33, 129.24, 128.95, 128.75, 128.70, 126.58, 116.22, 115.35, 97.98, 24.38, 12.66.

ESI-HRMS: mass spectrometry: m/z calc. 444.05286 $[C_{24}H_{17}O_2NCl_2Na]^+$, measured 444.05215.

IR (neat, cm^{-1}): ṽ: 3470, 3086, 2927, 1740, 1608, 1457, 1404, 1331, 1224, 1141, 1065, 942, 870, 784, 748, 699.



6,7-oxazol-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

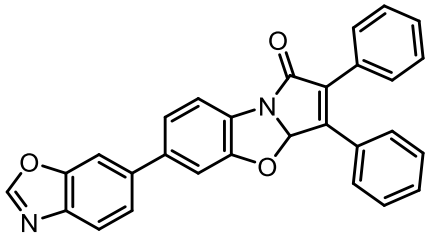
12v: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 43 mg product was obtained by 59% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.86 (s, 1H), 7.58 - 7.54 (m, 2H), 7.46 - 7.35 (m, 8H), 7.11 (s, 1H), 6.96 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.70, 154.22, 152.01, 150.38, 147.83, 134.81, 134.39, 131.00, 130.56, 130.12, 129.42, 129.26, 128.94, 128.72, 128.56, 128.27, 108.65, 98.10, 93.63.

ESI-HRMS: mass spectrometry: m/z calc. 367.10772 $[C_{23}H_{15}O_3N_2]^+$, measured 367.10771.

IR (neat, cm^{-1}): ṽ: 3445, 3112, 2922, 1726, 1619, 1457, 1373, 1347, 1208, 1163, 1122, 1066, 938, 838, 769, 687.



6-(benzo[*d*]oxazol-6-yl)-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

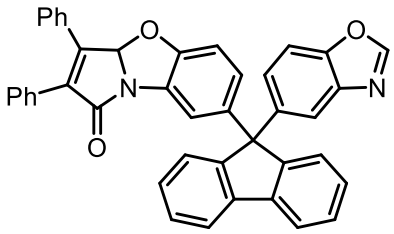
12w: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 20 mg product was obtained by 22% isolated yield as yellow solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.59 – 7.57 (m, 2H), 7.56 – 7.54 (m, 1H), 7.46 – 7.35 (m, 7H), 7.15 (d, J = 1.8Hz, 1H), 6.94 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.87, 155.87, 152.92, 150.76, 139.42, 139.13, 138.90, 134.77, 131.12, 130.49, 130.24, 129.97, 129.44, 129.19, 128.92, 128.70, 128.60, 124.17, 121.32, 120.57, 116.97, 109.42, 108.86, 97.45.

ESI-HRMS: mass spectrometry: m/z calc. 465.12096 $[C_{29}H_{18}O_3N_2Na]^+$, measured 465.11987.

IR (neat, cm^{-1}): $\tilde{\nu}$: 3423, 3125, 2922, 1719, 1592, 1504, 1468, 1352, 1250, 1219, 1144, 1061, 948, 867, 811, 694.



7-(9-(benzo[*d*]oxazol-5-yl)-9*H*-fluoren-9-yl)-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

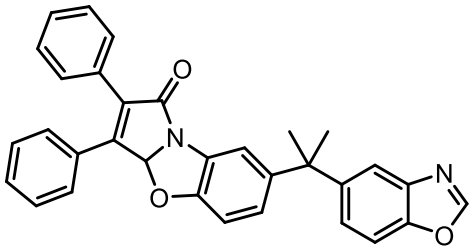
12x: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 67 mg product was obtained by 55% isolated yield as yellow oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.81 - 7.75 (m, 2H), 7.65 (d, J = 2.4 Hz, 1H), 7.57 - 7.54 (m, 2H), 7.52 - 7.50 (m, 1H), 7.50 - 7.46 (m, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.42 - 7.39 (m, 2H), 7.39 - 7.32 (m, 9H), 7.32 - 7.28 (m, 2H), 6.87 (dd, J = 9.0, 2.4 Hz, 1H), 6.81 (s, 1H), 6.72 (d, J = 8.4 Hz, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.79, 154.23, 152.84, 151.08, 150.92, 150.49, 148.94, 143.11, 140.02, 139.99, 139.95, 139.80, 134.71, 131.23, 130.46, 130.43, 130.30, 129.45, 129.16, 128.88, 128.69, 128.64, 128.03, 127.91, 127.72, 126.16, 126.13, 126.06, 125.00, 120.36, 120.30, 119.91, 117.41, 110.60, 108.90, 97.55, 65.05.

ESI-HRMS: mass spectrometry: m/z calc. 629.18356 $[C_{42}H_{26}O_3N_2Na]^+$, measured 629.18171.

IR (neat, cm^{-1}): $\tilde{\nu}$: 3450, 3061, 2923, 1724, 1606, 1513, 1481, 1443, 1340, 1243, 1201, 1122, 1065, 907, 807, 727.



7-(2-(benzo[*d*]oxazol-5-yl)propan-2-yl)-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

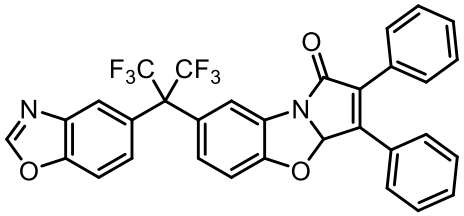
12y: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 58 mg product was obtained by 60% isolated yield as yellow liquid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.58 - 7.53 (m, 2H), 7.46 - 7.41 (m, 4H), 7.40 - 7.33 (m, 6H), 7.23 (dd, J = 8.4, 1.8 Hz, 1H), 6.90 (dd, J = 8.4, 1.8 Hz, 1H), 6.84 (s, 1H), 6.78 (d, J = 8.4 Hz, 1), 1.77 (s, 3H), 1.75 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.82, 153.20, 152.72, 150.65, 148.11, 147.74, 144.79, 139.83, 134.67, 131.24, 130.39, 130.31, 130.17, 129.47, 129.11, 128.87, 128.63, 128.61, 125.39, 123.96, 118.04, 115.67, 110.30, 108.79, 97.34, 43.01, 31.39, 31.37.

ESI-HRMS: mass spectrometry: m/z calc. 507.16791 $[C_{32}H_{24}O_3N_2Na]^+$, measured 507.16759.

IR (neat, cm^{-1}): ṽ: 3650, 3059, 2926, 1719, 1609, 1513, 1484, 1438, 1340, 1250, 1138, 1065, 958, 878, 811,692.



7-(2-(benzo[*d*]oxazol-5-yl)-1,1,1,3,3,3-hexafluoropropan-2-yl)-2,3-diphenylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12z: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 20:1). 48 mg product was obtained by 41% isolated yield as yellow solid.

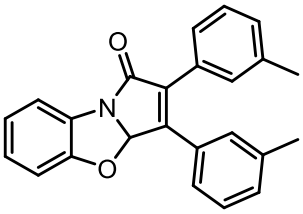
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 8.00 (s, 1H), 7.60 -7.54 (m, 3H), 7.49 - 7.46 (m, 1H), 7.46 - 7.32 (m, 9H), 7.19 - 7.14 (m, 1H), 6.90 (d, J = 9.0 Hz, 1H), 6.89 (s, 1H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 174.75, 155.64, 153.48, 150.52, 149.91, 140.04, 134.63, 131.06, 130.64, 130.59, 130.08, 130.00, 129.45, 129.29, 128.94, 128.69, 128.61, 128.06, 127.94, 126.97, 125.12(d, J = 285 Hz),, 123.05, 119.06, 110.74, 108.99, 97.94.

^{19}F NMR (564 MHz, Chloroform-*d*) δ -63.75.

ESI-HRMS: mass spectrometry: m/z calc. 615.11138 $[C_{32}H_{18}O_3N_2F_6Na]^+$, measured 615.11017.

IR (neat, cm^{-1}): ṽ: 3315, 3124, 2920, 1721, 1615, 1489, 1446, 1344, 1303, 1203, 1127, 1064, 961, 885, 811, 692.



2,3-di-*m*-tolylbenzo[*d*]pyrrolo[2,1-*b*]oxazol-1(3a*H*)-one

12aa: The crude mixture was purified by SiO_2 gel column chromatography with pentane/EA (from 60:1). 38 mg product was obtained by 54% isolated yield as yellow liquid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 (dd, J = 7.8, 1.2 Hz, 1H), 7.40 (s, 1H), 7.34 - 7.30 (m, 1H), 7.28 (s, 1H), 7.25 - 7.17 (m, 5H), 7.08 - 7.03 (m, 1H), 7.00 - 6.96 (m, 1H), 6.86 (s, 1H), 2.34 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*) δ 175.09, 155.16, 150.70, 138.56, 138.28, 134.70, 131.16, 130.33, 130.31, 129.95, 129.84, 129.01, 128.67, 128.45, 126.44, 125.85, 125.64, 121.83, 116.96, 109.60, 96.96, 21.44, 21.40.

ESI-HRMS: mass spectrometry: m/z calc. 378.13080 $[C_{24}H_{19}O_2NNa]^+$, measured 376.13056.

IR (neat, cm^{-1}): $\tilde{\nu}$: 3432, 3035, 2920, 1720, 1596, 1474, 1344, 1305, 1238, 1131, 1102, 1009, 933, 825, 748, 693.

5 List of Abbreviation

Ac	acetyl
acac	acetylacetonate
aq	aqueous
Ar	aryl
BINAP	(*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Boc	*tert*-butyloxycarbonyl
br	broad
Bu	butyl
Bz	benzoyl
℃	centigrade
Calcd.	calculated
d	doublet (NMR signal)
DCE	1,2-dichloroethane
DCM	dichloromethane
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
dr	diastereomeric excess
EI	electron ionization
equiv	equivalent
ESI	electrospray ionization
Et	ethyl
h	hour
HMPA	hexamethylphosphoramide
HRMS	high resolution mass spectroscopy
Hz	Hertz
IR	infrared spectroscopy
J	coupling constant (in NMR spectroscopy)
LDA	lithium diisopropylamide
m	multiplet (NMR signal)
m-	*meta*-
Me	methyl
min	minute
mol	mole
MS	mass spectroscopy
N. D.	no desired product
NMR	nuclear magnetic resonance
N. R.	no reaction
OTf	trifluoromethanesulfonate
p	para
Ph	phenyl

rt	Room temperature
s	singlet (NMR signal)
t	triplet (NMR signal)
t-Bu	*tert*-butyl
THF	tetrahydrofuran
TMS	trimethylsilyl
Tol	tolyl
Ts	*p*-toluenesulphonyl
δ	chemical shift

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