Doctoral Dissertation

Transition Metal-Catalyzed Non-Substitution Type Coupling Reactions via the Activation of Acyl Fluorides, Acylsilanes and Diarylacetylenes

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Preface and Acknowledgement

The research presented in this thesis was carried out under the direction of Professor Mamoru Tobisu of the Department of Applied Chemistry, Graduate School of Engineering, Osaka University. I joined to Tobisu's lab. in April 2017 and spent a life as a Ph.D. student from April 2020 to March 2023. The thesis is concerned with transition metal-catalyzed non-Substitution type coupling reactions via the activation of acyl Fluorides, acylsilanes and diarylacetylenes.

This thesis could not have been completed without the support of numerous people. Here, I wish to express my sincerest appreciation to all of these people.

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Tomoki Yoshida

Contents

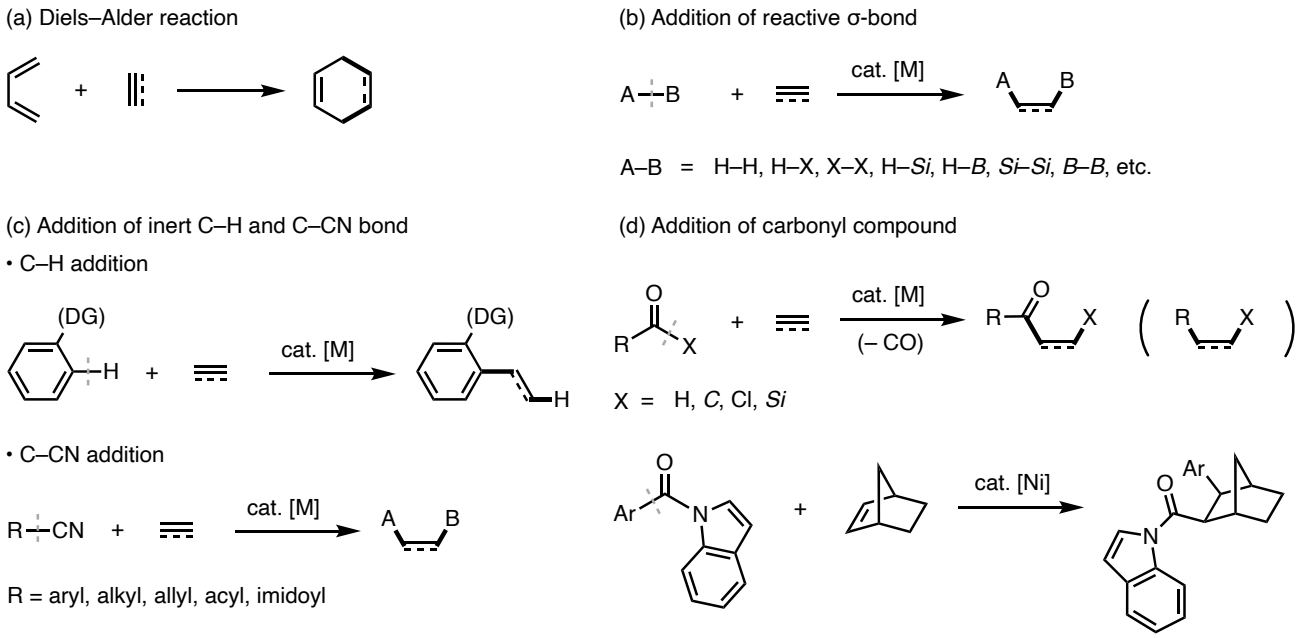
General Introduction

In 1991, Trost proposed the concept of atom economy (AE) as an index of the efficiency of a chemical transformation.[1] AE is defined as a ratio of the mass of the products to the sum of the mass of starting materials (eq 1).

$$AE\ (\%) = \frac{Mass\ of\ the\ product}{Sum\ of\ the\ mass\ of\ starting\ materials} \times 100 \qquad \text{(eq 1)}$$

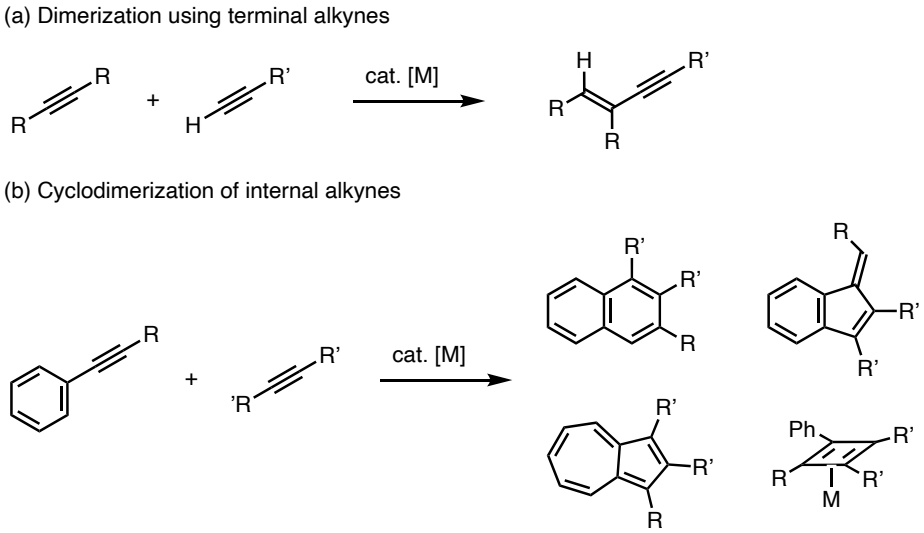
Trost also emphasized that, when designing new reactions for use in a sustainable society of the future, achieving high yield and selectivity in reactions is not sufficient and a high AE is also required. The keys to improving the AE of chemical reactions are 1) avoiding substitution type transformations and 2) the use of a catalyst. In substitution type reactions, a leaving group is essential. In most cases, the leaving group is a group or an atom other than hydrogen (*i.e.*, halogen and triflate etc), which leads to a decreased AE. Chemical reactions are often promoted by a stoichiometric amount of an activator (acid, base, etc.), which eventually produces a stoichiometric amount of chemical waste. If the amount of the activator can be reduced to a catalytic amount, then waste could be minimized. Since the concept of AE was established in 1991, numerous atom economical reactions have been developed that primarily involve the use of a transition metal complex as a catalyst. However, several issues remain to be addressed.

Addition reactions across unsaturated bonds are an ideal type of chemical reaction, because the AE of addition reactions is 100% (Scheme 1). For example, the classical Diels-Alder reaction represents an ideal method for constructing cyclohexene skeletons (Scheme 1a). [2] In addition to addition reactions between π-bonds, addition reactions of σ-bonds such as hydrogen (H–H),[3] halogen (X–X, H–X),[4] disilane (Si–Si) and diborane (B–B) have also been developed with the aid of suitable catalysts (Scheme 1b).[5] Despite these advances, the types of chemical bonds that can be used in catalytic addition reactions are still limited and the addition of inert σ-bonds lags far behind. As an exception, since Murai reported on the ruthenium-catalyzed hydroarylation of alkenes, remarkable advances have been made in addition reactions of inert C–H bonds (Scheme 1c).[6] A nickel-catalyzed addition reaction of C–CN bonds in nitriles has also been reported.[7] Regarding addition reactions of carbonyl compounds, several successes have been achieved (Scheme 1d). Hydroacylation using an aldehyde is one of the more typical reaction types of acyl functionalization reactions.[8] C–C bond addition reactions of ketones have also been achieved using substrates that have ring strain or a directing group.[9] The C–Cl bond of acyl chlorides can add across alkynes in the presence of a metal catalyst.[10] Recently, our group reported the nickel catalyzed C–C bond addition of amides across norbornene.[11] Our group also reported on the silylacylation of allenes via the cleavage of C–Si bonds in acylsilanes.[12] It is also known that the C–F bond of an acyl fluoride can be added across alkynes[13] and benzofurans[14] with the aid of organocatalytic system. As listed above, although addition reactions that proceed via the activation of an inert σ-bond have met with scattered success, broadening the scope of this reaction, both in terms of the nature of the σ-bonds and the type of the transformation is needed.



Scheme 1. (a) Diels-Alder reaction; (b) Addition of reactive σ-bonds; (c) Addition of inert C–H and C–CN bonds, (d) Addition of carbonyl compounds.

Transition metal-catalyzed dimerization of alkynes is also known as a type of addition reaction. It is known that there are two types of alkyne dimerization. One is liner dimerization using a terminal alkyne, in which an alkynic C–H bond adds across the other alkyne to form a conjugated enyne as a product (Scheme 2a).[15] Another type is cyclodimerization using aromatic internal alkynes, leading to π-extended products such as naphthalene,[16] indene,[17] and azulene.[18] A cyclobutadiene complex can also be obtained by cyclodimerization of alkynes, although the process is not catalytic (Scheme 2b).[19]

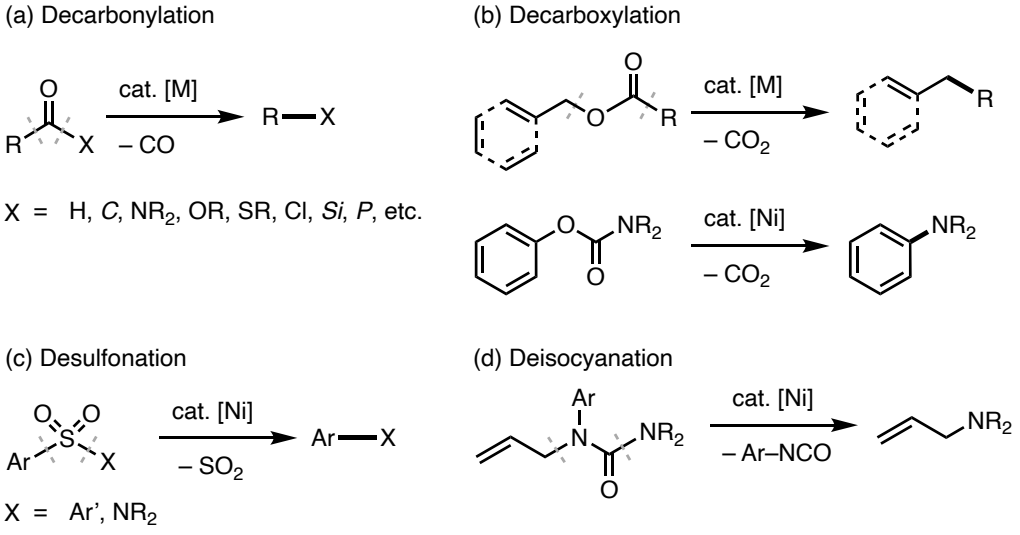


Scheme 2. (a) dimerization of terminal alkynes; (b) Cyclodimerization of aromatic alkynes.

Another type of highly atom economical reaction is transition metal-catalyzed unimolecular fragment coupling (UFC, Scheme 3). UFC is a reaction in which a small molecule such as CO or CO_2 is released and a new chemical

bond is formed between the remaining fragments of the original starting material. In typical cross-coupling reactions, aryl halides and organometallic reagents are required and the waste derived from both starting materials are generated at the end of the reaction, resulting in a low AE. In contrast, because only a small molecule is eliminated in UFC, the AE is generally higher than that for the cross-coupling reactions. Several types of UFC have been reported to date. The decarbonylation of aldehydes is a typical UFC (Scheme 3a),[20] a reaction known as Tsuji-Wilkinson decarbonylation, which is widely used in synthetic chemistry.[21] On the other hand, the decarbonylation of ketones has met with limited success due to the inertness of a carbon–carbon bond. It is known that ketones that contain a strained ring[22] or a directing group[23] can be decarbonylated catalytically. Some types of activated ketones such as β-diketones and alkynyl ketones can also participate in catalytic decarbonylation reactions.[24] It was recently reported that tropone derivatives can also be decarbonylated catalytically in the presence of a nickel complex.[25] The [d]ecarbonylation of unstrained simple ketones is also known but a stoichiometric amount of metal complexes is required for the success of these reactions.[26] Catalytic decarbonylation reactions of other carbonyl compounds such as esters[27], amides[28], thioesters[29], acyl chlorides[30], and others have also been reported.[31]

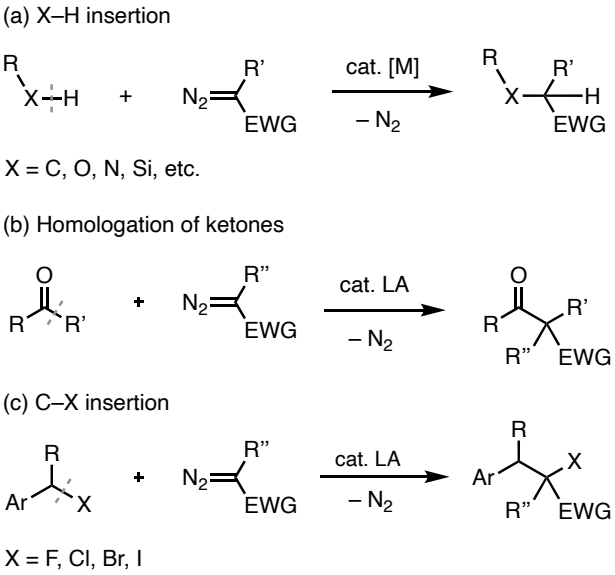
The decarboxylation of esters is another typical UFC (Scheme 3b), although these reactions are limited to allylic or benzylic esters in most cases,[32] and aryl esters derived from phenol derivatives cannot be used due to the inertness of a C(aryl)–O bond. Our group reported on the nickel-catalyzed decarboxylation of aryl carbamates via C(aryl)–O bond cleavage.[33] A UFC that releases molecules other than CO and CO_2 has also been reported. The nickel-catalyzed UFC of diaryl sulfones[34], sulfonamides[35], and sulfonates[36] with elimination of SO_2 has been reported (Scheme 3c). The catalytic elimination of isocyanate from N-allyl urea or amide derivatives has been developed (Scheme 3d).[37] Despite these successes of UFC, the range of applicable substrates is limited to activated carbonyl compounds due to the inertness of the C(acyl)–X bond. Therefore, the substrates that can be used in UFC needs to be expanded.



Scheme 3. Unimolecular Fragment Coupling Reactions: (a) Decarbonylation (b)Decarboxylation (c) Desulfonation (d) Deisocyanation

Bimolecular fragment coupling, a coupling reaction of two molecules with the elimination of only small molecules such as N_2, also represents atom-economical transformation. Transition metal-catalyzed carbene insertion into X–H bonds (X = C, O, N, Si etc) using diazo compounds is a representative bimolecular fragment coupling

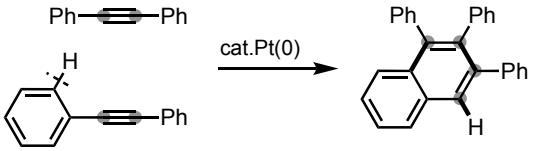
reaction with loss of N_2 (Scheme 4a).[38] Diazo compounds can also be inserted into a C–C bond of ketones. Lewis acid or Brønsted acid-catalyzed homologation reactions of ketones using diazo esters are known.[39] Recently, Lewis acid-catalyzed insertion reactions of carbenes into a C–X bond (X = halogen) of benzyl halides were also reported.[40] These bimolecular fragment coupling reactions are useful for the synthesis of highly functionalized molecules with high AE.



Scheme 4. Coupling reactions using diazo compounds (a) X–H insertion; (b) C–C insertion; (c) C–X insertion.

In this thesis, non-substitution type catalytic reactions were developed in the hope of realizing novel atom economical processes. In chapter 1, the platinum-catalyzed cyclodimerization of diaryl alkynes is described. In chapter 2, the decarbonylative UFC of acylsilanes via C–Si bond cleavage is described. Chapter 3 deals with the zinc(II)-catalyzed formal cross-dimerization of carbenes using acylsilanes and diazo esters. Chapter 4 is concerned with the cationic rhodium tetrafluoroborate-catalyzed intramolecular carbofluorination of alkenes via the activation of the C–F bond in an acyl fluoride.

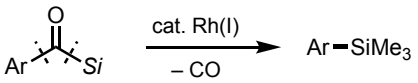
Chapter 1: Platinum/silylene-catalyzed cyclodimerization of diarylacetylenes



Addition

AE = 100%

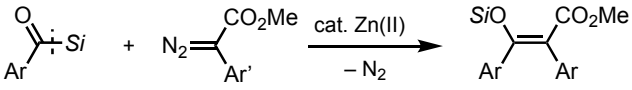
Chapter 2: Rh(I)-catalyzed decarbonylation of acylsilanes



Unimolecular Fragment Coupling

AE >84%

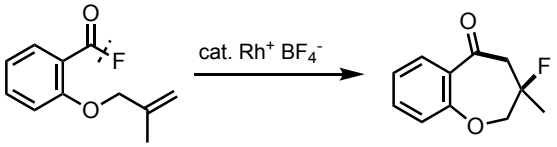
Chapter 3: Catalytic formal cross-dimerization of carbenes using acylsilanes



Bimolecular Fragment Coupling

AE >92%

Chapter 4: $Rh^+BF_4^-$-catalyzed carbofluorination via C–F bond cleavage of acyl fluorides



Addition

AE = 100%

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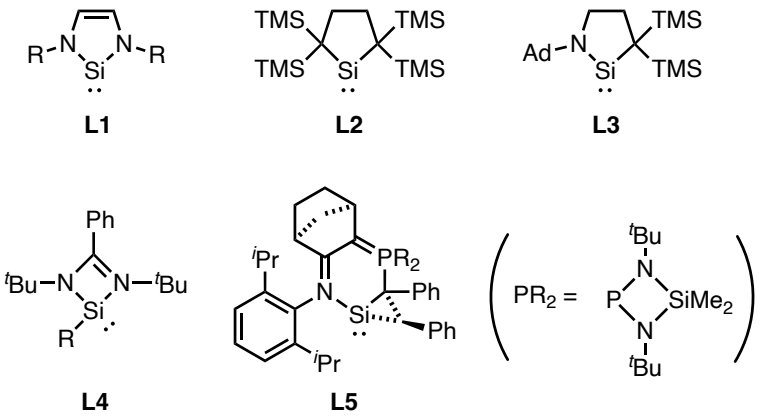
Chapter 1

Catalytic Cyclodimerization of Alkynes via C–H Bond Cleavage by a Platinum-Silylene Complex

1.1. Introduction

Silylenes are the heavier congeners of carbenes, which contain divalent silicon atoms typically in a singlet ground state. Since the first isolation of a stable silylene in 1986,[1] various stable silylenes, such as N-heterocyclic silylenes (**L1**), cyclic dialkylsilylenes (**L2**), cyclic amino silylenes (**L3**), and acyclic silylenes have been isolated.[2] Silylene can be used as a ligand in transition-metal-catalyzed reactions. In 2001, Fürstner et al. reported on the preparation of a Pd(0)-NHSi (**L1**: R = ^{t}Bu) complex and its use in Suzuki-Miyaura coupling reactions.[3] Since this first report, several additional catalytic reactions using silylene ligands have been investigated.[4] Three coordinate base-stabilized silylenes, such as **L4**, are another class of stable silylenes.[2c,d] Kato and Baceiredo reported the synthesis and isolation of base-stabilized silacycloprop-1-ylidene **L5** in 2012.[5] The silylene **L5** is an excellent ligand for transition metals, and Cu(I) and Pt(0) complexes of **L5** serve as efficient hydrosilylation catalysts,[6] highlighting a better performance of **L5** compared with other phosphine or N-heterocyclic carbene (NHC) ligands. However, the applications of **L5** in catalysis is limited to hydosilylation reactions of carbonyl compounds and alkenes, and, therefore, other types of reactions need to be explored to unveil the full potential of **L5** as a ligand. The author report herein that a platinum-**L5** complex is a potent catalyst for use in C-H activation reactions[7] of diphenylacetylene derivatives, which leads to the cyclodimerization of two alkynes to form naphthalene derivatives. Although this type of cyclodimerization of alkynes has been accomplished using Rh,[8] Au,[9] Ru[10] or Ir[11] catalysts, no platinum complexes that are capable of catalyzing the cyclodimerization of alkynes have been reported to date.



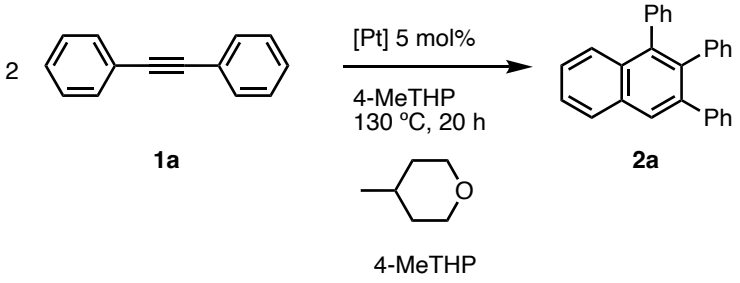
Scheme 1. Selected stable silylenes.

1.2. Results and Discussion

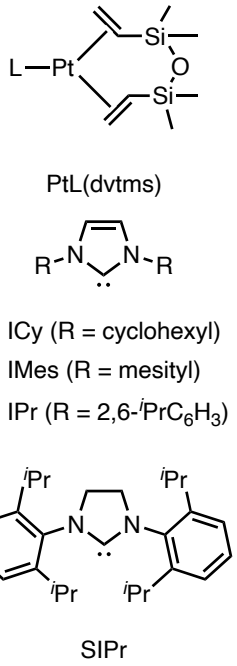
During the course of our study of catalytic reactions using Pt(**L5**)(dvtms) (dvtms = 1,3-divinyltetramethyldisiloxane), we found that the cyclodimerization of diphenylacetylene (**1a**) is catalyzed by it. Thus, when alkyne **1a** was reacted in 4-MeTHP at 130 °C for 20 h in the presence of 5.0 mol% of Pt(**L5**)(dvtms), 1,2,3-triphenylnaphthalene **2a** was formed in 72% yield (entry 1, Table 1). In marked contrast, the corresponding NHC-Pt complexes (entries 2-5) and $Pt_2(dvtms)_3$ (Karstedt's catalyst, entry 6) were completely inactive for the cyclodimerization of **1a**. These results clearly highlight the uniqueness of the silylene ligand **L5**. The thermal stability

of Pt(**L5**)(dvtms) complex has been confirmed by the absence of decomposition after its heating in 4-methyltetrahydropyran at 130 °C for 20 h. It was previously reported that π-acidic Au(I) complexes-catalyzed cyclodimerization of push-pull alkynes.[9] Therefore, we first considered the initiation of the reaction by electrophilic Pt(II) complexes generated in situ. However, this possibility was excluded since electrophilic Pt(II) complexes such as $[PtCl_2(MeCN)_2]$ did not show any catalytic activity (entry 7). It was also reported that Rh(I) complexes, in the presence of a Brϕnsted acid, can generate a Rh(III)-hydride as a key catalytically active species, which initiates the dimerization of alkynes by a hydrorhodation process.[8a,b] To verify the possibility that such a metal-hydride species is involved in our platinum system, the reaction was conducted in the presence of 20 mol% of Py·HBr. However, no reaction occured when a proton source was added (entry 8). Therefore, it is unlikely that the reaction is catalyzed by a platinum-hydride species that is formed by the reaction of Pt(**L5**)(dvtms) with residual water.

Table 1. Platinum-catalyzed cyclodimerization of **1a**[a]



entry	[Pt]	yield of **2a** (%)[b]
1	Pt(**L5**)(dvtms)	72
2	Pt(ICy)(dvtms)	0
3	Pt(IMes)(dvtms)	0
4	Pt(IPr)(dvtms)	0
5	Pt(SIPr)(dvtms)	0
6	$Pt_2(dvtms)_3$ (Karstedt's catalyst)	0
7	$PtCl_2(MeCN)_2$	0
8	Pt(**L5**)(dvtms) + 20 mol% Py•HBr	0

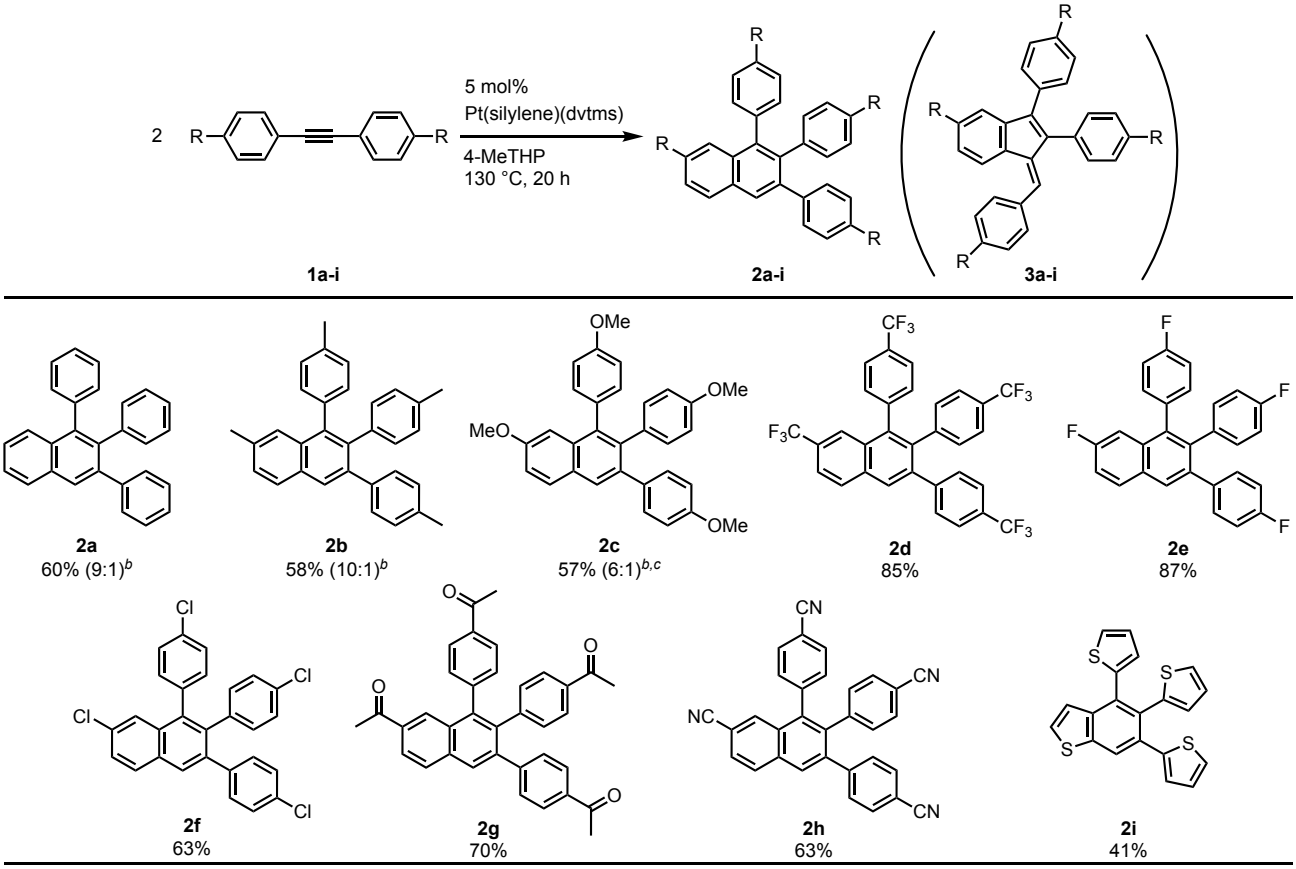


[a]Reaction conditions: **1a** (0.20 mmol), [Pt] (0.010 mmol), 4-MeTHP (0.50 mL) in a screw-capped vial under N_2 for 20 h. [b]Yields were determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

The scope of the platinum-silylene-catalyzed cyclodimerization of diarylacetylenes was investigated (Table 2). Substrates bearing an electron-donating group, such as methyl (**1b**) and methoxy groups (**1c**), were applicable to this reaction, although the yields were relatively low compared with that for electron-neutral alkyne **1a** due to the formation of indene derivative **3**[12] as a byproduct. On the other hand, electron-deficient alkynes, such as those bearing a trifluoromethyl group (**1d**), were efficiently cyclodimerized without an indene-type byproduct being formed. Halogen atoms, such as fluorine (**1e**) and chlorine (**1f**), were tolerated, with the corresponding cyclodimerization

products being formed in 87% and 63%, respectively. Acetyl (**1g**) and cyano (**1h**) groups were also compatible. The reaction is not limited to aromatic alkynes, and heteroaromatic substrates also participated in this reaction. When di(2-thienyl)acetylene (**1i**) was used, benzothiophene was obtained in 41% yield. However, Pt(**L5**)(dvtms) did not show any catalytic activity for the cyclodimerization of aliphatic alkynes and 2-phenyl-1-trimethylsilylacetylene.

Table 2. Platinum-catalyzed cyclodimerization of various alkynes.[a]

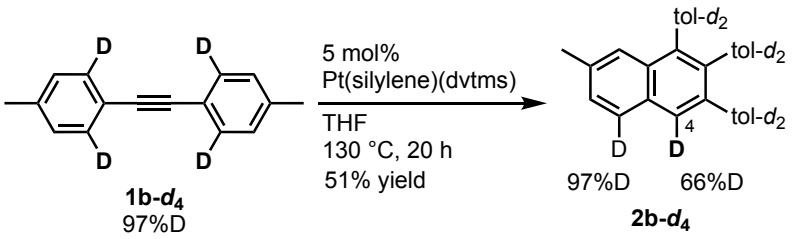


[a]Reaction conditions: **1a** (0.20 mmol), Pt(silylene)(dvtms) (0.010 mmol), 4-MeTHP (0.50 mL) in a screw-capped vial under N_2 for 20 h. [b]Isolated as a mixture of **2** and **3**. Ratio of **2** and **3** was determined by GC or NMR analysis. [c]0.3mmol scale

To obtain mechanistic insights of this cyclodimerization reaction, deuterium labelling experiments were conducted. The platinum-silylene catalyzed reaction of 2,6,2',6'-tetradeuteroditolylacetylene (**1b-*d*$_4$**) under the standard reaction conditions led to the formation of a naphthalene derivative with deuterium being incorporated at the 4-position (*i.e.*, **2b-*d*$_4$**), in addition to the positions where deuterium atoms were originally located (Scheme 2a). Although the deuterium content at the 4-position was 66%,[13] the majority of the cleaved deuterium atom is incorporated into the product, indicating that the cleaved hydrogen atom migrates in an intramolecular manner rather than via an intermolecular proton transfer pathway. In terms of the reaction rates, deuterium labeling had no significant effect on the yields at the early stage of cyclodimerization reaction (Scheme 2b), which indicates that the rate-determining step of this reaction is not the step of C-H bond cleavage. We next examined substituent effect on

the cyclodimerization reaction by comparing the yields of cyclodimerization of **1a**, **1c** and **1d** at 1 and 3 h (Scheme 2c). The yields for alkynes **1a** and **1c** were significantly lower compared with alkyne **1d**, and the reaction of **1d** was complete within 3 h, revealing that this cyclodimerization is strongly promoted by electron-withdrawing groups.

(a)



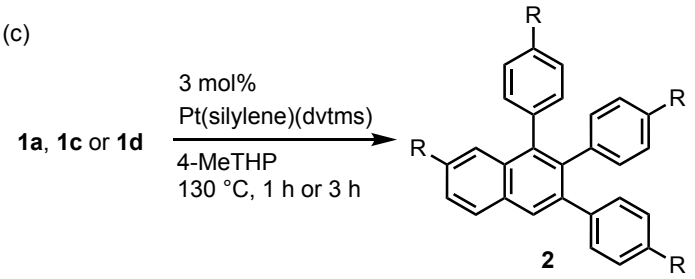
1b-d_4
97%D

2b-d_4

(b)

substrate	product yield (%)	
	1 h	3 h
1b	22	30
1b-d_4	17	25

(c)



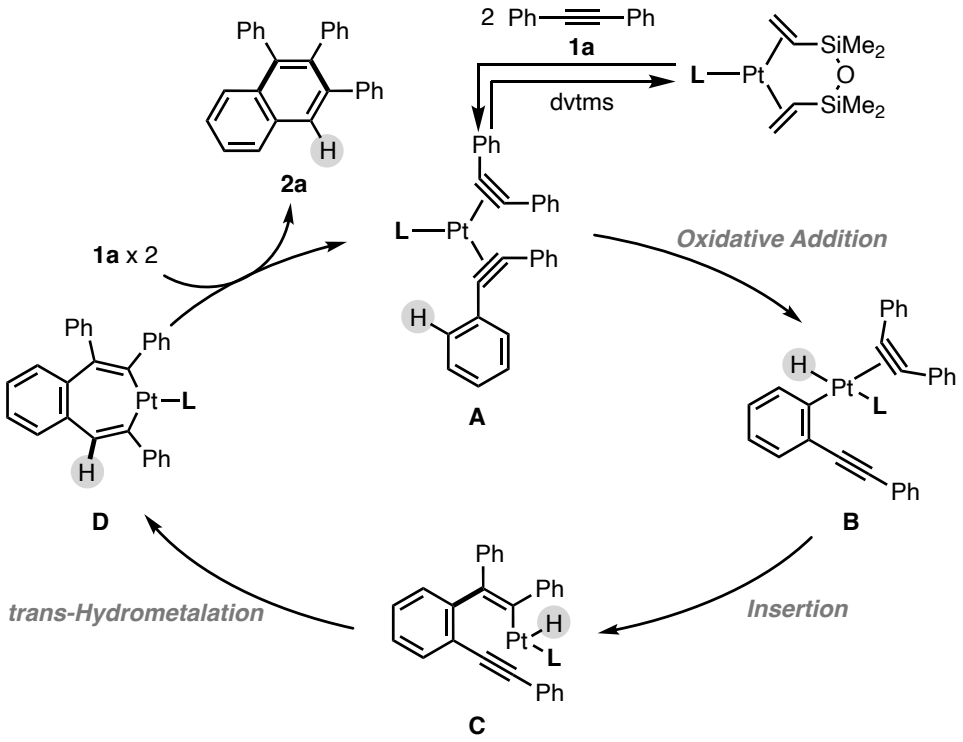
1a, **1c** or **1d**

2

R	yield of **2** (%)	
	1 h	3 h
H (**1a**)	17	18
OMe (**1c**)	15	30
CF_3 (**1d**)	83	>95

Scheme2. Mechanistic studies

A possible mechanism is shown in Scheme 3. First, ligand exchange between dvtms and two alkynes forms Pt(alkyne)$_2$ complex **A**. The ortho C-H bond of alkyne **1a** then oxidatively adds to a platinum, in which an alkyne serves as an ortho directing group,[11,12,14] to provide Pt(II)-hydride intermediate **B**. The insertion of a second alkyne into an aryl-platinum bond forms alkenyl-Pt complex **C**, which leads to the formation of seven-membered platinacycle **D** via intramolecular *trans*-hydrometalation.[15] Finally, reductive elimination from **D** affords naphthalene **2a** with the regeneration of Pt(0). In this reaction, the silylene ligand **L5** is specifically effective. The silylene ligand **L5** is a strong σ-donor, as evidenced by its TEP value of 2027 cm^{-1} which is lower than the values for typical NHC ligands (e.g., 2037 cm^{-1} for ICy).[6] Nevertheless, the Pt-vinyl bond distance in Pt(**L5**)(dvtms) (2.123-2.151 Å) is longer than that in Pt(NHC)(dvtms) (2.114-2.132 Å), probably because of the greater π-backdonation of Pt→silylene than Pt→NHC.[6] In addition, the silicon center of **L5** is tricoordinate due to the coordination of the imine, rendering the silicon center more sterically demanding than typical NHCs. These electronic and steric features of silylene **L5** would be expected to facilitate the dissociation of dvtms and reductive elimination. We confirmed that both Pt(**L5**)(dvtms) and Pt(ICy)(dvtms) release dvtms at similar rates upon the addition of **1a**, indicating that the initial ligand exchange step is not specifically accelerated by **L5** (See Supporting Information). Given that a kinetic isotope effect was not observed in this reaction (Scheme 2b), the rate-determination step of this catalytic cycle is most probably the reductive elimination step, which would be expected to be facilitated by silylene ligand **L5**, as discussed above. This conclusion is also in agreement with the experimental observation that electron-deficient alkynes react more rapidly (Scheme 2c).[16]



Scheme 3. Possible mechanism.

1.3. Conclusion

The author have developed the platinum-silylene complex-catalyzed cyclodimerization of diarylacetylenes, leading to the formation of naphthalene derivatives. This reaction includes the cleavage of an *ortho*- C-H bond of aromatic alkynes. The present study demonstrated a utility of platinum-silylene complexes in catalytic C-H functionalization.[7]

1.4. Experimental Section

I. General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. The data is reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-700 spectrometer. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-2014 gas chromatograph, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Silicycle SilicaFlash F60 (230-400 mesh).

II. Materials

Diphenylacetylene (TCI), $Pt_2(dvtms)_3$ (TCI), $PtCl_2(MeCN)_2$ (Aldrich) and Py·HBr (Wako), THF (Wako) and THF-d_8 (Aldrich) were purchased from the commercial suppliers and used as received. All alkynes were prepared by a

sequential Sonogashira coupling reaction between the corresponding aryl iodides and trimethylsilylacetylene (TCI)/desilylation/second Sonogashira coupling.[17] 4-Methyltetrahydropyran (4-MeTHP, Kuraray) was distilled from CaH_2 prior to use. Silylene **L5** [CAS: 1399296-36-6] was prepared according to the literature procedure.[5] Pt(**L5**)(dvtms) (dvtms = 1,3-divinyltetramethyldisiloxane) [CAS: 1979169-16-8] was prepared according to the literature procedure.[6] Pt(ICy)(dvtms) [CAS: 400758-55-6], Pt(IMes)(dvtms) [CAS: 441018-47-9], Pt(IPr)(dvtms) [CAS: 849830-54-2] and Pt(SIPr)(dvtms) [CAS: 873311-51-4] were prepared from the reaction of H_2PtCl_6 (Wako), dvtms (TCI) and KO^{t}Bu (TCI) with ICy · HCl (TCI), IMes · HCl (TCI), IPr·HCl (TCI) and SIPr·HCl (TCI), respectively, according to the literature procedure.[18] 2,6-Deuterio-4-methylphenol [CAS: 2876-02-0] was prepared from *p*-cresol (Wako), D_2O (Aldrich) and PBr_3 (TCI) by the literature procedure.[19]

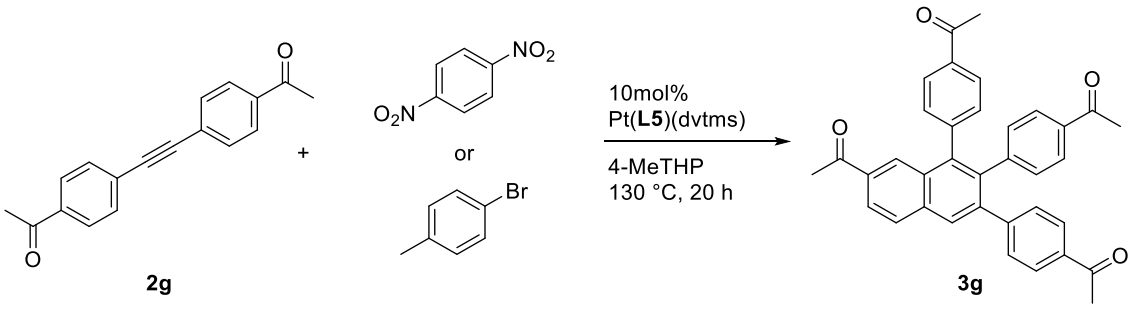
III. Typical Procedure of Cyclodimerization of Alkynes

In a glovebox filled with nitrogen, Pt(**L5**)(dvtms) (11.1 mg, 0.010 mmol, 0.05 equiv) and alkyne (0.20 mmol, 1.0 equiv) were added to a 10 mL screw-capped vial. 4-MeTHP (0.5 mL) was added, and the vial was sealed with the cap. The resulting mixture was stirred at 130 °C for 20 h. After allowing the reaction mixture to cool to room temperature, the solvent was removed. The residue was analyzed by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as the internal standard. The mixture was purified by flash column chromatography over silica gel (eluting with hexane/EtOAc) to give a product.

IV. Procedure of Cyclodimerization of Alkynes Using Pt/PPh_3 System

In a glovebox filled with nitrogen, $Pt_2(dvtms)_3$ (10.3 mg, 0.010 mmol, 0.05 equiv), **1a** (35.7 mg , 0.20 mmol, 1.0 equiv), and PPh_3 (5.2 mg, 0.020 mmol, 0.10 equiv) were added to a 10 mL screw-capped vial. 4-MeTHP (0.5 mL) was added, and the vial was sealed with the cap. The resulting mixture was stirred at 130 °C for 20 h. After allowing the reaction mixture to cool to room temperature, the solvent was removed. The residue was analyzed by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as the internal standard. As a result, no dimerization product was obtained and most of **1a** was remained. Therefore, this Pt/PPh_3 catalytic system is not effective for the cyclodimerization of **1a**.

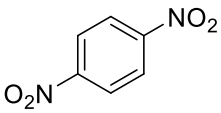
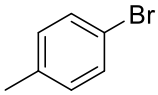
V. Procedure of Robustness Screening of NO_2 and Br Group[20]



In a glovebox filled with nitrogen, Pt(**L5**)(dvtms) (11.1 mg, 0.010 mmol, 0.1 equiv), **1g** (26.2 mg, 0.10 mmol, 1.0 equiv) and 1,4-dinitrobenzene (33.6 mg, 0.20 mmol, 2.0 equiv) or *p*-bromotoluene (34.2 mg, 0.20 mmol, 2.0 equiv) were added to a 10 mL screw-capped vial. 4-MeTHP (0.5 mL) was added, and the vial was sealed with the cap. The

resulting mixture was stirred at 130 °C for 20 h. After allowing the reaction mixture to cool to room temperature, the solvent was removed. The residue was analyzed by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as the internal standard. As a result, a NO_2 group inhibited the catalytic reaction completely. Thus, a NO2 group is not compatible for the cyclodimerization reaction. On the other hand, 56 % of **3g** was obtained in the presence of *p*-bromotoluene. Although the yields of **3g** was lowered from standard conditions, Br group is compatible to a certain extent for the cyclodimerization. (Table S1)

Table S1. Robustness Screening of NO_2 and Br Group

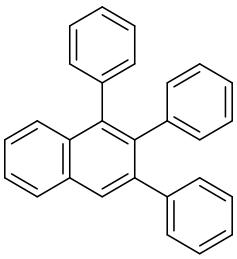
additive	NMR yields		
	3g	**2g**	additive
	0	85	90
	56	16	64
none[1]	70[2]	0	

[1]0.2 mmol scale, 5 mol% of Pt(**L5**)(dvtms) was used.

[2]Isolated yield.

VI. Spectroscopic Data

1,2,3-Triphenylnaphthalene (2a). [1942-39-8]



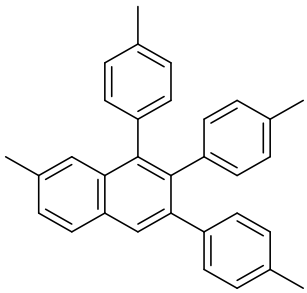
Rf = 0.20 (Hexane). Pale yellow solid (21.4 mg, 60%). Isolated as a mixture of **2a** and **3a** (9:1). Pure **2a** was obtained by recrystallization from MeOH.

^{1}H NMR ($CDCl_3$, 400 MHz): 6.84-6.87 (m, 2H), 6.92-6.95 (m, 3H), 7.14-7.26 (m, 10H), 7.37-7.42 (m, 1H), 7.49-7.53 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 6.8 Hz, 1H), 7.94 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): 125.6, 126.07, 126.13, 126.2, 126.4, 126.8, 126.9, 127.50 (two peaks are overlapped), 127.9, 128.7, 130.0, 131.2, 131.5, 132.0, 132.6, 138.0, 139.1, 139.3, 139.8, 140.0, 141.9.

HRMS (DART+, [M+H$^+$]): Calcd for $C_{28}H_{20}$ 357.1638, Found 357.1630.

7-Methyl-1,2,3-tris(4-methylphenyl)naphthalene (2b). [218617-78-8]



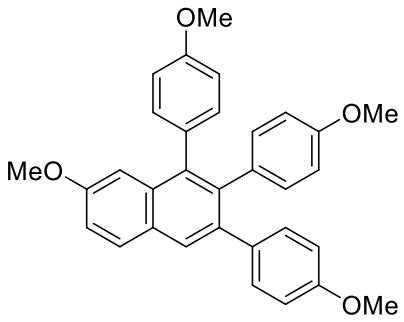
Rf = 0.40 (Hexane/EtOAc = 9/1). Yellow solid (26.6 mg, 58%). Isolated as a mixture of **2b** and **3b** (10:1). Pure **2b** was obtained by recrystallization from MeOH.

^{1}H NMR ($CDCl_3$, 400 MHz): 2.17 (s, 3H), 2.28 (s, 3H), 2.33 (s, 3H), 2.39 (s, 3H), 6.71-6.75 (m, 4H), 6.96-7.06 (m, 8H), 7.306 (s, 1H), 7.314 (d, *J* = 6.4 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.83 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): 21.11, 21.14, 21.3, 22.0, 125.7, 127.6, 127.7, 128.11, 128.2 (two peaks are overlapped), 128.4, 129.8, 130.9, 131.1, 131.3, 132.2, 134.7, 135.48, 135.54 (two peaks are overlapped), 136.56, 137.24, 138.1, 138.5, 139.0, 139.4.

HRMS (DART+, [M+H$^+$]): Calcd for $C_{32}H_{29}$ 413.2264, Found 413.2256.

7-Methoxy-1,2,3-tris(4-methoxyphenyl)naphthalene (2c). [218617-75-5]



The reaction was run on a 0.30 mmol scale.

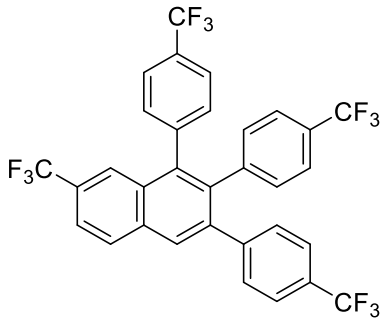
Rf = 0.30 (Hexane/EtOAc = 4/1). Pale yellow solid (40.5 mg, 57%). Isolated as a mixture of **2c** and **3c** (6:1). Pure **2c** was obtained by the second column chromatography (0.2 mmol scale, 14.0 mg, 29%).

^{1}H NMR ($CDCl_3$, 400 MHz): 3.68 (s, 3H), 3.71 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 6.49-6.53 (m, 2H), 6.71-6.75 (m, 4H), 6.78-6.80 (m, 2H), 6.88 (d, *J* = 2.4 Hz, 1H), 7.03-7.07 (m, 4H), 7.15 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.801 (d, *J* = 8.8 Hz, 1H), 7.803 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): 54.9, 55.08, 55.11, 55.13, 105.4, 112.4, 112.96, 113.08, 118.3, 128.19, 128.21, 129.3, 131.0, 132.0, 132.1, 132.5, 132.8, 133.4, 134.7, 137.5, 137.8, 138.4, 157.1, 157.6, 157.8 (two peaks are overlapped).

HRMS (EI+, [M$^+$]): Calcd for $C_{32}H_{28}O_4$ 476.1988, Found 476.1992.

7-(Trifluoromethyl)-1,2,3-tris(4-(trifluoromethyl)phenyl)naphthalene (2d).



Rf = 0.29 (Hexane/EtOAc = 9/1). White solid (53.3 mg, 85%). Mp = 121-123 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): 6.97 (d, *J* = 7.6 Hz, 2H), 7.25-7.28 (m, 6H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.75-7.77 (m, 1H), 7.80 (s, 1H), 8.05 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H).

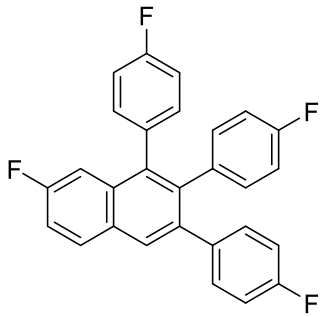
^{13}C NMR ($CDCl_3$, 100 MHz): Multiple peaks due to C-F coupling.

^{19}F NMR ($CDCl_3$, 375 MHz): -63.59, -63.74, -63.84, -63.90. [Perfluorobenzene (-163.0 ppm) was used as an internal standard.]

IR (KBr): 3059 w, 2936 w, 1923 w, 1803 w, 1617 s, 1574 m, 1443 m, 1407 s, 1324 s, 1298 s, 1167 s, 1117 s, 1069 s, 1018 s, 981 m, 925 s, 910 s, 840 s, 703 s, 645 s, 636 s.

HRMS (EI+, [M^+]): Calcd for $C_{32}H_{16}F_{12}$ 628.1060, Found 628.1056.

7-Fluoro-1,2,3-tris(4-fluorophenyl)naphthalene (2e). [1208342-15-7]



Rf = 0.12 (Hexane). Pale yellow solid (40.5 mg, 87%).

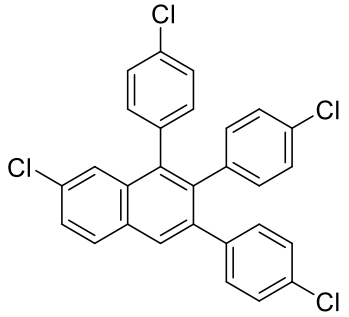
^{1}H NMR ($CDCl_3$, 400 MHz): 6.69 (t, *J* = 8.4 Hz, 2H), 6.75-6.79 (m, 2H), 6.89 (t, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 8.8 Hz, 2H), 7.05-7.10 (m, 4H), 7.14 (dd, *J* = 11.2, 2.5 Hz, 1H), 7.31 (td, *J* = 8.6, 2.6 Hz, 1H), 7.90 (s, 1H), 7.93 (dd, *J* = 8.9, 5.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): 110.0, 110.2, 114.2, 114.4, 114.6, 114.8, 114.9, 115.1, 116.7, 117.0, 128.8, 129.7, 130.4, 130.5, 131.4, 131.5, 132.4, 132.5, 132.65, 132.73, 133.0, 133.1, 134.47, 134.51, 135.39, 135.43, 137.29, 137.32, 137.89, 137.95, 138.11, 138.13, 138.2, 159.8, 160.38, 160.44, 162.3, 162.8, 162.9. (Multiple peaks due to C-F coupling. All observed peaks are in agreement with those reported in the literature.[7])

^{19}F NMR ($CDCl_3$, 375 MHz): -113.83 (s), -116.41 (s), -117.24 (s) (two peaks arew overlapped). [Perfluorobenzene (-163.0 ppm) was used as an internal standard.]

HRMS (DART+, [M+H^+]): Calcd for $C_{28}H_{16}F_4$ 429.1261, Found 429.1258.

7-Chloro-1,2,3-tris(4-chlorophenyl)naphthalene (2f). [1208342-13-5]



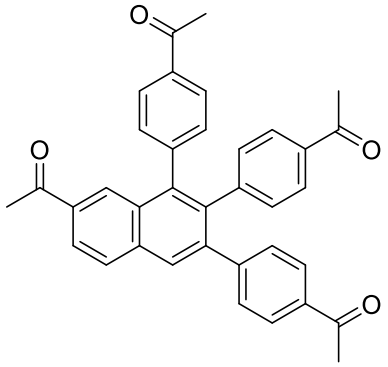
Rf = 0.44 (Hexane/EtOAc = 9/1). Pale yellow solid (31.1 mg, 63%).

^{1}H NMR ($CDCl_3$, 400 MHz): 6.74 (d, *J* = 8.2 Hz, 2H), 6.97-7.00 (m, 2H), 7.01-7.05 (m, 4H), 7.16-7.19 (m, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.47-7.49 (m, 2H), 7.86 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): 125.4, 127.5, 127.7, 128.1, 128.3, 129.0, 129.6, 130.97, 131.09, 132.2, 132.3, 132.4, 132.6, 132.7, 132.9, 133.1, 136.6, 137.5, 137.6, 137.7, 138.7, 139.5.

HRMS (DART+, [M+H$^+$]): Calcd for $C_{28}H_{17}Cl_4$, 493.0079, Found 493.0087.

1,1',1''-[(7-Acetylnaphthalene-1,2,3-triyl)tris(benzene-4,1-diyl)]tris(ethan-1-one) (2g).



Rf = 0.52 (Hexane/EtOAc = 3/7). Pale yellow solid (38.1 mg, 70%). Mp = 240-242 °C.

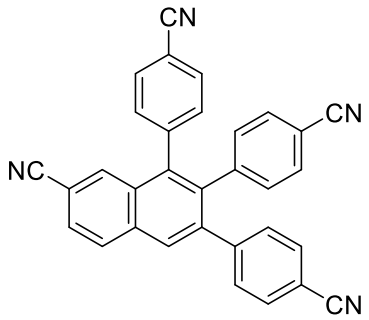
^{1}H NMR ($CDCl_3$, 400 MHz): 2.49 (s, 3H), 2.52 (s, 3H), 2.57 (s, 3H), 2.62 (s, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 7.25-7.29 (m, 4H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 8.02-8.05 (m, 2H), 8.12-8.13 (m, 2H).

^{13}C NMR ($CDCl_3$, 150 MHz): 26.5, 26.58 (two peaks are overlapped), 26.61, 124.9, 127.5, 127.9, 128.0, 128.4, 128.8, 129.2, 130.0, 131.0, 131.3, 131.4, 134.8, 135.0, 135.4, 135.5, 135.9, 137.5, 139.9, 140.8, 143.1, 144.0, 145.6, 197.60 (two peaks are overlapped), 197.61, 197.7.

IR (KBr): 1679 s, 1605 s, 1402 w, 1358 m, 1267 s, 1237 m, 1184 w, 1016 w, 960 m, 706 w.

HRMS (DART+, [M+H$^+$]): Calcd for $C_{36}H_{29}O_4$ 525.2060, Found 525.2069.

4,4',4''-(7-Cyanonaphthalene-1,2,3-triyl)tribenzonitrile (2h). [1208342-17-9]



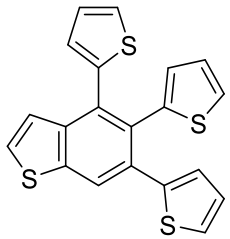
Rf = 0.40 (Hexane/EtOAc = 1/1). Pale yellow solid (30.0 mg, 63%).

^{1}H NMR ($CDCl_3$, 400 MHz): 6.93-6.95 (m, 2H), 7.22-7.25 (m, 4H), 7.33-7.36 (m, 2H), 7.53-7.56 (m, 2H), 7.65-7.67 (m, 2H), 7.76 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.83 (d, *J* = 0.8 Hz, 1 H), 8.04 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): 111.29, 111.34, 111.6, 112.3, 117.95, 118.02, 118.2, 118.6, 127.9, 129.7, 130.0, 130.3, 130.7, 131.50, 131.57, 131.59, 132.0, 132.2, 132.4, 134.0, 137.4, 138.4, 140.3, 141.7, 142.7, 144.4.

HRMS (EI+, [M^+]): Calcd for $C_{32}H_{16}N_4$ 456.1375, Found 456.1372.

4,5,6-Tri(thiophen-2-yl)benzo[*b*]thiophene (2i). [441284-37-3]



Rf = 0.12 (Hexane). White solid (15.6 mg, 41%).

^{1}H NMR ($CDCl_3$, 400 MHz): 6.72 (q, *J* = 1.5 Hz, 1H) 6.83 (q, *J* = 2.7 Hz, 1H), 6.87 (q, *J* = 1.5 Hz, 1H), 6.91 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.96-7.00 (m, 2H), 7.21 (dd, *J* = 5.2, 1.4 Hz, 1H), 7.23 (dd, *J* = 5.2, 1.4 Hz, 1H), 7.26 (t, *J* = 2.7 Hz, 1H), 7.30 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.46 (d, *J* = 5.5 Hz, 1H), 8.10 (s, 1H).

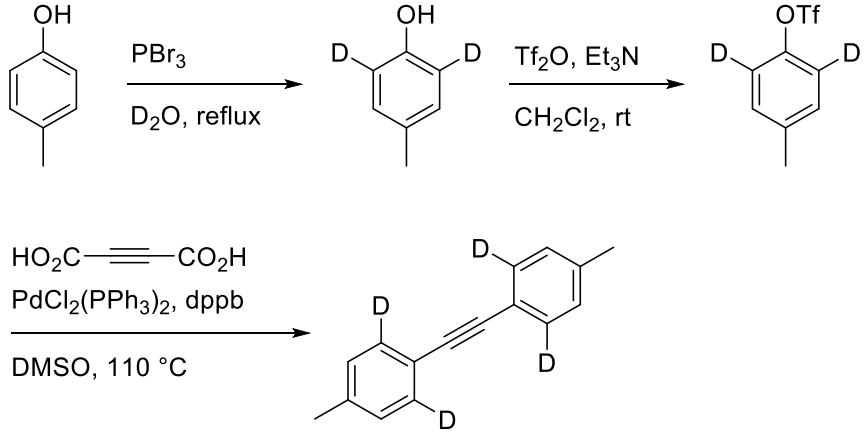
^{13}C NMR ($CDCl_3$, 100 MHz): 123.9, 124.5, 126.2, 126.3 (two peaks are overlapped), 126.55, 126.64, 127.0, 127.5, 128.4, 129.8 (two peaks are overlapped), 129.9, 131.4, 132.3, 139.7, 139.9, 140.0, 140.2, 143.2.

HRMS (DART+, [M+H^+]): Calcd for $C_{20}H_{13}S_4$ 380.9895, Found 380.9901.

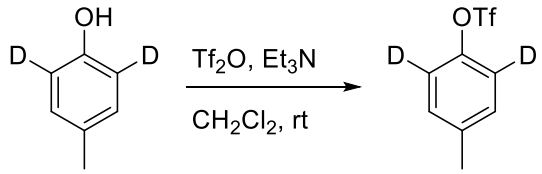
VII. Mechanistic Studies

VII-I. Preparation of alkyne 1b-d_4.

Alkyne **1b-d_4** was prepared based on the following scheme. 2,6-Dideuterio-4-methylphenol was prepared according to the literature procedure.[19]



2,6-Dideuterio-4-methyltrifluoromethanesulfonate.



To a mixture of 2,6-dideuterio-4-methylphanol (1.1 g, 10 mmol) and Et_3N (2.1 mL, 13 mmol) in CH_2Cl_2 (20 mL), Tf_2O (2.5 mL, 13 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to rt and stirred overnight. All volatiles were then removed in vacuo. Thus obtained residual materials were purified by column chromatography using hexane/EtOAc = 1~3% gradient to give desired 2,6-dideuterio-4-methyltrifluoromethanesulfonate as colorless oil (1.78 g, 73%).

Rf = 0.29 (hexane). Colorless oil (1.78 g, 73%). Deuterium content at the 2,6-positions of the benzene ring was determined to be 97% by ^{1}H NMR spectroscopy

^{1}H NMR ($CDCl_3$, 400 MHz): 2.37 (s, 3H), 7.23 (s, 2H).

^{2}H NMR ($CHCl_3$, 400 MHz): 7.07 (s). [Methanol-d_4 (3.31 ppm) was used as an internal standard.]

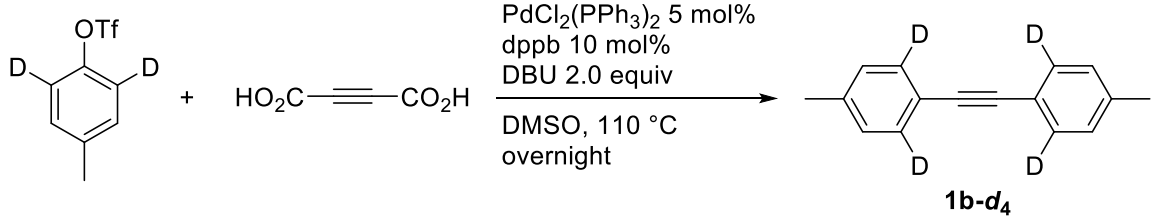
^{13}C NMR ($CDCl_3$, 100 MHz): 20.8, 118.8 (q, J = 319.4 Hz), 120.7 (t, J = 24.8 Hz), 130.6, 138.5, 147.5.

^{19}F NMR ($CDCl_3$, 375 MHz): 73.95 (s). [Perfluorobenzene (-163.0 ppm) was used as an internal standard.]

IR (ATR): 1454 m, 1420 s, 1248 m, 1203 s, 1139 s, 1047 m, 896 s, 850 m, 793 m, 606 s, 502 m, 455 m.

HRMS (DART+, [M+H$^+$]): Calcd for $C_8H_6D_2F_3O_3S$ 243.0266, Found 243.0257.

2,6,2',6'-Tetradeuterioditolylacetylene (1b-*d*$_4$).



1b-*d*$_4$

To a flame-dried two-necked round-bottom flask, 2,6-dideuterio-4-metyltrifluoromethanesulfonate (1.45 g, 6.0 mmol), acetylenedicarboxylic acid (342 mg, 3.0 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), dppb (128 mg, 0.3 mmol),

DBU (913 mg, 6.0 mmol), DMSO (15.0 mL) were added. This mixture was heated at 110 °C under an atmosphere of N_2 for 12 h. After cooling to rt, H_2O (30 mL) was added to the reaction mixture. The mixture was extracted with Et_2O (30 mL × 3) and combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The residual materials were purified by column chromatography using hexane/EtOAc = 1~3% gradient, followed by bulb-to-bulb distillation to give 2,6,2',6'-tetradeuterioditolylacetylene (**1b-*d*$_4$**) as a colorless crystalline solid (191 mg, 30 %).

Rf = 0.17 (hexane). Colorless crystalline solid (191 mg, 30%). Mp = 130~133 °C.

Deuterium content at the 2,6,2',6'-positions of the benzene rings was determined to be 97% by ^{1}H NMR spectroscopy.

^{1}H NMR ($CDCl_3$, 400 MHz): 2.36 (s, 6H), 7.15 (s, 4H).

^{2}H NMR ($CHCl_3$, 400 MHz): 7.34 (s). [Methanol-d_4 (3.31 ppm) was used as an internal standard.]

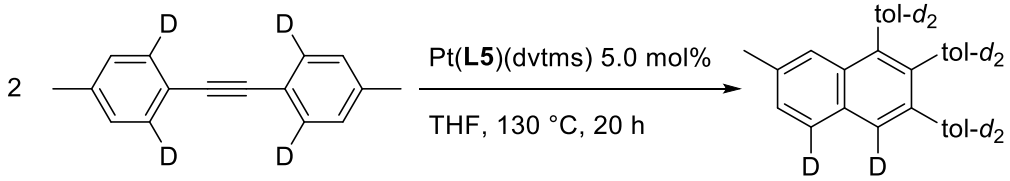
^{13}C NMR ($CDCl_3$, 100 MHz): 21.5, 88.8, 120.1, 129.0, 131.1 (t, J = 23.8 Hz), 138.2.

IR (KBr): 3019 w, 2921 w, 1480 s, 1037 m, 887 m, 765 s, 485 s.

HRMS (DART+, [M+H$^+$]): Calcd for $C_{16}H_{11}D_4$ 211.1419, Found 211.1427.

VII-II. Labelling experiments

Cyclodimerization of 1b-*d*$_4$.



1b-*d*$_4$ **2b-*d*$_8$**

In a glovebox filled with nitrogen, **1b-*d*$_4$** (0.20 mmol, 42.0 mg) and Pt(**L5**)(dvtms) (0.010 mmol, 11.1 mg) were added to a 10 mL-sample vial with a Teflon-sealed screwcap. THF (0.5 mL) was then added, and the vial was sealed with the cap. The vial was stirred at 130 °C for 20 h. After allowing the reaction mixture to cool to rt, the crude mixture was filtered through a pad of silica gel, which was eluted with EtOAc. The volatiles were removed in vacuo and 1,1,2,2-tetrachloroethane was added as an internal standard. The crude material was analyzed by ^{1}H NMR. After ^{1}H NMR analysis, the solvent was removed and purified by column chromatography (hexane/Et_2O = 0~5%) to give **2b-*d*$_4$** as a pale-yellow solid (22.2 mg, 51%).

Rf = 0.40 (Hexane/EtOAc = 9/1). Pale-yellow solid (22.2 mg, 51%). Mp = 102-104 °C.

Deuterium content at the 4-position of the naphthalene ring was determined to be 66% by ^{1}H NMR spectroscopy (Figure S2).

^{1}H NMR ($CDCl_3$, 400 MHz): 2.16 (s, 3H), 2.28 (s, 3H), 2.33 (s, 3H), 2.39 (s, 3H), 6.74 (s, 2H), 6.97 (s, 2H), 7.04 (s, 2H), 7.31 (s, 2H).

^{2}H NMR ($CHCl_3$, 400 MHz): 6.64 (s, 2H), 6.94 (s, 4H), 7.72 (s, 2H). [Methanol-d_4 (3.31 ppm) was used as an internal standard.]

^{13}C NMR ($CDCl_3$, 100 MHz): 21.11, 21.14, 21.3, 22.0, 125.7, 127.4, 128.0, 128.1, 128.3, 129.3, 129.5, 129.76, 129.82, 130.5, 130.7, 130.8, 131.0, 131.2, 131.3, 132.2, 134.7, 135.48, 135.54, 136.4, 137.1, 138.1, 138.4, 138.8,

138.9, 139.19, 139.22 (The ^{13}C NMR spectrum was quite complex due to ^{13}C-D coupling. All signals observed were shown).

IR (ATR): 3024 m, 2919 m, 2863 w, 1471 m, 911 s, 884 s, 874 s, 740 s.

HRMS (DART+, [M+H$^+$]): Calcd for $C_{32}H_{21}D_8$ 421.2766, Found 421.2770.

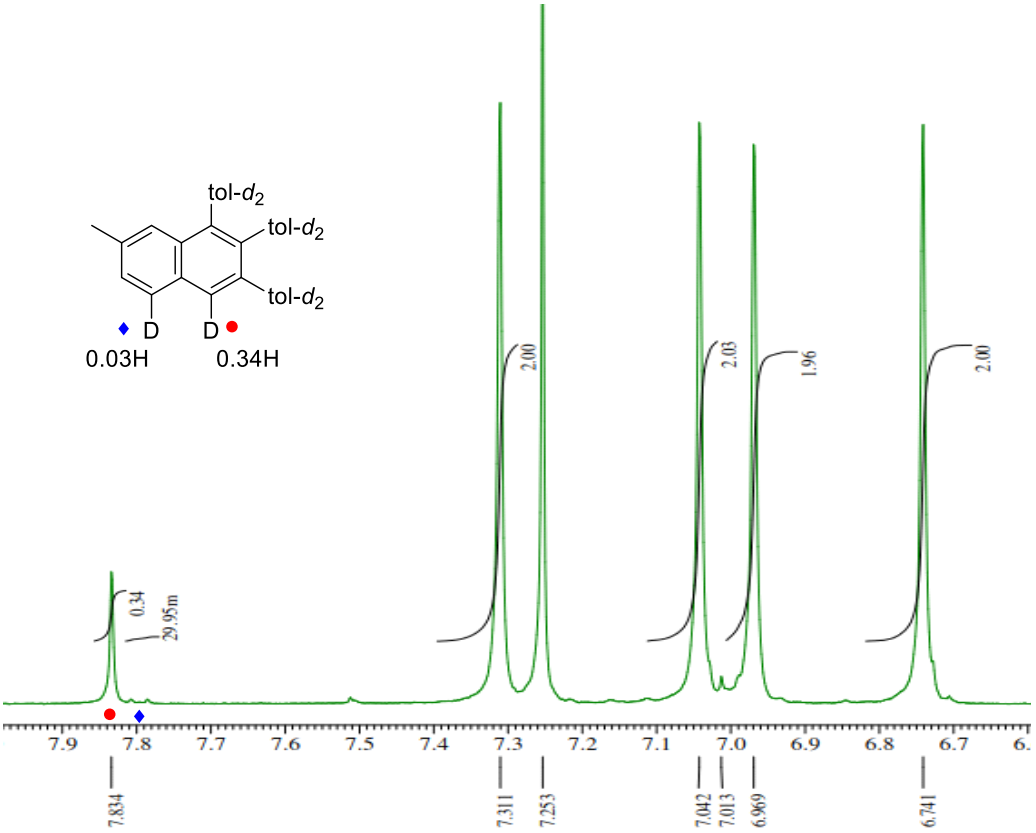
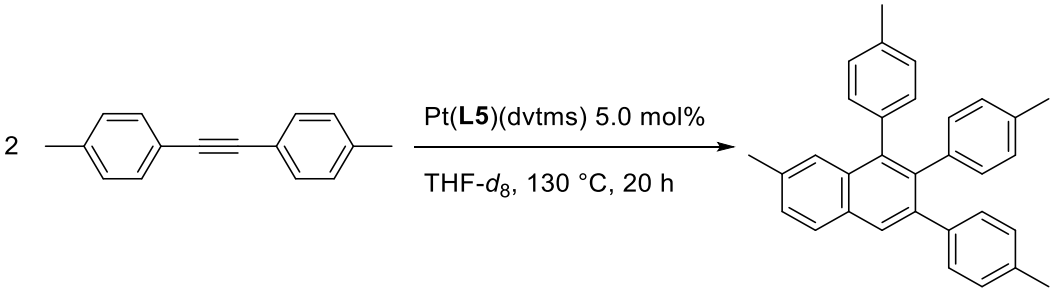


Figure S1. ^{1}H NMR Spectrum of **2b-*d*$_8$**(400 MHz, $CDCl_3$)

Cyclodimerization of 1b in THF-*d*$_8$.



In a glovebox filled with nitrogen, **1b** (0.20 mmol, 41.2 mg) and Pt(**L5**)(dvtms) (0.005 mmol, 11.1 mg) were added to a 10 mL-sample vial with a Teflon-sealed screwcap. THF-d_8 (0.5 mL) was then added, and the vial was then sealed with the cap. The vial was stirred at 130 °C for 20 h. After allowing the reaction mixture to cool to rt, the crude mixture was filtered through a pad of silica gel, which was eluted with EtOAc. The volatile was removed in vacuo and 1,1,2,2-tetrachloroethane was added as an internal standard. The crude material was analyzed by ^{1}H NMR, which indicated that no deuterium was incorporated into the product (Figure S3). Therefore, H/D exchange with THF-d_8 does not occur under these conditions.

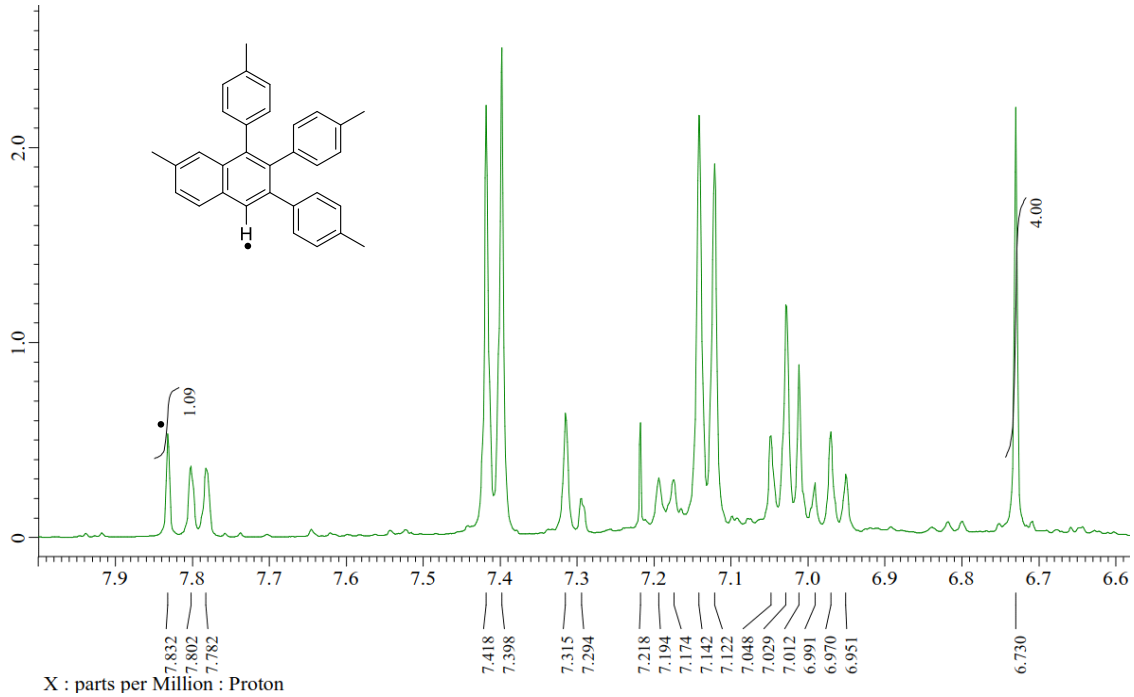


Figure S2. ^{1}H NMR Spectrum of Crude Material of **2b** (400 MHz, $CDCl_3$)

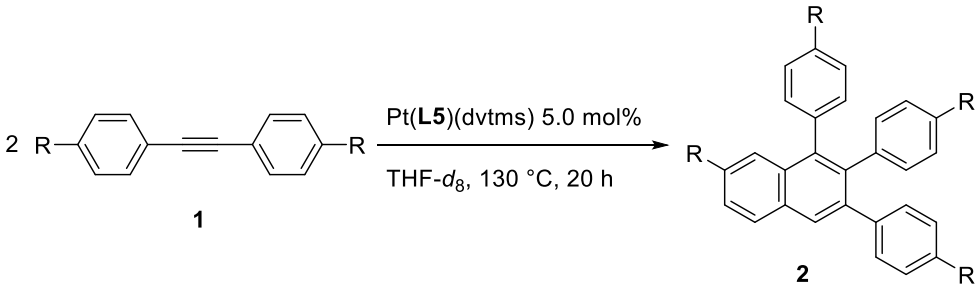
A comparison of initial yields between 1b and 1b-*d*$_4$.

In a glovebox filled with nitrogen, **1b** (0.10 mmol, 20.6 mg) or **1b-*d*$_4$** (0.10 mmol, 21.0 mg) and Pt(**L5**)(dvtms) (0.005 mmol, 5.6 mg) were added to a 10 mL-sample vial with a Teflon-sealed screwcap. 4-MeTHP (0.5 mL) was then added, and the vial was then sealed with the cap. The vial was stirred at 130 °C for 1 h. After allowing the reaction mixture to cool to rt, the crude mixture was filtered through a pad of silica gel, which was eluted with EtOAc. The volatile was removed in vacuo and 1,1,2,2-tetrachloroethane was added as an internal standard. Yields of the products were determined by ^{1}H NMR analysis of the crude material. The yields at 3 h were determined in a similar manner. No significant difference in yields was observed between **1b** and **1b-*d*$_4$**, indicating that the C-H bond cleavage is not involved in the turnover-limiting step (Table S2).

Table S2. Comparison of Initial Yields between **1b** and **1b-*d*$_4$**

substrate	product yield (%)	
	1 h	3 h
1b	22	30
1b-*d*$_4$	17	25

A comparison of initial yields among 1b, 1c and 1d.



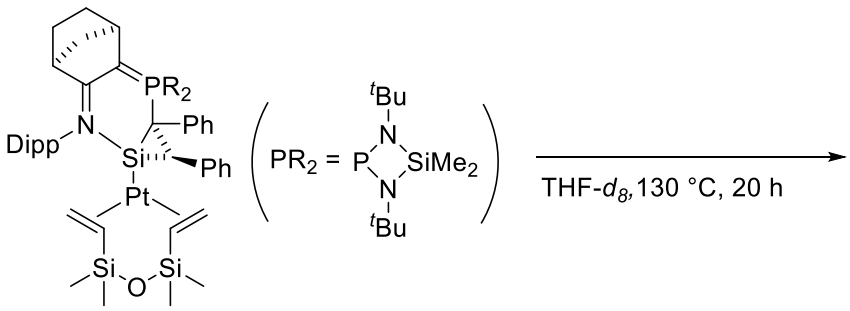
In a glovebox filled with nitrogen, **1a** (0.10 mmol, 17.8 mg) or **1c** (0.10 mmol, 23.8 mg), **1d** (0.10 mmol, 31.4 mg) or **1e** (0.10 mmol, 21.4 mg) and Pt(**L5**)(dvtms) (0.003 mmol, 3.3 mg) were added to a 10 mL-sample vial with a Teflon-sealed screwcap. 4-MeTHP (0.5 mL) was then added, and the vial was then sealed with the cap. The vial was stirred at 130 °C for 1 h. After allowing the reaction mixture to cool to rt, the crude mixture was filtered through a pad of silica gel, which was eluted with EtOAc. The volatile was removed in vacuo and 1,1,2,2-tetrachloroethane was added as an internal standard. Yields of the products were determined by ^{1}H NMR analysis of the crude material. The yields at 3 h were determined in a similar manner. These experiments revealed that electron-deficient **1d** and **1e** reacts significantly faster than electron-neutral **1a** and electron-rich **1c** (Table S3).

Table S3. Comparison of Initial Yields among **1b**, **1c**, **1d** and **1e**

R	yield of **2** (%)	
	1 h	3 h
H (**1a**)	17	18
OMe (**1c**)	15	30
CF_3 (**1d**)	83	>95
F (**1e**)	49	62

VII-III. NMR experiments

Thermal stability of Pt(L5)(dvtms).



In a glovebox filled with nitrogen, Pt(**L5**)(dvtms) (0.010 mmol, 11.1 mg) and THF-d_8 (0.75 mL) were added to an NMR tube equipped with a J-Young valve. The mixture was heated at 130 °C for 20 h using oil bath. After allowing the reaction mixture to cool to rt, this mixture was analyzed by ^{1}H NMR. ^{1}H NMR spectra before (Figure S4) and after (Figure S5) heating are virtually identical, indicating that Pt(**L5**)(dvtms) did not decompose by heating at 130 °C

for 20 h.

Before heating

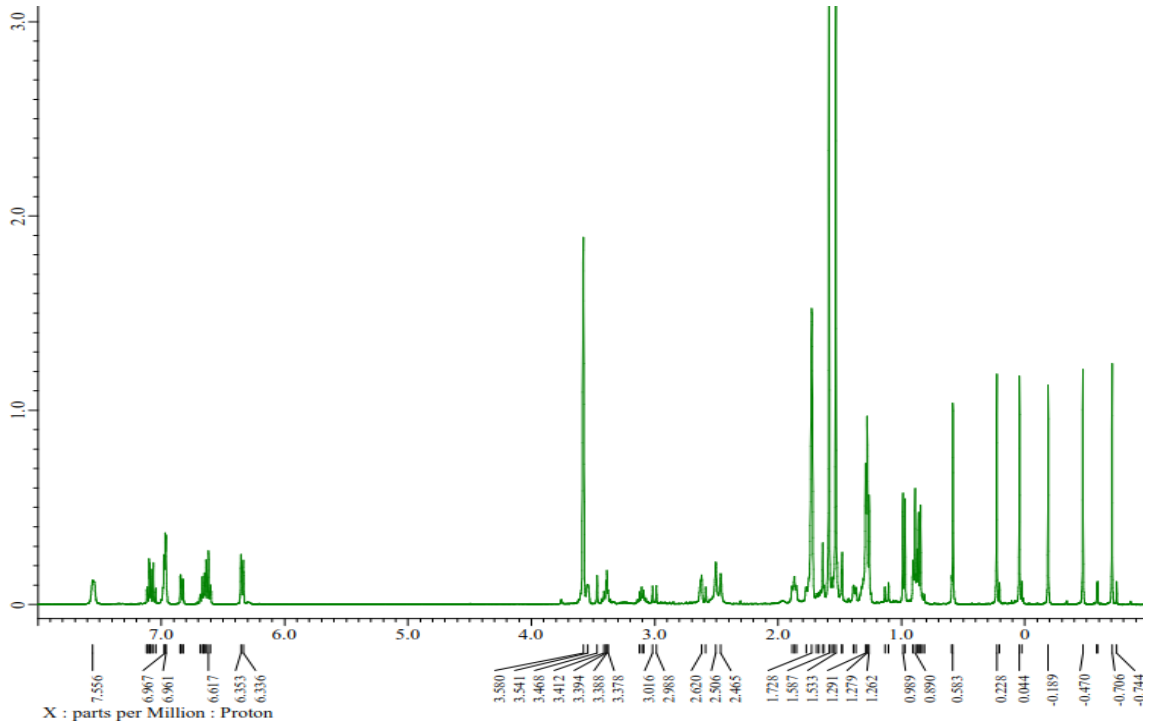


Figure S3. ^{1}H NMR Spectrum of Pt(**L5**)(dvtms) (400 MHz, THF-d_8)

After heating at 130 °C for 20 h

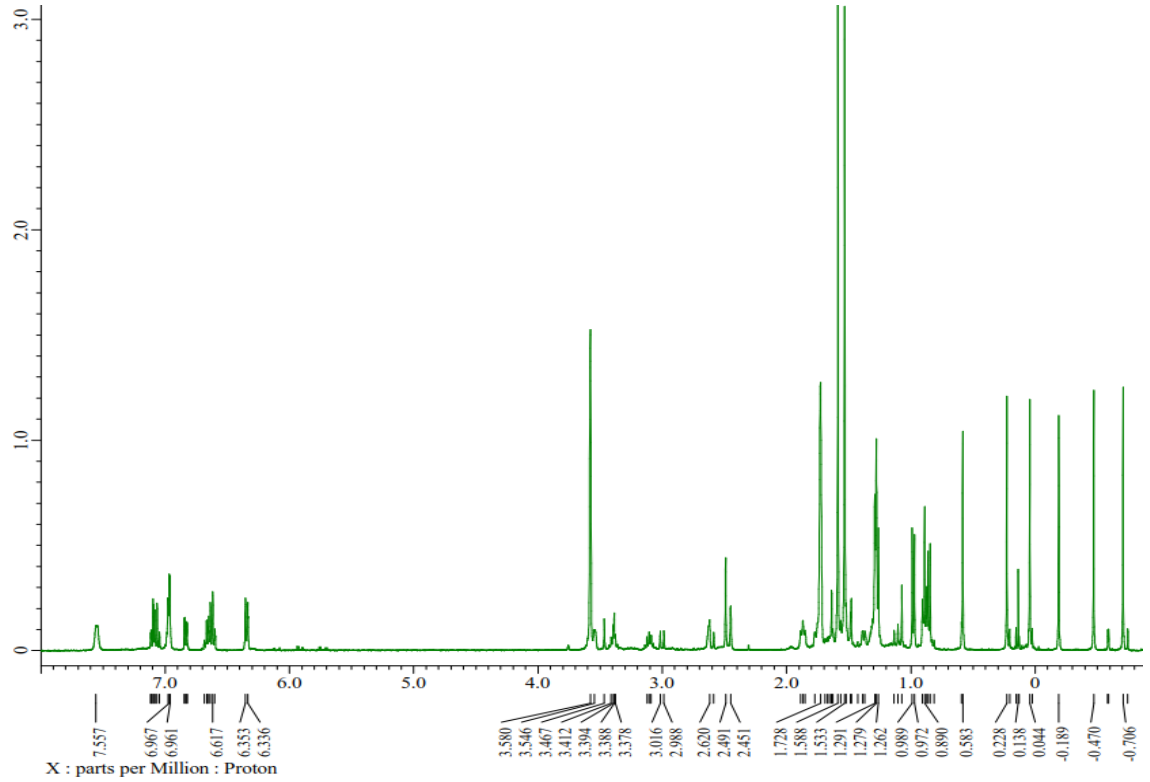
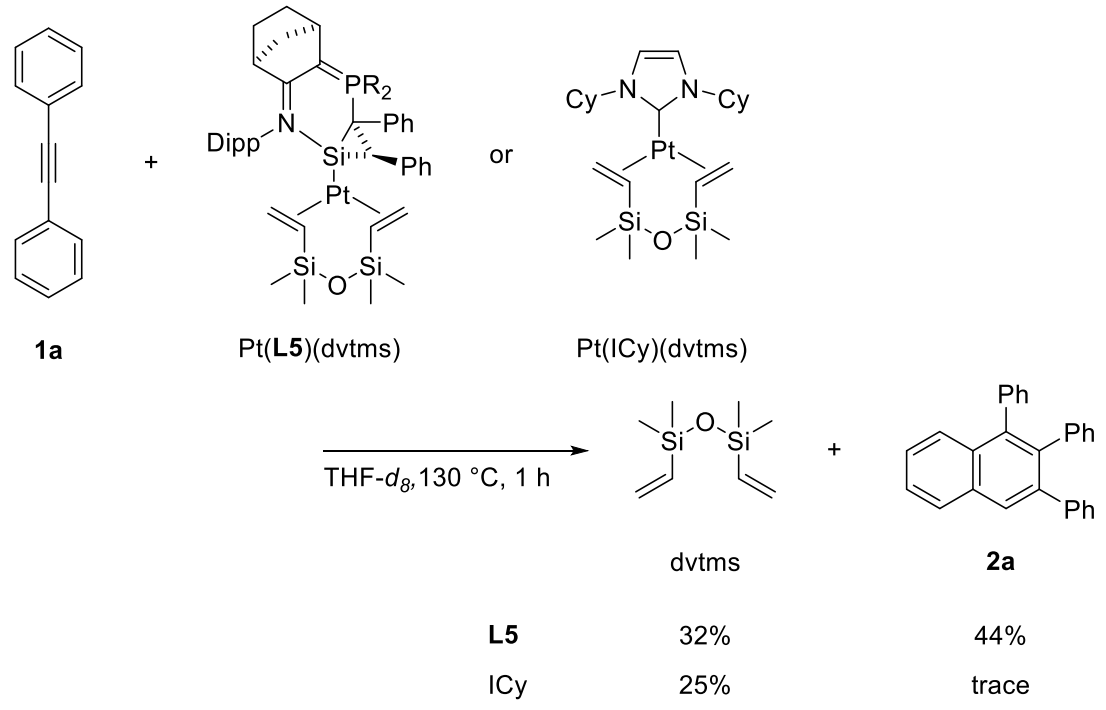


Figure S4. ^{1}H NMR Spectrum of Pt(**L5**)(dvtms) after heating (400 MHz, THF-d_8)

Ligand exchange between dvtms and 1a on platinum.



1a + Pt(**L5**)(dvtms) or Pt(ICy)(dvtms)

	dvtms	**2a**
L5	32%	44%
ICy	25%	trace

In a glovebox filled with nitrogen, **1a** (0.050 mmol, 8.9 mg), Pt(**L5**)(dvtms) (0.025 mmol, 27.8 mg) and anisole (4.0 mg, internal standard) were added to an NMR tube equipped with a J-Young volve. These mixtures were dissolved in THF-d_8 (0.50 mL) and heated at 130 °C for 1 h using oil bath. After allowing to cool to rt, the reaction mixture was analyzed by ^{1}H NMR, which revealed that 32% of dvtms was released along with the formation of dimerized product **2a** (44%). The same experiment was conducted using Pt(ICy)(dvtms) (0.025 mmol, 15.3 mg), resulting in the formation of dvtms in 25%, whereas **2a** was not observed. These results indicate that the initial ligand exchange can occur with both **L5** and ICy ligands, while the subsequent product formation requires **L5**.

1.5. References

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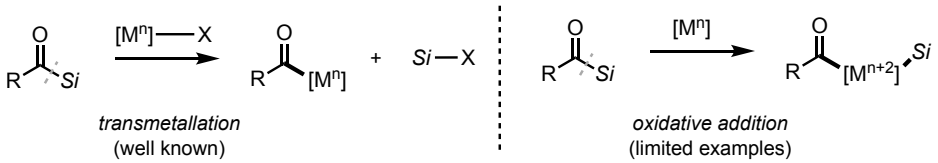
Chapter 2

Rhodium-Catalyzed Decarbonylation of Acylsilanes

2.1. Introduction

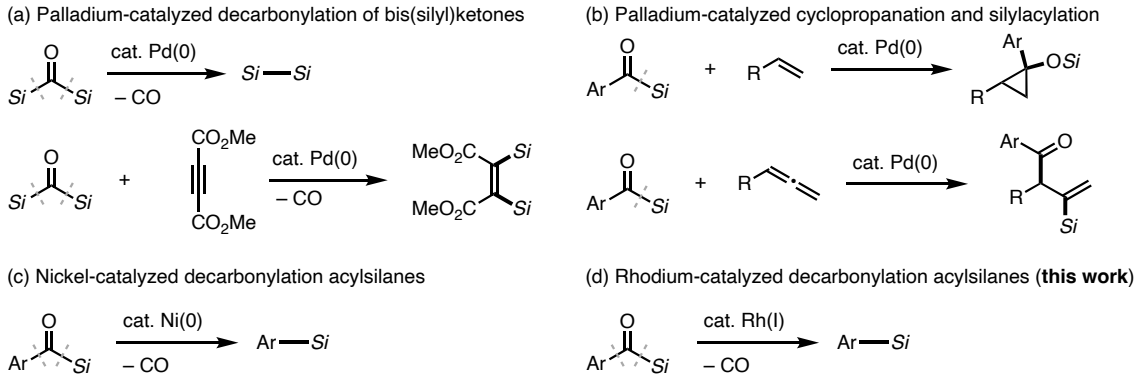
The transition metal-catalyzed decarbonylation of aldehydes, or Tsuji-Wilkinson decarbonylation, has been used extensively in organic synthesis.[1] If such a decarbonylation process could be applied to other carbonyl compounds, it would serve as a powerful method for forging new chemical bonds other than C–H bonds.[2] Although the scope of the reaction is somewhat limited, catalytic decarbonylation reactions of ketones,[3] esters,[4] amides,[5] and some other carbonyl compounds[6,7] have been reported to date. Our group[8a] and Rueping[8b] independently reported that acylsilanes[9] can also be decarbonylated by nickel catalysts via the cleavage of C–C and C–Si bonds.

Regarding the cleavage of a carbon–silicon bond in acylsilanes, two mechanistic modes appear to be involved. One is a transmetallation reaction, in which a silyl group serves as a leaving group to generate an acylmetal species (Scheme 1, left).[10] In this process, the oxidation state of the metal center remains unchanged. The other mode is oxidative addition, in which an (acyl)(silyl)metal species is formed with the increase of the oxidation state of the metal center by two (Scheme 1, right).



Scheme 1. Transition metal-mediated C–Si bond cleavage of acylsilane

The transmetallation process has been applied to cross-coupling type reactions using acylsilanes.[10] In contrast, there are only a limited number of reports of catalytic reactions that involve the oxidative addition of acylsilanes, despite the potential utility of such reactions in the synthesis of organosilicon compounds by incorporating both an acyl and a silyl group of acylsilanes into the product. Narasaka reported that bis(silyl)ketones can be decarbonylated by the use of a palladium catalyst, a reaction that likely includes oxidative addition of a C–Si bond (Scheme 2a).[11] This process was further applied to decarbonylative addition across electron-deficient alkynes. However, the applicability of these reactions to acylsilanes was not mentioned. Our group recently reported on the palladium-catalyzed siloxycyclopropanation of alkenes[12] and silylacylation of allenes[13] using acylsilanes, in which the oxidative addition of a C–Si bond in acylsilanes to a palladium(0) complex is involved (Scheme 2b). As described above, our group[8a] and Rueping's group[8b] independently developed the nickel-catalyzed decarbonylation of acylsilanes, which suggests that a nickel(0) complex can mediate the oxidative addition of acylsilanes (Scheme 2c). The author report herein that the decarbonylation of acylsilanes can also be catalyzed by a rhodium(I) complex, which suggests that carbon–silicon bond of acylsilanes can oxidatively add to a rhodium(I) center (Scheme 2d).[14]

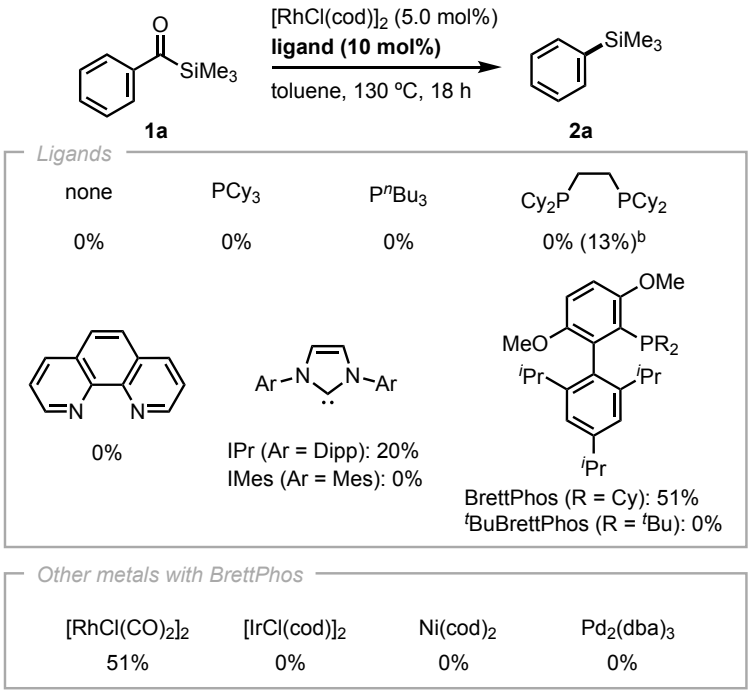


Scheme 2. Catalytic reactions involving oxidative addition of C–Si bond of acylsilanes

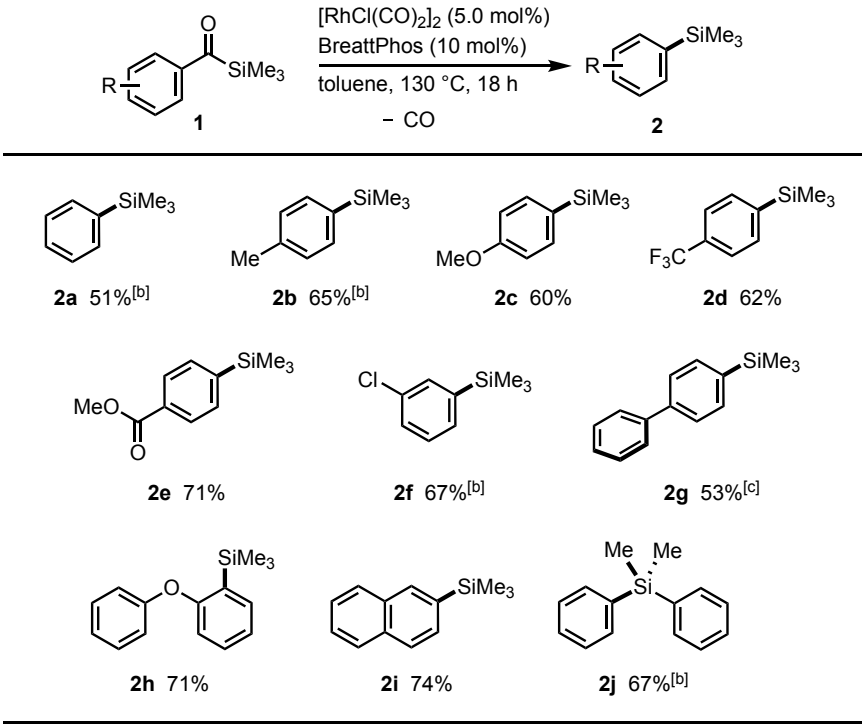
2.2. Results and Discussion

We began our investigation with examination of the reaction of acylsilane **1a** in the presence of 5.0 mol% of $[RhCl(cod)]_2$ at 130 °C for 18 h. (Scheme 3). No reaction occurred in the absence of an added ligand. The addition of monodentate phosphines, such as PCy_3 and P^nBu_3, also failed to promote the reaction. The use of a P-based bidentate ligand dcype at 160 °C led to the formation of decarbonylated product **2a**, albeit in low yield (13%). Phenanthroline (0%) and NHC ligands, such as IPr (20%) and IMes (0%), which were effective ligands for nickel-catalyzed decarbonylation of acylsilanes,[8a] were also not as effective for this rhodium system. When Brettphos was used as a ligand, **2a** was obtained in 51% yield. When the Cy groups of Brettphos were replaced with ^{t}Bu groups (*i.e.*, ^{t}BuBrettphos), no reaction occurred. The use of $[RhCl(CO)_2]_2$ as a catalyst precursor resulted in the formation of **2a** in a yield comparable to that obtained with $[RhCl(cod)]_2$. This indicate that the eliminated CO does not completely deactivate the catalyst, which is in sharp contrast to nickel-catalyzed decarbonylation of carbonyl compounds.[3c,5b] When other metal catalysts such as iridium(I), nickel(0), and palladium(0), were used instead of rhodium(I), **2a** was not formed under these conditions using a BrettPhos ligand.

With the optimized conditions in hand, the scope of this rhodium-catalyzed decarbonylation of acylsilanes was next examined (Scheme 4). Both electron-rich (**1b**, **1c**) and electron-deficient (**1d**, **1e**) acylsilanes could be applied to decarbonylation with the formation of the corresponding arylsilanes **2b**, **2c**, **2d**, and **2e**, in which ether and ester groups were tolerated. A chloroarene moiety was also applicable for this reaction without loss of the chlorine atom, as exemplified by the formation of **2f**. When a substrate containing a biphenyl moiety (**1g**) was used, the corresponding arylsilane **2g** was obtained in 53% yield. Substrates bearing an ortho substituent, such as 2-phenoxybenzoylsilane (**1h**), were also good substrates for this reaction. An acylsilane having a π-extended naphthalene ring (**1i**) also participated in this decarbonylation to form 2-naphthylsilane **2i** in 74% yield. Regarding the substituents on the silicon atom, a bulkier $SiMe_2Ph$ group (**1j**) can also be used for this rhodium-catalyzed decarbonylation, with biarylsilane **2j** being produced in 67% yield.



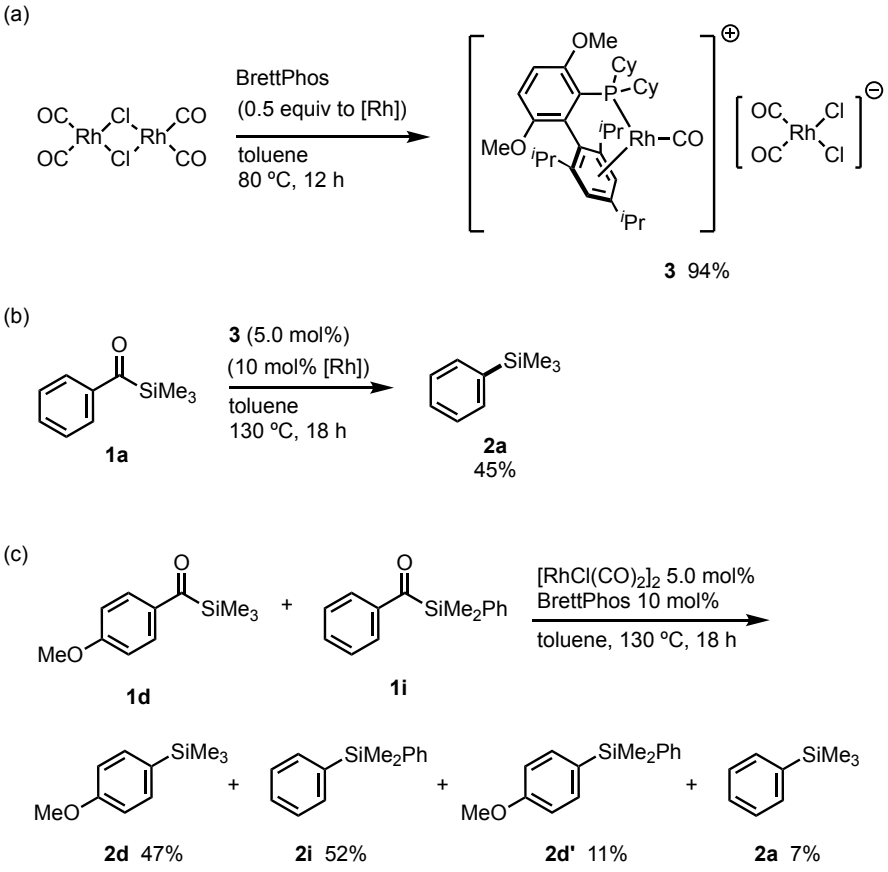
Scheme 3. Reaction optimization[a] [a]Yield of **2a** was determined by GC using pentadecane as an internal standard due to volatility of **2a**. [b]Run at 160 °C.



Scheme 4. Scope of Rh-catalyzed decarbonylation of acylsilanes.[a] [a]Isolated yields are shown unless otherwise noted. [b]Yield of 2 was determined by GC using pentadecane as an internal standard due to the volatility of the product.

To obtain mechanistic insights, several preliminary mechanistic experiments were conducted for this decarbonylation reactions. When $[RhCl(CO)_2)]_2$ and a BrettPhos ligand (0.50 equiv) were reacted in toluene at 80 °C, a yellow

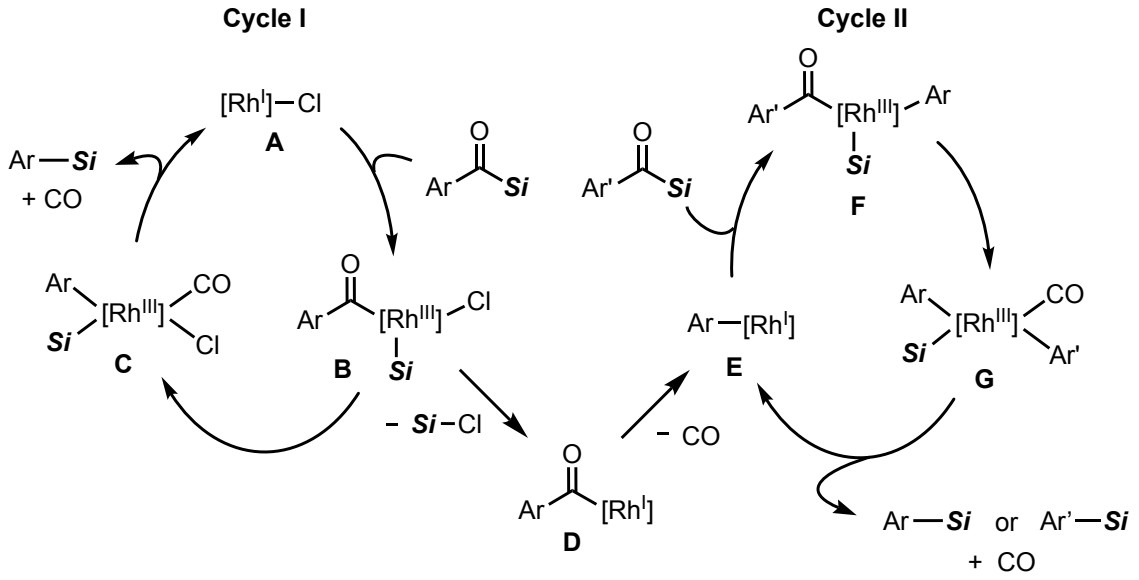
precipitate was formed. X-ray crystallographic analysis of a recrystallized sample unambiguously determined that an ion pair consisting of cationic and anionic rhodium complexes (*i.e.*, **3**) was generated, presumably by disproportionation of a neutral rhodium(I)–Cl complex (Scheme 5a). Complexes with a Buchwald-type ligand has not been reported, to the best of our knowledge, although similar ion pair rhodium complexes are known to be formed with several ligands.[15]. The catalytic activity of **3** for the decarbonylation of **1a** was next examined (Scheme 5b). As a result, **2a** was obtained in a yield comparable to that obtained with a $[RhCl(CO)_2]_2$/BrettPhos catalyst, although it is unclear whether **3** is the catalytically active species or a resting-state species in this reaction. A crossover experiment using acylsilanes **1c** and **1j** resulted in the formation of crossover products **2c'** and **2a**, in addition to intramolecular decarbonylation products **2c** and **2j** (Scheme 5c). These results indicate that the aryl groups on the rhodium center are interchangeable under the catalytic conditions being used.[16]



Scheme 5. Mechanistic studies

Based on the results of a crossover experiment, proposed catalytic cycles for this reaction are showed in Scheme 6. The reaction is initiated by the oxidative addition of a carbon–silicon bond of acylsilane **1** across Rh(I)–Cl (**A**) to give (acyl)(silyl)rhodium(III) intermediate **B**. The elimination of CO subsequently gives arylrhodium(III) species **C**, which finally leads to the formation of product **2** by reductive elimination (Cycle I). Alternatively, intermediate **B** can release chlorosilane (*Si*–Cl) by reductive elimination to generate acylrhodium(I) **D**,[17] which leads to the formation of arylrhodium(I) **E** by the extrusion of CO. This complex **E** can also mediate the catalytic decarbonylation of acylsilane (Cycle II). Cycle II is basically the same as Cycle I, except that the chloro ligand is replaced by an aryl group. The oxidative addition of an acylsilane, followed by decarbonylation forms intermediate **G**, which has two

aryl ligands. Both of the aryl ligands can reductively eliminate with the silyl ligand to form a decarbonylated product, which explains the experimental observations of the crossover products.



Scheme 6. A possible mechanism

2.3. Conclusion

In summary, we report on the rhodium-catalyzed decarbonylation of acylsilanes, in which BrettPhos serves as an optimized ligand. In previously reported catalytic reactions of acylsilanes that involves the oxidative addition of a carbon–silicon bond, Ni(0) and Pd(0) catalysts were used. This work demonstrates that a utility of rhodium(I) complex in the catalytic transformation of acylsilanes via oxidative addition of C–Si bond in which a substituent of the acyl group and the silyl group are both incorporated into the product.

2.4. Experimental Section

I. General Information

^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$. The chemical shifts in ^{1}H NMR spectra were recorded relative to tetramethyl silane (δ 0.00) or $CHCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.16). The chemical shifts in ^{19}F NMR spectra were recorded relative to hexafluorobenzene (C_6F_6, δ –163.0).^{31}P NMR spectra were recorded relative to H_3PO_4(δ 0.00). The data is reported as follows: chemical shift (δ) in ppm, coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silicycle SilicaFlash F60 (230-400 mesh)). Data collection for X-ray crystal analysis were performed on a Rigaku/XtaLAB Pro P200 Hybrid Photon Counting diffractometer (Cu-Kα, λ = 1.54184 Å). The structures were solved with olex2.solve 1.5. SHELXL−2018/3 was used

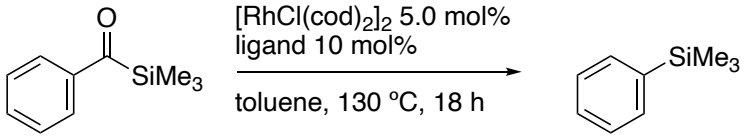
for structure refinement.

II. Materials

Unless otherwise stated, all commercially available reagents and solvents were supplied from TCI, Wako Chemical, and Aldrich and used as received. Toluene (deoxygenated) was purchased from Wako Chemical and used as received. Acylsilane phenyl(trimethylsilyl)methanone **1a** [CAS: 5908-41-8] was prepared from benzyltrimethylsilane (TCI) according to the literature method.[18] *p*-Tolyl(trimethylsilyl)methanone **1b** [CAS: 68185-94-4], (4-methoxyphenyl)(trimethylsilyl)methanone **1c** [CAS: 75748-09-3], (4-(trifluoromethyl)phenyl)(trimethylsilyl)methanone **1d** [CAS: 103411-25-2], methyl 4-((trimethylsilyl)carbonyl)benzoate **1e** [CAS: 75748-12-8], (3-chlorophenyl)(trimethylsilyl)methanone **1f** [CAS: 68185-97-7], [1,1'-biphenyl]-4-yl(trimethylsilyl)methanone **1g** [CAS: 648428-46-0], (2-phenoxyphenyl)(trimethylsilyl)methanone **1h** [CAS: 2416830-79-8], naphthalen-2-yl(trimethylsilyl)methanone naphthalen-2-yl(trimethylsilyl)methanone **1i** [CAS: 22364-54-1] were prepared from corresponding acyl chlorides according to literature method.[19, 20] (Dimethyl(phenyl)silyl)(phenyl)methanone **1j** [CAS: 17909-51-2] was prepared according to literature procedure from benzylchloride.[21]

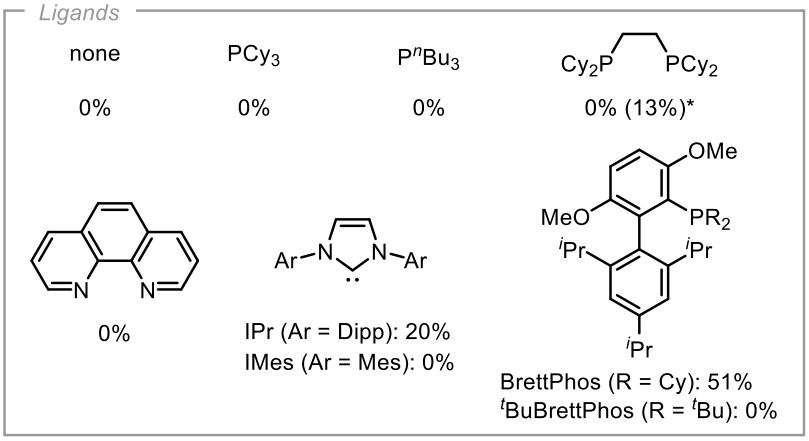
III. Optimization Studies

III-I. Ligand screening



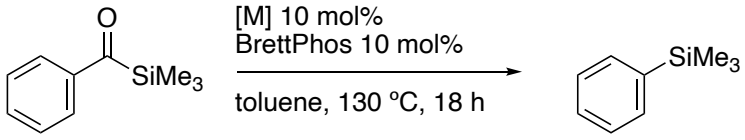
1a **2a**

In a glovebox filled with N_2, $[RhCl(cod)_2]_2$ (4.9 mg, 0.010 mmol, 10 mol% [Rh]), ligand (0.020 mmol, 10 mol%), and toluene (0.50 mL) were added to a screw-capped vial. After stirring at rt for 5 min, acylsilane **1a** (35.6 mg, 0.20 mmol) and toluene (0.50 mmol) were added to the vial. The screw-cap was then closed and the vial was removed from the glove box. The reaction mixture was stirred at 130 ºC for 18 h. After cooling to rt, the reaction mixture was filtered through a short silica gel pad. The crude mixture was analyzed by GC using pentadecane as an internal standard.



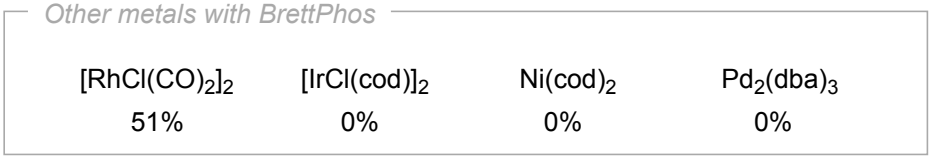
*At 160 °C.

III-II. Catalyst screening

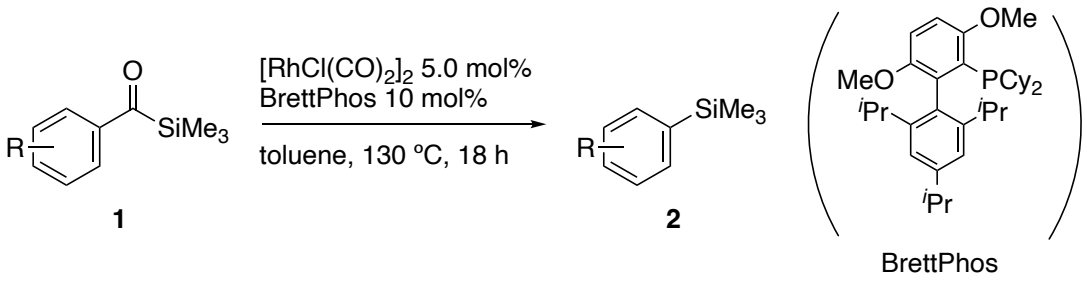


1a **2a**

In a glovebox filled with N_2, a catalyst precursor (10 mol%), BrettPhos (10.7 mg, 10 mol%), and toluene (0.50 mL) were added to a screw-capped vial. After stirring at rt for 5 min, acylsilane **1a** (35.6 mg, 0.20 mmol) and toluene (0.50 mL) were added to the vial. The screw-cap was then closed and the vial was removed from the glove box. The reaction mixture was stirred at 130 ºC for 18 h. After cooling to rt, the reaction mixture was filtered through a short silica gel pad. The crude mixture was analyzed by GC using pentadecane as an internal standard.



IV. General Procedure for Rhodium-Catalyzed Decarbonylation of Acylsilanes



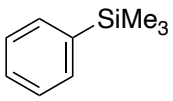
1 **2**

In a glovebox filled with N_2, $[RhCl(CO)_2]_2$ (3.9 mg, 0.010 mmol, 10 mol% [Rh]), BrettPhos (10.7 mg, 0.020 mmol, 10 mol%), and toluene (0.50 mL) were added to a screw-capped vial. After stirring at rt for 5 min, acylsilane

1 (0.20 mmol) and toluene (0.50 mmol) were added to the vial. The screw-cap was then closed and the vial was removed from the glove box. The reaction mixture was stirred at 130 ºC for 18 h. After cooling to rt, all volatiles were removed in vacuo and the residue was purified by flash column chromatography to give desired arylsilane **2**.

Spectroscopic Data of Products

Trimethyl(phenyl)silane (2a). [CAS: 768-32-1]



General procedure was followed using **1a** (36.5 mg, 0.205 mmol).

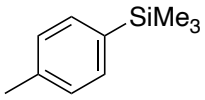
Colorless oil (51%, GC yield using pentadecane as an internal standard due to the volatility).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.28 (s, 9H), 7.35–7.38 (m, 3H), 7.52–7.56 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -1.0, 127.9, 128.9, 133.4, 140.6.

HRMS (EI, $[M]^+$): Calcd for $C_9H_{14}Si$: 150.0865. Found: 150.0869.

Trimethyl(*p*-tolyl)silane (2b). [CAS: 3728-43-6]



General procedure was followed using **1b** (40.6 mg, 0.211 mmol).

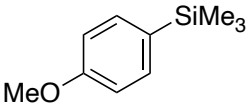
Colorless oil (65%, GC yield using pentadecane as an internal standard due to the volatility).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.28 (s, 9H), 2.38 (s, 3H), 7.20–7.22 (m, 2H), 7.45–7.47 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -0.91, 21.6, 128.7, 133.5, 136.9, 138.7.

HRMS (EI, $[M]^+$): Calcd for $C_{10}H_{16}Si$: 164.1021. Found:164.1023.

(4-Methoxyphenyl)trimethylsilane (2c). [CAS: 877-68-9]



General procedure was followed using **1c** (42.5 mg, 0.204 mmol).

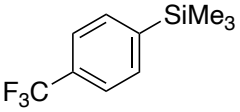
Colorless oil (22.1 mg, 60%). R_f = 0.86 (SiO_2, hexane/Et_2O = 7/3)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.26 (s, 9H), 3.82 (s, 3H), 6.93 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -0.79, 55.2, 113.6, 131.5, 134.9, 160.3.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{10}H_{17}OSi$: 181.1043. Found: 181.1043.

Trimethyl(4-(trifluoromethyl)phenyl)silane (2d). [CAS: 312-75-4]



General procedure was followed using **1e** (53.5 mg, 0.217 mmol).

Colorless oil (29.4 mg, 62%). R_f = 0.74 (SiO_2, hexane)

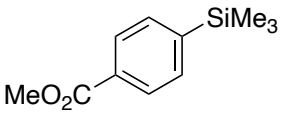
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.30 (s, 9H), 7.58–7.65 (m, 4H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -1.2, 123.7 (q, $J_{C–F}$ = 272.2 Hz), 124.4 (q, $J_{C–F}$ = 3.8 Hz) 130.9 (q, $J_{C–F}$ = 32.6 Hz) 133.7, 145.6.

^{19}F NMR ($CDCl_3$, 375 MHz) δ: -65.17.

HRMS (EI+, $[M]^+$) Calcd for $C_{10}H_{13}F_3Si$: 218.0739. Found: 218.0741.

Methyl 4-(trimethylsilyl)benzoate (2e). [CAS: 22515-30-6]



General procedure was followed using **1d** (47.5 mg, 0.201 mmol).

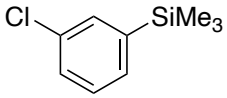
Colorless oil (29.5 mg, 71%). R_f = 0.74 (SiO_2, hexane/Et_2O = 7/3)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.29 (s, 9H), 3.92 (s, 3H), 7.60 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -1.2, 52.2, 128.6, 130.4, 133.4, 147.0, 167.5.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{11}H_{17}O_2Si$: 209.0992. Found: 209.0989.

(3-Chlorophenyl)trimethylsilane. (**2f**) [CAS: 4405-42-9]



General procedure was followed using **1f** (50.3 mg, 0.24 mmol).

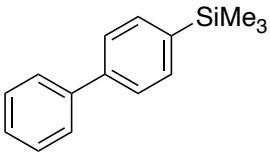
Colorless oil (67%, GC yield using pentadecane as an internal standard).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.27 (s, 9H), 7.28–7.33 (m, 2H), 7.36–7.39 (m, 1H), 7.456–7.462 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -1.1, 129.0, 129.4, 131.4, 133.2, 134.3, 143.4.

MS, *m/z* (EI+, relative intensity, %): 186 (14, $[M+2]^+$), 184 (38, $[M]^+$), 172 (12), 171 (85), 170 (35), 169 (100), 168 (10), 141 (11), 93 (12), 91 (60), 85 (14), 73 (15), 65 (21), 63 (32), 43 (18).

[1,1'-Biphenyl]-4-yltrimethylsilane (2g). [CAS: 1625-88-3]



General procedure was followed using **1g** (42.7 mg, 0.168 mmol).

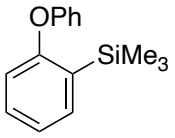
Colorless solid (20.3 mg, 53%). R_f = 0.48 (SiO_2, hexane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.32 (s, 9H), 7.36 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.3 Hz, 2H), 7.59–7.64 (m, 6H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -0.94, 126.6, 127.3, 127.5, 128.9, 134.0, 139.4, 141.3, 141.7.

HRMS (EI+, $[M]^+$) Calcd for $C_{15}H_{18}Si$: 226.1178. Found: 226.1172.

Trimethyl(2-phenoxyphenyl)silane (2h). [CAS: 17049-42-2]



General procedure was followed using **1h** (55.4 mg, 0.205 mmol).

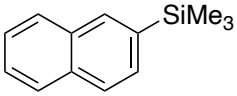
Colorless oil (35.4 mg, 71%). R_f = 0.88 (SiO_2, hexane/Et_2O = 7/3)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.32 (s, 9H), 6.84 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 7.09–7.15 (m, 2H), 7.31–7.38 (m, 3H), 7.53 (dd, *J* = 7.3, 1.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -0.78, 117.6, 118.9, 123.0, 123.1, 129.8, 130.8 (two peaks are overlapped), 135.5, 157.6, 162.1.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{19}OSi$: 243.1200. Found: 243.1198.

Trimethyl(naphthalen-2-yl)silane (2i). [CAS: 18052-85-2]



General procedure was followed using **1i** (48.5 mg, 0.213 mmol).

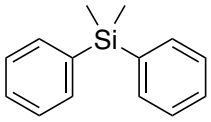
Colorless oil (31.2 mg, 74%). R_f = 0.54 (SiO_2, hexane)

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.39 (s, 9H), 7.49–7.53 (m, 2H), 7.64 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.84–7.89 (m, 3H), 8.05 (s, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -0.93, 126.0, 126.3, 127.1, 127.8, 128.2, 129.9, 133.1, 133.8, 133.9, 138.0.

HRMS (EI+, $[M]^+$) Calcd for $C_{13}H_{16}Si$: 200.1021. Found: 200.1025.

Dimethyldiphenylsilane (2j). [CAS: 778-24-5]



General procedure was followed using **1j** (48.5 mg, 0.213 mmol).

67% (GC yield using pentadecane as an internal standard).

Product **2i** was isolated as a mixture with $(Me_2PhSi)_2O$. Analytically pure **2i** was obtained by purification by gel permeation chromatography.

Colorless oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.58 (s, 6H), 7.35–7.38 (m, 6H), 7.54–7.57 (m, 4H).

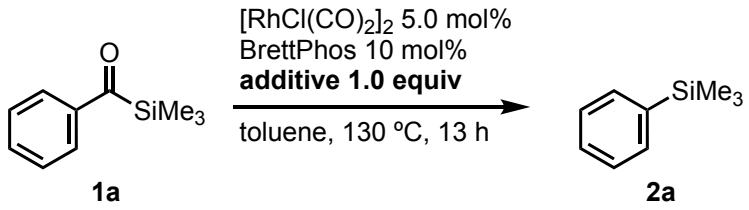
^{13}C NMR ($CDCl_3$, 101 MHz) δ: -2.2, 127.9, 29.2, 134.3, 138.4.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{14}H_{17}Si$: 213.1094. Found: 213.1097.

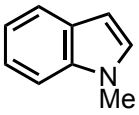
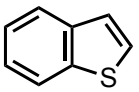
V. Applicability of Heteroarenes

In a glovebox filled with N_2, $[RhCl(CO)_2]_2$ (3.9 mg, 0.010 mmol, 10 mol% [Rh]) and BrettPhos (10.7 mg, 0.020 mmol, 10 mol%) were added to a screw-capped vial and dissolved in toluene (0.50 mL). After stirring at rt for 5 min,

acylsilane **1a** (35.6 mg, 0.20 mmol), additive (0.20 mmol, 1.0 equiv), and toluene (0.50 mmol) were added to the vial. The screw-cap was then closed and the vial was removed from the glove box. The reaction mixture was stirred at 130 ºC for 13 h. After cooling to rt, the reaction mixture was filtered through a silica gel pad. The crude mixture was analyzed by GC using pentadecane as an internal standard. As a result, it was revealed that addition of 1 equiv of *N*-methylindole or benzothiophene did not affect the yield of **2a**, and they were recovered in 59% and 72% yield, respectively.

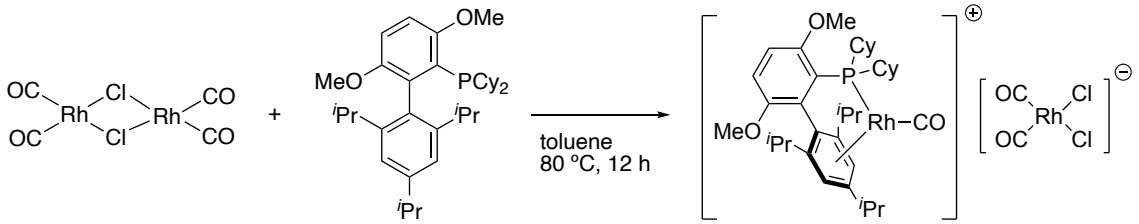


1a **2a**

Additive	**1a** [%]	**2a** [%]	Recovered additive [%]
None	0	51	---
	0	51	59
	0	53	72

VI. Mechanistic Studies

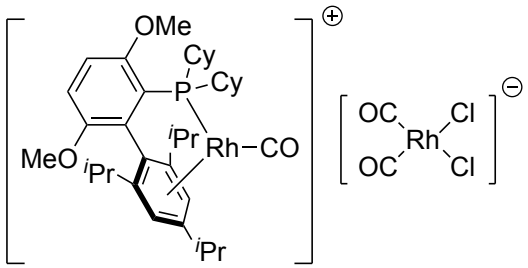
VI-I. Synthesis of Rh Complex 3



0.5 equiv to [Rh] **3**

In a glovebox filled with N_2, $[RhCl(CO)_2]_2$ (97.2 mg, 0.25 mmol) and BrettPhos (134.2 mg, 0.25 mmol, 0.5 equiv to [Rh]) were added to a 20 mL screw-capped vial and dissolved in toluene (5.0 mL). The screw-cap was closed and the vial was taken out of the glove box. The reaction mixture was stirred at 80 ºC for 12 h. After cooling to rt, a yellow precipitate was collected by filtration in a glovebox. The collected solid was washed with toluene (5.0 mL×3) and hexane (5.0 mL×3). The solid was dried under reduced pressure to give Rh complex **3** as yellow solid (214 mg, 94%).

Rh Complex 3



Yellow solid (214 mg, 94%). M. p. = 183.1–189.1 (decomp.)

The single crystal of **3** that is suitable for X-ray crystallography was obtained by recrystallization from toluene-d_8.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.88–1.00 (m, 2H), 1.09–1.38 (m, 22H), 1.44 (d, J = 6.9 Hz, 6H), 1.72–1.73 (br, 4H), 1.84–1.87 (br, 4H), 2.28 (sept, J = 6.9 Hz, 2H), 2.47–2.57 (m, 2H), 2.89 (sept, J = 6.9 Hz, 1H), 3.84 (s, 3H), 3.97 (s, 3H), 6.97 (s, 2H), 7.34 (dd, J = 9.2, 4.1 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H).

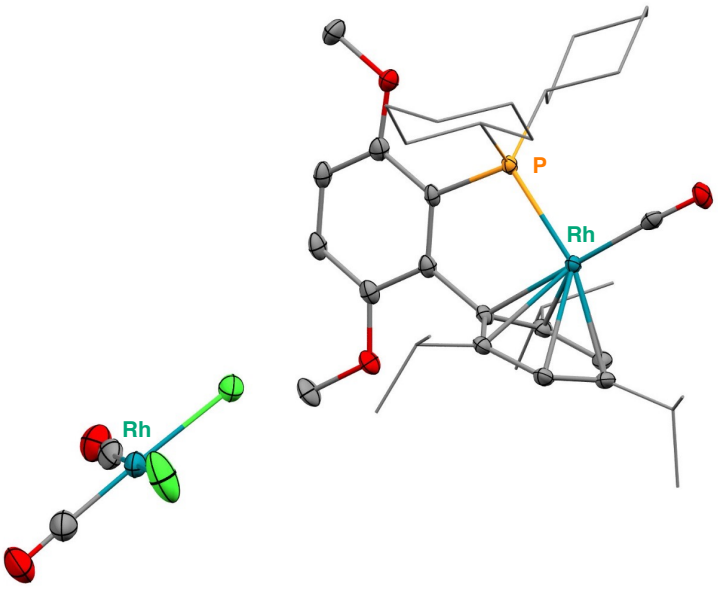
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 23.2, 24.2, 25.2, 25.7, 26.78 (d, J = 26.8 Hz), 26.79, 29.4, 30.4, 31.9, 33.5, 40.0 (d, J = 28.8 Hz), 55.6, 56.8, 103.0, 110.34, 110.35 (d, J = 8.6 Hz), 115.0 (d, J = 4.8 Hz), 117.3, 123.5 (d, J = 4.8 Hz), 129 4 (d, J = 40.3 Hz), 130.0 (d, J = 16.3 Hz), 135.2, 152.4 (d, J = 16.3 Hz), 154.1, 181.9 (d, J = 71.9 Hz), 184.5 (d, J = 16.3 Hz), 185.4 (d, J = 15.3 Hz).

^{31}P NMR ($CDCl_3$, 161 MHz) δ: 88.26 (d, $J_{P–Rh}$ = 164.6 Hz).

IR (KBr): 2969 (m), 2935 (m), 2854 (m), 1975 (s), 1577 (m), 1476 (s), 1364 (w), 1295 (m), 1259 (s), 1178 (w), 1100 (w), 1041 (m), 1009 (m), 888 (m), 808 (m), 744 (m), 706 (m), 621 (m), 558 (m), 477 9 (m).

Anal. Calcd for $C_{38}H_{53}Cl_2O_2PRh_2$: C, 50.85; H, 5.95; N, 0.00. Found: C, 50.74; H, 6.12; N, 0.00.

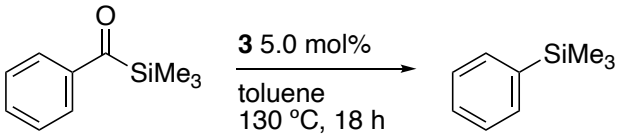
The structure of **3** was confirmed by X-ray crystallography.



ORTEP drawing of **3** with thermal ellipsoids set at the 50% probability level.[a]

[a]Crystal data for **3**, triclinic, space group $P\bar{1}$ (no. 2), a = 9.59780(10) Å, b = 12.04240(10) Å, c = 17.9402(2) Å, α = 101.5180(10)°, β = 105.2770(10)°, γ = 93.3790(10)°, V = 1946.29(4) Å^3, T = 123 K, Z = 2, $R1$ ($wR2$) = 0.0289 (0.0732) for 468 parameters and 7704 unique reflections. GOF = 1.061. CCDC 2214703.

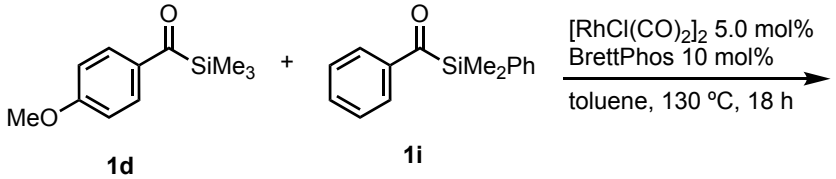
VI-II. Rh complex 3-catalyzed decarbonylation of 1a.



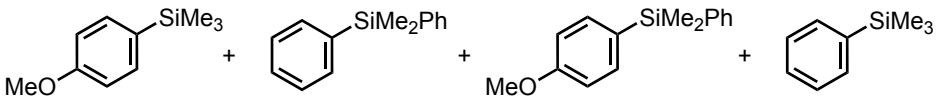
1a **2a** 45%

In a glovebox filled with N_2, complex **3** (9.1 mg, 0.010 mmol, 5.0 mol%) was added to a 10 mL screw-capped vial and dissolved in toluene (0.50 mL). Acylsilane **1a** (35.6 mg, 0.20 mmol) and toluene (0.5 mL) were added to the vial. The screw-cap was then closed and the vial was removed from the glove box. The reaction mixture was stirred at 130 ºC for 18 h. After cooling to rt, the reaction mixture was filtered through a silica gel pad. The crude mixture was analyzed by GC using pentadecane as an internal standard, which indicated that 45% of **2a** was formed.

VI-III. Crossover experiment



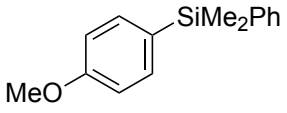
1d **1i**



2d 47% **2i** 52% **2d'** 11% **2a** 7%

In a glovebox filled with N_2, $[RhCl(CO)_2]_2$ (3.9 mg, 0.010 mmol, 10 mol% [Rh]) and BrettPhos (10.7 mg, 0.020 mmol, 10 mol%) were added to a screw-capped vial and dissolved in toluene (0.50 mL). After stirring at rt for 5 min, acylsilane **1c** (20.8 mg, 0.10 mmol), **1j** (24.0 mg, 0.10 mmol), and toluene (0.50 mmol) were added to the vial. The screw-cap was then closed and the vial was removed from the glove box. The reaction mixture was stirred at 130 ºC for 18 h. After cooling to rt, the reaction mixture was filtered through a silica gel pad. The crude mixture was analyzed by GC using pentadecane as an internal standard, which revealed that **2c** (47%), **2j** (52%), **2c'** (11%) and **2a** (7%) were formed.

(4-Methoxyphenyl)dimethyl(phenyl)silane (2c'). [CAS: 14311-78-5]



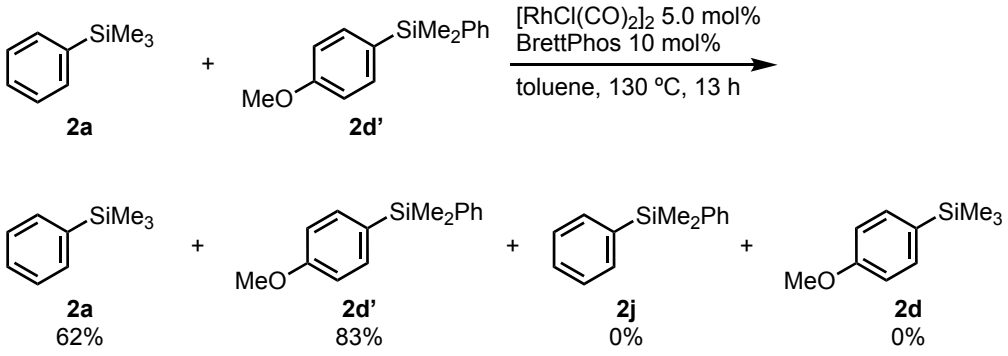
Colorless oil (11%, GC yield using pentadecane as an internal standard).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.54 (s, 6H), 3.82 (s, 3H), 6.92 (d, J = 8.2 Hz, 2H), 7.33–7.38 (m, 3H), 7.45–7.48 (m, 2H), 7.51–7.54 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -2.05, 55.2, 113.7, 127.9, 129.1 (two peaks are overlapped), 134.3, 135.8, 138.8, 160.6.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{19}OSi$: 243.1200. Found: 243.1196.

Based on the results of the following experiments, the crossover between arylsilane products did not occur under these conditions. In a glovebox filled with N_2, $[RhCl(CO)_2]_2$ (3.9 mg, 0.010 mmol, 10 mol% [Rh]) and BrettPhos (10.7 mg, 0.020 mmol, 10 mol%) were added to a screw-capped vial and dissolved in toluene (0.50 mL). After stirring at rt for 5 min, arylsilane **2a** (15.0 mg, 0.10 mmol), **2d'** (24.2 mg, 0.10 mmol), and toluene (0.50 mmol) were added to the vial. The screw-cap was then closed and the vial was removed from the glove box. The reaction mixture was stirred at 130 ºC for 13 h. After cooling to rt, the reaction mixture was filtered through a silica gel pad. The crude mixture was analyzed by GC using pentadecane as an internal standard, which revealed that **2a** (62%), **2d** (83%) were remained unreacted and crossover products **2j** and **2d** were not formed.



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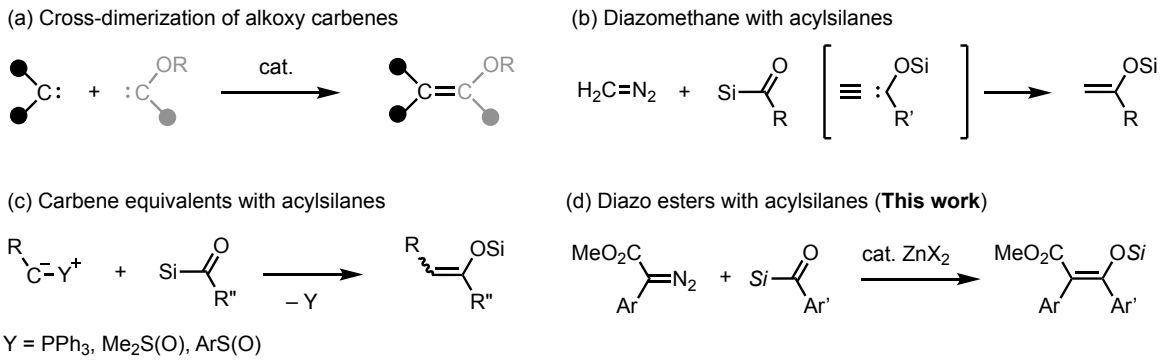
Chapter 3

Zn(II)-Catalyzed Formal Cross-Dimerization of Carbenes Using Acylsilanes and Diazo Esters

3.1. Introduction

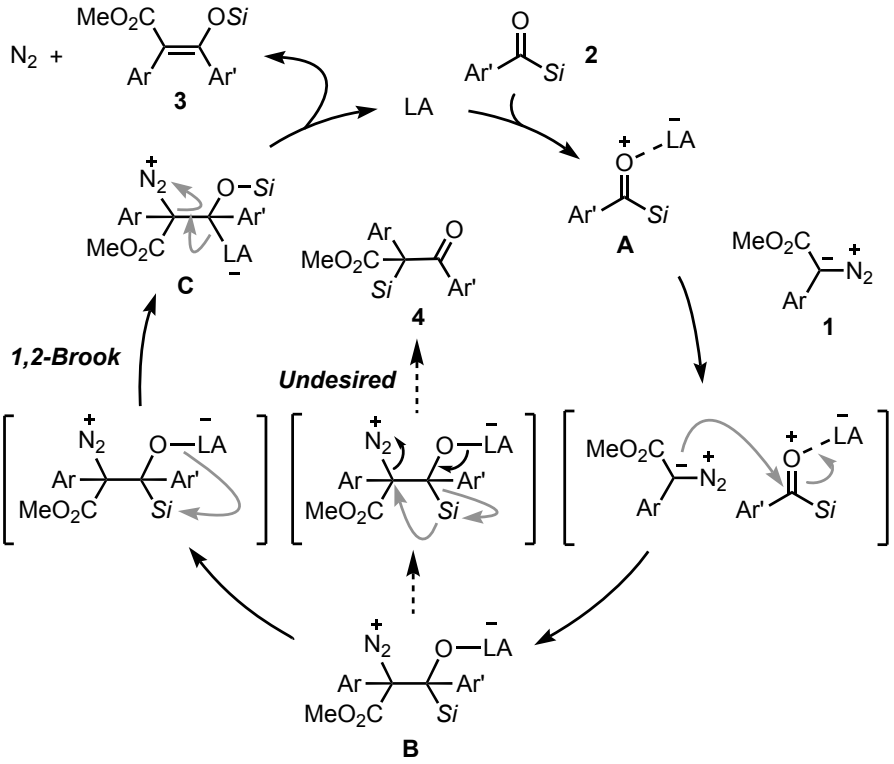
The dimerization of carbenes is known as an undesirable side reaction in catalytic carbene transfer reactions.[1] This dimerization process has also been investigated as a possible powerful method for the synthesis of alkenes. Of particular interest is the cross-dimerization of two different carbenes or their equivalents, which would allow for the assembly of densely substituted alkenes in a convergent manner. In this context, significant success has been achieved to date by the judicious choice of carbene precursors, including diazo esters and sulfur and phosphorus ylides.[2] If an alkoxy carbene could be used as one of the carbenes in the cross-dimerization reactions, it would provide a unique method for the synthesis of enol ethers (Scheme 1, top). However, only a limited number of examples have been reported to date, partly due to the limited availability of alkoxycarbene precursors. Barluenga reported that cross-dimerization of alkoxy carbene complexes of chromium and diazo esters proceeds by the use of a copper(I) catalyst, leading to the formation of enol ethers (Scheme 1a).[3] Recently, a related cross-coupling of Fischer carbene complexes of chromium with N-tosyl hydrazones in the presence of base, although the products were isolated as hydrolyzed ketones, rather than enol ethers.[4] It has been reported that acylsilanes[5] can function as siloxycarbene equivalents in carbene cross-dimerization reactions. Brook reported on cross-dimerization reactions between acylsilanes and diazomethane with the formation of silyl enol ethers (Scheme 1b).[6] Although this reaction represents a pioneering study on cross-dimerization reactions that involve non-metallic alkoxycarbene precursors, α-silylketones is formed as a main product as well as the fact that this reaction is not applicable for other diazo esters has limited the widespread use of this reaction in organic synthesis. It has also been reported that phosphorus-[7] and sulfur-based[8] ylides can be cross-dimerized with acylsilanes to form a series of silyl enol ethers (Scheme 1c). The author report herein that the selectivity and scope of Brook's cross-dimerization reaction (Scheme 1b) can be significantly improved by using a zinc(II) catalyst, which allows for the selective synthesis of tetra-substituted silyl enol ethers (Scheme 1d).



Scheme 1. Catalytic synthesis of enol ethers by the cross-dimerization of carbenes or their equivalents.

Based on Brook's thermal cross-dimerization using diazomethane and acylsilanes (Scheme 1b),[6] we envisioned that the use of a suitable Lewis acid (LA) catalyst would enhance the efficiency of the process, thereby allowing a diverse array of diazo esters to be used in this reaction (Scheme 2). This cross-dimerization is initiated by the nucleophilic addition of diazo ester **1** to acylsilane **2**, which would be expected to be accelerated by the electrophilic activation of **2** through the complexation with LA (*i.e.*, **A**). The resulting adduct **B** subsequently undergoes a 1,2-Brook

rearrangement to generate intermediate **C**, which then leads to the formation of the cross-dimerized alkene **3** by the β-elimination of N_2.[9] Another issue regarding Brook's reaction is the formation of α-silylketone **4** as a byproduct, presumably because the 1,2-Brook rearrangement of **B** competes with the Wagner-Meerwein type rearrangement of the silyl group. We also concluded that this issue could be addressed by using a LA catalyst, because the nature of the oxygen nucleophile would be expected to be affected by LA, thereby allowing the selectivity between **3** and **4** to be controlled.

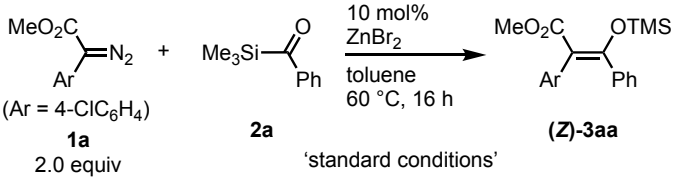


Scheme 2. Working hypothesis.

3.2. Results and Disccusion

We began our study with examining the reactions of diazo ester **1a** and acylsilane **2a** in the presence of catalytic amounts of LAs that are capable of activating **2a**. After numerous efforts, we found that the coupling of **1a** (2.0 equiv to **2a**) with **2a** in the presence of $ZnBr_2$ (10 mol%) in toluene at 60 °C resulted in the formation of the silyl enol ether **3aa** in 87% yield (determined by ^{1}H NMR) with a *Z*/*E* ratio of 90/10 (Scheme 3, Entry 1). This reaction did not procced with no catalyst, indicating that $ZnBr_2$ has a strong promoting effect on the reaction (Entry 2). When 1,2-dichloroethane (1,2-DCE) was used as a solvent instead of toluene, the yield of **3aa** was slightly lower (Entry 3). The use of $ZnCl_2$, which is a weaker Lewis acid than $ZnBr_2$,[10] also resulted in the yield of **3aa** being decreased to 40% with a *Z*/*E* ratio of 22/78 (Entry 4**)**. Other Lewis acids, involving $BF_3{\cdot}OEt_2$, $B(C_6F_5)_3$, methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide) (MAD), $Ni(OTf)_2$, $Cu(OTf)_2$, $FeCl_3$, $InCl_3$ and $Zn(OTf)_2$ failed to catalyze this reaction (Entry 5).

With the optimized conditions in hand, the substrate scope of this zinc(II)-catalyzed coupling reaction of acylsilanes and diazo esters was next explored (Scheme 4). The silyl enol ether **3** could be isolated by silica gel column chromatography, although a fraction of **3** was desilylated during the purification. Diazo esters bearing phenyl (**1b**) and CF_3 groups (**1c**) could also be used for this reaction to produce the corresponding silyl enol ethers with *Z*



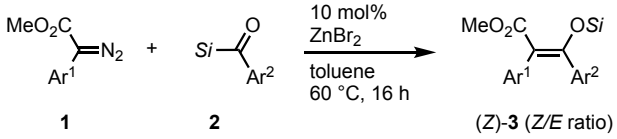
Entry	Deviation from the 'standard conditions'	**3aa** (%) (*Z*/*E*)[b]
1	none	87 (90/10)
2	no $ZnBr_2$	0
3	1,2-DCE instead of toluene	77 (84/16)
4[c]	$ZnCl_2$ instead of $ZnBr_2$	40 (22/78)
5[c,d]	$BF_3{\cdot}Et_2O$, $B(C_6F_5)_3$, MAD, $Ni(OTf)_2$, $Cu(OTf)_2$, $FeCl_3$, $InCl_3$, $Zn(OTf)_2$ instead of $ZnBr_2$	0–8

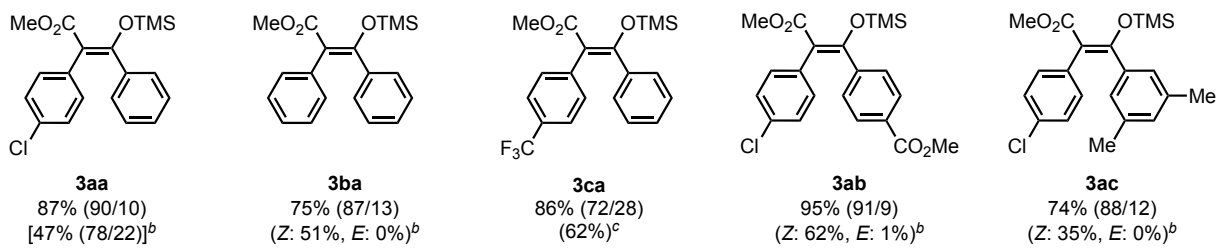
Scheme 3. Optimization studies.

MAD = methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide)

[a]Reaction conditions: **1a** (0.40 mmol), **2a** (0.20 mmol), catalyst (0.020 mmol, 10 mol%) and toluene (1.0 mL) at 60 °C for 16 h. [b]Yield and *Z*/*E* ratio of **3aa** were determined by ^{1}H NMR analysis using mesitylene as an internal standard. [c]Run in DCE with 20 mol% of the catalyst. [d]Run at 50 ºC.

selectivity. Both electron-deficient (**2b**) and electron-rich (**2c**) acylsilanes could be coupled with **1a** under these conditions with cross-dimerized products being formed in yields of 95% (**3ab**) and 74% (**3ac**), respectively. A methoxy group (i.e., **2d**) was also applicable with this reaction, although the *Z* selectivity was diminished. Fluorine (**2e**) and a CF_3 group (**2f**) were also tolerated in this reaction. Regarding the silyl group of the acylsilane, a bulkier TBS group could also be used for this reaction. In this case, although the yield was lower compared with that for TMS-substituted derivatives, the silyl enol ether **3ag** was more stable, allowing for its isolation by column chromatography without significant loss by hydrolysis.





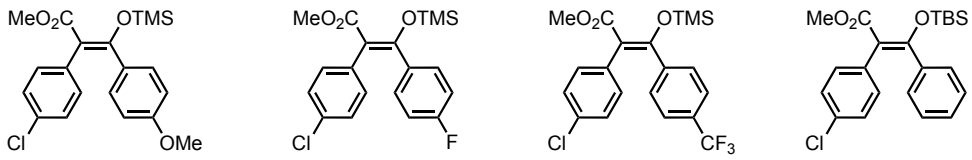
3aa
87% (90/10)
[47% (78/22)][b]

3ba
75% (87/13)
(*Z*: 51%, *E*: 0%)[b]

3ca
86% (72/28)
(62%)[c]

3ab
95% (91/9)
(*Z*: 62%, *E*: 1%)[b]

3ac
74% (88/12)
(*Z*: 35%, *E*: 0%)[b]



3ad
82% (57/43)
(*Z*: 38%, *E*: 39%)[b]

3ae
71% (87/13)
(*Z*: 64%, *E*: 0%)[b]

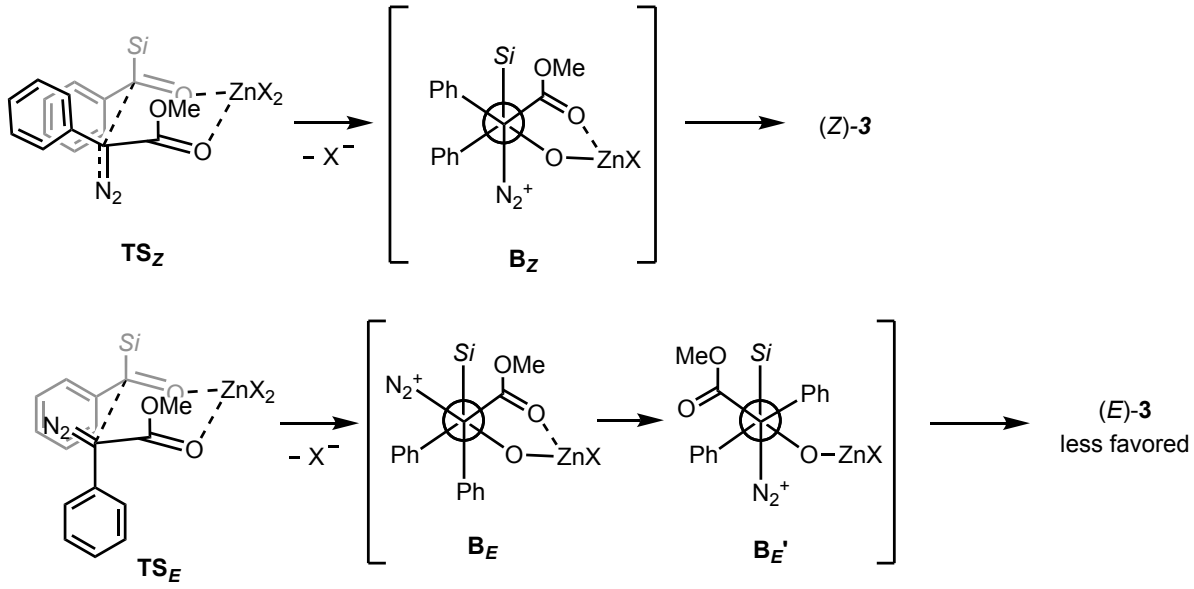
3af
71% (92/8)
(70%)[c]

3ag
36% (87/13)[b,d]

Scheme 4. Scope of the Zn(II)-catalyzed cross-dimerization of acylsilanes and diazo esters.[a]

[a]Reaction conditions: diazo ester 1 (0.40 mmol), acylsilane 2 (0.20 mmol), $ZnBr_2$ (0.020 mmol, 10 mol%) in toluene (1.0 mL) at 60 °C for 16 h. NMR yields are shown. [b]Isolated yield of each isomer with >95% purity after column chromatography. [c]Isolated as a hydrolyzed ketone due to instability of 3. [d]30 mol% of $ZnBr_2$ was used.

In this cross-dimerization reaction, *Z*-isomers of **3** were the major products, although *Z*-isomers are thermodynamically less stable than the corresponding *E*-isomers (See Supporting Information). This selectivity can be explained by the mechanistic model shown in Scheme 5. The initial nucleophilic attack of diazo ester **1** to acylsilane **2** possibly proceeds via a chair-like six-membered transition-state through chelation by ZnX_2.[11] Although four isomeric transition states are possible depending on the relative orientation of **1** and **2**, two (i.e., $\mathbf{TS}_{\boldsymbol{Z}}$ and $\mathbf{TS}_{\boldsymbol{E}}$) in which a relatively smaller $SiMe_3$ group of **2** , rather than a Ph group, occupies an axial position would be more favored to avoid 1,3-diaxial interaction with the axial methoxy group (cf. A values: 2.5 for $SiMe_3$, 3.0 for Ph).[12] The transition state $\mathbf{TS}_{\boldsymbol{Z}}$, in which a diazo group occupies an axial position, would lead to the formation of the intermediate $\mathbf{B}_{\boldsymbol{Z}}$, in which a silyl group and a diazo group are located in an antiperiplanar configuration. This conformation allows for immediate β-elimination of N_2 after a 1,2-Brook rearrangement to form (*Z*)-**3**.[7,8] Another transition state $\mathbf{TS}_{\mathbf{E}}$, in which a phenyl group occupies an axial position, would lead to the formation of intermediate $\mathbf{B}_{\mathbf{E}}$. In this intermediate, σ-bond rotation is required by breaking the chelation of Zn(II) in order to form conformer $\mathbf{B}_{\mathbf{E}}$**'**, which has antiperiplanar Si/N_2^+ groups that could subsequently undergo smooth b-elimination. However, this conformational change would be kinetically less favored, thus rendering (*E*)-**3** a minor product in this reaction.



Scheme 5. Rationalization of *Z* selectivity.

3.3. Conclusion

In summary, the author report on a method for the synthesis of highly substituted silyl enol ethers by zinc(II)-catalyzed formal cross-dimerization reactions between diazo esters and acylsilanes. The reaction proceeds via a 1,2-Brook rearrangement, in which acylsilanes act as an equivalent of siloxycarbene. This reaction represents one of the rare examples of transition metal-catalyzed reactions of acylsilanes, in which substituents derived from both acyl and silyl groups are incorporated into the final product.[13]

3.4. Experimental Section

I. General Information

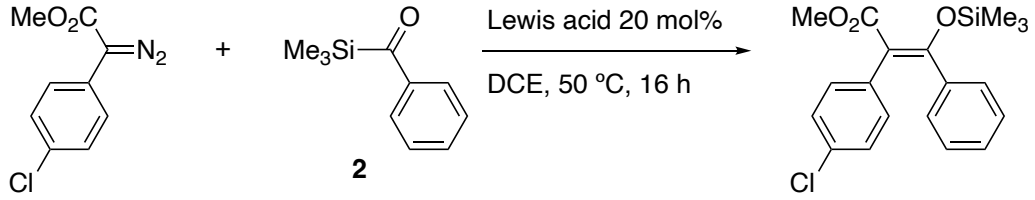
^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$. The chemical shifts in ^{1}H NMR spectra were recorded relative to tetramethyl silane (δ 0.00) or $CHCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.00). The chemical shifts in ^{19}F NMR spectra were recorded relative to benzotrifluoride (C_6F_6, δ –163.0). The data is reported as follows: chemical shift (δ) in ppm, coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silicycle SilicaFlash F60 (230-400 mesh)). Data collection for X-ray crystal analysis were performed on a Rigaku/XtaLAB Pro P200 Hybrid Photon Counting diffractometer (Mo-Kα, λ = 0.71073 Å). The structures were solved with olex2.solve 1.2-ac3. SHELXL−2017/1 was used for structure refinement.

II. Materials

Unless otherwise stated, all commercially available reagents and solvents were supplied from TCI, Wako Chemical, and Aldrich and used as received. DCE (dehydrated) was purchased from Wako Chemical and used as received. Toluene (deoxygenated) was purchased from Wako Chemical and used as received. $ZnBr_2$ was purchased from TCI and used as received. Diazo esters **1a** [CAS: 93961-29-6], methyl **1b** [CAS: 22979-35-7], and **1c** [CAS: 219564-85-9] were prepared according to literature procedure from the corresponding aryl acetates and 4-acetamidobenzenesulfonyl azide (*p*-ABSA, TCI).[14] Phenyl(trimethylsilyl)methanone (**2a**) [CAS: 5908-41-8] was prepared from benzyltrimethylsilane (TCI) according to the literature method.[15] Acylsilanes **2b** [CAS: 75748-12-8], **2c** [CAS: 1354579-01-3], **2d** [CAS: 75748-09-3], **2e** [CAS: 144968-85-4], and **2f** [CAS: 103411-25-2] were prepared from the corresponding acyl chlorides according to literature method.[16,17] (*tert*-Butyldimethylsilyl)(phenyl)methanone (**2g**) [CAS: 132868-67-8] was prepared from benzaldehyde according to a literature procedure.[18]

III. Optimization Studies

III-I. Screening of Catalysts

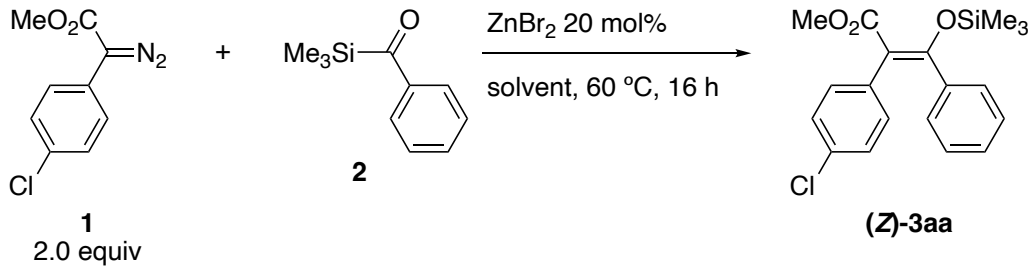


In a glovebox filled with N_2, Lewis acid (0.020 mmol), **1** (84.0 mg, 0.40 mmol, 2.0 equiv), **2** (35.6 mg, 0.20 mmol) and DCE (1.0 mL) were added to a 10 mL screw-capped vial and the cap was closed. The vial was removed from the glovebox and heated at 50 °C for 16 h. After cooling to rt, the solvent was removed in vacuo. The yield and a *Z*/*E* ratio of **3aa** was determined by ^{1}H NMR analysis of the crude mixture using mesitylene as an internal standard.

Lewis acid	**3aa** (%) (*Z*/*E*)	**2** (%)
$ZnBr_2$	59 (80/20)	15
$ZnCl_2$	45 (22/78)	12
$Zn(OTf)_2$	0	75
$B(C_6F_5)_3$	0	82
$BF_3{\cdot}Et_2O$	0	67
$Ni(OTf)_2$	0	59
$Cu(OTf)_2$	0	39
$Sc(OTf)_3$	0	79
$InCl_3$	7 (43/57)	20
$FeCl_3$	8 (63/37)	58
MAD	0	86

*All yields were determined by ^{1}H NMR analysis using mesitylene as an internal standard.

III-II. Screening of Solvents

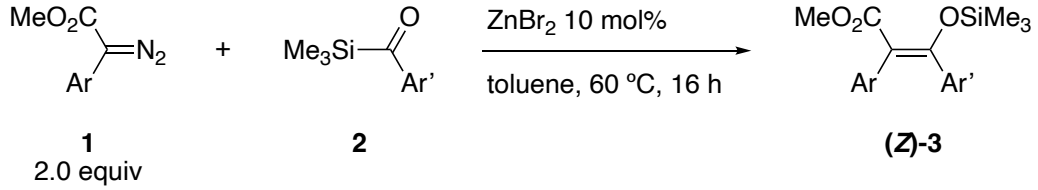


In a glovebox filled with N_2, $ZnBr_2$ (9.0 mg, 0.040 mmol, 20 mol%), **1** (84.0 mg, 0.40 mmol, 2.0 equiv), **2** (35.6 mg, 0.20 mmol) and solvent (1.0 mL) were added to a 10 mL screw-capped vial and the cap was closed. The vial was removed from the glovebox and heated at 50 °C for 16 h. After cooling to rt, the solvent was removed in vacuo. The yield and a *Z*/*E* ratio of **3aa** was determined by ^{1}H NMR analysis of the crude mixture using mesitylene as an internal standard.

solvent	**3aa** (%) (*Z*/*E*)	**2** (%)
MeCN	51 (75/25)	15
THF	33 (67/33)	0
DCE	92 (80/20)	3
DCE[a]	77 (84/16)	1
toluene	76 (88/12)	0
toluene[a]	87 (90/10)	0

*All yields were determined by ^{1}H NMR analysis using mesitylene as an internal standard.
[a]10 mol% of $ZnBr_2$ was used.

IV. General Procedure for Zinc-Catalyzed Synthesis of Silyl Enol Ethers from Acylsilanes and Diazo Esters.



1
2.0 equiv

2

(*Z*)-3

In a glovebox filled with N_2, $ZnBr_2$ (4.5 mg, 0.020 mmol, 10 mol%), **1** (0.40 mmol), **2** (0.20 mmol) and toluene (1.0 mL) were added to a 10 mL screw-capped vial and the cap was closed. The vial was removed from glovebox and heated at 60 °C for 16 h. After cooling to rt, the solvent was removed in vacuo. The yield and a *Z*/*E* ratio of **3aa** was determined by ^{1}H NMR analysis of the crude mixture using mesitylene as an internal standard. The crude mixture was further purified by silica gel column chromatography.

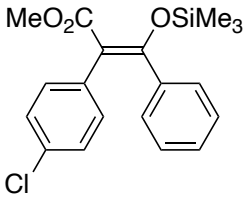
Spectroscopic Data of Products

NOTE: The stereochemistry of **(*E*)-3aa** was unambiguously determined by X-ray crystallography (see section VI). The stereochemistry of other products were determined by comparing the chemical shifts with authentic **(*E*)** and **(*Z*)-3aa**. Resonances assigned to the Si*Me*$_3$ (-0.2~0.2 ppm) and the CO_2*Me* (3.5-3.8 ppm) groups consistently appeared in lower field for *Z* isomers, compared with *E* isomers.

Methyl (*Z*) and (*E*)-2-(4-chlorophenyl)-3-phenyl-3-((trimethylsilyl)oxy)acrylate ((*Z*)- and (*E*)-3aa).

87% NMR yield, *Z*/*E* ratio = 90/10 (determined by ^{1}H NMR using mesitylene as an internal standard).
Pale-yellow oil, 34.3 mg (47% isolated yield, *Z*/*E* = 78/22). R_f 0.34 (SiO_2, hexane/EtOAc = 4/1). Part of each isomer was obtained in a stereochemically pure form.

Z-isomer:



^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.09 (s, 9H), 3.76 (s, 3H), 6.97 (dd, *J* = 6.6, 2.1 Hz, 2H), 7.10 (dd, *J* = 6.4, 1.8 Hz, 2H), 7.21-7.15 (m, 5H).

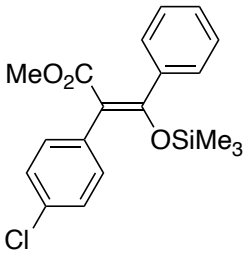
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.42, 51.72, 116.00, 127.87, 128.13, 128.98, 129.55, 132.12, 132.46, 134.85, 137.00, 158.14, 168.06.

IR (KBr): 2821 w, 2779 w, 2024 w, 1774 w, 1581 w, 1564 w, 1473 w, 1427 m, 1288 m, 1270 m, 1254 m, 1187 w, 1106 m, 780 w, 766 w, 740 m, 701 s, 564 w, 555 w, 522 s, 482 s, 473 s, 468 s, 452 s, 443 s, 419 s.

MS, *m/z* (relative intensity, %): 360 (M^+, 9), 347 (12), 345 (32), 89 (26), 77 (22), 75 (13), 73 (72), 59 (13), 45 (25).

HRMS (DART+): Calcd for $C_{19}H_{22}O_3SiCl$: 361.1021. Found: 361.1011.

E-isomer:



^{1}H NMR ($CDCl_3$, 400 MHz) δ: -0.15 (s, 9H), 3.45 (s, 3H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.42-7.37 (m, 7H).

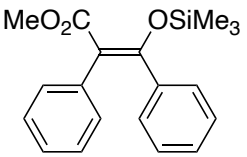
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.44, 51.6, 115.7, 128.0 (two peaks are overlapped), 128.3, 129.2, 131.3, 132.6, 134.0, 138.1, 159.4, 169.0.

MS, *m/z* (relative intensity, %): 360 (M^+, 9), 347 (12), 345 (32), 89 (26), 77 (22), 75 (13), 73 (72), 59 (13), 45 (25).

HRMS (DART+) Calcd for $C_{19}H_{22}O_3SiCl$: 361.1021. Found: 361.1015.

The structure of **(*E*)-3aa** was confirmed by X-ray analysis (see p. S14).

Methyl (*Z*)-2,3-diphenyl-3-((trimethylsilyl)oxy)acrylate ((*Z*)-3ba).



75% NMR yield, *Z*/*E* ratio = 87/13 (determined by ^{1}H NMR using mesitylene as an internal standard).

Pale yellow oil (34.7 mg, 51%). R_f 0.44 (SiO_2, hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.10 (s, 9H), 3.76 (s, 3H), 7.05-7.07 (m, 2H), 7.11-7.19 (m, 8H).

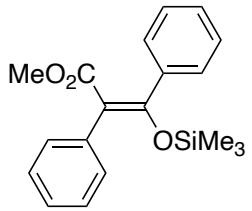
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.4, 51.7, 117.3, 126.6, 127.7, 127.9, 128.7, 129.6, 130.7, 136.2, 137.2, 157.1, 168.5.

IR (KBr): 1716 m, 1433 w, 1325 w, 1251 m, 1222 m, 1117 m, 1014 w, 850 m, 773 s, 698 w.

MS, *m/z* (relative intensity, %): 326 (M^+, 16), 312 (16), 311 (62), 105 (100), 89 (32), 77 (24), 75 (16), 73 (69), 59 (14), 45 (23).

HRMS (DART+): Calcd for $C_{19}H_{23}O_3Si$: 327.1411. Found: 327.1406.

Methyl (*E*)-2,3-diphenyl-3-((trimethylsilyl)oxy)acrylate ((*E*)-3ba).



^{1}H NMR resonances assignable to the *E* isomer: -0.17 (s, 9H), 3.45 (s, 3H).

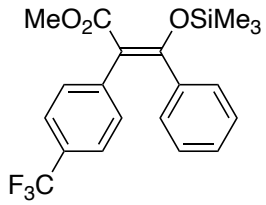
MS, *m/z* (relative intensity, %): 326 (M^+, 12), 312 (13), 311 (48), 105 (100), 89 (28), 77 (23), 75 (14), 73 (67), 59 (11), 45 (24).

(*E*)-3ba was completely decomposed after column chromatography.

Methyl (*Z*)- and (*E*)-3-phenyl-2-(4-(trifluoromethyl)phenyl)-3-((trimethylsilyl)oxy)acrylate ((*Z*)-and (*E*)-3ca).

86% NMR yield, *Z*/*E* = 72/28 (determined by ^{1}H NMR using mesitylene as an internal standard).

Z-isomer:

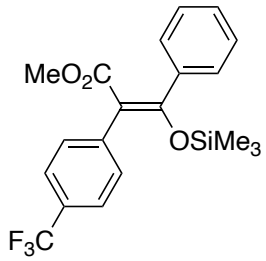


^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.10 (s, 9H), 3.77 (s, 3H), 7.17-7.14 (m, 6H), 7.21–7.24 (m, 1H), 7.37 (d, *J* = 8.2 Hz, 2H).

MS, *m/z* (relative intensity, %): 394 (M^+, 6), 380 (11), 379 (42), 105 (100), 89 (23), 75 (11), 73 (81), 59 (16), 45 (26).

HRMS (DART+) Calcd for $C_{20}H_{22}O_3F_3Si$: 395.1285. Found: 395.1283.

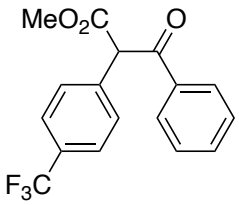
E-isomer:



^{1}H NMR resonances assignable to the *E* isomer: -0.17 (s, 9H), 3.46 (s, 3H).

Since **3ca** was desilylated during purification by column chromatography (SiO_2, hexane/Et_2O = 7/3), and this compound was isolated and characterized as the corresponding ketone **3ca'**.

Methyl 3-oxo-3-phenyl-2-(4-(trifluoromethyl)phenyl)propanoate (3ca').



Colorless solid (39.9 mg, 62%). R_f = 0.30 (SiO_2, hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.77 (s, 3H), 5.72 (s, 1H), 7.44–7.48 (m, 2H), 7.64–7.64 (m, 5H), 7.95–7.97 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 53.0, 59.8, 123.9 (q, *J* = 272.3 Hz), 125.7 (q, *J* = 4.6 Hz), 128.9 (two peaks are overlapped), 130.0, 130.4 (q, *J* = 32.3 Hz), 133.9, 135.2, 136.6, 168.6, 192.4.

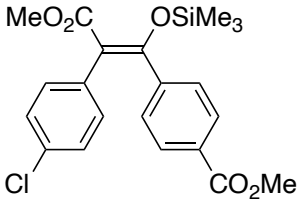
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -64.02.

IR (KBr): 1726 s, 1696 s, 1685 s, 1597 m, 1581 m, 1432 s, 1332 s, 1279 m, 1118 m, 1068 s, 1020 s, 992 s, 918 m, 862 m, 822 s, 792 s, 754 m, 689 s, 674 s, 617 m, 596 s, 484 m.

MS, *m/z* (relative intensity, %): 322 (M^+, 0.13), 105 (100), 77 (33).

HRMS (DART+) Calcd for $C_{17}H_{14}O_3F_3$: 323.0890. Found: 323.0887.

Methyl (*Z*)-4-(2-(4-chlorophenyl)-3-methoxy-3-oxo-1-((trimethylsilyl)oxy)prop-1-en-1-yl)benzoate ((*Z*)-3ab).



95% NMR yield, *Z*/*E* = 91/9 (determined by ^{1}H NMR using mesitylene as an internal standard).

Pale yellow solid (52.0 mg, 62%). R_f 0.20 (SiO_2, hexane/EtOAc = 4/1) (decomposed on TLC).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.09 (s, 9H), 3.76 (s, 3H), 3.88 (s, 3H), 6.96 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H).

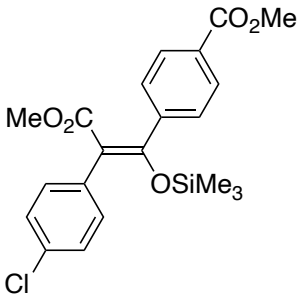
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.42, 51.9, 52.2, 117.2, 128.3, 129.1, 129.5, 130.3, 132.0, 132.9, 134.2, 141.6, 156.5, 166.4, 167.7.

IR (KBr): 1730 s, 1718 s, 1600 s, 1281 s, 1253 s, 1231 s, 1006 s, 863 s, 849 s, 835 s, 753 s, 709 s.

MS, *m/z* (relative intensity, %): 418 (M^+,10), 405 (17), 404 (12), 403 (45), 164 (10), 163 (84), 135 (11), 89 (27), 75 (16), 73 (100), 59 (20), 45 (29).

Exact Mass (DART+) Calcd for $C_{21}H_{24}O_5SiCl$: 419.1076. Found: 419.1081.

Methyl (*E*)-4-(2-(4-chlorophenyl)-3-methoxy-3-oxo-1-((trimethylsilyl)oxy)prop-1-en-1-yl)benzoate ((*E*)-3ab).



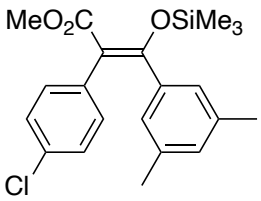
Pale-yellow solid (1.2 mg, 1%). R_f 0.20 (SiO_2, hexane/EtOAc = 4/1) (decomposed on TLC).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: -0.16 (s, 9H), 3.45 (s, 3H), 3.94 (s, 3H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 8.7 Hz, 2H)

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.5, 51.8, 52.3, 116.7, 128.1, 128.3, 129.3, 130.6, 131.3, 132.9, 133.5, 142.7, 158.2, 166.6, 168.6.

HRMS (DART+) Calcd for $C_{21}H_{24}O_5SiCl$: 419.1076. Found: 419.1081.

Methyl (*Z*)-2-(4-chlorophenyl)-3-(3,5-dimethylphenyl)-3-((trimethylsilyl)oxy)acrylate ((*Z*)-3ac).



74% NMR yield, *Z*/*E* = 88/12 (determined by ^{1}H NMR using mesitylene as an internal standard).

Colorless oil (27.2 mg, 35%). R_f 0.52 (SiO_2, hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.10 (d, *J* = 3.2 Hz, 9H), 2.15 (s, 6H), 3.75 (s, 3H), 6.74 (s, 2H), 6.84 (s, 1H), 6.97-6.99 (m, 2H), 7.10 (dd, *J* = 6.6, 2.1 Hz, 2H).

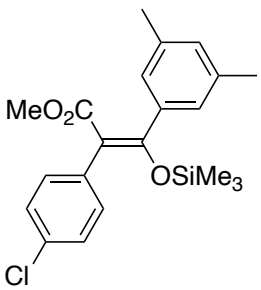
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.5, 21.1, 51.7, 115.5, 127.4, 128.0, 130.6, 132.1, 132.3, 135.1, 136.7, 137.2, 158.6, 168.2.

IR (KBr): 1718 s, 1335 m, 1261 m, 1250 s, 1203 m, 1124 m, 1091 w, 1004 m, 858 s, 850 s.

MS, *m/z* (relative intensity, %): 390 ($[M+2]^+$, 10), 388 (M^+, 25), 375 (30), 374 (22), 373 (70), 134 (10), 133 (100), 105 (18), 89 (26), 75 (12), 73 (65), 45 (15).

HRMS (DART+) Calcd for $C_{21}H_{26}O_3SiCl$: 389.1334. Found: 389.1339.

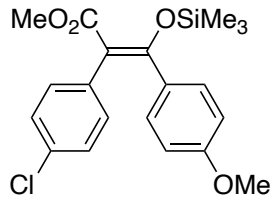
Methyl (*E*)-2-(4-chlorophenyl)-3-(3,5-dimethylphenyl)-3-((trimethylsilyl)oxy)acrylate ((*E*)-3ac).



^{1}H NMR resonances assignable to the *E* isomer: -0.150 (s, 9H), 3.47 (s, 3H).

The *E*-isomer was completely decomposed after column chromatography.

Methyl (*Z*)-2-(4-chlorophenyl)-3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)acrylate ((*Z*)-3ad).



82% NMR yield, *Z*/*E* = 57/43 (determined by ^{1}H NMR using mesitylene as an internal standard).

White solid (29.7 mg, 38%). R_f 0.20 (SiO_2, hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.11 (s, 9H), 3.74 (s, 3H), 3.76 (s, 3H), 6.68 (dd, *J* = 6.9, 2.3 Hz, 2H), 6.98 (dd, *J* = 6.6, 2.1 Hz, 2H), 7.07 (dd, *J* = 6.9, 1.8 Hz, 2H), 7.11 (dd, *J* = 6.4, 1.8 Hz, 2H).

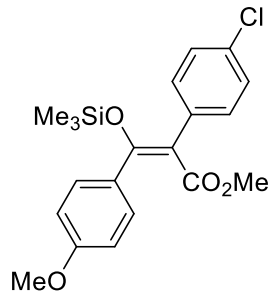
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.5, 51.7, 55.1, 113.2, 115.1, 128.2, 129.2, 131.2, 132.2, 132.3, 135.3, 158.3, 159.9, 168.2.

IR (KBr): 1717 m, 1607 m, 1509 m, 1491 w, 1324 m, 1252 s, 1226 s, 1174 w, 1119 m, 1099 w, 1092 w, 850 s.

MS, *m/z* (relative intensity, %): 392 ([M+2]$^+$, 12), 391 (10), 390 (M$^+$, 33), 377 (34), 376 (24), 375 (82), 135 (100), 89 (22), 75 (10), 73 (58), 59 (10), 45 (14).

HRMS (DART+) Calcd for $C_{20}H_{24}O_4SiCl$: 391.1127. Found: 391.1144.

Methyl (*E*)-2-(4-chlorophenyl)-3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)acrylate ((*E*)-3ad).



Pale-yellow solid (30.5 mg, 39%). R_f 0.20 (hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: -0.15 (s, 9H), 3.49 (s, 3H), 3.85 (s, 3H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.35–7.40 (m, 4H).

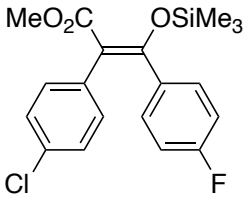
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.5, 51.7, 55.2, 113.3, 115.1, 127.9, 129.9, 130.3, 131.4, 132.4, 134.4, 159.4, 160.3, 169.2.

IR (KBr): 1726 s, 1695 s, 1609 s, 1509 s, 1492 s, 1324 s, 1297 s, 1279 m, 1248 s, 1227 s, 1179 s, 1127 s, 1111 s, 1089 m, 1030 m, 850 s, 828 s.

MS, *m/z* (relative intensity, %): 392 ([M+2]$^+$, 4), 390 (M$^+$, 11), 377 (12), 375 (31), 135 (100), 89 (20), 75 (11), 73 (72), 59 (11), 45 (22).

HRMS (DART+) Calcd for $C_{20}H_{24}O_4SiCl$: 391.1127. Found: 391.1138.

Methyl (*Z*)-2-(4-chlorophenyl)-3-(4-fluorophenyl)-3-((trimethylsilyl)oxy)acrylate ((*Z*)-3ae).



71% NMR yield, *Z*/*E* = 87/13 (determined by ^{1}H NMR using mesitylene as an internal standard).

Pale yellow solid (37.2 mg, 64%, *Z*/*E* = 93/7). R_f 0.48 (hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.10 (s, 9H), 3.75 (s, 3H), 6.87 (t, *J* = 8.7 Hz, 2H), 6.97 (dd, *J* = 6.6, 2.1 Hz, 2H), 7.11-7.15 (m, 4H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 0.4, 51.8, 115.1 (d, *J* = 21.1 Hz), 116.2, 128.3, 131.5 (d, *J* = 8.6 Hz), 132.1, 132.7, 133.1 (d, *J* = 3.8 Hz), 134.7, 157.0, 162.7 (d, *J* = 250.2 Hz), 167.9.

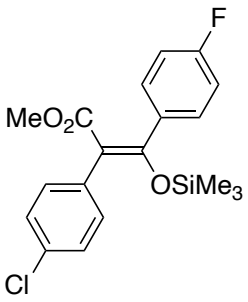
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -112.08.

IR (KBr): 1715 s, 1602 s, 1577 m, 1507 s, 1492 s, 1319 m, 1261 m, 1252 m, 1236 m, 1219 m, 1118 m, 1090 m, 1010 m, 978 m, 854 s, 843 s, 575 s, 515 s.

MS, *m/z* (relative intensity, %): 380 ($[M+2]^+$, 6), 378 (M^+, 14), 365 (24), 364 (15), 363 (60), 123 (100), 95 (12), 89 (24), 75 (12), 73 (74), 45 (17).

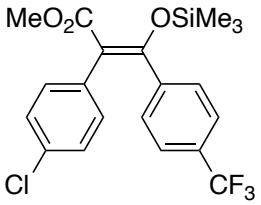
HRMS (DART+) Calcd for $C_{19}H_{21}O_3FSiCl$: 379.0927. Found: 379.0932.

Methyl (*E*)-2-(4-chlorophenyl)-3-(4-fluorophenyl)-3-((trimethylsilyl)oxy)acrylate ((*E*)-3ae).



^{1}H NMR resonances assignable to the *E* isomer: -0.16 (s, 9H), 3.48 (s, 3H).

Methyl (*Z*)-2-(4-chlorophenyl)-3-(4-(trifluoromethyl)phenyl)-3-((trimethylsilyl)oxy)acrylate ((*Z*)-3af).

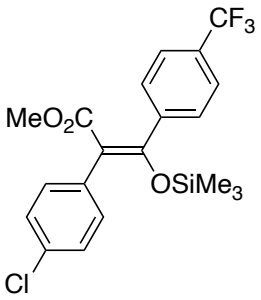


71% NMR yield, *Z*/*E* = 92/8 (determined by ^{1}H NMR using mesitylene as an internal standard).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.10 (s, 9H), 3.77 (s, 3H), 6.96–6.98 (m, 2H), 7.13–7.15 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H).

HRMS (DART+) Calcd for $C_{20}H_{21}O_3F_3SiCl$: 429.0895. Found: 429.0898.

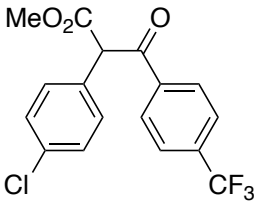
Methyl (E)-2-(4-chlorophenyl)-3-(4-(trifluoromethyl)phenyl)-3-((trimethylsilyl)oxy)acrylate ((*E*)-3af).



^{1}H NMR resonances assignable to the *E* isomer: -0.16 (s, 9H), 3.48 (s, 3H).

Because of the unstability of silyl enol ether **3af** toward chromatography, it was isolated and characterized as the corresponding ketone **3af'** by treating with HCl aq (2 M, 2.0 mL) in THF (1.0 mL) at 60 °C for 1 h.[4]

Methyl 2-(4-chlorophenyl)-3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (3af').



Colorless oil (49.7 mg, 70%). R_f = 0.20 (SiO_2, hexane/Et_2O = 7/3).

3af' was obtained as a mixture with an enol tautomer.[20]

ketone

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.77 (s, 3H), 5.58 (s, 1H), 7.32–7.37 (m, 4H), 7.71 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 53.1, 59.8, 123.3 (q, *J* = 272.2 Hz), 125.9 (q, *J* = 3.8 Hz), 129.17, 129.25, 130.7, 133.1, 134.7, 134.9 (q, *J* = 33.6 Hz), 138.0, 168.5, 191.9.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: -64.57.

enol

^{1}H NMR ($CDCl_3$, 400 MHz) δ:3.79 (s, 3H), 7.00–7.03 (m, 2H), 7.20–7.23 (m, 2H), 7.32–7.37 (m, 2H), 7.45 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): 52.5, 104.1, 124.8 (q, *J* = 3.8 Hz)), 128.5, 129.6, 130.6, 132.7, 133.3, 137.9, 169.6, 173.2.

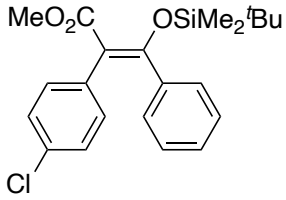
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -64.27.

IR (KBr): 2955 w, 1749 s, 1692 s, 1603 w, 1493 s, 1439 m, 1410 s, 1324 s, 1264 s, 1217 w, 1170 s, 1133 s, 1113 s, 1067 s, 991 s, 871 m, 850 m, 834 m, 744 m, 605 w, 509 m.

MS, *m/z* (relative intensity, %): 356 (M^+, 0), 297 ([M-CO_2Me]$^+$, 0.93), 174 (10), 173 (100), 145 (43), 125 (20), 89 (10).

HRMS (DART+) Calcd for $C_{17}H_{13}O_3F_3Cl$: 357.0500. Found: 357.0511.

Methyl (*Z*) and (*E*)-3-((*tert*-butyldimethylsilyl)oxy)-2-(4-chlorophenyl)-3-phenylacrylate ((*Z*) and (*E*)-3ag)



Pale-yellow oil, 28.8 mg (36% isolated yield *Z*/*E* = 87/13). Isolated using gel-permeation chromatography.

Z-isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: -0.09 (s, 6H), 0.91 (s, 9H), 3.76 (s, 3H), 6.98–7.01 (m, 2H), 7.06–7.09 (m, 2H), 7.12–7.24 (m, 5H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: -4.2, 18.2, 25.6, 51.8, 115.7, 127.90, 128.0, 128.8, 129.5, 131.9, 132.4, 134.5, 137.0, 156.9, 168.0.

E-isomer

^{1}H NMR ($CDCl_3$, 400 MHz) δ: -0.35 (s, 6H), 0.62 (s, 9H), 3.42 (s, 3H), 7.31–7.35 (m, 2H), 7.37–7.42 (m, 7H).

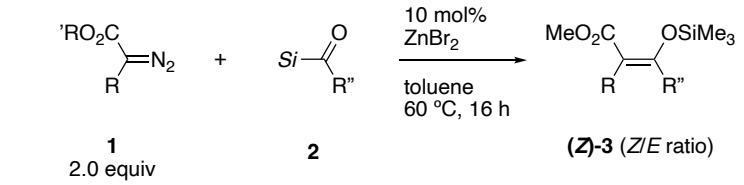
^{13}C NMR ($CDCl_3$, 101 MHz) δ: -4.3, 17.9, 25.1, 51.5, 115.4, 127.94, 128.3, 129.0, 129.5, 131.7, 132.7, 133.9, 138.1, 160.3, 168.6.

IR (KBr): 2952 w, 2931 w, 2859 w, 1721 s, 1492 m, 1433 w, 1325 m, 1258 m, 1226 s, 1118 s, 1092 m, 1011 m, 838 s, 817 m, 783 m, 700 w.

MS, *m/z* (relative intensity, %): 402 (M^+, 0.31), 348 (13), 347 (51), 346 (34), 345 (100), 212 (15), 105 (31), 89 (92), 77 (13), 75 (23), 73 (48).

HRMS (DART+) Calcd for $C_{22}H_{28}O_3SiCl$: 403.1491. Found: 403.1495.

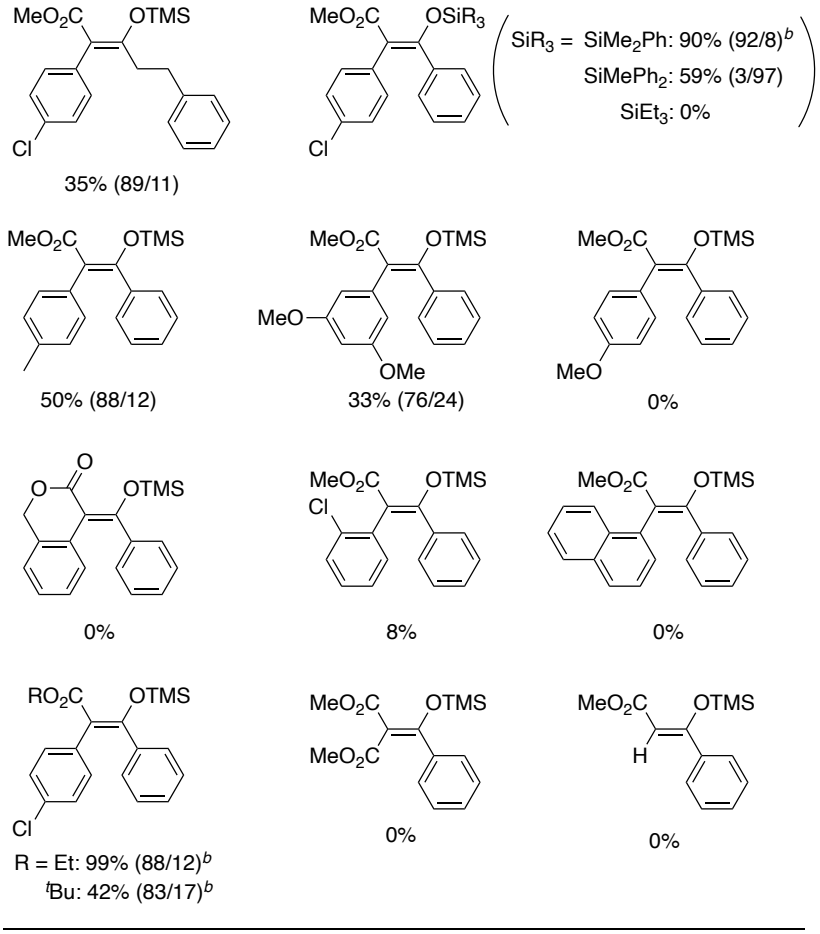
V. Additional Scope and Limitations



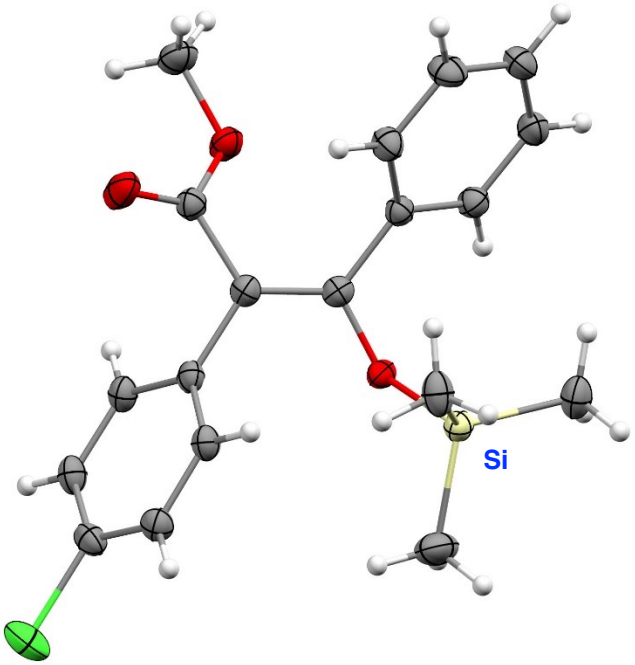
1
2.0 equiv

2

(*Z*)-3 (*Z*/*E* ratio)



VI. Crystallographic Information



ORTEP drawing of **(*E*)-3aa** with thermal ellipsoids set at the 50% probability level.[a]

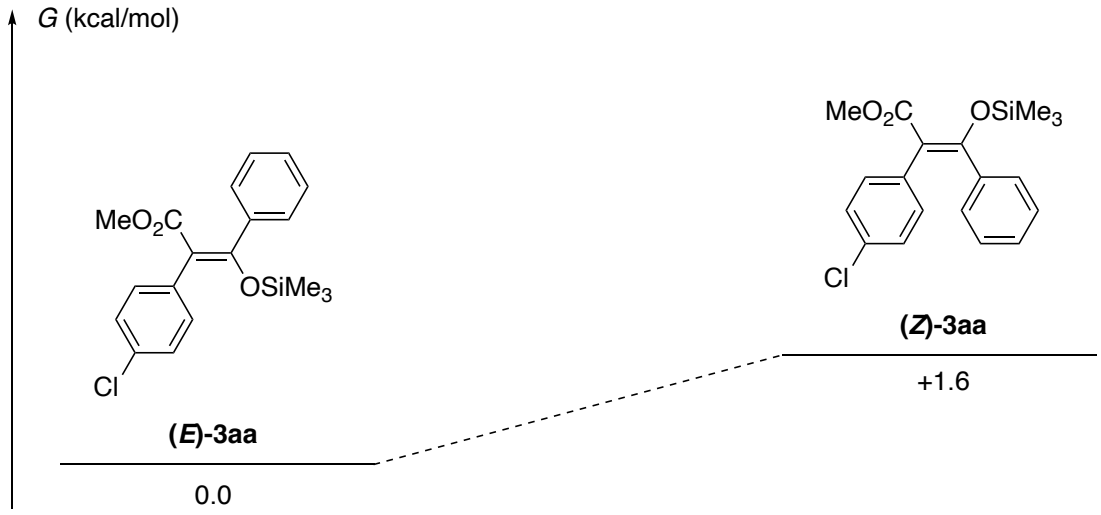
[a]Crystal data for **(*E*)-3aa**, triclinic, space group $P\bar{1}$ (no. 2), a = 9.4496(4) Å, b = 10.3840(4) Å, c = 10.6383(3) Å, α = 91.144(3)°, β = 104.854(3)°, γ = 111.876(4)°, V = 928.55(7) Å^3, T = 123 K, Z = 2, $R1$ ($wR2$) = 0.0360 (0.0879) for 221 parameters and 4613 unique reflections. GOF = 1.075. CCDC 2216894.

VII. DFT Calculation

VII-I. Computational Details

Calculations were performed with the Gaussian 09 (G09 Rev D.01) program.[21] Geometry optimizations for all reported structures were performed using M06-2X[22] with the 6-31G (d,p) basis set.

VII-II. Relative Gibbs Free Energies



(*E*)-3aa is more thermodynamically stable than **(*Z*)-3aa** for 1.6 kcal/mol.

VII-III. Cartesian Coordinates of the Optimized Geometries and Energies

· **(*Z*)-3aa** (G = -1711.350611 Hartree, no imaginary frequency)

C	0.93777600	4.35906500	-0.82897800
C	1.50972900	3.25986400	-1.46708600
C	0.94635400	1.99832600	-1.32696000
C	-0.20052500	1.81935500	-0.54467900
C	-0.78562900	2.93201800	0.06681100
C	-0.21250600	4.19260300	-0.06364400
C	3.18729400	-0.03997300	1.25874100
C	4.01821200	-0.82079900	0.46417000
C	3.50442800	-1.58328000	-0.57878600
C	2.13940500	-1.54818700	-0.83432100
C	1.28038400	-0.75223600	-0.06835600
C	1.82417600	-0.01789000	0.99026400
C	-0.85576000	0.48847400	-0.41178900
O	-2.19461500	0.58857400	-0.38138500
C	-0.17799100	-0.69456800	-0.35664300
C	-0.81941500	-2.02205000	-0.53642900
O	-2.02924700	-1.97919700	-1.14017000
O	-0.29693800	-3.07205600	-0.23798500
C	-2.60014000	-3.26061100	-1.39471800
Cl	5.73354100	-0.85422500	0.78833300
Si	-3.33338900	0.00490800	0.73489100
C	-2.60628100	-1.28065100	1.88730900
C	-3.83141200	1.49586900	1.76187000
C	-4.80845500	-0.58136500	-0.24378600
H	1.38263000	5.34303500	-0.93779600
H	2.39560900	3.38636100	-2.08081900
H	1.39227600	1.14616500	-1.82864800
H	-1.69699700	2.80274700	0.64090500
H	-0.67026400	5.04606600	0.42594200
H	3.60433500	0.53479400	2.07795700
H	4.16718800	-2.19611100	-1.17916800
H	1.73230600	-2.15259300	-1.63816500
H	1.16911700	0.59094100	1.60644500
H	-2.87229100	-3.75581000	-0.45775600

H	-3.48692200	-3.07769500	-2.00019700
H	-1.89297400	-3.89555600	-1.93094400
H	-2.52028400	-2.27681200	1.44733100
H	-1.61001100	-0.98269400	2.23042100
H	-3.24776100	-1.35540700	2.77179100
H	-4.67437100	1.24585100	2.41434300
H	-4.13829100	2.33060000	1.12448600
H	-3.01116100	1.83770300	2.40129900
H	-5.63666800	-0.83532200	0.42479400
H	-5.15011400	0.21148400	-0.91538400
H	-4.56955700	-1.45699500	-0.84859100

· **(*E*)-3aa** (G = -1711.353112 Hartree, no imaginary frequency)

C	-5.33643400	-0.06403900	-0.07715500
C	-4.69055500	-0.77511900	-1.08431600
C	-3.30610300	-0.71010200	-1.20225800
C	-2.55834300	0.09002000	-0.33193100
C	-3.21330600	0.79233600	0.68411900
C	-4.59403200	0.71268300	0.81053900
C	3.37614800	0.53186500	0.96793200
C	3.97124800	-0.00298400	-0.16916400
C	3.24690900	-0.18251500	-1.34200200
C	1.90340000	0.17456500	-1.36877100
C	1.27774800	0.71356600	-0.24155700
C	2.03262400	0.89049400	0.92117100
C	-1.07652900	0.04926300	-0.43962400
O	-0.60767200	-1.18820500	-0.73480000
C	-0.17684800	1.05060000	-0.26084100
C	-0.58553200	2.47402300	-0.14526700
O	0.45683200	3.25079700	0.21636600
O	-1.68297100	2.93523200	-0.36032600
C	0.15610100	4.64034500	0.31215000
Cl	5.65469200	-0.46182300	-0.12220700
Si	-0.36558400	-2.42085200	0.41414200
C	1.41382600	-2.95406800	0.23693500
C	-0.70996700	-1.70393300	2.10803100
C	-1.56068000	-3.79325800	-0.01274200
H	-6.41578200	-0.12062900	0.02251600
H	-5.26353000	-1.38573600	-1.77456300
H	-2.79002200	-1.27722500	-1.97026900

H	-2.63557200	1.39581300	1.37487200
H	-5.09307600	1.25573400	1.60634100
H	3.95837200	0.66542200	1.87286500
H	3.73026100	-0.60185600	-2.21720800
H	1.32326400	0.02108200	-2.27291400
H	1.56251100	1.32226200	1.79948600
H	-0.61563800	4.81458900	1.06532000
H	1.08802900	5.12619400	0.59629600
H	-0.20200000	5.02126800	-0.64638300
H	1.62694700	-3.84199100	0.83995100
H	1.64730400	-3.18681000	-0.80618800
H	2.08446700	-2.14934400	0.55625000
H	-0.04819700	-0.85496100	2.30797200
H	-0.53769000	-2.45615800	2.88370300
H	-1.74505800	-1.35882900	2.19121600
H	-1.44623200	-4.64441600	0.66540500
H	-2.59265600	-3.43593800	0.05680200
H	-1.39484700	-4.15059300	-1.03333800

3.4. References

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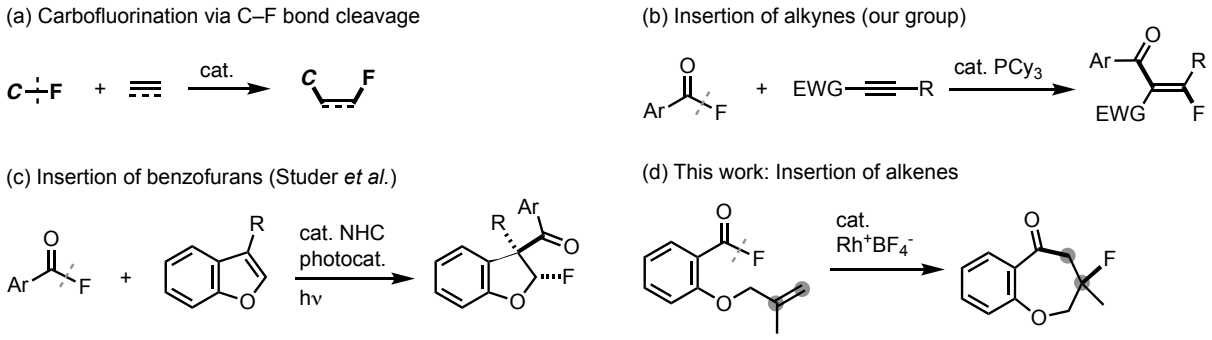
Chepter 4

Cationic Rhodium(I) Tetrafluoroborate-Catalyzed Intramolecular Carbofluorination of Alkenes via the Activation of a Carbon–Fluorine Bond in Acyl Fluorides

4.1. Introduction

It is well-known that the introduction of a fluorine atom into an organic molecule leads to a dramatic change in physical properties and chemical reactivity, thereby allowing for creation of new functional molecules and materials with a variety of functions. Because of this, introduction of a fluorine atom is now recognized as a powerful design principle in the fields of pharmaceutical, agrochemical, and material sciences.[1] In this context, numerous methods for converting non-fluorinated compounds into fluorinated derivatives have been developed to date.[2] If a C–F bond in readily available organic fluorine compounds is cleaved, and an alkene or alkyne is inserted into the C–F bond in a catalytic manner, it would offer a powerful method for the rapid synthesis of complicated organofluorine compounds using simple fluorine-containing molecules with an atom economy of 100% (Scheme 1a). However, only two reports regarding such insertion reactions into a C–F bond have appeared. Our group reported on the phosphine-catalyzed insertion of electron-deficient alkynes into C–F bonds of acyl fluorides via a five-coordinate fluorophosphorane intermediate (Scheme 1b).[3] Very recently, Studer reported that insertion of benzofuran derivatives into C–F bond of acyl fluorides is enabled by the dual use of carbene/photoredox catalysts via the formation of a radical intermediate (Scheme 1c).[4,5] Herein, the author report the rhodium-catalyzed intramolecular insertion of unactivated alkenes into a C–F bond of acid fluorides (Scheme 1d).



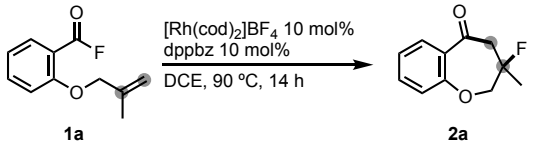
Scheme 1. Carbofluorination via the activation of C–F bond.

4.2. Results and Discussion

We began our study by examining the reaction of acyl fluoride **1a** with the hope that a tethered alkene could be inserted if a metal catalyst capable of activating a C–F bond is present. In contrast to our expectations, low valent metal species that typically mediate the oxidative addition of a C–F bond,[6] including Pd(0) and Ni(0), failed to promote the desired insertion reaction. After numerous efforts, it was founded that the reaction of **1a** in the presence of $[Rh(cod)_2]BF_4$ (10 mol%) and 1,2-diphenylphosphinobenzene (dppbz) (10 mol%) in 1,2-dichloroethane (DCE) at 90 °C in a sealed vial resulted in the formation of insertion product **2a** in 70% isolated yield (entry 1, Table 1). Interestingly, a seven-membered ring is selectively produced with no side products via a 6-exo cyclization being formed. Also noteworthy is the fact that sterically congested tertiary alkyl fluorides can be synthesized by transition metal catalysis.[7] This reaction did not proceed in the absence of a rhodium catalyst (entry 2). When the reaction was

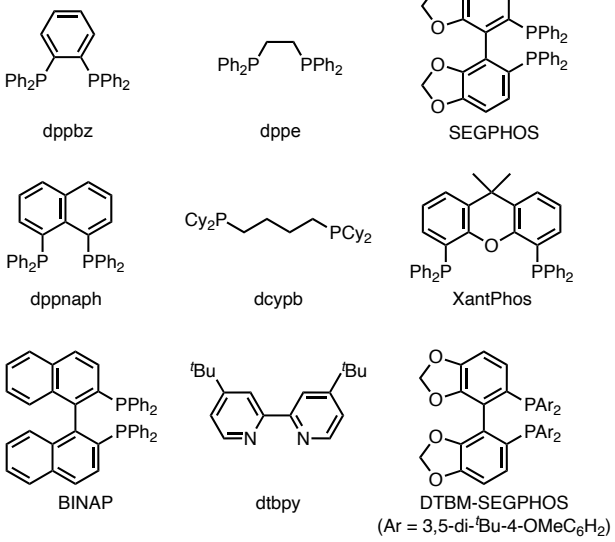
carried out without a dppbz ligand being present, the yield of **2a** was decreased to 51% (entry 3). Although several bisphosphines were also active for this carbofluorination reaction, the yields were somewhat lower than that obtained with dppbz (entry 4–6). Interestingly, electronically neutral $[RhCl(cod)]_2$ showed no catalytic activity, indicating that the cationic character of the rhodium is essential for this insertion reaction (entry 7). When the reaction temperature was lowered to 70 °C, no reaction occurred (entry 8).

Table 1. Rhodium-catalyzed cyclization of **1a** to **2a**.[a]



1a **2a**

entry	deviation from the standard conditions	NMR yield (%)	
		1a	**2a**
1	none	0	74 (70)
2	no rhodium	>99	0
3	no dppbz	0	51
4[b]	dppe, SEGPHOS or dppnaph, instead of dppbz	0	54-59
5[b]	dcypb, Xantphos or BINAP, instead of dppbz	0	0-6
6	1,10-phenanthroline, dtbpy or DTBM-SEGPHOS, instead of dppbz	>99	0
7	$[RhCl(cod)]_2$ instead of $[Rh(cod)_2]BF_4$	>99	0
8	run at 70 ºC	>99	0

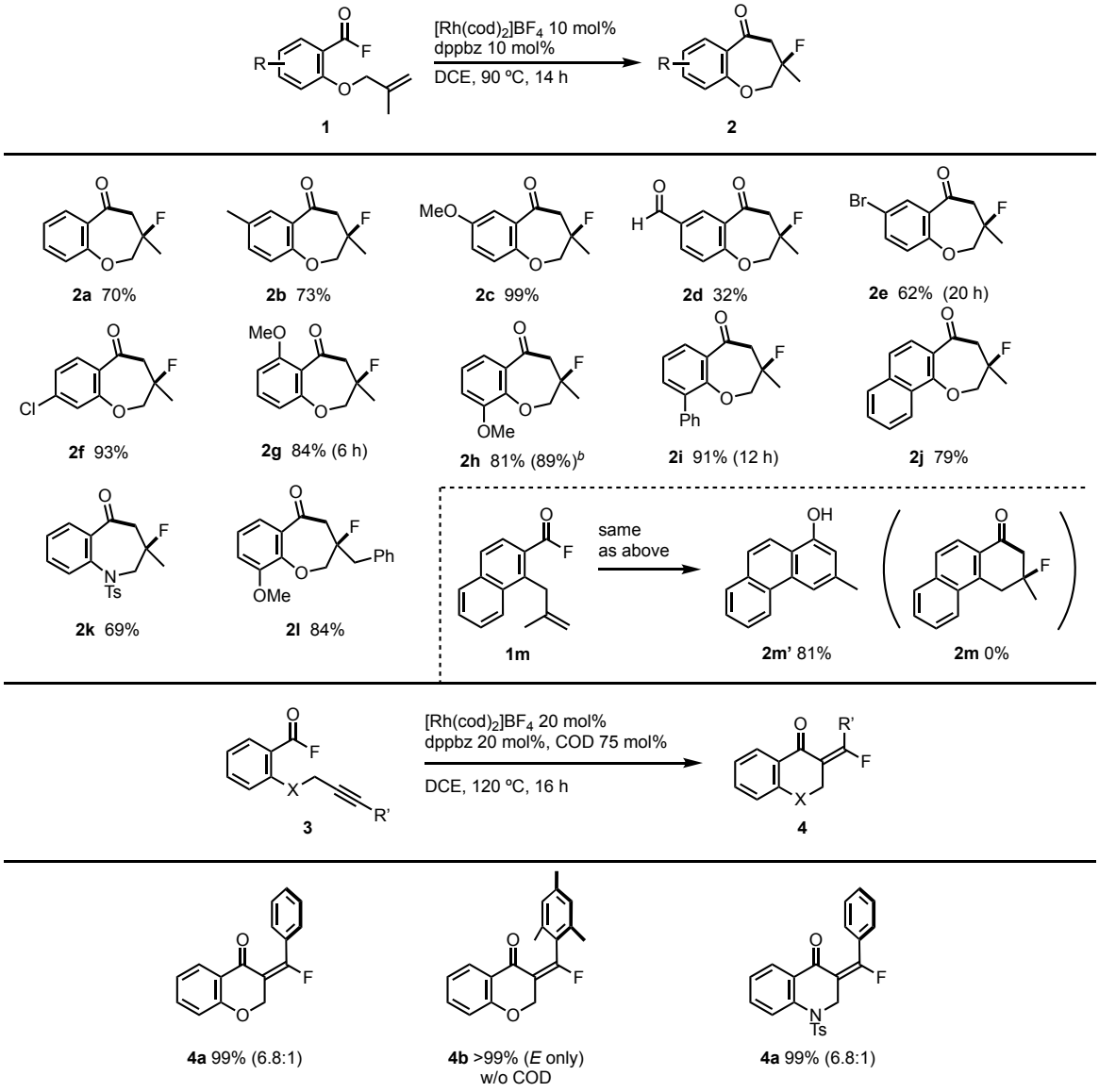


[a]**1a** (0.20 mmol), $[Rh(cod)_2]BF_4$ (0.020 mmol), dppbz (0.020 mmol), DCE (1.0 mL) in a sealed tube at 90 °C for 14 h. [b]Isolated yield. [c]Reaction was conducted for 16 h. dppbz = 1,2-bis(diphenylphosphino)benzene

With the optimized conditions in hand, the substrate scope for this reaction was next examined (Scheme 2). The starting acyl fluorides **1** can readily be prepared from the corresponding commercially available salicylic acid derivatives. A variety of functional groups, encompassing methyl (**2b**), methoxy (**2c**, **2g** and **2h**), and halogen (**2e** and **2f**) groups were compatible for this reaction, with the production of the corresponding carbofluorination products. It should be noted that the scaffold that can be constructed by this carbofluorination reaction (*i.e.*, 3,4-dihydro-2*H*-benzo[b]oxepin-5-one) is a common motif found in a number of pharmaceutical and agrochemical compounds.[8] Therefore, their fluorinated analogues can be rapidly accessed by this carbofluorination reaction. Acyl fluorides on a π-extended aryl group, such as biphenyl (**1i**) and naphthyl (**1j**) rings successfully participated in this carbofluorination reaction, thus allowing for the formation unique ring systems containing a 3,4-dihydro-2*H*-benzo[b]oxepin-5-one scaffold. In addition to oxygen-tethered substrates, a nitrogen linker can also be used, leading to the formation of a seven-membered nitrogen heterocycle **2k**.[9] This carbofluorination is sensitive to the substitution pattern of the alkene moiety. Although acyl fluorides bearing a mono-substituted alkene and an internal alkene both failed to participate in this carbofluorination, 1,1-disustituted alkenes were found to be widely tolerated. For example, benzyl-substituted substrate **1l** can be readily converted into the corresponding cyclized product with the formation of a highly congested tertiary alkyl fluoride moiety. In an attempt to synthesize a six-membered ring, substrate **1m**, which contains a one-carbon shorter tether, was examined for its applicability to this reaction. Phenol derivative **2m'** was obtained, instead

of carbofluorinated product **2m**, which is in sharp contrast to the result obtained for the reaction of **2j**. We assume that this is probably because the postulated carbocation intermediate is prone to deprotonation, which is driven by aromatization (*vide infra*).

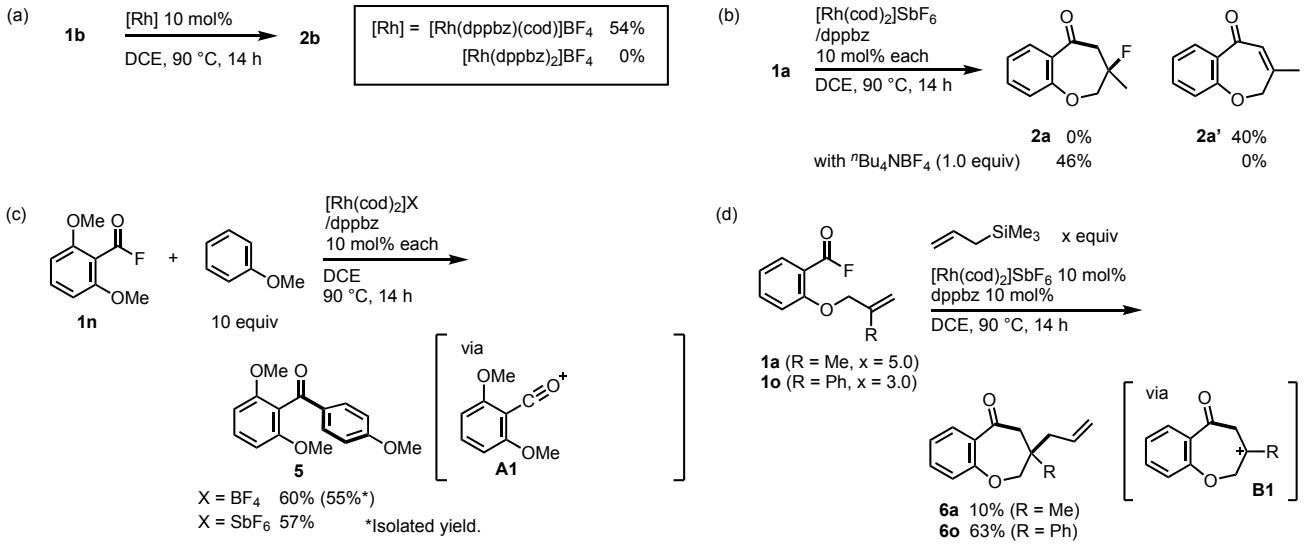
This carbofluorination reaction can also be applied to acyl fluorides which have alkyne moiety. Thus, the rhodium-catalyzed reaction of acyl fluoride **3a** gave 6-exo cyclization product **4a** without the formation of a seven-membered product. A bulky mesityl group (*i.e.*, **3b**) was also compatible as a substituent at the alkyne terminal to generate fluorinated 4-chromanone derivatives.[10a] Nitrogen-tethered acyl fluoride **3c** successfully participated in this catalytic carbofluorination, thereby demonstrating the broad utility of this reaction for the synthesis of fluorinated heterocycles.[10b]



Scheme 2. Scope of Rhodium-Catalyzed Intramolecular Acylfluorination of **1**[a]

[a]Reaction conditions: **1a** (0.20 mmol), $[Rh(cod)_2]BF_4$ (0.020 mmol. 10 mol%), dppbz (0.020 mmol, 10 mol%) in DCE (1.0 mL) at 90 °C for 14 h. [b]1.0 mmol scale.

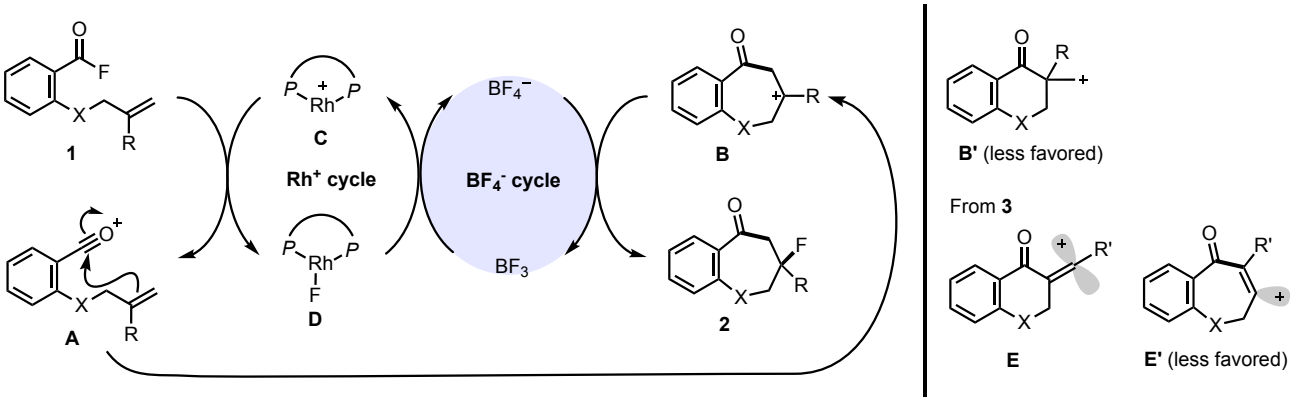
To obtain mechanistic insights of this carbofluorination, several mechanistic experiments were carried out (Scheme 3). First, the reaction of **1b** using independently synthesized Rh-dppbz complexes as a catalyst was examined to verify the catalytically active species (Scheme 3a). When $[Rh(dppbz)(cod)]BF_4$ was used as a catalyst, carbofluorinated product **2b** was obtained in 54% yield, whereas $[Rh(dppbz)_2]BF_4$ failed to promote the reaction. These results indicated that a metal to ligand ratio of 1:1 is essential for this insertion reaction, and the use of an excess amount of a ligand resulted in the deterioration of the catalytic activity by forming a 1:2 complex. The effect of the counter anion of a rhodium catalyst was next investigated. Interestingly, when $[Rh(cod)_2]SbF_6$ was used instead of $[Rh(cod)_2]BF_4$ in the reaction, **1a** did not form **2a** under the standard conditions and alkene **2a'** was instead obtained in 40% yield. When the same reaction was conducted in the presence of 1 equiv of $^nBu_4NBF_4$, **2a** was formed in 46% yield (Scheme 3b). These results indicate that BF_4^- is not merely a spectator but, rather, plays an indispensable role in this reaction, for example, as a fluoride donor. In fact, the fluoride ion affinity (FIA) value of BF_3 is significantly lower than for SbF_5, suggesting that BF_4^- is a better fluoride donor than SbF_6^-.[11] In an attempt to obtain additional insights into the intermediate involved in this reaction, the reactions of acyl fluorides with external nucleophiles were examined in the presence of a cationic rhodium catalyst. When acyl fluoride **1n** was reacted with anisole (10 equiv) in the presence of $[Rh(cod)_2]BF_4$ or $[Rh(cod)_2]SbF_6$ and dppbz (10 mol% each), Friedel–Crafts type acylation proceeded to form acylated anisole **5** in 60% and 57% yield, respectively (Scheme 3c).[12] This result indicates that the cationic rhodium complex, irrespective of the nature of its counter anion, is capable of abstracting a fluoride anion from acyl fluoride to form an acylium cation **A1**, which is likely involved as an intermediate in the carbofluorination reaction. Moreover, the use of allylsilane, instead of anisole, in the $[Rh(cod)_2]SbF_6$-catalyzed reaction of **1a** or **1o** provided allylated product **6a** (10% yield) or **6o** (63% yield), respectively (Scheme 3d).[13] These allylated products **6a** and **6o** were presumably formed by the reaction of a cyclic carbocation intermediate **B1** with allylsilane, when BF_4^- was not present.[14]



Scheme 3. Mechanistic studies.

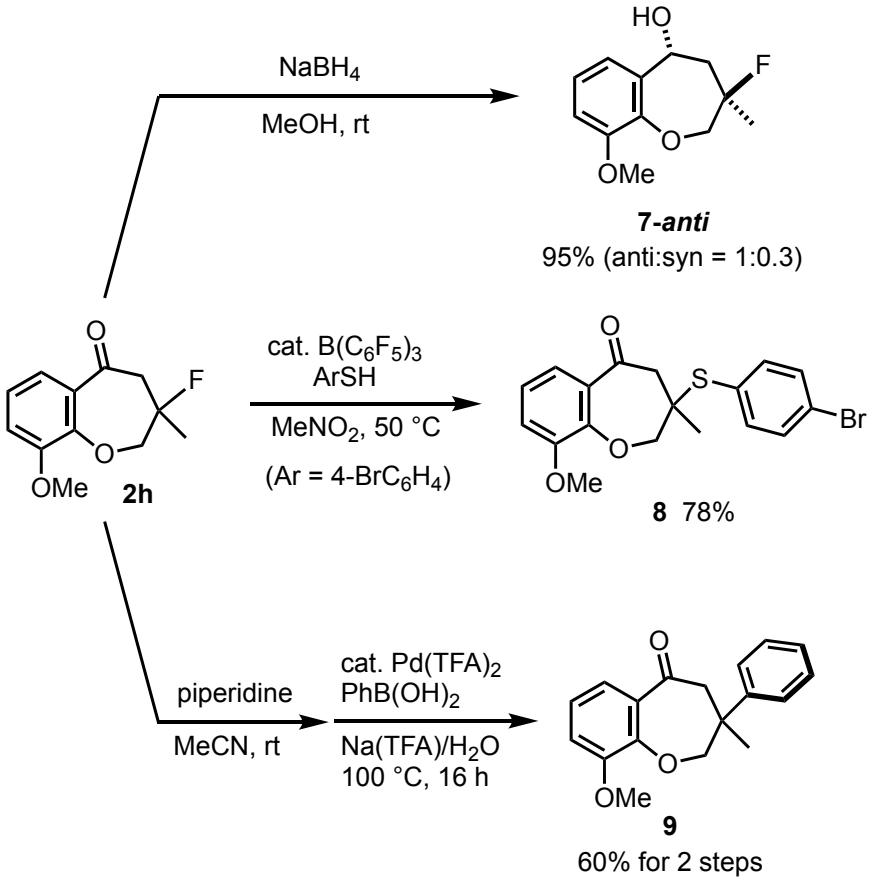
Based on above mechanistic studies, a possible mechanism for this rhodium-catalyzed carbofluorination of **1** is showed in Scheme 4. The catalytic cycle starts with the abstraction of a fluoride anion from acid fluoride **1** by a

Lewis acidic rhodium cation **C** to form an acylium cation **A**, along with a neutral rhodium(I)-fluoride complex **D**.[15] Acylium cation **A** is subsequently intercepted by a tethered alkene to generate a more stable cyclic tertiary carbocation intermediate **B**. This carbocation finally leads to the production of fluoride **2** by abstracting a fluoride from a BF_4^-, rather than from rhodium-fluoride **D**.[16] The resulting BF_3 subsequently abstracts a fluoride from **D** to regenerate cationic rhodium catalyst **C**.[17] In this proposed mechanism, BF_4^- serves as a fluoride anion shuttle, which explains the essential importance of BF_4^- in this carbofluorination reaction (see Scheme 3b). Interestingly, the use of $BF_3{\cdot}OEt_2$ as a catalyst, instead of $[Rh(cod)_2]BF_4$/dppbz, did not result in the formation of a carbofluorination product but, rather, resulted in a complicated mixture (See the SI for details). This result highlights the uniqueness of the cationic rhodium/BF_4^- dual catalytic system for catalytic carbofluorination reactions, presumably because undesired side reactions can be suppressed by lowering the concentration of the strongly Lewis acidic BF_3 in the system through the conjugation of another catalytic cycle mediated by a cationic rhodium complex. The preferred cyclization mode (7-endo vs 6-exo) can be rationalized by the relative stability of the carbocation intermediates. In the case of alkene-tethered substrate **1**, the 7-endo mode is preferred because more stable tertiary cation **B** is generated, rather than primary cation **B'**. The carbofluorination of alkyne **3** results in the exclusive formation of a six-membered ring, presumably because the postulated linear alkenyl cation **E** is more stable than the seven-membered alkenyl cation **E'**.[18]



Scheme 4. Possible mechanism

The fluorinated seven-membered compounds synthesized by this the carbofluorination reaction can serve as versatile intermediates and are amenable to further synthetic elaboration (Scheme 5). For example, the ketone moiety in **2h** can be reduced to the corresponding alcohol **7** with the fluorine moiety remaining intact. The fluorine group in **2h** can be substituted by various nucleophiles, which allows for the construction of quaternary stereocenters that contain a variety of substituents. When **2h** was reacted with 4-bromobenzenethiol in the presence of a $B(C_6F_5)_3$ catalyst,[19] sulfide **8** was obtained in 78% yield. An aryl group can also be introduced via dehydrofluorination,[20] followed by the palladium-catalyzed 1,4-addition of arylboronic acid to form **9** in 60% overall yield.[21]



Scheme 5. Synthetic applications.

4.3. Conclusion

In summary, we report on the intramolecular insertion of simple alkenes into a C–F bond of an acyl fluoride, which is catalyzed by a $Rh^{+}BF_4^{-}$ catalyst. Mechanistic studies indicated that the cleavage and formation of a C–F bond is mediated by a cooperative action of cationic rhodium and BF_4^{-}.

4.4. Experimental Section

I. General Information

^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$. The chemical shifts in ^{1}H NMR spectra were recorded relative to tetramethyl silane (δ 0.00) or $CHCl_3$ (δ 7.26). The chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.16). The chemical shifts in ^{19}F NMR spectra were recorded relative to benzotrifluoride ($PhCF_3$, δ –65.64). The data is reported as follows: chemical shift (δ) in ppm, coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer. Absorption is reported in reciprocal centimeters (cm^{-1}) with the following relative intensities: s (strong), m (medium), or w (weak). High resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silicycle SilicaFlash F60 (230-400 mesh)). Data collection for X-ray crystal analysis were performed on a

Rigaku/XtaLAB Pro P200 Hybrid Photon Counting diffractometer (Cu-Kα, λ = 1.54184 Å). The structures were solve with direct methods and refined with full-matrix least squares.

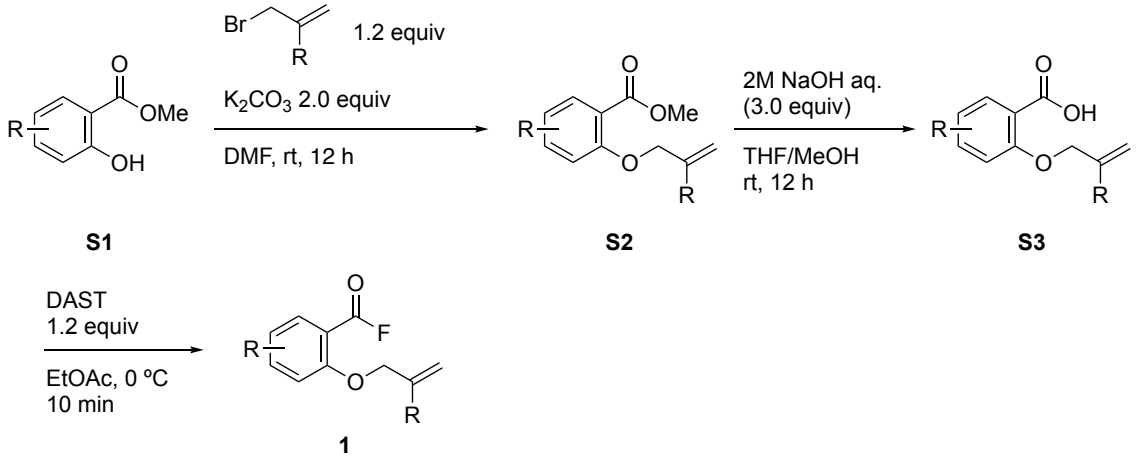
II. Materials

Unless otherwise stated, all commercially available reagents and solvents were supplied from TCI, Wako Chemical, and Aldrich and used as received. DCE (dehydrated) was purchased from Wako Chemical and used as received. $[RhCl(cod)]_2$,[22] $[Rh(cod)_2]BF_4$,[23] $[Rh(cod)_2]SbF_6$[23] were prepared according to literature procedure. Methyl 5-bromosalicylate [CAS: 4068-76-2], methyl 4-chlorosalicylate [CAS: 22717-55-1], methyl 6-hydroxy-2-anisate [CAS: 22833-69-8], methyl 3-phenylsalicylate [CAS: 4906-69-8], methyl 1-hydroxy-2-naphthoate [CAS: 948-03-8] were prepared according to the literature procedure from corresponding salicylic acid.[24] Methyl *N*-(*p*-toluenesulfonyl)anthranilate [CAS: 50998-74-8], [25] allyl bromides 3-bromo-2-phenyl-1-propene [CAS: 3360-54-1],[26] [2-(bromomethyl)allyl]benzene [CAS: 437709-07-4],[27] 1-(2-methyl-2-propen-1-yl)-2-naphthalenecarboxaldehyde [CAS: 1888391-97-6][28], 3-phenylprop-2-yn-1-yl methanesulfonate [CAS: 82490-61-7][29], 3-mesitylprop-2-yn-1-ol [CAS: 774-10-7][30] and 2,6-dimethoxybenzoyl fluoride [CAS: 130161-08-9][31] were prepared according to literature procedures. $[Rh(dppbz)(cod)]BF_4$ [CAS: 2068819-89-4] and $[Rh(dppbz)_2]BF_4$ [CAS: 2004725-12-4] were prepared according to literature procedure.[32]

III. Preparation of Starting Materials

General Procedures for the Synthesis of Starting Acyl Fluorides 1

Starting acyl fluorides **1** were synthesized according to the following schemes.



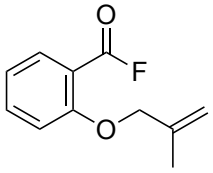
Synthesis of S2. In a round-bottom flask, methyl salicylate **S1** (10 mmol) and K_2CO_3 (20 mmol, 2.76 g) were dissolved in DMF (20 mL), 3-bromo-2-methylpropene (12 mmol, 1.2 equiv, 1.2 mL) was then added, and the resulting mixture was stirred for 12 h at rt. After **S1** was consumed completely (checked by TLC), Et_2O (50 mL) and water (50 mL) were added into the reaction mixture. The organic layer was separated and washed with water (30 mL). The organic layer was dried using Na_2SO_4. After filtration, the solvent was removed in vacuo to give crude allyl ether **S2**, which was used for next step without further purification.

Synthesis of S3. In a round-bottom flask, crude **S2** (10 mmol) was dissolved in THF/MeOH (1/1, 20 mL), and an aqueous solution of NaOH (2 M, 15 mL, 3.0 equiv of NaOH) was then added to the reaction mixture. After stirring for 12 h, the reaction mixture was extracted with Et_2O (50 mL × 3) and aqueous layer was acidified using 4 M HCl aq. The aqueous layer was extracted with Et_2O (30 mL × 3) and washed with brine. The combined organic extracts were dried using Na_2SO_4. After filtration and evaporation, crude carboxylic acid **S3** was obtained, which was used for the next step without further purification.

Synthesis of 1. Crude carboxylic acid (5.0 mmol) and dehydrated EtOAc (15 mL) were added to a round-bottom flask under N_2 atmosphere. After cooling to 0 ºC, DAST (6.0 mmol, 0.79 mL, 1.2 equiv) was slowly added and the resulting mixture was stirred at 0 ºC for 30 min. An aqueous saturated solution of $NaHCO_3$ (30 mL) was then added and organic layer was separated and dried using Na_2SO_4. After filtration, volatiles were removed in vacuo and the residue was purified by flash column chromatography to give desired acyl fluoride **1**.

Spectroscopic data of 1.

2-((2-Methylallyl)oxy)benzoyl fluoride (1a).



The synthesis was performed on a 10 mmol scale according to General Procedures using methyl salicylate (1.52 g, 10 mmol) and 3-bromo-2-methyl-1-propene (1.2 mL, 12 mmol).

Colorless oil (1.61 g, 82%). R_f 0.46 (SiO_2, Hexane/Et_2O = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.87 (s, 3H), 4.56 (s, 2H), 5.03-5.05 (m, 1H), 5.22 (t, J = 1.2 Hz, 1H), 7.00-7.06 (m, 2H), 7,57-7.62 (m, 1H), 7.94 (dd, J = 9.6, 1.6 Hz, 1H).

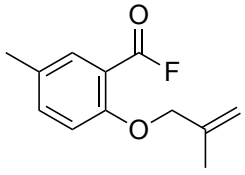
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.4, 72.3, 113.3, 113.5 (d, $J_{C–F}$ = 1.9 Hz), 113.7 (d, $J_{C–F}$ = 54.6 Hz), 120.6, 134.0 (d, $J_{C–F}$ = 2.9 Hz), 136.6, 139.8, 155.2 (d, $J_{C–F}$ = 343 Hz), 160.7 (d, $J_{C–F}$ = 3.8 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.22.

IR (KBr): 2978 w, 1813 s, 1601 s, 1490 s, 1450 s, 1301 m, 1221 s, 1168 m, 1051 w, 984 m, 908 w, 754 s, 692 m, 640 m.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{11}H_{12}O_2F$: 195.0816. Found: 195.0817.

5-Methyl-2-((2-methylallyl)oxy)benzoyl fluoride (1b).



The synthesis was performed on a 5.0 mmol scale according to General Procedures using methyl 5-methyl salicylate (850 mg, 5.0 mmol) and 3-bromo-2-methyl-1-propene (613 mL, 6.0 mmol).

Colorless oil (792 mg, 76%). R_f 0.48 (SiO_2, Hexane/Et_2O = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.85 (s, 3H), 2.32 (s, 3H), 4.52 (s, 2H), 5.02 (d, J = 1.6 Hz, 1H), 5.20 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 7.38 (dd, J = 8.7, 2.3 Hz, 1H), 7.73 (d, J = 1.7 Hz, 1H).

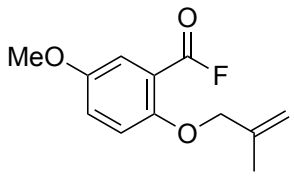
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.4, 20.3, 72.4, 113.1, 113.4 (d, $J_{C–F}$ = 55.6 Hz), 113.5 (d, J_{C-F} = 1.9 Hz), 130.1, 134.0 (d, J_{C-F} = 1.9 Hz), 137.3, 140.1, 155.5 (d, J_{C-F} = 343 Hz), 158.7 (d, J_{C-F} = 2.9 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.19.

IR (KBr): 2978 w, 1814 s, 1617 w, 1579 w, 1502 s, 1454 m, 1295 m, 1260 m, 1178 m, 1151 w, 1049 w, 990 m, 897 m, 812 w, 772 w, 721 w, 535 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{14}O_2F$: 209.0972. Found: 209.0979.

5-Methoxy-2-((2-methylallyl)oxy)benzoyl fluoride (1c).



The synthesis was performed on a 5.0 mmol scale according to General Procedures using Methyl 5-methoxysalicylate (911 mg, 5.0 mmol) and 3-bromo-2-methyl-1-propene (613 mL, 6.0 mmol).

Pale-yellow oil (851 mg, 76%). R_f 0.46 (SiO_2, Hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.85 (s, 3H), 3.80 (s, 3H), 4.50 (s, 2H), 5.02 (t, J = 1.0 Hz, 1H), 5.19 (d, J = 0.9 Hz, 1H), 6.95 (dd, J = 9.2, 0.92 Hz, 1H), 7.16 (dd, J = 9.2, 3.7 Hz, 1H), 7.40 (d, J = 3.2 Hz, 1H).

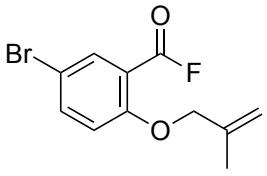
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.4, 55.7, 72.9, 113.1, 113.8 (d, J_{C-F} = 58.5 Hz), 115.1 (d, J_{C-F} = 2.9 Hz), 116.9 (d, J_{C-F} = 2.9 Hz), 123.4, 140.1, 153.1, 155.1 (d, J_{C-F} = 2.9 Hz), 155.2 (d, J_{C-F} = 346 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.19.

IR (KBr): 2943 w, 1816 s, 1583 w, 1499 s, 1456 m, 1420 w, 1286 m, 1236 m, 1196 m, 1176 m, 1038 m, 992 m, 902 w, 814 w, 768 w, 719 w, 658 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{14}O_3F$: 225.0922. Found: 225.0918.

5-Bromo-2-((2-methylallyl)oxy)benzoyl fluoride (1e).



The synthesis was performed on a 5.0 mmol scale according to General Procedures using methyl 5-bromosalicylate (1.16 g, 5.0 mmol) and 3-bromo-2-methyl-1-propene (613 mL, 6.0 mmol).

Colorless solid (929 mg, 68%). R_f 0.50 (SiO_2, Hexane/Et_2O = 4/1). M.p.: 77.4-78.3 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.85 (s, 3H), 4.54 (s, 2H), 5.05 (t, J = 1.4 Hz, 1H), 5.19 (s, 1H), 6.91 (dd, J = 8.9, 1.1 Hz, 1H), 7.67 (dd, J = 8.9, 2.5 Hz, 1H), 8.03 (d, J = 2.8 Hz, 1H).

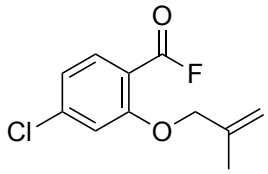
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.4, 72.7, 112.5, 113.6, 115.36 (d, J_{C-F} = 2.9 Hz), 115.43 (d, J_{C-F} = 60.6 Hz), 136.2 (d, J_{C-F} = 2.8 Hz), 139.2, 139.4, 153.9 (d, J_{C-F} = 347 Hz), 159.7 (d, J_{C-F} = 3.8 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz, C_6F_6) δ: 29.75.

IR (KBr): 3115 m, 2978 m, 2914 m, 1807 s, 1782 s, 1661 m, 1594 s, 1568 s, 1492 s, 1447 m, 1401 m, 1375 m, 1289 s, 1269 m, 1256 s, 1204 s, 1160 m, 1150 m, 1102 w, 1045 s, 988 s, 904 s, 844 m, 821 s, 770 s, 690 w, 666 s, 527 m, 432 m.

HRMS (EI+, $[M]^+$) Calcd for $C_{11}H_{10}{}^{79}BrFO_2$: 271.9848. Found: 271.9852.

4-Chloro-2-((2-methylallyl)oxy)benzoyl fluoride (1f).



The synthesis was performed on a 5.0 mmol scale according to General Procedures using Methyl 4-chlorosalicylate (933 mg, 5.0 mmol) and 3-bromo-2-methyl-1-propene (613 mL, 6.0 mmol).

Colorless solid (760 mg, 67%). R_f 0.60 (SiO_2, Hexane/Et_2O = 4/1). M.p. 49.7-50.6 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.87 (s, 3H), 4.54 (s, 2H), 5.06 (t, J = 1.4 Hz, 1H), 5.22 (s, 1H), 7.01-7.04 (m, 2H), 7.87 (d, J = 8.2 Hz, 1H).

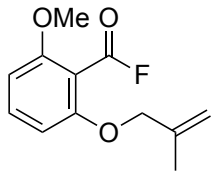
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.4, 72.8, 112.3 (d, $J_{C–F}$ = 59.4 Hz),113.8, 114.2 (d, $J_{C–F}$ = 2.9 Hz), 121.1, 134.9 (d, $J_{C–F}$ = 2.9 Hz), 139.2, 142.9, 154.5 (d, $J_{C–F}$ = 342 Hz), 161.1 (d, $J_{C–F}$ = 3.8 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz, C_6F_6) δ: 29.04.

IR (KBr): 3117 m, 2936 w, 1824 s, 1780 s, 1602 s, 1565 s, 1421 m, 1282 m, 1263 s, 1216 s, 1144 m, 1104 m, 1038 m, 1010 m, 965 s, 900 s, 864 m, 850 m, 834 w, 760 s, 683 m, 599 w, 471 m, 426 w.

HRMS (EI+, $[M]^+$) Calcd for $C_{11}H_{10}{}^{35}ClFO_2$: 228.0353. Found: 228.0355.

2-Methoxy-6-((2-methylallyl)oxy)benzoyl fluoride (1g).



The synthesis was performed on a 6.3 mmol scale according to General Procedures using methyl 6-methoxysalicylate (1.15 g, 6.3 mmol) and 3-bromo-2-methyl-1-propene (772 mL, 7.6 mmol).

Pale-yellow oil (1.2 g, 82%). R_f 0.42 (SiO_2, Hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.80 (s, 3H), 3.82 (s, 3H), 4.45 (s, 2H), 4.97 (s, 1H), 5.09 (s, 1H), 6.55 (d, J = 4.4 Hz, 1H), 6.57 (d, J = 4.8 Hz, 1H), 7.35 (t, J = 8.6 Hz, 1H).

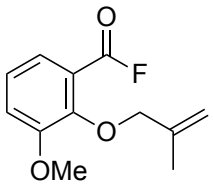
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.0, 56.0, 72.2, 103.9, 105.0, 106.9 (d, $J_{C–F}$ = 57.5 Hz), 112.8, 133.8, 139.8, 155.4 (d, $J_{C–F}$ =350 Hz), 158.0, 159.0.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 50.80.

IR (KBr): 2943 w, 1826 s, 1598 s, 1478 s, 1439 m, 1378 w, 1305 m, 1260 s, 1220 m, 1110 s, 1000 s, 904 w, 790 m, 750 w, 710 w, 634 w, 617 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{14}O_3F$: 225.0922. Found: 225.0926.

3-Methoxy-2-((2-methylallyl)oxy)benzoyl fluoride (1h).



The synthesis was performed on a 5.0 mmol scale according to General Procedures using methyl 3-methoxysalicylate (911 mg, 5.0 mmol) and 3-bromo-2-methyl-1-propene (613 mL, 6.0 mmol)

Pale-yellow oil (991.7 mg, 88%). R_f 0.36 (SiO_2, Hexane/Et_2O = 4/1).

^1H NMR ($CDCl_3$, 400 MHz) δ: 1.90 (s, 3H), 3.89 (s, 3H), 4.50 (s, 2H), 4.99 (s, 1H), 5.12 (d, J = 0.92 Hz, 1H), 7.12-7.21 (m, 2H), 7.46 (dd, J = 7.6, 1.6 Hz, 1H).

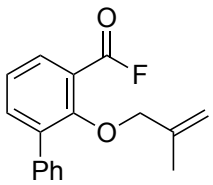
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.8, 56.3, 77.8, 113.8, 118.7, 120.0 (d, $J_{C–F}$ = 57.5 Hz), 124.0 (d, $J_{C–F}$ = 2.9 Hz), 124.1, 141.4, 150.6 (d, $J_{C–F}$ = 1.9 Hz), 154.0 (d, $J_{C–F}$ = 3.8 Hz), 155.4 (d, $J_{C–F}$ = 345 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 30.94

IR (KBr): 2945 w, 1818 s, 1582 w, 1479 s, 1440 m, 1317 m, 1270 s, 1252 s, 1090 w, 1015 m, 968 w, 906 w, 748 m, 734 w, 718 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{14}O_3F$: 225.0922. Found: 225.0925.

2-((2-Methylallyl)oxy)-[1,1'-biphenyl]-3-carbonyl fluoride (1i).



The synthesis was performed on a 5.0 mmol scale according to General Procedures using methyl 3-phenylsalicylate (1.14 g, 5.0 mmol) and 3-bromo-2-methyl-1-propene (613 mL, 6.0 mmol).

Colorless oil (1.03 g, 76%). R_f 0.60 (SiO_2, Hexane/Et_2O = 4/1).

^1H NMR ($CDCl_3$, 400 MHz) δ: 1.59 (s, 3H), 3.98 (s, 2H), 4.77 (s, 1H), 4.81 (s, 1H), 7.25-7.31 (m, 1H), 7.36-7.45 (m, 3H), 7.53-7.55 (m, 2H), 7.64 (dd, J = 7.8, 1.8 Hz, 1H), 7.90 (dd, J = 7.8, 1.8 Hz, 1H).

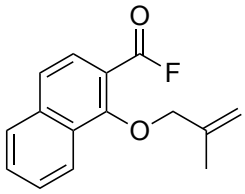
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.6, 78.4, 114.3, 119.9 (d, $J_{C–F}$ = 57.5 Hz), 124.4, 128.0, 128.5, 129.4, 132.2 (d, $J_{C–F}$ = 1.9 Hz), 137.0, 137.8 (d, $J_{C–F}$ = 2.9 Hz), 137.9, 140.7, 155.4 (d, $J_{C–F}$ = 345 Hz), 158.5 (d, $J_{C–F}$ = 2.9 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 30.48

IR (KBr): 3080 w, 2917 w, 2362 w, 1825 s, 1811 s, 1646 w, 1587 w, 1457 m, 1432 m, 1362 w, 1242 m, 1184 w, 1033 m, 990 m, 907 w, 763 m, 731 m, 698 m, 636 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{17}H_{16}O_2F$: 271.1129. Found: 271.1122.

1-((2-Methylallyl)oxy)-2-naphthoyl fluoride (1j).



The synthesis was performed on a 5.0 mmol scale according to General Procedures using methyl 1-hydroxy-2-naphthoate (1.01 g, 5.0 mmol) and 3-bromo-2-methyl-1-propene (613 mL, 6.0 mmol).

Pale-yellow oil (888 mg, 73%). R_f 0.60 (SiO_2, Hexane/Et_2O = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.99 (s, 3H), 4.57 (s, 2H), 5.11 (s, 1H), 5.27 (s, 1H), 7.59-7.63 (m, 1H), 7.66-7.70 (m, 2H), 7.87 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 7.3 Hz, 1H), 8.31 (d, J = 8.2 Hz, 1H).

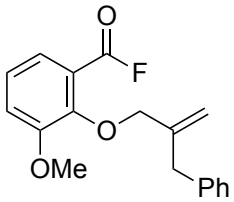
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.9, 80.0, 118.8 (d, $J_{C–F}$ =58.5 Hz), 113.9, 124.2, 124.4, 126.7 (d, $J_{C–F}$ = 2.9 Hz), 127.3, 128.2, 128.8 (d, $J_{C–F}$ = 2.9 Hz), 130.0, 138.1, 140.1, 155.6 (d, $J_{C–F}$ = 343 Hz), 161.0 (d, $J_{C–F}$ = 4.8 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.16.

IR (KBr): 3080 w, 2916 w, 1812 s, 1793 s, 1624 m, 1569 m, 1457 m, 1397 w, 1336 m, 1229 m, 1208 m, 1151 w, 1103 m, 1050 s, 986 w, 904 w, 822 w, 762 m, 737w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{14}O_2F$: 245.0972. Found: 245.0964.

2-((2-Benzylallyl)oxy)-3-methoxybenzoyl fluoride (1n).



The synthesis was performed on a 3.0 mmol scale according to General Procedures using methyl 3-methoxysalicylate (547 mg, 3.0 mmol) and (2-(bromomethyl)allyl)benzene (368 mL, 3.6 mmol).

Pale-yellow solid (245 mg, 27%). R_f 0.44 (SiO_2, Hexane/Et_2O = 7/3). M.p. 50.6-51.4 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.58 (s, 2H), 3.83 (s, 3H), 4.49 (s, 2H), 4.99 (d, J = 1.4 Hz, 1H), 5.28 (s, 1H), 7.11-7.19 (m, 2H), 7.20-7.32 (m, 5H), 7.45 (dd, J = 7.3, 1.8 Hz, 1H).

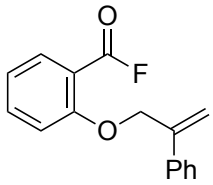
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 39.9, 56.2, 76.1, 115.5, 118.6, 119.9 (d, $J_{C–F}$ =57.5 Hz), 124.0 (d, $J_{C–F}$ =2.9 Hz), 124.2, 126.3, 128.4, 129.3, 139.3, 144.6, 150.5 (d, $J_{C–F}$ =2.9 Hz), 153.9 (d, $J_{C–F}$ =3.8 Hz), 155.4 (d, $J_{C–F}$ =345 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz, C_6F_6) δ: 32.93.

IR (KBr): 3023 w, 2942 w, 1822 s, 1790 s, 1651 w, 1596 m, 1581 m, 1479 s, 1435 m, 1324 s, 1273 s, 1247 s, 1090 m, 1036 s, 971 s, 920 s, 849 s, 832 m, 808 w, 727 s, 645 w, 498 w, 473 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{18}H_{18}O_3F$: 301.1235. Found: 301.1237.

2-((2-Phenylallyl)oxy)benzoyl fluoride (1o).



The synthesis was performed on a 9.4 mmol scale according to General Procedures using methyl salicylate (1.43 g, 9.4 mmol) and 3-bromo-2-phenyl-1-propene (2.22 g, 11.3 mmol).

Colorless solid (1.94 g, 81%). R_f 0.40 (SiO_2, Hexane/Et_2O = 4/1). M.p. 67.7-68.5 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.02 (t, J = 1.4 Hz, 2H), 5.63 (d, J = 0.92 Hz, 1H), 5.68 (d, J = 0.92 Hz, 1H), 7.04-7.09 (m, 2H), 7.31-7.40 (m, 3H), 7.45-7.48 (m, 2H), 7.59-7.63 (m, 1H), 7.95 (dd, J = 8.0, 1.8 Hz, 1H).

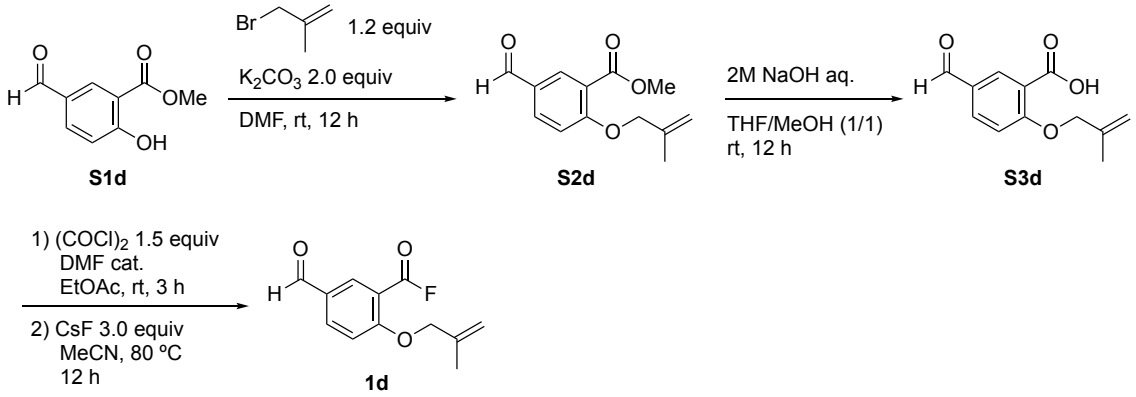
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 70.2, 113.7 (d, $J_{C–F}$ =2.9 Hz), 113.9 (d, $J_{C–F}$ =59.4 Hz), 114.8, 120.9, 126.2, 128.3, 128.7, 134.0 (d, $J_{C–F}$ =1.9 Hz), 136.7, 138.3, 142.1, 155.2 (d, $J_{C–F}$ =343 Hz), 160.4 (d, $J_{C–F}$ =2.9 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.28.

IR (KBr): 3090 w, 3064 w, 1809 s, 1780 m, 1491 s, 1449 s, 1389 m, 1301 s, 1217 m, 1140 m, 1025 s, 974 s, 912 s, 786 s, 756 s, 717 s, 690 s, 680 s, 641 s, 620 s, 528 m.

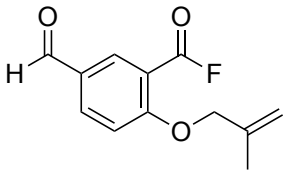
HRMS (EI+, $[M]^+$) Calcd for $C_{16}H_{13}FO_2$: 256.0900. Found: 256.0897.

Synthesis of 5-formyl-2-((2-methylallyl)oxy)benzoyl fluoride (1d).



Carboxylic acid **S3d** was prepared from **S1d** according to General Procedures. **S3d** (1.1 g, 5.0 mmol) was dissolved in EtOAc (20 mL) in a round-bottom flask under N_2 atmosphere and the flask was cooled to 0 °C using an ice/water bath. $(COCl)_2$ (643 mL, 7.5 mmol, 1.5 equiv) and DMF (several drops) were then added to the flask and the ice/water bath was removed. After stirring at rt for 3 h, volatiles were removed in vacuo and the residue was dissolved in MeCN (30 mL) under N_2 atmosphere. CsF (2.3 g, 15 mmol, 3.0 equiv) was then added and the resulting mixture was stirred at 80 °C for 12 h. After the mixture was cooled to rt, a precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography to give **1d** as a colorless solid (506 mg, 46%).

5-Formyl-2-((2-methylallyl)oxy)benzoyl fluoride (1d).



Colorless solid (506 mg, 46%). R_f 0.22 (SiO_2, Hexane/Et_2O = 7/3). M.p. 72.5-73.4 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.88 (s, 3H), 4.67 (s, 2H), 5.08-5.09 (m, 1H), 5.22-5.23 (m, 1H), 7.16 (d, J = 8.8 Hz, 1H), 8.14 (dd, J = 8.9, 2.1 Hz, 1H), 8.45 (d, J = 1.6 Hz, 1H), 9.94 (s, 1H).

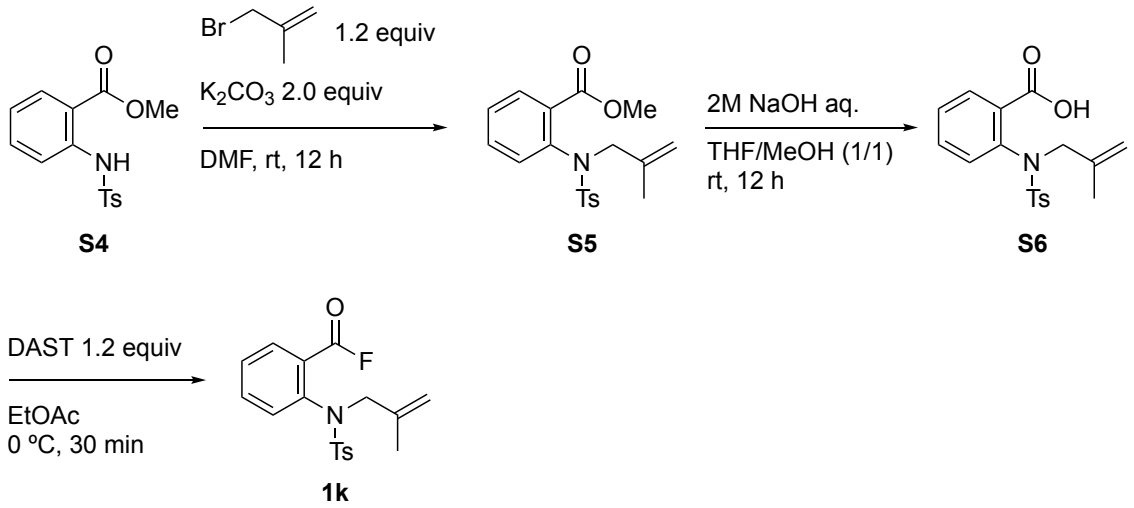
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.3, 73.1, 114.0 (d, $J_{C–F}$ =1.9 Hz), 114.1, 114.4 (d, $J_{C–F}$ =65.2 Hz), 129.5, 136.7, 136.9 (d, $J_{C–F}$ =1.9 Hz), 138.9, 154.1 (d, $J_{C–F}$ =343 Hz), 164.7 (d, $J_{C–F}$ =3.8 Hz), 189.4.

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.87.

IR (KBr): 3093 w, 2877 m, 1823 s, 1782 s, 1709 m, 1698 s, 1611 m, 1504 m, 1450 w, 1430 m, 1366 w, 1312 m, 1281 s, 1238 s, 1181 s, 1148 m, 1137 m, 1060 w, 991 s, 978 s, 967 m, 921 w, 776 m, 625 m, 535 m.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{12}O_3F$: 223.0765. Found: 223.0759.

Synthesis of 2-((4-methyl-N-(2-methylallyl)phenyl)sulfonamido)benzoyl fluoride (1k).

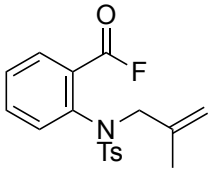


Synthesis of S5. In a round-bottom flask, **S4**[25] (10 mmol, 3.33 g) and K_2CO_3 (20 mmol, 2.76 g) were dissolved in DMF (20 mL). 3-Bromo-2-methylpropene (12 mmol, 1.2 equiv, 1.2 mL) was then added and the resulting mixture was stirred for 12 h at rt. After **S4** was completely consumed (checked by TLC), Et_2O (50 mL) and water (50 mL) were added to the reaction mixture. The organic layer was separated and washed with water (30 mL). The organic layer was dried using Na_2SO_4. After filtration, the solvent was removed in vacuo, crude **S5** was obtained, which was used for next step without further purification.

Synthesis of S6. In a round-bottom flask, crude **S5** (10 mmol) was dissolved in THF/MeOH (1/1, 20 mL). An aqueous solution of NaOH (2 M, 15 mL, 3.0 equiv of NaOH) was added to the reaction mixture. After stirring for 12 h, the reaction mixture was extracted with Et_2O (50 mL × 3) and aqueous layer was acidified using 4 M HCl aq. The aqueous layer was extracted with Et_2O (30 mL × 3) and washed with brine. The combined organic extracts were dried using Na_2SO_4. After filtration and evaporation, crude carboxylic acid **S6** was obtained, which was used for the next step without further purification.

Synthesis of 1k. Crude carboxylic acid **S6** (2.6 mmol, 911 mg) and dehydrated EtOAc (8.0 mL) were added to a round-bottom flask under N_2 atmosphere. After cooling to 0 ºC, DAST (3.2 mmol, 0.34 mL, 1.2 equiv) was slowly added to reaction mixture, and the resulting mixture was stirred at 0 ºC for 30 min. A saturated aqueous solution of $NaHCO_3$ (30 mL) was added and organic layer was separated. The organic extract was dried using Na_2SO_4. After filtration, volatiles were removed in vacuo and the residue was purified by flash column chromatography to give desired acyl fluoride **1k** (626 mg, 68%).

2-((4-Methyl-N-(2-methylallyl)phenyl)sulfonamido)benzoyl fluoride (1k).



Colorless solid (626 mg, 68%). R_f 0.34 (SiO_2, Hexane/EtOAc = 7/3). M.p.: 154.4-155.0 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.79 (s, 3H), 2.43 (s, 3H), 4.14 (brs, 2H), 4.68 (s, 1H), 4.78 (t, J = 1.4 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 8.7 Hz, 2H), 7.42-7.47 (m, 3H), 7.56 (td, J = 7.7, 1.8, 1.4 Hz, 1H), 7.98 (dd, J = 7.9, 1.9 Hz, 1H).

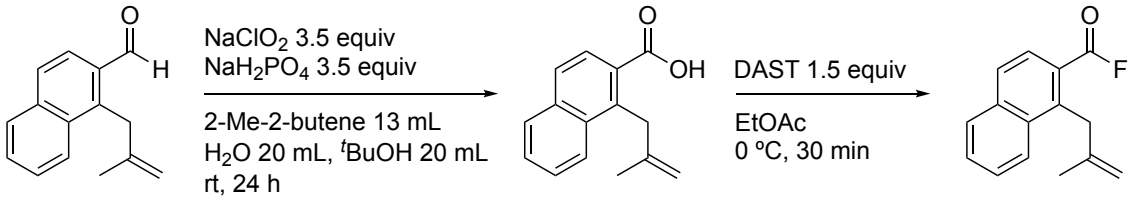
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 20.4, 21.7, 57.2, 116.6, 126.5 (d, $J_{C–F}$ = 58.5 Hz), 128.0, 128.2, 129.6, 130.1 (d, $J_{C–F}$ = 2.9 Hz), 133.1 (d, $J_{C–F}$ = 1.9 Hz), 134.4, 135.0, 139.9, 140.0 (d, $J_{C–F}$ = 1.9 Hz), 144.0, 155.4 (d, $J_{C–F}$ = 347 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ:29.59.

IR (KBr): 3078 w, 1830 s, 1810 s, 1655 w, 1596 s, 1489 s, 1450 s, 1282 m, 1230 s, 1166 s, 1092 m, 1023 s, 995 s, 903 s, 862 s, 791 m, 708 s, 637 m, 579 s, 542 m.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{18}H_{19}NO_3FS$: 348.1064. Found: 348.1057.

Synthesis of 1-(2-methylallyl)-2-naphthoyl fluoride (1o).



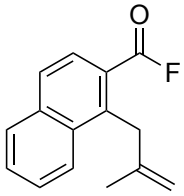
S7 **S8** **1o**

A round-bottom flask was charged with **S7**[28] (210 mg, 1.0 mmol), H_2O (20 mL), 2-methyl-2-butene (13 mL), ^{t}BuOH (20 mL), NaH_2PO_4 (420 mg, 3.5 mmol, 3.5 equiv), and $NaClO_2$ (317 mg, 3.5 mmol, 3.5 equiv). The mixture was stirred at rt for 24 h. The organic layer was then separated and the aqueous layer was extracted with EtOAc (20 mL × 3). The combined organic extracts were dried using Na_2SO_4. After filtration, the filtrate was concentrated to give crude **S8**.

Crude **S8** and dehydrated EtOAc (10 mL) were added to a round-bottom flask under N_2 atmosphere. After cooling to 0 ºC, DAST (1.5 mmol, 0.20 mL, 1.5 equiv) was slowly added to reaction mixture, which was stirred at 0 °C for 30 min. A saturated aqueous solution of $NaHCO_3$ (30 mL) was added and organic layer was separated. The organic extract was dried using Na_2SO_4. After filtration, volatiles were removed and the residue was purified by flash

column chromatography to give desired acyl fluoride **1m** (135 mg, 59%).

1-(2-Methylallyl)-2-naphthoyl fluoride (1m).



Colorless solid (135 mg, 59%). R_f 0.66 (SiO_2, Hexane/Et_2O = 4/1). M.p. 72.1-72.9 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.95 (s, 3H), 4.11 (s, 1H), 4.23 (s, 2H), 4.78 (t, J = 1.4 Hz, 1H), 7.58-7.66 (m, 2H), 7.84 (d, J = 8.7 Hz, 1H), 7.89-7.91 (m, 1H), 7.97 (d, J = 8.7 Hz, 1H), 8.16 (d, J = 8.7 Hz, 1H).

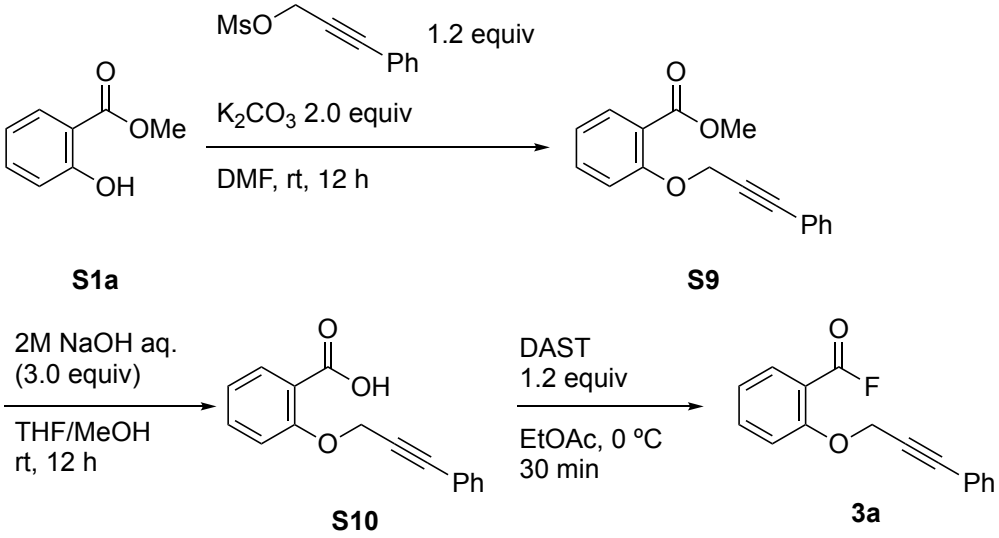
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 23.8, 36.8, 111.6, 121.7 (d, $J_{C–F}$ = 56.6 Hz), 126.4, 127.4, 127.7, 128.7, 129.0, 132.9 (d, $J_{C–F}$ = 3.8 Hz), 136.1, 144.4, 144.47, 144.50, 157.1 (d, $J_{C–F}$ = 345 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 32.23.

IR (KBr): 3077 w, 1812 s, 1781 s, 1654 w, 1622 m, 1600 w, 1470 w, 1450 w, 1344 w, 1216 s, 1089 m, 1020 m, 929 m, 875 m, 812 w, 761 s, 717 w, 580 w, 512 w, 443 w.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{14}OF$: 229.1023. Found: 229.1015.

Synthesis of 2-((3-phenylprop-2-yn-1-yl)oxy)benzoyl fluoride (3a).



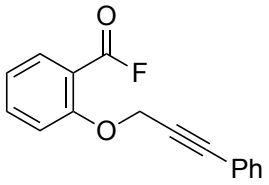
Synthesis of S9. In a round-bottom flask, methyl salicylate (**S1a**, 1.52 g, 10 mmol) and K_2CO_3 (2.76 g, 20 mmol) were dissolved in DMF (20 mL), and 3-phenylprop-2-yn-1-yl methanesulfonate (2.52 g, 12 mmol) was then added. The resulting mixture was stirred at rt for 12 h. After **S1a** was consumed completely (checked by TLC), Et_2O (50 mL) and water (50 mL) were added to the reaction mixture. The organic layer was separated and washed with brine (30 mL). The organic layer was dried using Na_2SO_4. After filtration, the solvent was removed in vacuo to give crude **S9**, which was used for next step without further purification.

Synthesis of S3. In a round-bottom flask, crude **S9** (ca. 10 mmol) was dissolved in THF/MeOH (1/1, 20 mL), and an

aqueous solution of NaOH (2 M, 15 mL) was then added to the reaction mixture. After stirring for 12 h, the reaction mixture was wahsed with Et_2O (50 mL × 3) and the separated aqueous layer was acidified using 4 M HCl aq. The aqueous layer was then extracted with Et_2O (30 mL × 3) and washed with brine. The combined organic extracts were dried using Na_2SO_4. After filtration and evaporation, crude carboxylic acid **S10** was obtained, which was used for the next step without further purification.

Synthesis of 3a. Crude **S10** (ca. 5.0 mmol) and dehydrated EtOAc (15 mL) were added to a round-bottom flask under N_2 atmosphere. DAST (6.0 mmol, 0.79 mL) was slowly added at 0 °C and the resulting mixture was stirred at 0 °C for 30 min. A saturated aqueous solution of $NaHCO_3$ (30 mL) was then added and organic layer was separated and dried using Na_2SO_4. After filtration, volatiles were removed in vacuo and the residue was purified by flash column chromatography (hexane to hexane:Et_2O = 7:3) to give desired acyl fluoride **3a** as a colorless solid (1.10 g, 87%).

2-((3-Phenylprop-2-yn-1-yl)oxy)benzoyl fluoride (3a).



Colorless solid (1.10 g, 87%). R_f 0.44 (SiO_2, Hexane/Et_2O = 7/3). M.p. 47.5–48.8 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.08 (s, 2H), 7.10 (t, J = 7.8 Hz, 1H), 7.28–7.36 (m, 4H), 7.40–7.43 (m, 2H), 7.63–7.67 (m, 1H), 7.96 (dd, J =7.8, 1.8 Hz, 1H).

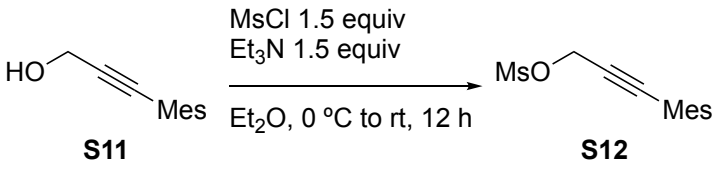
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 57.6, 82.9, 88.4, 114.40 (d, $J_{C–F}$ = 2.9 Hz), 114.40 (d, $J_{C–F}$ = 59.4 Hz), 121.4, 122.0, 128.5, 129.0, 131.9, 134.0, (d, $J_{C–F}$ = 2.9 Hz), 136.5, 155.1 (d, $J_{C–F}$ = 343 Hz), 159.3 (d, $J_{C–F}$ = 3.8 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.44.

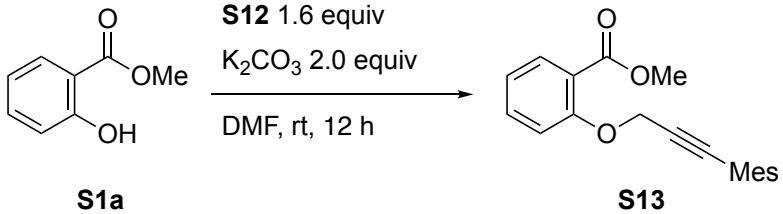
IR (KBr): 3078 (w), 1816 (s), 1799 (s), 1599 (s), 1580 (s), 1490 (s), 1448 (s), 1377 (s), 1299 (s), 1251 (s), 1224 (s), 1167 (m), 1119 (m), 1015 (s), 982 (s), 838 (m), 759 (s), 641 (m).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{12}O_2F$: 255.0816 Found: 255.0815.

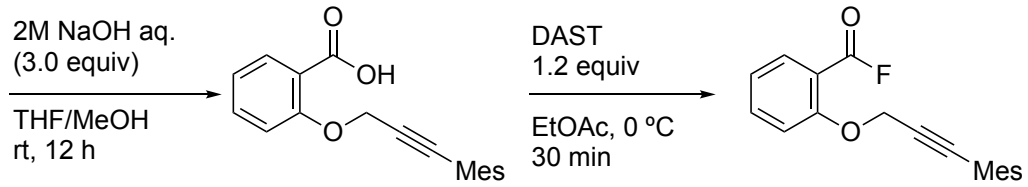
Synthesis of 2-((3-mesitylprop-2-yn-1-yl)oxy)benzoyl fluoride (3b).



S11 **S12**



S1a **S13**



S14 **3b**

Synthesis of S12. In a round-bottom flask, **S11** (1.39 g, 8.0 mmol) and Et_3N (1.7 mL, 12 mmol) were dissolved in Et_2O (30 mL). MsCl (1.0 mL, 12 mmol) was then added slowly at 0 ºC, and the resulting mixture was stirred at rt for 12 h. After **S11** was consumed completely, water (30 mL) was added and the mixture was extracted with Et_2O (30 mL × 3). The combined organic extracts were dried using Na_2SO_4. After filtration and evaporation, crude **S12** was obtained, which was used for the next step without further purification.

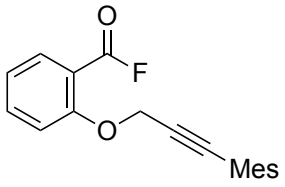
Synthesis of S13. In a round-bottom flask, methyl salicylate (**S1a**, 1.52 g, 5.0 mmol) and K_2CO_3 (1.38 g, 10 mmol) were dissolved in DMF (15 mL), and crude **S12** (ca. 8.0 mmol) was then added, and the resulting mixture was stirred at rt for 12 h. After **S1a** was consumed completely (checked by TLC), Et_2O (50 mL) and water (50 mL) were added to the reaction mixture. The organic layer was separated and washed with brine (30 mL). The organic layer was dried using Na_2SO_4. After filtration, the solvent was removed in vacuo to give crude **S13**, which was used for next step without further purification.

Synthesis of S14. In a round-bottom flask, crude **S13** (ca. 5.0 mmol) was dissolved in THF/MeOH (1/1, 20 mL), and an aqueous solution of NaOH (2 M, 7.5 mL) was then added to the reaction mixture. After stirring for 12 h, the reaction mixture was washed with Et_2O (50 mL × 3) and the separated aqueous layer was acidified using 4 M HCl aq. The aqueous layer was extracted with Et_2O (30 mL × 3) and washed with brine. The combined organic extracts were dried using Na_2SO_4. After filtration and evaporation, crude **S14** was obtained, which was used for the next step without further purification.

Synthesis of 3a. Crude **S14** (ca. 5.0 mmol) and dehydrated EtOAc (15 mL) were added to a round-bottom flask under N_2 atmosphere. DAST (6.0 mmol, 0.79 mL, 1.2 equiv) was slowly added 0 ºC and the resulting mixture was stirred at 0 ºC for 30 min. A saturated aqueous solution of $NaHCO_3$ (30 mL) was then added and organic layer was separated and dried using Na_2SO_4. After filtration, volatiles were removed in vacuo and the residue was purified by flash column chromatography (hexane to hexane:Et_2O = 4:1) to give desired acyl fluoride **3b** as a colorless solid (174 mg,

11%).

2-((3-Mesitylprop-2-yn-1-yl)oxy)benzoyl fluoride (3b).



Colorless solid (174 mg, 11%). R_f 0.60 (SiO_2, Hexane/Et_2O = 7/3). M.p. 89.4–90.1 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.26 (s, 3H), 2.30 (s, 6H), 5.18 (s, 2H), 6.83 (s, 2H), 7.0 (t, J = 7.8 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.61–7.66 (m, 1H), 7.96 (dd, J = 8.0, 1.8 Hz, 1H).

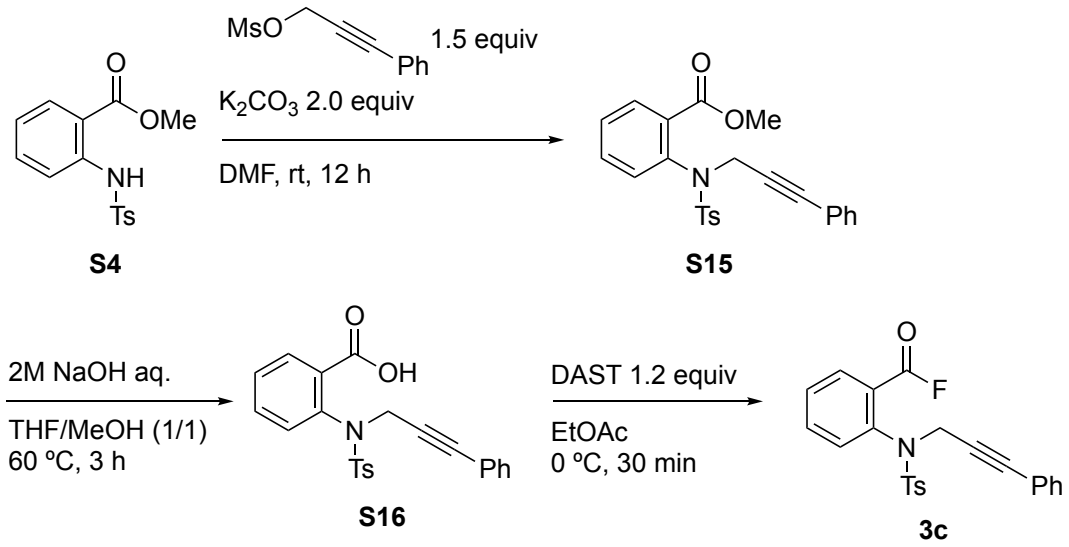
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.0, 21.4, 57.7, 86.4, 90.2, 114.3 (d, $J_{C–F}$ = 58.5 Hz), 114.6 (d, $J_{C–F}$ = 2.9 Hz), 118.8, 121.2, 127.7, 133.9 (d, $J_{C–F}$ =1.9 Hz), 136.3, 138.5, 140.7, 155.1 (d, $J_{C–F}$ = 342 Hz), 159.7 (d, $J_{C–F}$ = 3.8Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.32.

IR (KBr): 2973 (w), 2920 (w), 1819 (s), 1789 (m), 1603 (m), 1579 (w), 1489 (w), 1456 (w), 1372 (w), 1293 (m), 1239 (w), 1221 (w), 986 (w), 848 (w), 750 (m), 688 (w), 640 (w).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{19}H_{18}O_2F$: 297.1285. Found: 297.1283.

Synthesis of 2-((4-methyl-*N*-(3-phenylprop-2-yn-1-yl)phenyl)sulfonamido)benzoyl fluoride (3c).



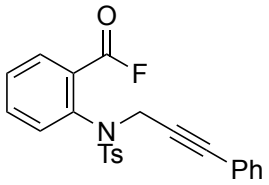
Synthesis of S15. In a round-bottom flask, **S4**[25] (2.33 g, 7.6 mmol) and K_2CO_3 (2.10 g, 15.2 mmol) were dissolved in DMF (30 mL). 3-Phenylprop-2-yn-1-yl methanesulfonate (2.40 g, 11.4 mmol) was then added and the resulting mixture was stirred at rt for 12 h. After **S4** was completely consumed (checked by TLC), Et_2O (50 mL) and water (50 mL) were added to the reaction mixture. The organic layer was separated and washed with water (30 mL). The organic layer was dried using Na_2SO_4. After filtration, the solvent was removed in vacuo, crude **S15** was obtained, which was used for next step without further purification.

Synthesis of S16. In a round-bottom flask, crude **S15** (ca. 7.6 mmol) was dissolved in THF/MeOH (1/1, 20 mL). An aqueous solution of NaOH (2 M, 11.4 mL) was added to the reaction mixture. After stirring at 60 ºC for 3 h, the

reaction mixture was washed with Et_2O (50 mL × 3) and the separated aqueous layer was acidified using 4 M HCl aq. The aqueous layer was extracted with Et_2O (30 mL × 3) and washed with brine. The combined organic extracts were dried using Na_2SO_4. After filtration and evaporation, crude carboxylic acid **S16** was obtained, which was used for the next step without further purification.

Synthesis of 3c. Crude carboxylic acid **S16** (ca. 7.6 mmol) and dehydrated EtOAc (20 mL) were added to a round-bottom flask under N_2 atmosphere. DAST (1.1 mL, 9.1 mmol) was slowly added at 0 ºC to the reaction mixture, and the resulting mixture was stirred at 0 ºC for 30 min. A saturated aqueous solution of $NaHCO_3$ (30 mL) was added and organic layer was separated. The organic extract was dried using Na_2SO_4. After filtration, volatiles were removed in vacuo and the residue was purified by flash column chromatography (hexane:Et_2O = 7:3 to 1:1) then recrystallized from $CHCl_3$/hexane to give desired acyl fluoride **3c** as a colorless solid (975 mg, 32%).

2-((4-Methyl-*N*-(3-phenylprop-2-yn-1-yl)phenyl)sulfonamido)benzoyl fluoride (3c).



Colorless solid (975 mg, 32%). R_f 0.24 (SiO_2, Hexane/EtOAc = 4/1). Recrystallized from $CHCl_3$/Hexane. M.p. 91.2–92.3 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.40 (s, 3H), 4.76 (brs, 2H), 7.18–7.31 (m, 7H), 7.34 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.60 (td, J = 7.8, 1.8 Hz, 1H), 7.64 (d, J = 8.7 Hz, 2H), 8.02 (dd, J = 7.6, 1.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.7, 41.9, 83.4, 86.1, 122.3, 126.9 (d, $J_{C–F}$ = 58.5 Hz), 128.1, 128.4, 128.7, 129.3, 129.6, 131.6, 131.9 (d, $J_{C–F}$ = 2.9 Hz), 133.0, 134.8, 136.5, 140.1 (d, $J_{C–F}$ = 2.9 Hz), 144.1 (d, $J_{C–F}$ = 56.6 Hz), 155.2 (d, $J_{C–F}$ = 347 Hz).

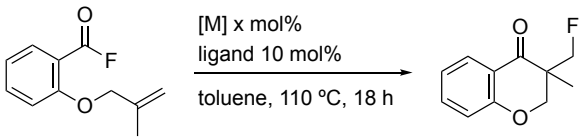
^{19}F NMR ($CDCl_3$, 376 MHz) δ: 29.38.

IR (KBr): 3065 (w), 1821 (s), 1594 (s), 1488 (s), 1451 (m), 1442 (w), 1355 (s), 1311 (w), 1240 (m), 1163 (s), 1080 (m), 1016 (s), 958 (w), 863 (s), 815 (m), 781 (m), 703 (m), 661 (s).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{23}H_{19}NO_3F$: 408.1064. Found: 408.1063.

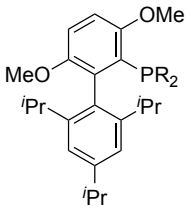
IV. Optimization Studies

IV-I. Catalyst screening on the reaction of 1a

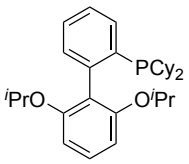


1a **S17**

entry	[M] (x)	ligand	yield of **S17** (%)
1	$Pd_2(dba)_3$ (5.0)	BrettPhos	0
2	$Pd_2(dba)_3$ (5.0)	^{t}BuBrettPhos	0
3	$Pd_2(dba)_3$ (5.0)	RuPhos	0
4	$Pd_2(dba)_3$ (5.0)	PCy_3	0
5	$Pd_2(dba)_3$ (5.0)	PAd_3	0
6	$Ni(cod)_2$ (10)	PCy_3 (20 mol%)	0
7	$Ni(cod)_2$ (10)	dppbz	0



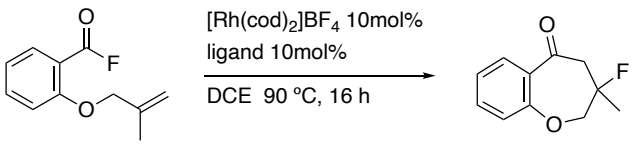
R = Cy: BrettPhos
= ^{t}Bu: ^{t}BuBrettPhos



RuPhos

In a glove box filled with nitrogen, $Pd_2(dba)_3$ (9.2 mg, 0.010 mmol, 10 mol% [Pd]), ligand (10 mol%), and toluene (0.50 mL). After stirring for 5 min, **1a** (38.8 mg, 0.20 mmol) and toluene (0.50 mL) were added to the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 110 ºC for 18 h. After cooling to room temperature, the reaction mixture was added pentadecane as an internal standard. The mixture was analyzed by GC-MS analysis. None of these Pd(0)/L systems were active for the reaction of **1a**.

IV-II. Ligand screening for the reaction of 1a using a $[Rh(cod)_2]BF_4$ catalyst



1a **2a**
NMR yield

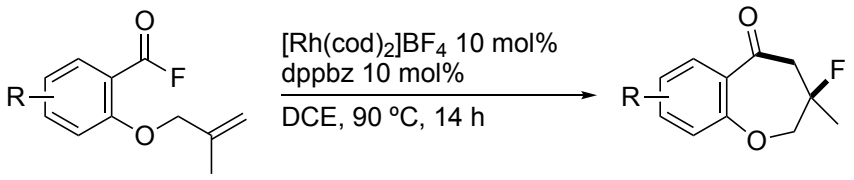
entry	ligand	**1a** (%)	**2a** (%)
1	BINAP	n.d.	6
2	dcype	92	n.d.
3	dppe	n.d.	57
4	(*S*)-SEGPHOS	21	59
5	dcypb	n.d.	n.d.
6	H_8-BINAP	>99	n.d.
7	(*R*)-DTBM-SEGPHOS	>99	n.d.
8	Xantphos	n.d.	n.d.
9	BIPHEP	n.d.	19
10	dppbz	n.d.	72
11	dppnaph	55	54
12	PhDavePhos	>99	n.d.
13	dtbbpy	>99	trace
14	phen	>99	n.d.

*All the yields were determined by ^{19}F NMR analysis using $PhCF_3$ as an internal standard.

In a glove box filled with nitrogen, $[Rh(cod)_2]BF_4$ (8.1 mg, 0.020 mmol, 10 mol%) and ligand (10 mol%) were added

to a screw-capped vial and dissolved in DCE (0.50 mL). After stirring for 5 minutes, acyl fluoride **1a** (0.20 mmol) and DCE (0.50 mL) were added to the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 90 °C for 14 h. After cooling to room temperature, $PhCF_3$ was added into the reaction mixture as an internal standard and the reaction was analyzed using ^{19}F NMR. Among the ligands examined, dppbz was found to be the most effective ligand.

V. General Procedure for Rhodium-Catalyzed Intramolecular Carbofluorination of Alkenes

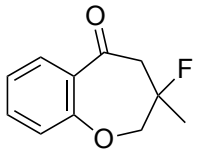


1 **2**

In a glove box filled with nitrogen, $[Rh(cod)_2]BF_4$ (8.1 mg, 0.020 mmol, 10 mol%) and dppbz (8.9 mg, 0.020 mmol, 10 mol%) were added to a screw-capped vial and dissolved in DCE (0.50 mL). After stirring for 5 minutes, acyl fluoride **1** (0.20 mmol) and DCE (0.50 mL) were added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 90 ºC for 14 h. After cooling to room temperature, all volatiles were removed in vacuo and the residue was purified by flash column chromatography to give desired compounds **2**.

Spectroscopic Data of Products

3-Fluoro-3-methyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2a).



Colorless oil (27.2 mg, 70%). R_f 0.36 (SiO_2, Hexane/Et_2O = 4/1).

^1H NMR ($CDCl_3$, 400 MHz) δ: 1.50 (d, *J* = 1.50 Hz, 3H), 3.08 (dd, *J* = 11.4, 8.2 Hz, 1H), 3.55 (dd, *J* = 18.3, 11.5 Hz, 1H), 3.88 (dd, *J* = 29.5, 13.7 Hz, 1H), 4.50 (dd, *J* = 16.9, 13.7 Hz, 1H), 7.12-7.15 (m, 2H), 7.44-7.48 (m, 1H), 7.81 (dd, *J* = 8.0, 1.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.9 (d, $J_{C–F}$ = 24.9 Hz), 53.8 (d, $J_{C–F}$ = 24.0 Hz), 81.1 (d, $J_{C–F}$ = 26.8 Hz), 96.9 (d, $J_{C–F}$ = 179 Hz), 120.7, 123.3, 127.5, 129.8, 134.4, 163.3, 194.8 (d, $J_{C–F}$ = 12.5 Hz).

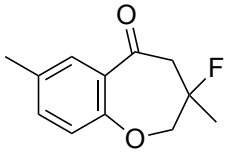
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -140.68.

IR (KBr): 2981 w, 2934 w, 1685 s, 1603 m, 1474 m, 1457 s, 1322 m, 1298 m, 1042 m, 880 m, 768 w, 604 w, 458 w, 419 w.

MS, *m/z* (relative intensity, %): 194 (47), 164 (21), 149 (19), 121 (16), 120 (50), 117 (14), 105 (32), 104 (11), 92 (38), 77 (18), 76 (23), 64 (15), 63 (16), 55 (100), 51 (11), 50 (16).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{11}H_{12}O_2F$: 195.0816. Found: 195.0810.

3-Fluoro-3,7-dimethyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2b).



Colorless oil (30.4 mg, 73%). R_f 0.40 (SiO_2, Hexane/Et_2O = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.48 (d, *J* = 21.1 Hz, 3H), 2.32 (s, 3H), 3.07 (ddd, *J* = 11.7, 8.9, 0.92 Hz, 1H), 3.52 (dd, *J* = 17.9, 11.5 Hz, 1H), 3.84 (dd, *J* = 29.5, 13.5 Hz, 1H), 4.46 (ddd, *J* = 17.3, 13.6, 0.92 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 7.26 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 20.6, 22.9 (d, $J_{C–F}$ = 24.9 Hz), 53.7 (d, $J_{C–F}$ = 24.0 Hz), 81.1 (d, $J_{C–F}$ = 26.8 Hz), 96.9 (d, $J_{C–F}$ = 179 Hz), 120.5, 127,1, 129.5, 132.9, 135.2, 161.3, 194.9 (d, $J_{C–F}$ = 12.5 Hz).

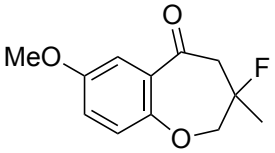
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -140.78.

IR (KBr): 2982 w, 2931 w, 1683 s, 1613 s, 1558 w, 1490 s, 1457 m, 1407 m, 1385 m, 1309 m, 1284 m, 1251 w, 1210 m, 1142 m, 1089 m, 1036 m, 997 w, 904 m, 868 s, 816 s, 770 m, 602 s, 530 s, 464 s, 424 m.

MS, *m/z* (relative intensity, %): 209 (14), 208 (M^+, 100), 178 (20), 163 (32), 157 (11), 135 (21), 134 (63), 131 (25), 119 (32), 91 (30), 90 (15), 89 (19), 78 (21), 77 (22), 55 (62), 51 (15).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{14}O_2F$: 209.0972. Found: 209.0966.

3-Fluoro-7-methoxy-3-methyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2c).



Colorless oil (44.4 mg, 99%). R_f 0.36 (SiO_2, Hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.48 (d, *J* = 20.6 Hz, 3H), 3.07-3.13 (m, 1H), 3.53 (dd, *J* = 17.2, 11.7 Hz, 1H), 3.81 (s, 3H), 3.84 (dd, *J* = 29.5, 13.5 Hz, 1H), 4.46 (ddd, *J* = 17.8, 13.3, 0.92 Hz, 1H), 7.01-7.07 (m, 2H), 7.27 (d, *J* = 3.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 23.0 (d, $J_{C–F}$ = 25.9 Hz), 53.6 (d, $J_{C–F}$ = 24.9 Hz), 55.9, 81.4 (d, $J_{C–F}$ = 26.8 Hz), 97.0 (d, $J_{C–F}$ = 178 Hz), 111.1, 122.1, 122.4, 127.7, 155.4, 157.7, 194.6 (d, $J_{C–F}$ = 12.5 Hz).

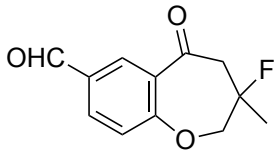
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -140.19.

IR (KBr): 2996 m, 2963 m, 1682 s, 1608 s, 1491 s, 1456 m, 1418 s, 1339 m, 1281 s, 1199 s, 1085 m, 993 w, 897 m, 827 s, 731 w, 667 w, 603 m, 531 m, 429 w.

MS, *m/z* (relative intensity, %): 225 (14), 224 (M^+, 100), 195 (12), 161 (10), 151 (19), 150 (38), 135 (33), 122 (14), 107 (34), 79 (23), 63 (15), 55 (20), 53 (12), 51 (11).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{14}O_3F$: 225.0922. Found: 225.0917.

3-Fluoro-3-methyl-5-oxo-2,3,4,5-tetrahydrobenzo[b]oxepine-7-carbaldehyde (2d).



Colorless oil (14.2 mg, 32%). R_f 0.44 (SiO_2, Hexane/EtOAc = 3/2).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.54 (d, *J* = 21.1 Hz, 3H), 3.13 (ddd, *J* = 11.5, 7.8, 0.92 Hz, 1H), 3.54 (dd, *J* = 18.8, 11.9 Hz, 1H), 3.96 (dd, *J* = 28.9, 13.7 Hz, 1H), 4.53-4.61 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 8.02 (dd, *J* = 8.5, 2.1 Hz, 1H), 8.30 (d, *J* = 1.8 Hz, 1H), 9.97 (s, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.8 (d, $J_{C–F}$ = 24.9 Hz), 53.6 (d, $J_{C–F}$ = 24.0 Hz), 81.0 (d, $J_{C–F}$ = 26.8 Hz), 96.4 (d, $J_{C–F}$ = 180 Hz), 121.9, 127.5, 131.9, 133.4, 133.9, 167.4, 190.2, 193.6 (d, $J_{C–F}$ = 12.5 Hz).

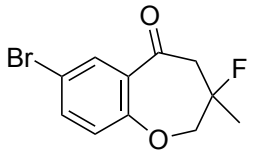
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -141.08.

IR (KBr): 2937 w, 2859 w, 1699 s, 1684 s, 1570 m, 1488 m, 1423 m, 1374 w, 1329 w, 1215 m, 1182 m, 1145 w, 1084 w, 943 w. 867 m, 814 m, 758 w, 584 w, 420 w.

MS, *m/z* (relative intensity, %): 222 ([M]$^+$, 60), 192 (18), 161 (16), 149 (11), 148 (22), 147 (18), 133 (16), 120 (11), 119 (23), 105 (11), 103 (16), 77 (11), 75 (14), 63 (15), 55 (100).

HRMS (DART+, [M+H]$^+$) Calcd for $C_{12}H_{12}O_3F$: 223.0765. Found: 223.0754.

7-Bromo-3-fluoro-3-methyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2e).



Colorless oil (33.9 mg, 62%). R_f 0.44 (SiO_2, Hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.49 (d, *J* = 20.6 Hz, 3H), 3.08 (ddd, *J* = 11.5, 8.7, 0.92 Hz, 1H), 3.51 (dd, *J* = 17.9, 11.5 Hz, 1H), 3.86 (dd, *J* = 29.3, 13.7 Hz, 1H), 4.49 (ddd, *J* = 16.9, 13.7, 0.92 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 7.54 (dd, *J* = 10.1, 2.8 Hz, 1H), 7.91 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.9 (d, $J_{C–F}$ = 24.9 Hz), 53.5 (d, $J_{C–F}$ = 24.9 Hz), 81.2 (d, $J_{C–F}$ = 26.8 Hz), 96.6 (d, $J_{C–F}$ = 179Hz), 116.1, 122.7, 128.9, 132.2, 137.0, 162.2, 193.4 (d, $J_{C–F}$ = 12.5 Hz).

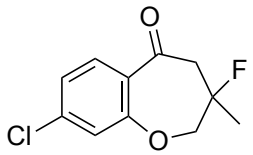
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -140.96.

IR (KBr): 2983 m, 2941 w, 1684 s, 1592 s, 1473 s, 1402 m, 1385 m, 1303 m, 1270 m, 1150 m, 1091 m, 1030 s, 953 w, 900 s, 880 s, 835 s, 812 m, 731 w, 637 s, 587 s, 524 m, 460 s, 421 m.

MS, *m/z* (relative intensity, %): 274 ([M$^+$+2], 55), 272 ([M]$^+$, 56), 244 (15), 242 (14), 200 (21), 198 (22), 172 (13), 170 (14), 145 (12), 115 (13), 77 (14), 75 (31), 63 (37), 59 (10), 55 (100), 53 (11).

HRMS (DART+, [M+H]$^+$) Calcd for $C_{11}H_{11}O_2F^{79}Br$: 272.9921. Found: 272.9916.

8-Chloro-3-fluoro-3-methyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2f).



Colorless solid (42.5 mg, 93%). R_f 0.42 (SiO_2, Hexane/Et_2O = 4/1). M.p. 92.4-92.9 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.49 (d, *J* = 20.6 Hz, 3H), 3.08 (ddd, *J* = 11.5, 8.7, 0.92 Hz, 1H), 3.50 (dd, *J* = 18.1, 11.7 Hz, 1H), 3.88 (dd, *J* = 29.1, 13.5 Hz, 1H), 4.49 (ddd, *J* = 17.2, 14.0, 0.92 Hz, 1H), 7.12 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.9 (d, $J_{C–F}$ = 24.9 Hz), 53.6 (d, $J_{C–F}$ = 24.0 Hz), 81.2 (d, $J_{C–F}$ = 26.9 Hz), 96.5 (d, $J_{C–F}$ = 179 Hz), 121.0, 124.0, 126.1, 130.9, 140.1, 163.6, 193.6 (d, $J_{C–F}$ = 12.5 Hz).

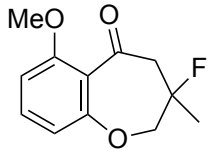
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -140.93.

IR (KBr): 2985 m, 1683 s, 1594 s, 1559 s, 1459 s, 1435 m, 1382 s, 1323 s, 1293 s, 1248 m, 1201 s, 1146 m, 1097 m, 1078 s, 1037 s, 993 m, 914 m, 887 s, 862 s, 832 s, 807 s, 743 m, 654 m, 602 m, 563 m, 528 s, 471 s, 414 m.

MS, *m/z* (relative intensity, %): 230 (M^++2, 15), 228 (M^+, 45), 198 (18), 183 (14), 163 (13), 155 (10), 154 (21), 139 (22), 126 (28), 110 (17), 75 (22), 55 (100).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{11}H_{11}O_2F^{35}Cl$: 229.0426: XX. Found: 229.0415.

3-Fluoro-6-methoxy-3-methyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2g).



Colorless oil (37.6 mg, 84%). R_f 0.20 (SiO_2, Hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.49 (d, *J* = 21.1 Hz, 3H), 2.95 (dd, *J* = 10.8, 6.6 Hz, 1H), 3.52 (dd, *J* = 19.0, 10.8 Hz, 1H), 3.858 (dd, *J* = 30.2, 13.7 Hz, 1H), 3.859 (s, 3H), 4.42 (t, *J* = 14.2 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.7 (d, $J_{C–F}$ = 23.4 Hz), 54.8 (d, $J_{C–F}$ = 24.0 Hz), 56.4, 79.6 (d, $J_{C–F}$ = 25.9 Hz), 97.0 (d, $J_{C–F}$ = 181 Hz), 106.0, 112.6, 117.9, 133.4, 159.2, 163.3, 194.3 (d, $J_{C–F}$ = 12.5 Hz).

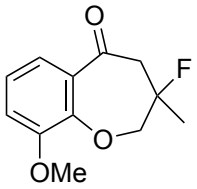
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -143.82.

IR (KBr): 2989 w, 2971 w, 1685 s, 1599 s, 1575 m, 1474 s, 1436 m, 1384 m, 1327 m, 1296 m, 1266 s, 1211 m, 1157 w, 1109 m, 1093 s, 1046 m, 993 w, 882 m, 820 m, 797 m, 734 m, 586 m, 547 w, 440 w.

MS, *m/z* (relative intensity, %): 225 (14), 224 ($[M]^+$, 100), 179 (19), 159 (18), 151 (15), 150 (12), 149 (14), 135 (26), 122 (72), 121 (36), 120 (26), 107 (43), 92 (18), 79 (15), 77 (17), 76 (22), 65 (19), 63 (13), 55 (49), 53 (15), 51 (27), 50 (10).

HRMS (DART+, $[M+H]^+$) $C_{12}H_{14}O_3F$: 225.0922. Found: 225.0916.

3-Fluoro-9-methoxy-3-methyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2h).



Colorless solid (36.3 mg, 81%). R_f 0.30 (SiO_2, Hexane/Et_2O = 3/2). M.p. 76.7-77.4 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.51 (d, *J* = 20.6 Hz, 3H), 3.10 (t, *J* = 11.2 Hz, 1H), 3.52 (dd, *J* = 17.4, 11.5 Hz, 1H), 3.92 (s, 3H), 3.95 (dd, *J* = 30.7, 13.5 Hz, 1H), 4.56 (dd, *J* = 16.5, 13.7 Hz, 1H), 7.06 (s, 1H), 7.07 (d, *J* = 1.4 Hz, 1H), 7.36-7.41 (m, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 23.0 (d, $J_{C–F}$ = 24.9 Hz), 53.8 (d, $J_{C–F}$ = 24.0 Hz), 56.5, 81.7 (d, $J_{C–F}$ = 27.8 Hz), 96.8 (d, $J_{C–F}$ = 179 Hz), 116.0, 120.7, 123.1, 128.5, 150.7, 153.0, 194.9 (d, $J_{C–F}$ = 11.5 Hz).

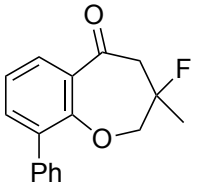
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -141.67.

IR (KBr): 2985 m, 2958 m, 1697 s, 1578 s, 1483 s, 1438 s, 1336 m, 1283 m, 1227 m, 1146 m, 1085 m, 1043 s, 1027 s, 1001 s, 884 s, 818 m, 737 s, 642 w, 548 m, 434 m, 412 m.

MS, *m/z* (relative intensity, %): 225 (14), 224 ([M]$^+$, 100), 178 (19), 159 (18), 151 (15), 150 (12), 149 (14), 135 (26), 122 (72), 120 (26), 107 (43), 92 (18), 79 (15), 77 (17), 76 (22), 65 (19), 63 (13), 55 (49), 53 (15), 51 (27), 50 (10).

HRMS (DART+, [M+H]$^+$) Calcd for $C_{12}H_{14}O_3F$: 225.0922. Found: 225.0915.

3-Fluoro-3-methyl-9-phenyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2i).



Colorless oil (49.2 mg, 91%). R_f 0.34 (SiO_2, Hexane/Et_2O = 4/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.48 (d, *J* = 21.1 Hz, 3H), 3.11 (ddd, *J* = 11.0, 8.9, 0.92 Hz, 1H), 3.60 (dd, *J* = 17.9, 11.5 Hz, 1H), 3.86 (dd, *J* = 29.1, 13.5 Hz, 1H), 4.45 (ddd, *J* = 17.4, 13.7, 0.92 Hz, 1H), 7.20 (t, *J*= 7.8 Hz, 1H), 7.36-7.40 (m, 1H), 7,42-7.46 (m, 2H), 7.49- 7.54 (m, 3H), 7.84 (dd, *J* = 7.8, 1.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.8 (d, $J_{C–F}$ = 24.9 Hz), 53.7 (d, $J_{C–F}$ = 24.9 Hz), 81.4 (d, $J_{C–F}$ = 26.8 Hz), 96.8 (d, $J_{C–F}$ = 179 Hz), 123.3, 127.7, 128.3 (two peaks are overlapped), 129.3, 129.7, 134.0, 135.6, 137.2, 160.3, 195.0 (d, $J_{C–F}$ = 12.5 Hz).

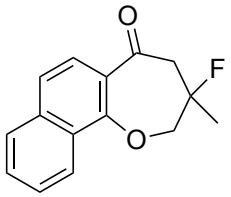
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -140.87.

IR (KBr): 2992 m, 2980 m, 1675 s, 1588 m, 1498 m, 1459 s, 1421 s, 1383 s, 1312 s, 1227 m, 1205 s, 1148 m, 1091 m 1032 s, 996 m, 914 m, 886 s, 797 m, 766 s, 726 m, 703 s, 616 s, 566 s, 470 m, 442 m, 419 w.

MS, *m/z* (relative intensity, %): 271 (20), 270 (M$^+$, 100), 205 (24), 196 (11), 195 (13), 181 (12), 168 (31), 152 (16), 139 (33), 55 (25).

HRMS (DART+, [M+H]$^+$) Calcd for $C_{17}H_{16}O_2F$: 271.1129. Found: 271.1125.

3-Fluoro-3-methyl-3,4-dihydronaphtho[1,2-b]oxepin-5(2H)-one (2j).



Colorless solid (38.6 mg, 79%). R_f 0.44 (SiO_2, Hexane/Et_2O = 7/3). M.p. 78.7-79.3 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.56 (d, *J* = 20.6 Hz, 3H), 3.17 (ddd, *J* = 11.0, 7.8, 0.92 Hz, 1H), 3.67 (dd, *J* = 18.8, 11.5 Hz, 1H), 4.05 (dd, *J* = 30.0 Hz, 13.5 Hz, 1H), 4.74 (ddd, *J* = 17.2, 13.5, 0.92 Hz, 1H), 7.52-7.64 (m, 3H), 7.81 (d, *J* = 8.7 Hz, 2H), 8.40 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.9 (d, $J_{C–F}$ = 24.9 Hz), 54.3 (d, $J_{C–F}$ = 24.0 Hz), 82.5 (d, $J_{C–F}$ = 26.8 Hz), 97.5 (d, $J_{C–F}$ = 179 Hz), 121.9, 122.9, 123.7, 124.4, 126.7 (two peaks are overlapped), 127.7, 129.4, 136.7, 162.0, 194.9 (d, $J_{C–F}$ = 13.4 Hz).

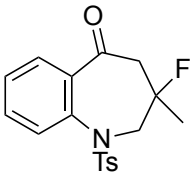
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -140.34.

IR (KBr): 3076 w, 2981 w., 1670 s, 1624 s, 1598 m, 1571 s, 1505 m, 1405 m, 1370 s, 1346 s, 1284 m, 1226 m, 1145 m, 1094 s, 1020 m, 957 w, 875 s, 826 s, 805 s, 751 s, 684 s, 630 m, 572 m, 510 m, 466 m, 428 s.

MS, *m/z* (relative intensity, %): 245 (17), 244 (M^+, 100), 199 (19), 171 (16), 167 (18), 155 (19), 142 (10), 128 (11), 127 (26), 126 (24), 115 (22), 114 (80), 113 (16), 88 (11), 63 (11), 55 (27).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{14}O_2F$: 245.0972. Found: 245.0964.

3-Fluoro-3-methyl-1-tosyl-1,2,3,4-tetrahydro-5H-benzo[b]azepin-5-one (2k).



Colorless oil (48.0 mg, 69%). R_f 0.64 (SiO_2, Hexane/EtOAc = 1/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.48 (d, *J* = 21.5 Hz, 3H), 2.43 (s, 3H), 2.88-3.00 (m, 2H), 4.01 (dd, *J* = 27.3, 15.8 Hz, 1H), 4.20 (dd, *J* = 19.0, 15.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.35-7.39 (m, 1H), 7.49-7.57 (m, 2H), 7.63-7.66 (m, 2H), 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.7, 25.3 (d, $J_{C–F}$ = 24.0 Hz), 52.4 (d, $J_{C–F}$ = 24.0 Hz), 60.2 (d, $J_{C–F}$ = 27.8 Hz), 96.5 (d, $J_{C–F}$ = 175 Hz), 127.3, 127.7, 128.0, 130.0, 130.2, 133.7, 134.5, 137.5, 140.7, 144.4, 195.0 (d, $J_{C–F}$ = 8.6 Hz).

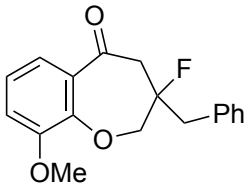
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -138.16.

IR (KBr): 2982 w, 1683 s, 1597 m, 1541 w, 1456 m, 1350 m, 1291 w, 1164 s, 1085 m, 938 w, 905 w, 814 w, 757 m, 662 m, 573 m, 544 w, 521 w.

MS, *m/z* (relative intensity, %): 347 (M^+, 17), 283 (29), 155 (11), 132 (100), 91 (43), 77 (41), 65 (12).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{18}H_{19}O_3NFS$: 348.1064. Found: 348.1055.

3-Benzyl-3-fluoro-9-methoxy-3,4-dihydrobenzo[b]oxepin-5(2H)-one (2l).



Colorless oil (50.9 mg, 84%). R_f 0.28 (SiO_2, Hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.03-3.17 (m, 3H), 3.32 (dd, *J* = 16.9, 11.9 Hz, 1H), 3.92 (s, 3H), 4.09 (dd, *J*= 25.9, 13.5 Hz, 1H), 4.41 (dd, *J* = 16.3, 13.5 Hz, 1H), 7.04-7.09 (m, 2H), 7.26-7.34 (m, 5H), 7.40 (dd, *J* = 6.4, 3.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 42.4 (d, J_{C-F} = 22.0 Hz), 51.4 (d, J_{C-F} = 23.4Hz), 56.5, 81.1 (d, J_{C-F} = 27.8 Hz), 98.1 (d, J_{C-F} = 185.0 Hz), 116.1, 120.4, 123.2, 127.4, 128.5, 128.8, 130.7, 134.1, 150.8, 153.0, 195.0 (d, J_{C-F} = 10.5 Hz).

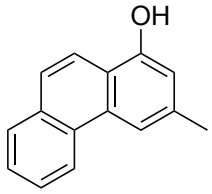
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -149.96.

IR (KBr): 2936 w, 1683 s, 1579 s, 1480 s, 1456 m, 1265 s, 1211 m, 1186 m, 1084 m, 1037 s, 964 w, 901 w, 784 w, 761 m, 702 m, 552 w.

MS, *m/z* (relative intensity, %): 301 (21), 300 (M^+, 100), 151 (79), 150 (18), 135 (13), 129 (10), 122 (60), 121 (23), 120 (14), 115 (11), 107 (15), 92 (17), 91 (78), 65 (20), 51 (11).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{18}H_{18}O_3F$: 301.1235. Found: 301.1235.

3-Methylphenanthren-1-ol (1m').



Off-white solid (33.7 mg, 81%). R_f 0.14 (SiO_2, Hexane/Et_2O = 4/1). M.p. 135.4-136.2 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.53 (s, 3H), 5.21 (s, 1H), 6.78 (s, 1H), 7.55–7.64 (m, 2H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.06 (s, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 8.63 (d, *J* = 7.8 Hz, 1H).

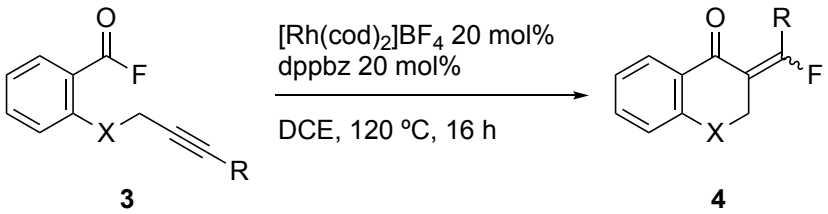
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.3, 112.4, 115.5, 119.9, 120.0, 123.2, 125.4, 126.5, 126.7, 128.7, 129.9, 132.0, 132.5, 136.8, 151.8.

IR (KBr): 3292 brw, 1625 m, 1604 m, 1573 w, 1457 m, 1434 m, 1362 m, 1293 m, 1265 m, 1222 w, 1149 w, 1130 m, 1081 w, 1039 w, 983 m, 944 m, 881 m, 865 m, 844 s, 817 s, 754 s, 701 m, 643 m, 588 m, 452 m, 418 s.

MS, *m/z* (relative intensity, %): 209 ($[M]^+$, 17), 208 (100), 207 (11), 179 (32), 178 (21), 165 (35), 104 (13), 95 (10), 89 (18), 88 (11), 76 (15).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{15}H_{13}O$: 209.0961. Found: 209.0953.

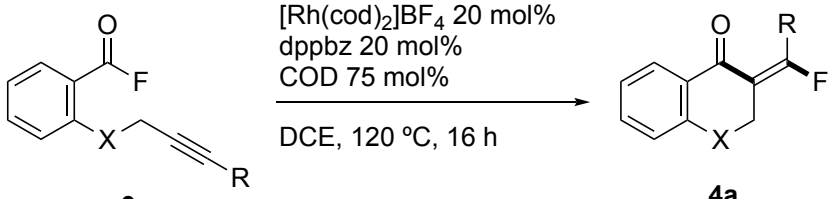
VI. General Procedure for Rhodium-Catalyzed Intramolecular Carbofluorination of Alkynes



3 **4**

In a glove box filled with nitrogen, $[Rh(cod)_2]BF_4$ (16.2 mg, 0.040 mmol, 20 mol%) and dppbz (17.8 mg, 0.040 mmol, 20 mol%) were added to a screw-capped vial and dissolved in DCE (0.50 mL). After stirring for 5 minutes, acyl fluoride **3** (0.20 mmol), COD (16.2 mg, 0.15 mmol, 75 mol%), and DCE (0.50 mL) were added to the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 120 ºC for 16 h. After cooling to room temperature, all volatiles were removed in vacuo and the residue was purified by flash column chromatography to give desired compound **4**.

Effect of COD.



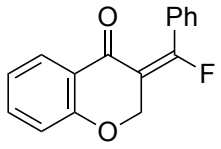
3a

4a
99%
(*E*/*Z* = 5.2/1)

w/o COD: 59%
(*E*/*Z* = 3.3/1)

Spectroscopic Data of Products

(*E*)-3-(Fluoro(phenyl)methylene)chroman-4-one (4a-*E*)



Off-white solid (42.2 mg, 83%), R_f 0.44 (SiO_2, Hexane/Et_2O = 7/3). M.p. 97.4–97.8 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.25 (d, J = 3.2 Hz, 2H), 6.99-7.05 (m, 2H), 7.41-7.51 (m, 4H), 7.67 (d, J = 7.8 Hz, 2H), 7.92 (dd, J = 8.0, 1.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 65.7 (d, $J_{C\text{-}F}$ = 12.3 Hz), 112.1 (d, $J_{C\text{-}F}$ = 18.5 Hz), 117.9, 121.9, 122.6 (d, $J_{C\text{-}F}$ = 4.6 Hz), 127.9, 128.1, 129.6 (d, $J_{C\text{-}F}$ = 4.6 Hz), 130.5 (d, $J_{C\text{-}F}$ = 26.2 Hz), 131.6, 136.0, 161.5, 164.0 (d, $J_{C\text{-}F}$ = 272.3 Hz), 181.7 (d, $J_{C\text{-}F}$ = 12.3 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: -79.82.

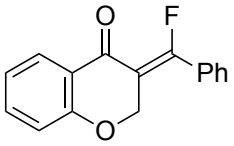
IR (KBr): 2878 (w), 1685 (s), 1645 (m), 1636 (m), 1604 (m), 1492 (m), 1475 (s), 1465 (m), 1457 (m), 1378 (w), 1327 (m), 1279 (m), 1268 (m), 1217 (m), 1185 (w), 1149 (m), 1086 (w), 1033 (w), 1012 (s), 1003 (s), 947 (w), 844 (w), 783 (m), 759 (s), 740 (s), 690 (m), 635 (m).

MS, *m/z* (relative intensity, %): 254 ([M]$^+$, 59), 253 (100), 134 (23), 133 (73), 126 (15), 121 (51), 120 (35), 92 (47),

64 (16), 63 (15).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{12}O_2F$: 255.0816. Found: 255.0821.

(*Z*)-3-(Fluoro(phenyl)methylene)chroman-4-one (4a-*Z*)



A part of the product isomerized to **4a-*E*** during the 1H NMR measurement in $CDCl_3$.

Pale-yellow oil (7.9 mg, 16%). R_f 0.28 (SiO_2, Hexane/Et_2O = 7/3).

^1H NMR ($CDCl_3$, 400 MHz) δ: 5.08 (d, J = 3.2 Hz, 2H), 6.95 (d, J = 8.2 Hz, 1H), 7.06–7.10 (m, 1H), 7.46–7.57 (m, 6H), 8.05 (dd, J = 7.8, 1.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 67.9 (d, $J_{C\text{-}F}$ = 5.8 Hz), 111.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 117.8, 122.1, 122.7, 128.0, 128.9, 129.1 (d, $J_{C\text{-}F}$ = 4.8Hz), 130.1 (d, $J_{C\text{-}F}$ = 25.9 Hz), 131.7, 135.9, 160.7, 162.3 (d, $J_{C\text{-}F}$ = 282.8 Hz), 181.5.

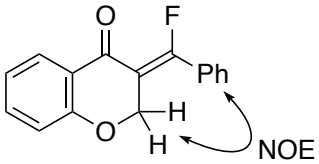
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -83.37.

IR (KBr): 2929 (w), 1689 (s), 1680 (s), 1640 (m), 1630 (m), 1620 (m), 1604 (s), 1477 (s), 1465 (s), 1450 (w), 1326 (m), 1306 (m), 1013 (m), 1000 (m), 759 (m), 697 (m).

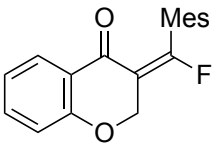
MS, *m/z* (relative intensity, %): 254 ($[M]^+$, 50), 253 (100), 134 (24), 133 (79), 126 (14), 121 (53), 120 (36), 92 (51), 64 (19), 63 (17).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{12}O_2F$: 255.0816. Found: 255.0820.

The stereochemistry of **4a-*Z*** was determine by NOESY spectroscopy.



(*E*)-3-(Fluoro(mesityl)methylene)chroman-4-one (4b)



The reaction was conducted without COD.

Off-white solid (59.3 mg, 100%). R_f 0.72 (SiO_2, Hexane/Et_2O = 7/3). M.p. 83.0–83.7 °C.

^1H NMR ($CDCl_3$, 400 MHz) δ: 2.23 (d, J = 2.3 Hz, 6H), 2.30 (d, J = 2.8 Hz, 3H), 5.30 (d, J = 3.2 Hz, 2H), 6.91 (s, 2H), 6.98–7.02 (m, 2H), 7.44–7.48 (m, 1H), 7.83 (dd, J = 8.1, 1.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 19.6, 21.5, 65.0 (d, $J_{C\text{-}F}$ = 9.2 Hz), 114.5 (d, $J_{C\text{-}F}$ = 18.5 Hz), 118.0, 121.9, 122.4 (d, $J_{C\text{-}F}$ = 4.6 Hz), 127.7, 128.2, 128.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 135.8, 137.1, 140.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 161.4, 164.1 (d, $J_{C\text{-}F}$ = 280 Hz), 181.1 (d, $J_{C\text{-}F}$ = 13.8 Hz).

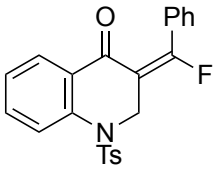
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -75.20.

IR (KBr): 2977 (w), 2947 (w), 2924 (w), 1693 (s), 1635 (s), 1603 (s), 1573 (m), 1473 (s), 1463 (s), 1450 (m), 1378 (w), 1315 (s), 1277 (m), 1227 (m), 1196 (w), 1155 (m), 1146 (s), 1078 (s), 1007 (s), 931 (w), 842 (s), 779 (s), 761 (s), 738 (m), 650 (m), 596 (w).

MS, *m/z* (relative intensity, %): 296 ([M]$^+$, 18), 282 (21), 281 (100), 279 (19). 276 (19), 275 (11), 261 (11), 178 (15), 161 (11), 160 (10), 159 (11), 156 (20), 146 (14), 141 (14), 140 (20), 121 (12).

HRMS (DART+, [M+H]$^+$) Calcd for $C_{19}H_{18}O_2F$: 297.1285. Found: 297.1283.

(*E*)-3-(Fluoro(phenyl)methylene)-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one (4c)



The product was obtained as a mixture of *E*/*Z* isomers (*E*/*Z* = 8/1, determined by ^{1}H NMR).

4c-*E*:

Pale-yellow solid (44.8 mg, 55%). R_f 0.52 (SiO_2, Hexane/Et_2O = 1/1). M.p. 175.8–176.6 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.29 (s, 3H), 4.97 (d, *J* = 2.3 Hz, 2H), 7.09–7.11 (m, 4H), 7.31–7.46 (m, 6H), 7.61–7.66 (m, 1H), 7.88–7.91 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 21.6, 46.2 (d, $J_{C\text{-}F}$ = 10.5 Hz), 110.7 (d, $J_{C\text{-}F}$ = 19.2 Hz), 127.0, 127.2, 127.4, 127.8, 128.1, 128.4 (d, $J_{C\text{-}F}$ = 5.8 Hz), 129.4 (d, $J_{C\text{-}F}$ = 5.8 Hz), 130.0, 130.1 (d, $J_{C\text{-}F}$ = 25.9 Hz), 131.6, 134.5, 135.6, 141.7, 144.5, 164.8 (d, $J_{C\text{-}F}$ = 272 Hz), 182.0 (d, $J_{C\text{-}F}$ = 13.4 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz) δ: -73.87

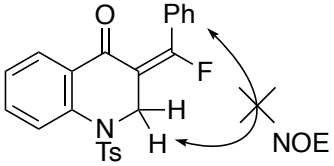
IR (KBr): 3068 (w), 2924 (w), 1683 (s), 1617 (s), 1598 (s), 1493 (w), 1474 (m), 1460 (s), 1361 (s), 1350 (m), 1275 (m), 1184 (m), 1166 (s), 1089 (m), 1068 (m), 1007 (m), 957 (m), 876 (m), 789 (w), 739 (w), 716 (s), 670 (s), 565 (m).

MS, *m/z* (relative intensity, %): 407 ([M]$^+$, 34), 253 (14), 252 (83), 251 (53), 250 (100), 233 (13), .232 (44), 204 (19), 133 (19), 128 (27), 91 (38), 77 (14), 65 (12).

HRMS (DART+, [M+H]$^+$) Calcd for $C_{23}H_{19}NO_3FS$: 408.1064. Found: 408.1075.

The stereochemistry of **4c-*E*** was determined by NOESY spectroscopy.

(The Ph group on an alkene moiety and NTs-CH_2 did not have correlation in a NOESY spectra)



4c-*Z*:

Although most of the resonances were overlapped with those of **4c-*E***, two resonances that are characteristic of **4c-*Z*** were observed in ^{1}H NMR spectra (most of **4c-*Z*** isomerized to **4c-*E*** during analysis). ^{19}F NMR spectra also showed

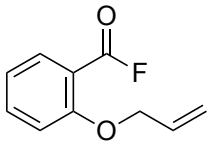
a resonance that is assignable to **4c-*Z***.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.39 (s, 3H), 4.91 (d, J = 2.8 Hz, 2H).

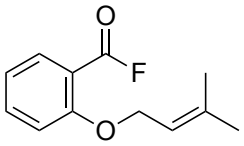
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -82.93.

MS, *m/z* (relative intensity, %): 407 ([M]$^{+}$, 34), 253 (16), 252 (86), 251 (57), 250 (100), 233 (14), 232 (51), 204 (22), 133 (22), 128 (30), 91 (44), 77 (16), 65 (16).

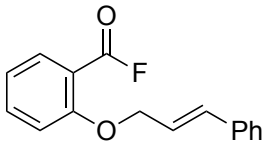
VII. Problematic Substrates



No pdt (<10% conversion)



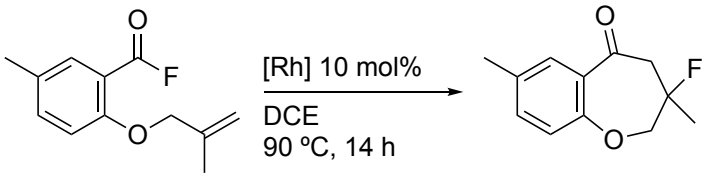
No pdt (>90% conversion)



No pdt (>90% conversion)

VIII. Mechanistic Studies

VIII-I. Intramolecular carbofluorination of 2a using [Rh(dppbz)(cod)]BF_4 and [Rh(dppbz)$_2$]BF_4



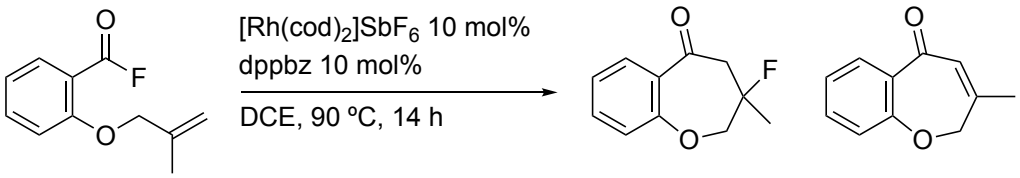
1b **2b**

entry	[Rh]	yield of **2b** (%)
1	[Rh(cod)(dppbz)]BF_4	54
2	[Rh(dppbz)$_2$]BF_4	0

*All the yields were determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

In a glove box filled with nitrogen, rhodium catalyst (14.9 mg for [Rh(dppbz)(cod)]BF_4, 21.7 mg for [Rh(dppbz)$_2$]BF_4,0.020 mmol, 10 mol%) were added to a screw-capped vial and dissolved in DCE (0.50 mL). Acyl fluoride **1b** (41.6 mg, 0.20 mmol) and DCE (0.50 mL) were added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 90 ºC for 14 h. After cooling to room temperature, the reaction mixture was added $PhCF_3$ and diluted with $CDCl_3$. The mixture was analyzed by ^{19}F NMR.

VIII-II. Intramolecular carbofluorination of 1a using [Rh(cod)$_2$]SbF_6 in the presence of Bu_4NBF_4



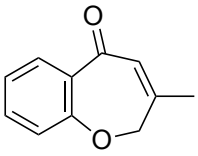
1a **2a** **2a'**

entry	deviation of reaction conditions	**2a** (%)	**2a'** (%)	**1a** (%)
1	none	0	40	0
2	with 1.0 equiv of NBu_4BF_4	46	0	51

* All the yields were determined by ^1H or ^{19}F NMR analysis using 1,3,5-trimethoxybenzene (^1H) and $PhCF_3$ (^{19}F) as internal standards.

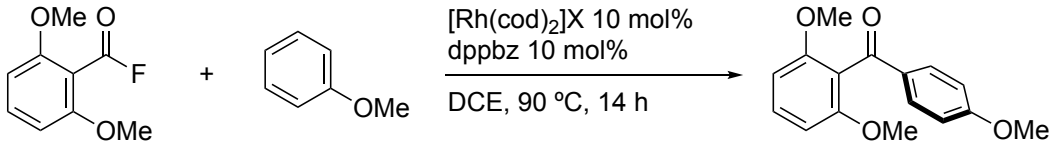
In a glove box filled with nitrogen, $[Rh(cod)_2]SbF_6$ (11.1 mg, 0.020 mmol, 10 mol%) and dppbz (8.9 mg, 0.020 mmol, 10 mol%) were added into a screw-capped vial and dissolved in DCE (0.50 mL). After stirring for 5 min, **1a** (38.8 mg, 0.20 mmol), Bu_4NBF_4 (65.9 mg, 0.20 mmol, 1.0 equiv) and DCE (0.50 mL) were added to the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 90 ºC for 14 h. After cooling to room temperature, the reaction mixture was added $PhCF_3$ and diluted with $CDCl_3$. The mixture was analyzed by ^{19}F NMR.

3-Methylbenzo[b]oxepin-5(2H)-one (2a') [CAS: 60505-35-3].[33]



^1H NMR ($CDCl_3$, 400 MHz) δ: 2.03 (d, *J* = 1.4 Hz, 3H), 4.63 (s, 2H), 6.31 (d, *J* = 1.4 Hz, 1H), 7.06 (dd, *J* = 8.2, 0.92 Hz, 1H), 7.15-1.19 (m, 1H), 7.43-7.47 (m, 1H), 7.95 (dd, *J* = 8.0, 1.8 Hz, 1H).
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 22.7, 73.2, 121.1, 124.0, 129.7, 131.2, 131.3, 134.5, 153.8, 159.0, 188.8.
HRMS (DART+, $[M+H]^+$) Calcd for $C_{11}H_{11}O_2$: 175.0754. Found: 175.0755.

VIII-III. Rhodium-catalyzed Friedel-Crafts acylation of anisole using 1n



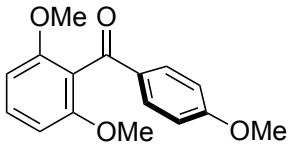
1n 10 equiv **5**

entry	X	NMR yield of **5** (%)
1	BF_4	60 (55*)
2	SbF_6	57

*Isolated yield.

In a glove box filled with nitrogen, $[Rh(cod)_2]BF_4$ (8.1 mg, 0.020 mmol, 10 mol%) and dppbz (8.9 mg, 0.020 mmol, 10 mol%) were added to a screw-capped vial and dissolved in DCE (0.50 mL). After stirring for 5 min, **1n** (38.4 mg, 0.20 mmol), anisole (216 mg, 2.0 mmol, 10 equiv) and DCE (0.50 mL) were added into the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 90 ºC for 14 h. After cooling to room temperature, all volatiles were removed in vacuo. Then 1,1,2,2-tetrachloroethane was added to the residue as an internal standard and analyzed by ^{1}H NMR. The residue was purified by flash column chromatography to give desired ketone **3**.

(2,6-Dimethoxyphenyl)(4-methoxyphenyl)methanone (5) [CAS: 52856-15-2].[34]



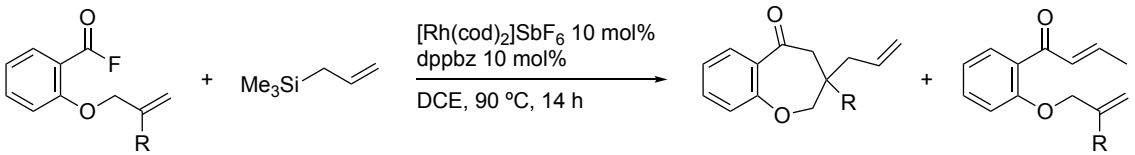
Colorless oil (28.5 mg, 55%). R_f 0.40 (SiO_2, Hexane/EtOAc = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.71 (s, 6H), 3.85 (s, 3H), 6.62 (d, J = 8.4 Hz, 2H), 6.88–6.92 (m, 2H), 7.33 (t, J = 12.8 Hz, 1H), 7.80–7.84 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 55.7, 56.0, 104.1, 113.7, 118.2, 130.7, 131.0, 131.9, 157.6, 163.8, 194.1.

HRMS (DART+, $[M+H]^+$) Calcd for $C_{16}H_{17}O_4$: 273.1121. Found: 273.1117.

VIII-IV. Procedure for allylative cyclization of 1a and 1o using allylsilane

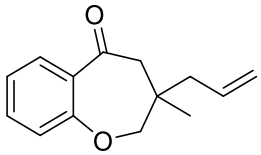


1a (R = Me) **6a** (R = Me) **6a'** (R = Me)
1o (R = Ph) **6o** (R = Ph) **6o'** (R = Ph)

In a glove box filled with nitrogen, $[Rh(cod)_2]SbF_6$ (11.1 mg, 0.020 mmol, 10 mol%) and dppbz (8.9 mg, 0.020 mmol, 10 mol%) were added to a screw-capped vial and dissolved in DCE (0.50 mL). After stirring for 5 min, **1a** (38.8 mg,

0.20 mmol) or **1o** (51.3 mg, 0.20 mmol), allyltrimethylsilane (114.3 mg, 1.0 mmol, 5.0 equiv for **1a** or 68.6 mg, 0.60 mmol, 3.0 equiv for **1o**), and DCE (0.50 mL) were added to the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 90 ºC for 14 h. After cooling to room temperature, all volatiles were removed in vacuo and the residue was purified by flash column chromatography to give desired compounds **6** and **6'**.

3-Allyl-3-methyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (6a).



Colorless oil (4.6 mg, 10%). R_f 0.60 (SIO_2, hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.09 (s, 3H), 2.18-2.33 (m, 2H), 2.58 (d, *J* = 11.0 Hz, 1H), 2.85 (d, *J* = 11.4 Hz, 1H), 3.79 (d, *J* = 12.4 Hz, 1H), 4.05 (d, *J* = 12.4 Hz, 1H), 5.14-5.18 (m, 2H), 5.80-5.90 (m, 1H), 7.04-7.08 (m, 2H), 7.40 (td, *J* = 7.6, 1.5 Hz, 1H), 7.74 (dd, *J* = 8.2, 1.8 Hz, 1H).

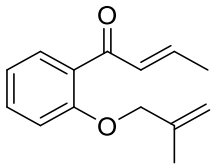
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 22.4, 41.7, 43.7, 53.3, 83.2, 119.2, 120.0, 122.4, 128.2, 129.4, 133.3, 133.5, 164.1, 199.3.

IR (KBr): 2821 w, 2779 w, 2024 w, 1774 w, 1581 w, 1564 w, 1473 w, 1427 m, 1288 m, 1270 m, 1254 m, 1187 w, 1106 m, 780 w, 766 w, 740 m, 701 s, 564 w, 555 w, 522 s, 482 s, 473 s, 468 s, 452 s, 443 s, 419 s.

MS, *m/z* (relative intensity, %): 216 (M^+, 25), 175 (44), 161 (15), 133 (41), 123 (18), 122 (20), 121 (100), 120 (41), 105 (16), 94 (12), 93 (16), 92 (48), 91 (23), 81 (27), 77 (12), 76 (15), 65 (17), 64 (12), 41 (12).

Exact Mass (DART+) Calcd for $C_{14}H_{17}O_2$: 217.1223. Found: 217.1223.

(*E*)-1-(2-((2-Methylallyl)oxy)phenyl)but-2-en-1-one (6a').



Pale yellow oil (8.6 mg, 19%). R_f 0.52 (SiO_2, hexane/EtOAc = 4/1).

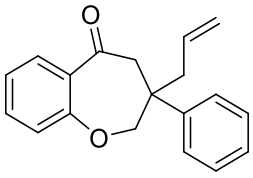
^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.82 (s, 3H), 1.91-1.93 (m, 3H), 4.47 (s, 2H), 4.98 (s, 1H), 5.09 (s, 1H), 6.73-6.77 (m, 1H), 6.83-6.94 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.38-7.42 (m, 1H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 18.4, 19.5, 72.3, 112.7, 112.9, 120.9, 129.6, 130.3, 132.5, 132.6, 140.4, 143.8, 157.1, 193.7.

IR (KBr): 2821 w, 2779 w, 2024 w, 1774 w, 1581 w, 1564 w, 1473 w, 1427 m, 1288 m, 1270 m, 1254 m, 1187 w, 1106 m, 780 w, 766 w, 740 m, 701 s, 564 w, 555 w, 522 s, 482 s, 473 s, 468 s, 452 s, 443 s, 419 s.

Exact Mass (DART+) Calcd for $C_{14}H_{17}O_2$: 217.1223. Found: 217.1223.

3-Allyl-3-phenyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (6o).



Colorless oil (39.7 mg, 63%). R_f 0.43 (SiO_2, hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.63 (q, *J* = 7.0 Hz, 1H), 2.80 (q, *J* = 7.2 Hz, 1H), 3.05 (d, *J* = 11.9 Hz, 1H), 3.33 (d, *J* = 11.9 Hz, 1H), 4.27 (d, *J* = 12.4 Hz, 1H), 4.52 (d, *J* = 12.8 Hz, 1H), 4.99 (dt, *J* = 10.1, 0.9 Hz, 1H), 5.05-5.09 (m, 1H), 5.39-5.47 (m, 1H), 7.10-7.06 (m, 2H), 7.29-7.25 (m, 1H), 7.37-7.43 (m, 3H), 7.49 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.80 (dd, *J* = 8.2, 1.8 Hz, 1H).

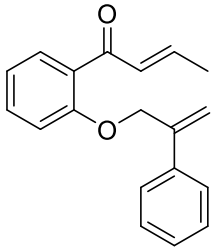
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 44.3, 48.9, 52.3, 83.2, 118.8, 120.2, 122.6, 126.4, 127.1, 128.0, 128.9, 129.6, 133.0, 133.8, 143.1, 164.3, 198.6.

IR (KBr): 2821 w, 2779 w, 2024 w, 1774 w, 1581 w, 1564 w, 1473 w, 1427 m, 1288 m, 1270 m, 1254 m, 1187 w, 1106 m, 780 w, 766 w, 740 m, 701 s, 564 w, 555 w, 522 s, 482 s, 473 s, 468 s, 452 s, 443 s, 419 s.

MS, *m/z* (relative intensity, %): 278 (M^+, 2), 238 (20), 237 (100), 195 (42), 167 (24), 120 (11), 118 (10), 117 (95), 116 (12), 115 (60), 105 (15), 92 (20), 91 (39), 77 (16), 65 (15).

Exact Mass (DART+) Calcd for $C_{19}H_{19}O_2$: 279.1380. Found: 279.1379.

(*E*)-1-(2-((2-Phenylallyl)oxy)phenyl)but-2-en-1-one (6o').



Colorless oil (15.4mg, 24%). R_f 0.33 (SiO_2, hexane/EtOAc = 4/1).

^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.75 (dd, *J* = 6.8, 1.9 Hz, 3H), 4.96 (s, 2H), 5.47 (d, *J* = 1.4 Hz, 1H), 5.59 (d, *J* = 0.9 Hz, 1H), 6.60 (dq, *J* = 15.5, 1.5 Hz, 1H), 6.76-6.85 (m, 1H), 7.00-7.04 (m, 2H), 7.32-7.47 (m, 6H), 7.54 (dd, *J* = 7.8, 1.8 Hz, 1H).

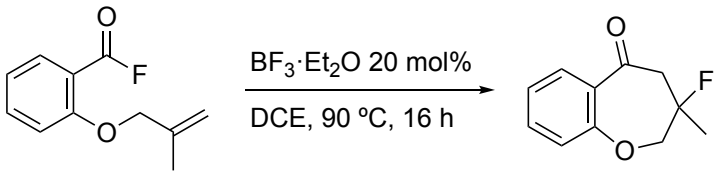
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 18.3, 70.3, 112.8, 115.2, 121.1, 126.2, 128.2, 128.7, 129.7, 130.5, 132.3, 132.7, 138.3, 142.8, 143.8, 156.9, 193.4.

IR (KBr): 2821 w, 2779 w, 2024 w, 1774 w, 1581 w, 1564 w, 1473 w, 1427 m, 1288 m, 1270 m, 1254 m, 1187 w, 1106 m, 780 w, 766 w, 740 m, 701 s, 564 w, 555 w, 522 s, 482 s, 473 s, 468 s, 452 s, 443 s, 419 s.

MS, *m/z* (relative intensity, %): 279 (12), 278 (M^+, 58), 277 (12), 264 (21), 263 (100), 237 (16), 208 (12), 157 (12), 147 (11), 133 (28), 131 (13), 121 (20), 117 (30), 116 (11), 115 (54), 105 (18), 91 (37), 77 (42), 69 (37), 51 (15), 41 (21).

Exact Mass (DART+) Calcd for $C_{19}H_{19}O_2$: 279.1380. Found: 279.1379.

VIII-V. Reaction of 1a using BF_3·Et_2O as a catalyst



1a **2a**

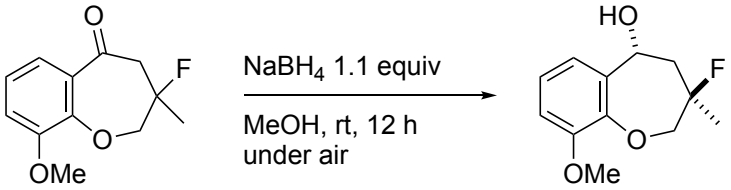
0% (**SM** 0%)

10 mol% BF_3 at -15–30 ºC: 0% (**SM** 0%)

In a glove box filled with nitrogen, $BF_3{\cdot}Et_2O$ (5.7 mg, 0.040 mmol, 20 mol%) in DCE (0.50 mL) and **1a** (38.8 mg, 0.20 mmol) in DCE (0.50 mL) were added to the vial. The screw-cap was closed and the vial was taken out from glove box. The reaction mixture was heated at 90 ºC for 16 h. After cooling to rt, $PhCF_3$ was added to the reaction mixture and diluted with $CDCl_3$. The mixture was analyzed by ^{19}F NMR.

IX. Synthetic Applications

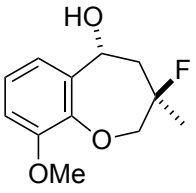
IX-I. Reduction of 2h using $NaBH_4$



2h ***7-anti***

In a round-bottom flask, **2h** (44.8 mg, 0.20 mmol) was dissolved in MeOH (2.0 mL) and the solution was cooled to 0 ºC. $NaBH_4$ (8.3 mg, 0.22 mmol, 1.1 equiv) was added into the solution at 0 ºC. The reaction was warmed to rt and stirred for 12 h. The reaction mixture was then quenched with water (10 mL) and extracted with Et_2O (10 mL × 3). The combined organic extracts were dried with Na_2SO_4. After the solvent was removed in vacuo, the residue was purified by flash column chromatography (SiO_2).

anti-3-Fluoro-9-methoxy-3-methyl-2,3,4,5-tetrahydrobenzo[_b_]oxepin-5-ol (7-_anti_) and _syn_-3-fluoro-9-methoxy-3-methyl-2,3,4,5-tetrahydrobenzo[_b_]oxepin-5-ol (7-_syn_).



+ *syn* isomer

7-anti

Colorless oil (42.7 mg, 95%). R_f 0.48 (SiO_2, Hexane/Et_2O = 1/1). Alcohol **5** was isolated as a mixture of diastereomers *(anti* : *syn* = 1 : 0.3).

^1H NMR ($CDCl_3$, 400 MHz) δ: 1.30 (d, J = 20.6 Hz, $3H_{syn}$ + $3H_{anti}$), 1.45 (d, J = 22.4 Hz, $3H_{syn}$), 1.81–1.99 (m, $1H_{anti}$ + $1H_{syn}$), 2.37–2.55 (m, $2H_{anti}$ + $1H_{syn}$), 3.13 (brs, $1H_{syn}$), 3.52 (ddd, J = 33.7, 13.3, 1.15 Hz, $1H_{anti}$), 3.85 (s, $3H_{anti}$), 3,86 (s, $3H_{syn}$), 4.20 (t, J = 11.0 Hz, $1H_{syn}$), 4.30–4.36 (m, $1H_{anti}$), 6.82–6.85 (m, $1H_{anti}$), 6.88–6.92 (m, $2H_{syn}$), 7.03–

7.05 (m, $1H_{syn}$), 7.07–7.10 (m, $2H_{anti}$).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: *anti*: 24.0 (d, $J_{C–F}$ = 22.0 Hz), 46.1 (d, $J_{C–F}$ = 23.0 Hz), 56.2, 65.5, 76.9, 94.5 (d, $J_{C–F}$ = 172.5 Hz), 111.3, 116.6, 124.6, 139.5, 145.5, 151.4. *syn*: 24.2 (d, $J_{C–F}$ = 24.0 Hz), 43.8 (d, $J_{C–F}$ = 20.1 Hz), 56.7, 70.8, 77.8, 96.4 (d, $J_{C–F}$ = 169.7 Hz), 112.0, 119.8, 124.7, 137.5, 147.3, 151.6.

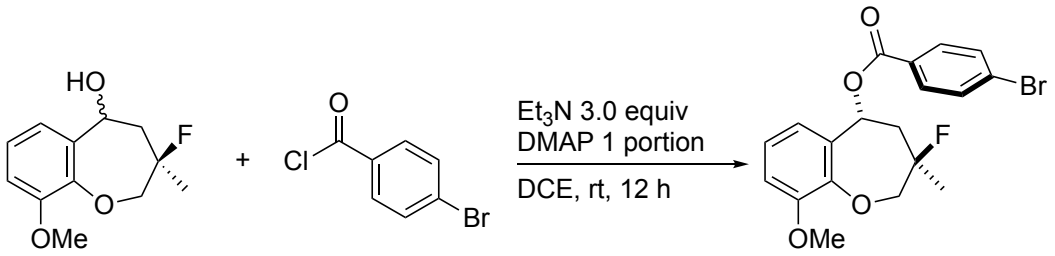
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -148.8 (*syn*), -153.7 (*anti*).

IR (KBr): 3458 brm, 2940 m, 2840 w, 1603 m, 1585 m, 1440 m, 1379 w, 1312 m, 1274 s, 1214 m, 1180 m, 1112 m, 1084 s, 1053 s, 959 w, 892 m, 863 m, 792 s, 752 m, 714 m, 444 w.

MS, *m/z* (relative intensity, %): 227 (14), 226 ([M]$^+$, 100), 195 (10), 175 (51), 152 (14), 151 (30), 149 (17), 148 (16), 147 (13), 145 (11), 137 (13), 135 (39), 133 (13), 122 (31), 121 (27), 120 (12), 119 (10), 109 (35), 108 (13), 107 (20), 106 (59), 105 (17), 93 (24), 92 (11), 91 (33), 81 (16), 79 (10), 78 (15), 77 (35), 65 (27), 55 (34), 53 (21), 52 (11), 51 (18), 43 (11).

HRMS (DART+, $[M+H]^+$) Calcd for $C_{12}H_{16}O_3F$: 227.1078. Found: 227.1081.

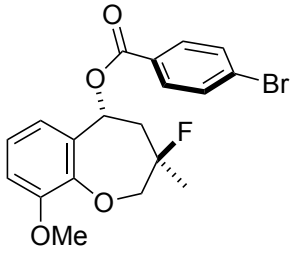
The stereochemistry of the major diastereomer was determined by converting **7** into *p*-bromobenzoyl ester **S18** according to literature procedure.[35]



7 1.2 equiv **S18-anti**

In a round-bottom flask, **7** (42.9 mg, 0.19 mmol) and 4-bromobenzoyl chloride (50.0 mg, 0.23 mmol, 1.2 equiv) were added and the flask was purged with nitrogen. The materials were dissolved in DCE (1.0 mL) and Et_3N (90 mL, 0.57 mmol, 3.0 equiv) was added to the mixture. DMAP (1 portion) was then added and the mixture was stirred for 12 h. After **7** was completely consumed (checked by TLC), water (5.0 mL) was added and the resulting mixture was extracted with EtOAc (5.0 mL × 3). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography to give the major isomer. The single crystal of the major isomer that is suitable for X-ray crystallography was obtained by recrystallization from $CHCl_3$/hexane. The stereochemistry of the major isomer proved to be **S20-*anti*** by X-ray analysis.

***anti*-7-Fluoro-1-methoxy-7-methyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-yl 4-bromobenzoate (S18-*anti*).**



Colorless solid (42.0 mg, 54%). R_f 0.28 (SiO_2, Hexane/Et_2O = 7/3). M.p. 163.8–164.2 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.37 (d, J = 20.6 Hz, 3H), 2.14–2.28 (m, 1H), 2.54 (t, J = 13.1 Hz, 1H), 3.70 (dd, J = 31.4, 13.1 Hz, 1H), 3.87 (s, 3H), 4.39 (t, J = 12.4 Hz, 1H), 6.64n (d, J = 10.1 Hz, 1H), 6.87 (s, 1H), 6.89 (s, 1H), 7.05 (t, J = 8.02 Hz, 1H), 7.62 (d, J = 8.7 Hz, 2H), 7.99 (d, J = 8.7 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 24.0 (d, $J_{C\text{-}F}$ = 23.0 Hz), 43.0 (d, $J_{C\text{-}F}$ = 24.0 Hz), 56.3, 69.1 (d, $J_{C\text{-}F}$ = 3.8 Hz), 77.3, 94.2 (d, $J_{C\text{-}F}$ = 173 Hz), 111.9, 117.3, 124.7, 128.6, 129.0, 131.4, 132.0, 134.9, 146.3, 151.8, 164.4.

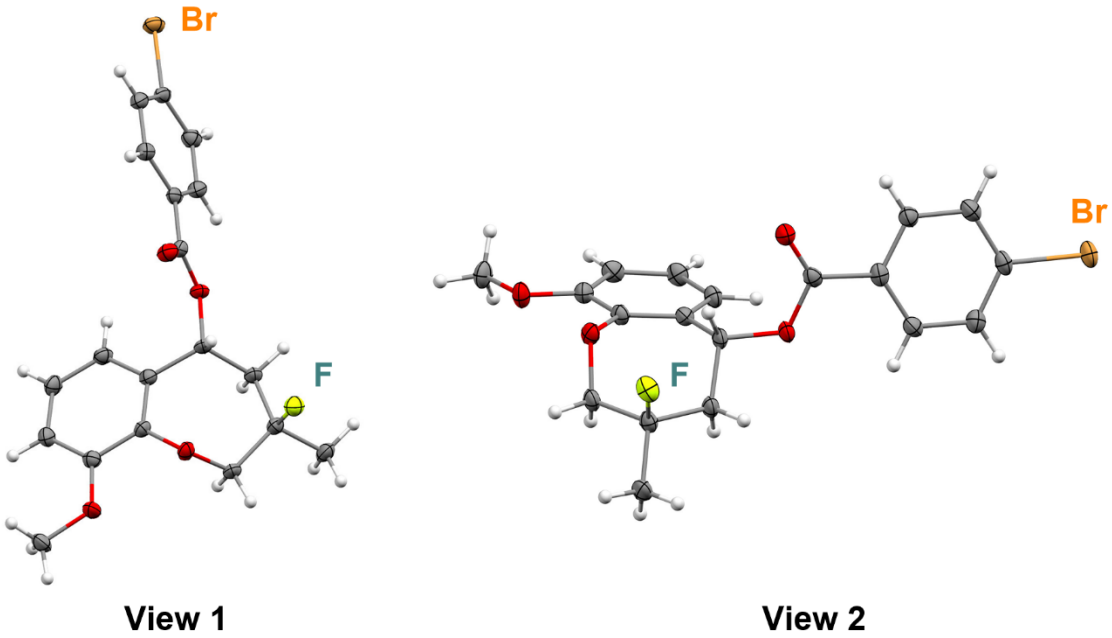
^{19}F NMR ($CDCl_3$, 376 MHz) δ: -152.3.

IR (KBr): 2939 w, 2839 w, 1719 s, 1592 s, 1484 s, 1440 m, 1397 m, 1362 w, 1299 s, 1273 s, 1185 m, 1173 m, 1119 s, 1077 m, 1011 s, 983 m, 859 m, 787 s, 755 m, 744 m, 681 w, 488 m.

MS, *m/z* (relative intensity, %): 411 (10), 410 ([M+2]$^+$, 54), 409 (11), 408 ([M]$^+$, 52), 335 (22), 333 (20), 225 (77), 224 (32), 206 (13), 205 (86), 193 (14), 189 (41), 188 (15), 185 (100), 183 (98), 177 (23), 161 (30), 157 (30), 155 (28), 149 (16), 148 (43), 145 (15), 137 (31), 133 (16), 129 (15), 123 (34), 121 (35), 117 (10), 115 (13), 109 (10), 107 (10), 105 (17), 104 (27), 91 (36), 78 (19), 77 (41), 76 (44), 75 (27), 73 (18), 65 (17), 55 (19), 53 (11), 51 (15), 43 (21).

HRMS (DART+, [M+H]$^+$) Calcd for $C_{19}H_{19}O_4F^{79}Br$: 409.0445. Found: 409.0440.

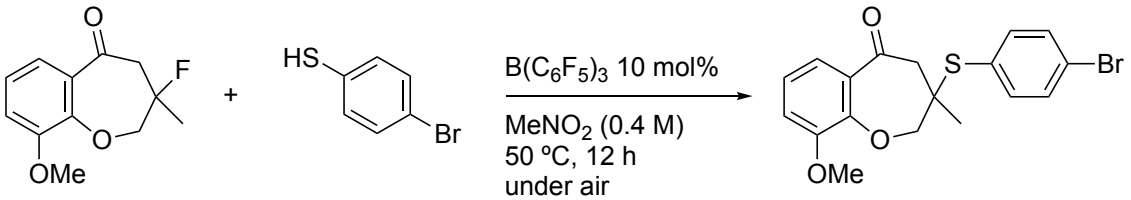
The structure of **S18-anti** was confirmed by X-ray crystallography.



ORTEP drawing of **S18-anti** with thermal ellipsoids set at the 50% probability level.[a]

[a]Crystal data for **S18-anti**, monoclinic, space group $P\,2_1/c$ (no. 14), a = 9.7593(2) Å, b = 16.7915(3) Å, c = 10.5285(2) Å, □ = 94.007(2) °, V = 1721.13(7) Å^3, T = 123 K, Z = 4, $R1$ ($wR2$) = 0.0335 (0.0898) for 228 parameters and 3444 unique reflections. GOF = 1.055. CCDC 2177625.

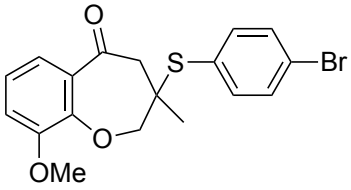
IX-II. Reaction of 2h with 4-bromobenzenethiol using a $B(C_6F_5)_3$ catalyst



2h 2.0 equiv **8**

This reaction was carried out according to the literature procedure with slight modification.[19] A round-bottom flask was added **5b** (44.8 mg, 0.20 mmol), 4-bromobenzenethiol (75.6 mg, 0.40 mmol, 2.0 equiv), and $B(C_6F_5)_3$ (10.4 mg, 0.020 mmol, 10 mol%). $MeNO_2$ (0.50 mL) was then added and the mixture was heated at 50 ºC for 12 h under air. After cooling to rt, the reaction was concentrated in vacuo. The residue was purified by flash column chromatography to give desired sulfide **8**.

3-((4-Bromophenyl)thio)-9-methoxy-3-methyl-3,4-dihydrobenzo[*b*]oxepin-5(2*H*)-one (8).



Colorless oil (61.1 mg, 78%). R_f 0.24 (SiO_2, hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.42 (s, 3H), 2.90 (d, *J* = 11.9 Hz, 1H), 3.01 (d, *J* = 11.9 Hz, 1H), 3.90 (s, 3H), 4.15 (d, *J* = 12.4 Hz, 1H), 4.29 (d, *J* = 12.4 Hz, 1H), 7.03 (d, *J* = 5.0 Hz, 2H), 7.36 (t, *J* = 4.8 Hz, 1H), 7.50 (s, 4H).

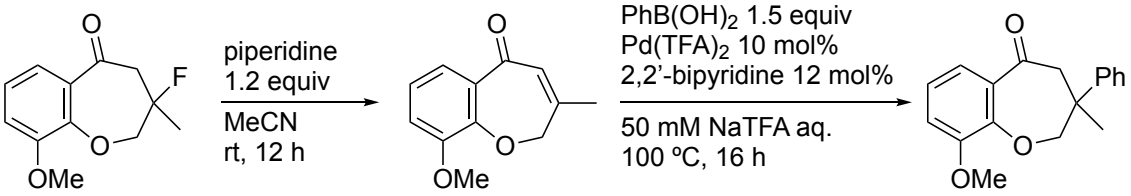
^{13}C NMR ($CDCl_3$, 101 MHz) δ: 26.1, 53.0, 53.6, 56.5, 83.4, 115.7, 120.7, 122.7, 124.7, 128.8, 128.9, 132.2, 139.5, 150.5, 153.5, 196.3.

IR (KBr): 2963 w, 1682 s, 1578 m, 1480 s, 1439 m, 1384 w, 1304 m, 1263 s, 1207 w, 1177 m, 1086 w, 1069 m, 1038 s, 1007 s, 821 m, 787 m, 755 m, 738 m, 667 w, 579 w, 487 w.

MS, *m/z* (relative intensity, %): 394 ([M^++2], 6), 392 ([M^+], 5), 204 (10), 192 (12), 191 (100), 151 (33), 122 (33), 121 (17), 108 (14), 55 (23).

Exact Mass (DART+, $[M+H]^+$) Calcd for $C_{18}H_{18}O_3S^{79}Br$: 393.0155. Found: 393.0154.

IX-III. Dehydrofluorination and 1,4-addition of 2h

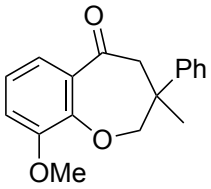


2h **2h'** **9**

These reactions were carried out according to the literature procedure with slight modification.[20,21] In round-bottom flask, **2h** (44.8 mg, 0.20 mmol) and piperidine (23.7 mL, 1.2 equiv) were stirred in MeCN (5.0 mL) for 12 h. Volatiles were then removed in vacuo, and the residue was filtered through short silica pad using Et_2O as an eluent. The filtrate was concentrated in vacuo to provide a crude product **2h'**, which was used for the next step without further purification.

Thus obtained **2h'** (0.20 mmol), $PhB(OH)_2$ (36.6 mg, 0.30 mmol, 1.5 equiv), $Pd(TFA)_2$ (6.6 mg, 0.020 mmol, 10 mol%), and 2,2'-bipyridine (3.7 mg, 0.024 mmol, 12 mol%) were added to a two-necked flask under N_2 atmosphere. An aqueous solution of Na(TFA) (50 mM, 1.0 mL) was added to the flask and the reaction was stirred at 100 ºC for 12 h. After cooling to rt, the reaction mixture was extracted with Et_2O (5.0 mL × 2) and the combined organic extracts were dried using Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography to give **9**.

9-Methoxy-3-methyl-3-phenyl-3,4-dihydrobenzo[b]oxepin-5(2H)-one (9).



Colorless oil (33.8 mg, 60% for two steps). R_f 0.26 (SiO_2, hexane/Et_2O = 7/3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.54 (s, 3H), 2.97 (d, *J* = 11.5 Hz, 1H), 3.42 (d, *J* = 11.9 Hz, 1H), 3.91 (s, 3H), 4.22 (d, *J* = 12.4 Hz, 1H), 4.58 (d, *J* = 12.4 Hz, 1H), 7.02 (d, *J* = 1.4 Hz, 1H), 7.03 (s, 1H), 7.24-7.27 (m, 1H), 7.35-7.43 (m, 3H), 7.54 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz) δ: 25.7, 45.9, 54.5, 56.5, 85.2, 115.5, 120.8, 122.3, 125.9, 127.0, 128.8, 129.0, 145.5, 150.5, 154.1, 198.6.

IR (KBr): 2965 m, 2838 w, 1682 s, 1599 m, 1578 s, 1481 s, 1441 s, 1386 w, 1321 m, 1262 s, 1175 w, 1082 w, 1038 m, 1011 m, 797 w, 764 m, 740 w, 700 m, 573 w.

MS, *m/z* (relative intensity, %): 282 ([M^+], 12), 192 (12), 191 (100), 190 (11), 151 (38), 122 (46), 121(17), 120(11), 115 (10), 107 (13), 91 (16), 77 (12).

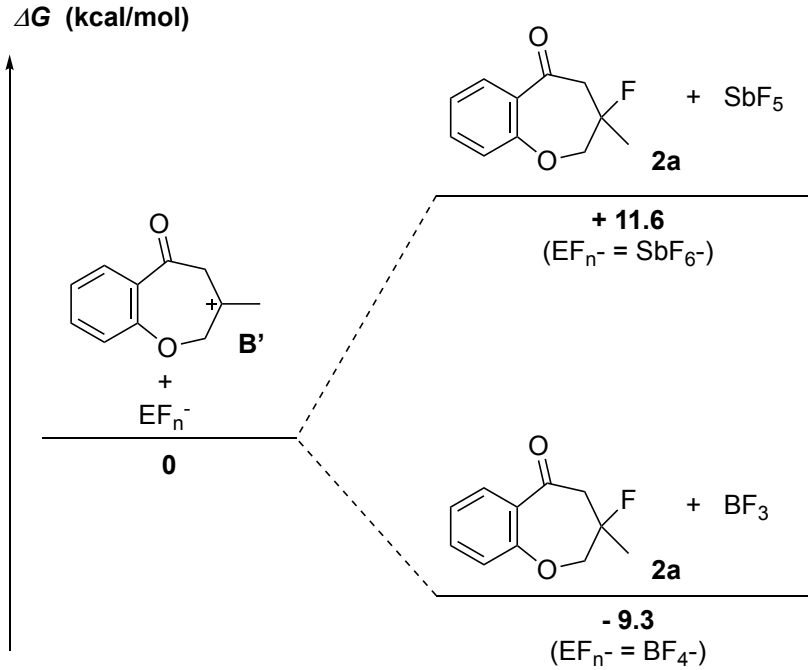
Exact Mass (DART+, $[M+H]^+$) Calcd for $C_{18}H_{19}O_3$: 283.1328. Found: 283.1827.

IX. DFT Calculations

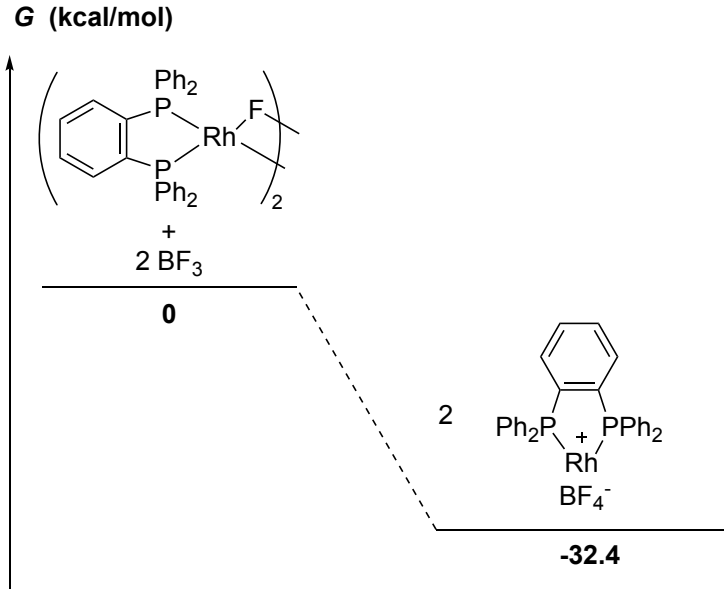
IX-I. Computational Details

Calculations were performed with the Gaussian 09 (G09RevD.01) program.[36] Geometry optimizations and frequency calculations for all reported structures were performed using the B3LYP functional with a basis set consisting of the LANL2DZ basis set for metallic atoms (Rh, Sb) and 6-31G(d,p) for the rest. PCM[37-39] solvent effects were incorporated for all calculations with dichloroethane as the solvent. Single-point calculations on optimized geometries were separately calculated using the B3LYP functional with a basis set consisting of the LANL2DZ basis set for metallic atoms (Rh, Sb) and 6-31G+(d,p) for the rest. Energy changes were shown by the use of Gibbs free energies (T = 298.15 K and P = 1 atm).

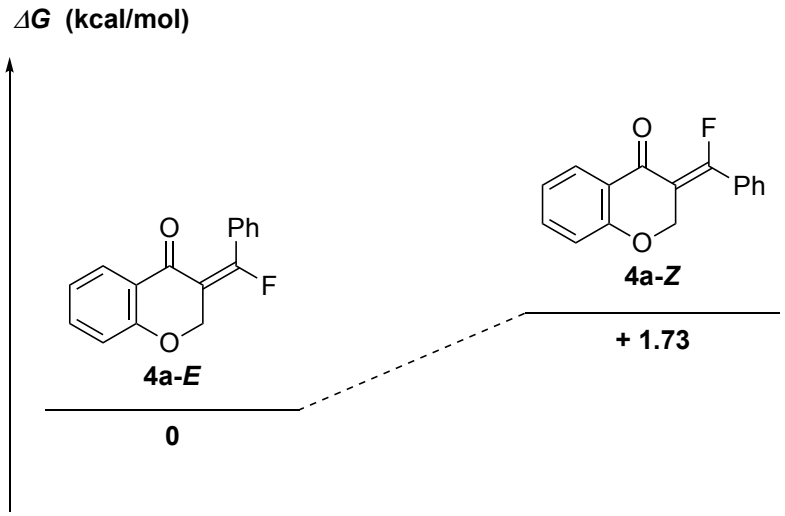
IX-II. Relative Gibbs Free Energies



The step of fluoride anion abstraction from EF_n^- (BF_4^- or SbF_6^-) by carbocation **B'** is exergonic for BF_4^- (-9.3 kcal/mol) whereas it is endergonic for SbF_6^- (+12.8 kcal/mol).



Fluoride anion abstraction step from Rh–F complex by BF_3 is exergonic.



4a-*E* is more thermodynamically stable than **4a-*Z***.

IX-III. Cartesian coordinates of the optimized geometries and energies

· **2a** (G = -675.9690285 Hartree, no imaginary frequency)

C	-2.11086400	1.18783300	0.25892200
C	-3.25928300	0.44446700	0.49921700
C	-3.24383500	-0.93808200	0.28279400
C	-2.08176100	-1.56392600	-0.16200000
C	-0.92472900	-0.81489200	-0.39245400
C	-0.92548200	0.58010100	-0.19137100
O	0.15958000	-1.48425400	-0.91420500
C	1.34270000	-1.59164400	-0.11238600
C	2.01967200	-0.25444900	0.21273300
C	1.61166300	0.84516900	-0.77520000
C	0.25356800	1.45823400	-0.44985800
O	0.14387300	2.67753000	-0.40028800
C	3.52880000	-0.41807900	0.33450800
F	1.55362100	0.15657400	1.49323900
H	-2.09839700	2.26198600	0.40850800
H	-4.16269400	0.93366800	0.84871600
H	-4.13666200	-1.52928200	0.46257700
H	-2.04935300	-2.63313700	-0.34249400
H	2.01411000	-2.21026100	-0.71120200
H	1.12486000	-2.11102400	0.82825200
H	2.33340300	1.66468600	-0.75949600
H	1.58623100	0.42855900	-1.78895000
H	3.97386300	-0.63385100	-0.64072400

H	3.96931500	0.50250200	0.72478900
H	3.77241800	-1.23762200	1.01738900

·Carbocation **B'** (G = -575.8862373 Hartree, no imaginary frequency)

C	-1.88371000	1.29904200	0.27718900
C	-3.10700700	0.65953700	0.39515700
C	-3.18913800	-0.72234100	0.18103600
C	-2.04963200	-1.46117800	-0.12780900
C	-0.81656600	-0.82241300	-0.23773500
C	-0.71774600	0.57593700	-0.05658000
O	0.26025600	-1.62028800	-0.56821000
C	1.39926400	-1.56278500	0.26506300
C	2.25772500	-0.38276600	0.04088000
C	1.80368600	0.60583900	-0.89437000
C	0.51200800	1.35178900	-0.25243900
O	0.64619700	2.53110400	-0.04355200
C	3.49627000	-0.22629100	0.81001400
H	-1.79812200	2.37014800	0.42001200
H	-3.99550600	1.22822300	0.64563200
H	-4.14447100	-1.22948100	0.26793300
H	-2.09269900	-2.53404400	-0.27643400
H	2.00230500	-2.46324500	0.07487900
H	1.13056700	-1.60554400	1.33482100
H	1.39012600	0.12424600	-1.79013500
H	2.52920900	1.38201100	-1.12209700
H	3.50334700	0.76567300	1.28400500
H	3.65485000	-1.00838300	1.55196300
H	4.33784500	-0.20236300	0.10107800

· BF_4^- (G = -424.6619272 Hartree, no imaginary frequency)

B	0.00000000	0.00000000	0.00000000
F	0.81229600	0.81229600	0.81229600
F	-0.81229600	-0.81229600	0.81229600
F	0.81229600	-0.81229600	-0.81229600
F	-0.81229600	0.81229600	-0.81229600

· BF_3 (G = -324.5938944 Hartree, no imaginary frequency)

B	0.00000000	0.00000000	0.00000000

F	0.00000000	1.31773900	0.00000000
F	1.14119500	-0.65886900	0.00000000
F	-1.14119500	-0.65886900	0.00000000

· SbF_6^- (G = -604.8531824 Hartree, no imaginary frequency)

Sb	0.00000000	0.00000000	0.00000000
F	0.00000000	0.00000000	1.86756000
F	0.00000000	0.00000000	-1.86756000
F	0.00000000	1.86756000	0.00000000
F	0.00000000	-1.86756000	0.00000000
F	-1.86756000	0.00000000	0.00000000
F	1.86756000	0.00000000	0.00000000

· SbF_5 (G = -504.7519502 Hartree, no imaginary frequency)

Sb	0.00000000	0.00000000	0.00105900
F	0.00000000	1.84180400	0.00278900
F	0.00000000	-1.84180400	0.00278900
F	-1.57695700	0.00000000	-0.91930000
F	1.57695700	0.00000000	-0.91930000
F	0.00000000	0.00000000	1.82702200

· $[(dppbz)RhF]_2$ (G = -4098.962395 Hartree, no imaginary frequency)

C	-6.07486600	1.39798000	-0.75964100
C	-7.24982800	0.69877500	-1.04335300
C	-7.24954700	-0.69779900	-1.04512500
C	-6.07434900	-1.39727100	-0.76303700
C	-4.89545900	-0.70411000	-0.45813500
C	-4.89570200	0.70448700	-0.45655000
P	-3.25982000	-1.51192000	-0.13397100
Rh	-1.63949500	0.00039100	-0.16402800
P	-3.26019700	1.51212100	-0.13158300
F	0.00862200	-1.37176800	-0.05880900
Rh	1.65931000	0.00010000	-0.02890900
F	0.00889800	1.37241400	-0.06191800
C	-3.40774400	-2.36873500	1.49538700
C	-4.62197900	-2.73061900	2.09703700
C	-4.63043200	-3.36324600	3.34377200
C	-3.42950100	-3.63896100	3.99948200

C	-2.21586100	-3.27442300	3.40916600
C	-2.20144000	-2.63790100	2.16779900
C	-3.18764700	-2.88600900	-1.36471000
C	-2.60481600	-2.61715500	-2.61406000
C	-2.55260400	-3.60555800	-3.59779000
C	-3.07303900	-4.87675400	-3.34108700
C	-3.64130900	-5.15721500	-2.09657400
C	-3.69703500	-4.16894000	-1.11096200
C	-3.40716900	2.36546300	1.49963600
C	-2.20028600	2.63610300	2.17042200
C	-2.21393900	3.27015000	3.41304700
C	-3.42738500	3.63059100	4.00630100
C	-4.62884300	3.35329400	3.35223800
C	-4.62116200	2.72322100	2.10419400
C	-3.18937300	2.88913300	-1.35917300
C	-2.60784100	2.62351500	-2.60982100
C	-2.55659600	3.61447500	-3.59101600
C	-3.07667700	4.88504100	-3.33046300
C	-3.64367900	5.16227600	-2.08466100
C	-3.69846500	4.17141700	-1.10158700
P	3.27183600	1.51683700	0.04242900
C	3.37658000	2.70321600	-1.37246400
C	2.90512200	2.28398400	-2.62645100
C	2.99681800	3.12625800	-3.73594300
C	3.55438100	4.40015600	-3.60285600
C	4.01519000	4.83076600	-2.35629700
C	3.92507400	3.98941800	-1.24558200
C	3.19763700	2.62959600	1.50995300
C	1.97428000	3.29489000	1.71567900
C	1.81763000	4.15825300	2.79883700
C	2.86861900	4.35418200	3.70091800
C	4.07627300	3.68101900	3.51414800
C	4.24407200	2.82339500	2.42200200
C	3.37534300	-2.70497400	-1.36872800
C	3.92494400	-3.99063800	-1.24115000
P	3.27136000	-1.51702300	0.04488500
C	4.01446100	-4.83300600	-2.35113200
C	3.55194300	-4.40397000	-3.59761300

C	2.99318200	-3.13066900	-3.73133900
C	2.90207900	-2.28737500	-2.62256900
C	3.19712600	-2.62815300	1.51359200
C	1.97423500	-3.29430800	1.71929700
C	1.81768600	-4.15664400	2.80328000
C	2.86829900	-4.35068000	3.70620900
C	4.07544600	-3.67659800	3.51948700
C	4.24314700	-2.81998800	2.42652900
C	4.93541500	-0.70413700	0.05384200
C	4.93562100	0.70345000	0.05258500
C	6.15218300	1.39681000	-0.02047400
C	7.35880000	0.69791100	-0.06907800
C	7.35860300	-0.69947600	-0.06779500
C	6.15179300	-1.39795500	-0.01793200
H	-6.07396600	2.48306600	-0.80041900
H	-8.15846900	1.24373300	-1.28097800
H	-8.15796100	-1.24251200	-1.28417200
H	-6.07307500	-2.48224900	-0.80655900
H	-5.56506100	-2.51328200	1.60648500
H	-5.57716100	-3.63512000	3.80176500
H	-3.43893100	-4.12675500	4.96995600
H	-1.27887600	-3.47203700	3.92182800
H	-1.26216700	-2.32810100	1.71688200
H	-2.18231600	-1.63318000	-2.79995800
H	-2.09832000	-3.38593700	-4.55960300
H	-3.02780000	-5.64802900	-4.10452500
H	-4.03808700	-6.14686400	-1.88910900
H	-4.13012100	-4.40264100	-0.14335200
H	-1.26110600	2.32918600	1.71733800
H	-1.27649200	3.46897900	3.92439300
H	-3.43620900	4.11639400	4.97777800
H	-5.57537900	3.62197100	3.81251100
H	-5.56457400	2.50462300	1.61483500
H	-2.18550000	1.64006300	-2.79878700
H	-2.10331300	3.39735000	-4.55386700
H	-3.03213000	5.65830500	-4.09192700
H	-4.04018900	6.15139900	-1.87419400
H	-4.13061500	4.40258700	-0.13295300

H	2.45477200	1.29956200	-2.71886900
H	2.62552700	2.79084700	-4.70000300
H	3.62180800	5.05808500	-4.46445800
H	4.44041600	5.82420300	-2.24596100
H	4.27224700	4.34159100	-0.27897400
H	1.14766200	3.11012100	1.03493000
H	0.87255700	4.67430900	2.94222000
H	2.74312800	5.02321800	4.54730700
H	4.89382000	3.82236100	4.21530100
H	5.19065300	2.30995200	2.29058300
H	4.27341200	-4.34161700	-0.27456800
H	4.44055700	-5.82601600	-2.24030600
H	3.61894200	-5.06269700	-4.45863900
H	2.62050100	-2.79653100	-4.69530400
H	2.45065200	-1.30345900	-2.71523300
H	1.14784600	-3.11100900	1.03788800
H	0.87300200	-4.67342600	2.94660500
H	2.74289700	-5.01896200	4.55320500
H	4.89268700	-3.81645200	4.22129300
H	5.18934000	-2.30582000	2.29515200
H	6.16082900	2.48174100	-0.05547500
H	8.29663000	1.24241700	-0.12361900
H	8.29627900	-1.24434400	-0.12133400
H	6.16017700	-2.48294700	-0.05095400

· [Rh(dppbz)]BF_4 (G = -2374.100924 Hartree, no imaginary frequency)

C	-1.30010900	3.09287200	1.37467900
C	-0.56679800	4.16903600	1.87734600
C	0.83013200	4.13528800	1.86260300
C	1.50068500	3.02492400	1.34652200
C	0.77207700	1.94746400	0.82599400
C	-0.63403500	1.98280500	0.83914100
P	1.52558600	0.39123300	0.17790300
Rh	-0.02148000	-1.15319900	-0.15160000
P	-1.47386200	0.47146700	0.19884600
F	-1.28405400	-2.96365900	-0.64268700
C	2.43407200	0.82539200	-1.36222000
C	2.60497900	2.13822200	-1.82331700

C	3.28731200	2.38010000	-3.01900600
C	3.80273600	1.31735200	-3.76175600
C	3.62947300	0.00481900	-3.31172000
C	2.94490600	-0.24243800	-2.12312700
C	2.84108300	-0.04856400	1.38598700
C	2.50996500	-0.89303500	2.45804200
C	3.46811700	-1.21955000	3.41832600
C	4.76500900	-0.71043800	3.31382300
C	5.10406300	0.12261200	2.24487500
C	4.14905600	0.45119000	1.28116100
C	-2.37073700	0.94659700	-1.33560900
C	-2.90914500	-0.09999200	-2.10713000
C	-3.58793100	0.17801100	-3.29230500
C	-3.72797800	1.49937700	-3.72766500
C	-3.18597900	2.54069200	-2.97341400
C	-2.50921200	2.26857900	-1.78102400
C	-2.79703400	0.08952100	1.41753400
C	-2.48187200	-0.73738400	2.50815900
C	-3.44680900	-1.02748500	3.47290100
C	-4.73520800	-0.49972900	3.35438900
C	-5.05797200	0.31685500	2.26809800
C	-4.09561900	0.60995200	1.29994500
H	-2.38466200	3.11272500	1.42004000
H	-1.08547100	5.02635800	2.29501900
H	1.39799200	4.96665300	2.26860500
H	2.58557500	2.99355000	1.37014300
H	2.20652700	2.97464100	-1.25929000
H	3.41298200	3.40107700	-3.36715300
H	4.33197600	1.50837300	-4.69055200
H	4.02067400	-0.82686000	-3.88993400
H	2.79411000	-1.26642700	-1.79161000
H	1.50320800	-1.29625700	2.52707500
H	3.20384800	-1.87513200	4.24264600
H	5.51156900	-0.96800400	4.05925100
H	6.11338300	0.51354500	2.15698900
H	4.42530000	1.08872800	0.44719600
H	-2.78241000	-1.13051600	-1.78665500
H	-4.00005800	-0.63708300	-3.87955700

H	-4.25224400	1.71396400	-4.65415100
H	-3.28625300	3.56823400	-3.31025800
H	-2.08955800	3.08838800	-1.20801500
H	-1.48250100	-1.15637300	2.58757900
H	-3.19506800	-1.67000800	4.31129600
H	-5.48768200	-0.73035800	4.10268900
H	-6.06052300	0.72235300	2.16958400
H	-4.35955500	1.23518100	0.45281200
B	-0.20385300	-3.88500100	-0.97314600
F	-0.25462200	-4.96927100	-0.13300500
F	-0.26833800	-4.21146600	-2.30473800
F	1.00095700	-3.11744600	-0.71119700

· **4a-*E*** (G = -866.432052 Hartree, no imaginary frequency)

C	4.19502200	-1.78112500	-0.21727200
C	4.85350800	-0.67665700	0.34657700
C	4.17199500	0.50981500	0.59257300
C	2.81192100	0.60295100	0.27222000
C	2.12883100	-0.50279400	-0.27246200
C	2.84355900	-1.68968200	-0.51462100
O	2.18592100	1.78207000	0.53085600
C	0.99630500	2.02637600	-0.24168500
C	0.03721900	0.85750200	-0.21393100
C	0.66046900	-0.46481400	-0.48107400
O	0.03819400	-1.46447800	-0.84179700
C	-1.28928400	1.08471700	-0.07210000
F	-1.65620000	2.39704400	-0.02344000
C	-2.46333000	0.21068700	0.05123800
C	-2.41324200	-1.02919100	0.71016300
C	-3.56734300	-1.79469900	0.84789000
C	-4.78377500	-1.33909700	0.33121300
C	-4.84464600	-0.10347900	-0.31604600
C	-3.69568600	0.67295400	-0.44619800
H	4.73869100	-2.70001200	-0.41020400
H	5.91030400	-0.74205800	0.58776600
H	4.67087600	1.37441600	1.01708200
H	2.29820600	-2.53185600	-0.92722100
H	0.54960900	2.92424600	0.17948600

H	1.30516000	2.24152700	-1.27489500
H	-1.47676200	-1.38798800	1.11635600
H	-3.51909300	-2.74740100	1.36595400
H	-5.68015400	-1.94232600	0.43866900
H	-5.78683000	0.25909300	-0.71496600
H	-3.74627900	1.63745300	-0.93844900

· **4a-*Z*** (G = --866.429300 Hartree, no imaginary frequency)

C	-2.45322600	0.40918400	0.09292400
C	-2.36268300	-0.99866500	0.13389000
O	-1.18890700	-1.64444100	0.38296000
C	-0.21227600	-0.83488300	1.06575900
C	0.01678700	0.48192200	0.37222800
C	-1.23561800	1.26246200	0.16872100
C	-3.70591200	0.99927800	-0.15238700
C	-4.83444400	0.22043900	-0.36006400
C	-4.71990200	-1.17864200	-0.34061900
C	-3.49523200	-1.78942000	-0.09646300
O	-1.28646700	2.48008900	0.00920600
C	1.23156900	0.91354400	-0.03006400
C	2.51933200	0.19854200	-0.07325800
F	1.35447900	2.18457500	-0.47005400
C	3.69277500	0.88772700	0.27867600
C	4.92657900	0.24381600	0.22817900
C	5.00738300	-1.08651100	-0.19145400
C	3.84900400	-1.76936300	-0.56943400
C	2.61074600	-1.13213800	-0.51595700
H	0.68411300	-1.44299900	1.15064400
H	-0.59488600	-0.64030000	2.07837000
H	-3.75246300	2.08261300	-0.18877500
H	-5.79658200	0.68643700	-0.54544100
H	-5.59721400	-1.79600500	-0.50921300
H	-3.39531700	-2.86911700	-0.06523100
H	3.63030400	1.92259400	0.59741600
H	5.82571200	0.78102200	0.51323700
H	5.97064800	-1.58536100	-0.23463300
H	3.90987500	-2.79486600	-0.91976900
H	1.71920600	-1.65412000	-0.84751600

4.5. References

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Conclusions

The research described in this thesis focuses on the development of non-substitution type catalytic reactions including the cleavage of an inert chemical bond.

In chapter 1, the platinum-catalyzed cyclodimerization of diarylalkynes was described. This reaction proceeds through the activation of an *ortho* C–H bond and the cleaved hydrogen atom is then incorporated into the product, resulting in an atom economy of 100%. A three-membered silylene ligand is critical for the cyclodimerization reaction to be effective.

In chapter 2, the rhodium-catalyzed decarbonylation of acylsilanes was described. In this reaction, only CO is generated as byproduct. The nature of reaction suggests that a C–Si bond is oxidatively added to a rhodium(I) center. The use of Brettphos as a ligand is essential for promoting the reaction. Catalytic silylation of phenyl iodide using hydrosilanes requires the use of stoichiometric base, which leads to low AE (for example, AE is 36% when K_3PO_4 is used as a base). In contrast, the AE of decarbonylation of acylsilanes is 84%.

In Chapter 3, the $ZnBr_2$-catalyzed formal cross-dimerization of carbenes using acylsilanes and diazo esters was described. In this reaction, the coupling reaction proceeds with the loss of only N_2 to give tetrasubstituted alkene derivatives. Acylsilanes act as equivalents of siloxycarbenes through a 1,2-Brook rearrangement in this reaction. The alkenes are formed with high *Z*-selectivity based on the chelation effect of the zinc catalyst. This cross-dimerization proceeds with higher AE (>92%) than classical Wittig reaction or coupling reactions of acylsilanes with ylides.

In chapter 4, the cationic rhodium-tetrafluoroborate-catalyzed intramolecular carbofluorination of alkenes via the activation of a C–F bond of an acyl fluoride was described. In this reaction, the C–F bond adds across the double bond of the alkene moiety in an intramolecular manner with an atom economy of 100%. The rhodium catalyst functions as a Lewis acid, which abstracts a fluoride anion from the acyl fluoride. The BF_4 anion, the counter anion of the catalyst, serves as a fluoride donor to a carbocation intermediate. Not only alkenes, but alkynes are also applicable to this carbofluorination reaction.

In this thesis, the utility of addition reactions and unimolecular fragment coupling was expanded through the development of the four above-described reactions. These reactions demonstrate that inert chemical bonds, such as C–H, C–Si, and C–F bonds can be used in addition reactions and UFC reactions when a suitable catalyst is available.

These findings and knowledge gained in this study will contribute to the further development of highly atom-economical catalytic reactions including the activation of chemical bonds that are now considered to be inert.

List of Publications

1. **Yoshida, T.**; Ohta, M.; Innocent, J.; Kato, T.; Tobisu, M.
   Catalytic Dimerization of Alkynes via C–H Bond Cleavage by a Platinum-Silylene Complex
   Organometallics, **2020**, *39*, 1678–1682.
2. **Yoshida T.**; Kodama, T.; Tobisu, M.
   Rhodium-Catalyzed Decarbonylation of Acylsilanes
   Asian J. Org. Chem. **2022**, e202200610.
3. **Yoshida, T.**; Ohta, M.; Emmei, T.; Kodama, T.; Tobisu, M.
   Zinc-Catalyzed Alkene Synthesis using Acylsilanes and Diazoesters via 1,2-Brook Rearrangement.
   Chem. Lett. in press. (DOI: 10.1246/cl.220476)
4. **Yoshida, T.**; Ohta, M.; Kodama, T.; Tobisu, M.
   Cationic Rhodium(I) tetrafluoroborate-Catalyzed Intramolecular Carbofluorination of Alkenes via the Activation of a Carbon–Fluorine Bond in Acyl Fluorides,
   Submitted.

Supplementary List of Publications

1. Sakurai, S.; **Yoshida, T.**; Tobisu, M. Iridium-catalyzed Decarbonylative Coupling of Acyl Fluorides with Arenes and Heteroarenes via C–H Activation. *Chem. Lett.* **2019**, *48*, 94.
2. Shimazumi, R.; Morita, K.; Yoshida, T.; Yasui, K.; Tobisu, M. Late-Stage Derivatization of Buflavine by Nickel-Catalyzed Direct Substitution of a Methoxy Group via C–O Bond Activation, *Synthesis*, **2021**, *53*, 3037–3044.
3. Yoshida, T.; Tobisu, M.
   Nickel-Catalyzed Cross Coupling via C–O and C–N Activation.
   Science of Synthesis: Base-Metal Catalysis, **2022**, *1,* 591–630.