Synthesis and Reactivity of

Highly Stabilized Cyclopentadienes

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ABSTRACT

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This dissertation focuses on the development of cyclopentadienes as an emerging class of compounds for use in catalysis. Previous work in the Lambert group had established pentacarboxycyclopentadienes (PCCPs) as a promising class of Brønsted acids capable of being used as catalysts in acid-promoted reactions. The ease of their synthesis distinguished them from the comparable BINOL-derived phosphoric acids, and their unique mode of enantioinduction created opportunities for their use in enantioselective reactions.

Initial efforts were focused on the synthesis of leading to the development of two complementary methods for their synthesis. Chapter 2 details the improvements made to the transesterification of penta(methoxycarbonyl)cyclopentadiene, which allowed for sterically encumbered alcohols to be used. Further, a new method for accessing the penta-acyl chloride intermediate was developed, leading to the ability for a wide array of electron-deficient PCCPs to be synthesized.

The second half of the dissertation examines the use of electrophilic silicon reagents and their use as Lewis acids. Given our ability to access highly electron-deficient cyclopentadienes, the silyl cyclopentadienes were targeted as potential Lewis acids. Chapter 4 details the synthesis of these species, and their characterization. Having established a convenient route to silyl mono(carboxy)tetracyanocyclopentadienides, we examined their use as catalysts in halide abstraction reactions. Benzylic bromides could be activated and subsequently allylated, or arylated with a nuclephilic arene using allyltrimethylsilane as a sacrificial silyl source.

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List of Abbreviations

1D	one dimensional
2,6-diClPy	2,6-dichloropyridine
Ac	acetyl
ACDC	asymmetric counterion directed catalysis
Ar	aryl
B	generic base
BCF	tris(pentafluorophenyl)borane
BINOL	1,1'-bi-2-naphthol
Bn	benzyl
Boc	*t*-butoxycarbonyl
Bz	benzoyl
cat.	catalyst
Cp	cyclopentadiene
Cy	cyclohexyl
DCE	1,2-dichloroethane
DCM	dichloromethane
DMA	dimethylacetamide
DMAP	4-(dimethylamino)pyridine
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DTBMP	2,6-dimethyl-4-*t*-butylpyridine
d.r.	diastereomeric ratio

e.e.	enantiomeric excess
e.r.	enantiomeric ratio
Et	ethyl
EtOAc	ethyl acetate
EWG	electron withdrawing group
FLP	frustrated Lewis pair
HFIP	1,1,1,3,3,3-hexafluoroisopropanol
HMBC	heteronuclear multiple-bond correlation spectroscopy
HOMO	highest occupied molecular orbital
iPr	*i*-propyl
IR	infrared
LA	Lewis acid
LUMO	lowest unoccupied molecular orbital
Me	methyl
MeCN	acetonitrile
MOM	methoxymethyl
MS	mass spectrometry
MsOH	methanesulfonic acid
NMI	*N*-methylimidazole
NMP	*N*-methylpyrrolidone
NMR	nuclear magnetic resonance
P	polymer chain
PCCP	pentacarboxycyclopentadiene

Ph	phenyl
Pin	pinacol
PMB	*p*-methoxybenzyl
PMHS	polymethylhydrosiloxane
Pr	propyl
PS	polystyrene
quant.	quantitative (yield)
SKA	silyl ketene acetal
SPINOL	1,1′-spirobiindane-7,7′-diol
TBS	*t*-butyldimethylsilyl
t-Bu	*t*-butyl
Tf	triflyl
TFA	2,2,2-trifluoroacetic acid
TFE	2,2,2-trifluoroethanol
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
TMP	2,2,6,6-tetramethylpiperidine
TMS	trimethylsilyl
tol	toluene
TON	turnover number
TPFPB	tetrakis(perfluorophenyl)borate
Ts	*p*-toluenesulfonyl

TTP   1,1,3,3-tetratriflylpropene

VAPOL   3,3'-biphenanthrol

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Chapter 1: Organic Brønsted Acids

The focus of this thesis is the development of a specific class of organic molecules that can function as Brønsted acids (and in later chapters, anions for Lewis acidic silicon species). To contextualize this, a brief history of acids will be presented, with an eye towards organic molecules and how various scientists tackled generating highly acidic species. Particular attention will be paid to molecules where the acidic functionality is most directly generated by organic functional groups.

Acid-Base Theory

The theory of acids and bases is one of the bedrocks of chemical education, and one of the first concepts one learns in school. The idea that chemical reactions occur when acids and bases are mixed is illustrated to kids through the effervescence of acetic acid and bicarbonate. All of this is situated about the proton, and its transfer between species. The proton, being the naked, positively charged hydrogen nucleus, represents one of the smallest quanta of chemical reactivity (redox chemistry, involving the transfer of electrons, along with energy-transfer phenomena being competitors).

Acids were well-known in the ancient world. Probably the first was acetic acid derived from fermentation, which takes center stage in Cleopatra's most expensive meal, where she reportedly dissolved a pearl in vinegar to win a bet with Marc Anthony. Metal sulfates and sulfuric acid were recognized as vitriols, giving rise to the modern word vitriolic.

Though it is so fundamental to modern chemical analysis, acid-base theories only began to take their modern form some two hundred years ago. Many ideas were circulating in the

1800's, the most powerful of which was Arrhenius' theory based on dissociation of acids in aqueous solution. The key contribution of Brønsted and Lowry was to notice that water, hydroxide ion and hydronium ion were not privileged species, but were rather only particularly important in the context of aqueous solutions. The true unifying characteristic of acids is their ability to lose protons (H^+), and, in water, they generate a hydronium ion.

The proceeding forms the basis of Brønsted-acid catalysis, with the stronger acid catalyst protonating the weaker acid substrate, activating it towards the desired reaction. Probably the most salient concept to arise from the formalism of Brønsted acid theory is the relation between thermodynamic stability and Brønsted acidity; in order to make a stronger acid, one can think of creating a more stable conjugate base. In the case of neutral Brønsted acids, the conjugate base is an anion, and so one may think of ways of stabilizing the negative charge. The better this charge is stabilized, through induction or resonance, etc., the stronger the acid should be.

Measures of Aciditiy

Throughout this thesis, we will be discussing the acidity of species, and ultimately comparing diverse kinds of acids against one another. To do perform these comparisons quantitatively, the chemical community has developed measurements for quantitatively measuring acidity. While a comprehensive discussion of the various techniques used to measure and calculate these is beyond the scope of this work, it is instructive to note the common methods that are referenced in this thesis.

pK_a is fundamentally tied to solvent (or lack thereof in the case of gas phase), with solvation effects having a large impact on the acidity of species, having an influence on self-association of the acidic species and the formation of ion pairs. pK_a is usually measured by

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looking at the equilibrium constant between the desired acid and a known acid. Where the equilibrium lies can be used to calculate the pK_a of the unknown acid. For some common acids, a direct measurement of the ionized and non-ionized form of the analyte in solution (e.g. spectroscopically or electrochemically) can yield the pK_a. For highly acidic species, and on the other side of the coin, highly basic species, the ionization under standard conditions is too low to be measured directly, and alternative methods must be used.

An early method for determining the strengths of strong acids was to establish an acidity function for concentrated acid solutions. These acidity functions take into account the changing activity of the solution with increasing concentration of the acid. Starting at low H_2SO_4 concentrations and using a weakly acidic indicator, the concentration of H_2SO_4 is increased until the indicator is mostly protonated. Then a second, more acidic indicator is used, and the percent ionization is compared, tying the relative pK_a of the two indicators together. This process is repeated, with more acidic indicators being used for higher concentrations of H_2SO_4, creating an overlapping scale. With a measured acidity function, a compound's pK_a can be determined by dissolving a compound in a concentrated H_2SO_4 solution and determining its ionization. For example, tricyanomethane is approximately 50% protonated in 60% H_2SO_4, corresponding to a pK_a of -5.

While there are an enormous number of measured aqueous acidities, measurement of acidities in organic solvents is comparatively understudied. Bordwell and others have diligently collected over 2000 values for pK_a's in DMSO.[1] Leito and Koppel[2] recently have pursued the creation of a self-consistent pK_a scale for organic solvents, mainly MeCN and DCE. By titrating mixtures of compounds with a strong acid or base, a pK_a difference can be directly measured by the relative abundance of each compound's protonation state, which they do using

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spectrophotometry. The scale is then composed of many difference measurements establishing a relative order of acidities. The scales are anchored by a reference compound, picric acid, that has a known pK_a of 11.0 in MeCN. Since picric acid has no absolute pKa measurement in DCE, the scale is purely relative, though Leito has shown the DCE and MeCN pK_as to be tightly correlated, allowing them to predict MeCN pKa's from their DCE measurements.
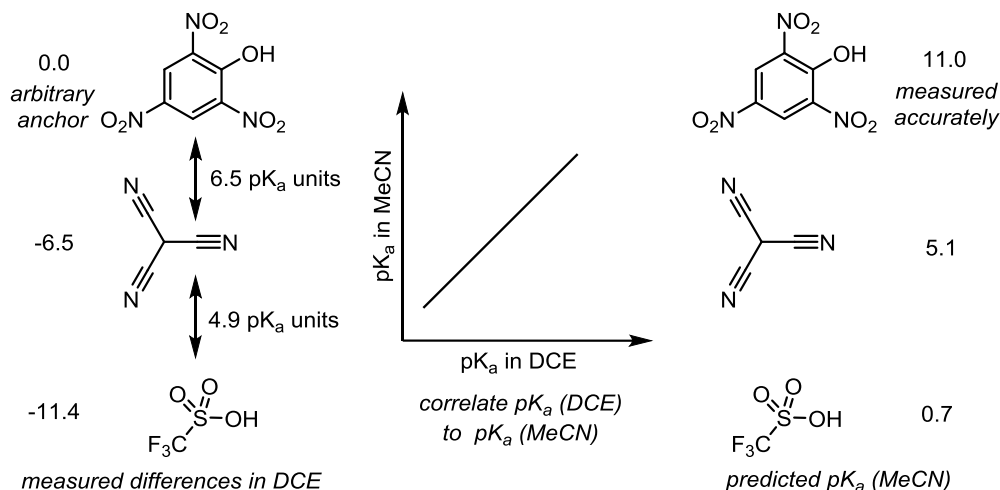
Figure 1: Self-consistent DCE scale leads to predicted MeCN pK_a's.

Phosphoric Acids and Derivatives

It would be hard to argue against the success of the BINOL phosphoric acids (and their various derivatives) in enabling synthetic chemistry generally, and catalysis specifically. The axially-chiral derivatives are probably the most widely used organic Brønsted acids in catalysis. Rueping's "Field Guide" to enantioselective catalysis[3] is a tome with >500 references, a testament to their the widespread adoption across the chemical community. Akiyama was the first to report an enantioselective reaction using a BINOL phosphoric acid.[4] The addition of a silyl ketene acetal to a (2-hydroxyphenyl)imine proceeds with 94.5:5.5 e.r. and 98% yield. Since this seminal report in 2004, myriad alterations of the binaphthyl scaffold have been reported, and

new scaffolds have been designed, such as the SPINOL **2** and VAPOL **3** catalysts (Figure 2, bottom).
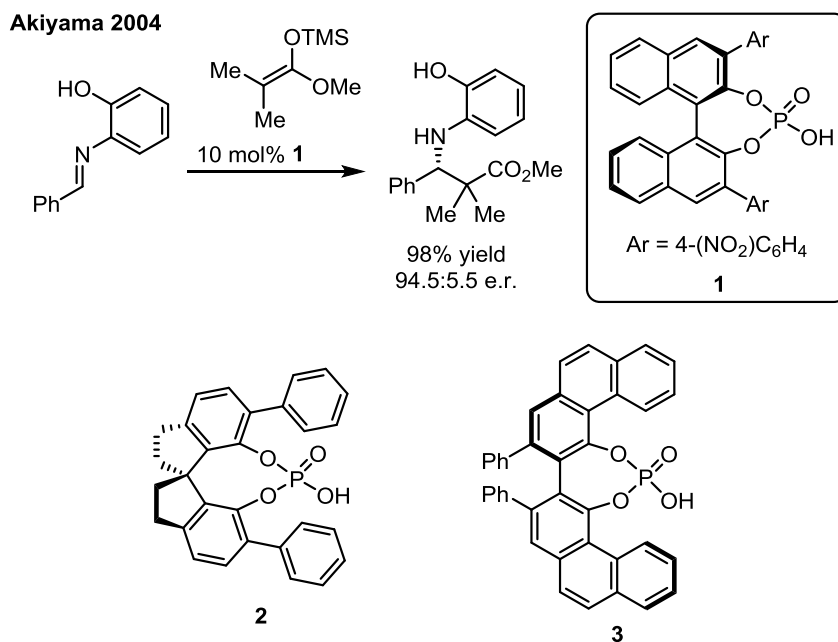
Figure 2: (top) Akiyama's original report of a phosphoric acid catalyzed reaction. **(bottom)** More recently reported SPINOL and VAPOL phosphoric acids.

Additionally, efforts have gone into enhancing the acidic functionality of these acids. Yamamoto developed the *N*-trifyl phosphoramides as much more acidic derivatives,[5] following Koppel's work showing that a =O to =NTf substitution should lead to a dramatic increase in acidity, in this case ~7 pK_a units (MeCN).[6] Yamamoto's first demonstration showed they could catalyze a Diels–Alder for which the phosphoric acid was completely ineffective. More recently, List has reported imidodiphosphoric acids, so called "confined Brønsted acids," that tie two binaphthyl units together around the extremely acidic functionality, creating a sterically demanding binding site (Figure 3).[7] These catalysts have shown impressive stereoselectivity in challenging reactions; for instance, in the formation of spiroketals, catalyst **4** provides the non-thermodynamic ketal in 5:1 d.r., when the thermodynamic isomer is favored 124:1.
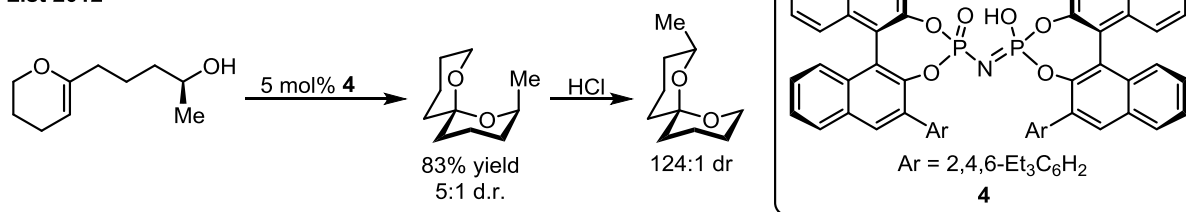
Figure 3: Diastereoselective spiroketalization catalyzed by imidodiphosphoric acid *4*.

While these phosphoric acids have proven themselves to be extremely versatile catalysts, their synthesis requires many steps and can be tedious. Figure 4 outlines a typical synthesis of a BINOL-phosphoric acid catalyst. Four steps are required to introduce the 3,3'-disubstitution that is crucial for the formation of the C_2-symmetric chiral pocket, including protection of the phenolic functionality and subsequent deprotection. The synthesis makes accessing large libraries of these acids tedious, even when starting from the enantioenriched BINOL as the chiral pool. The other axially chiral backbones have similar syntheses, along with the concomitant problems.
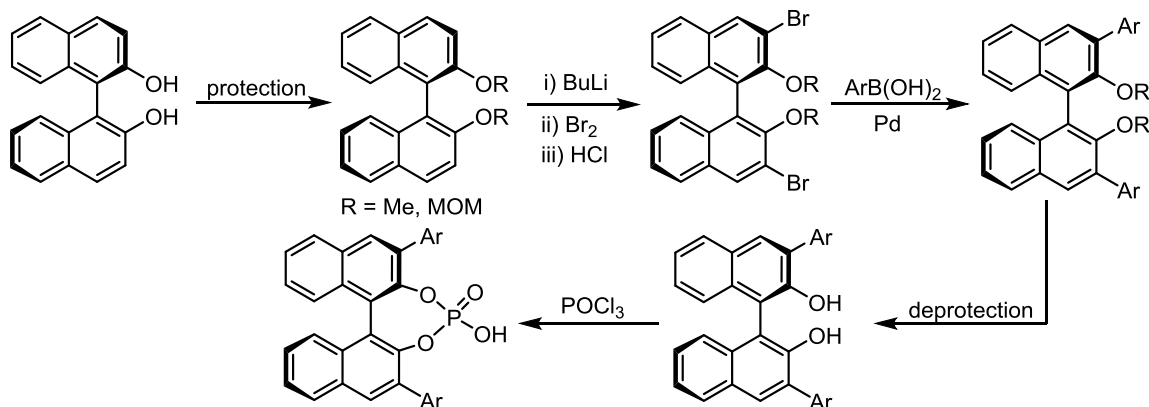
Figure 4: Schematic of a typical BINOL-phosphoric acid synthesis.

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Sulfonic Acids and Derivatives

Sulfonic acids are also well-utilized in organic chemistry. *p*-Toluenesulfonic acid (or the sometimes more convenient liquid methanesulfonic acid) are often used as general-purpose, organic-soluble acids. The highly acidic trifluoromethanesulfonic acid (TfOH) and bis(trifluoromethane)sulfinimide (HNTf$_2$) are potent Brønsted acids and can be used to promote a variety of transformations. They can be used to activate relatively unreactive substrates. An example is cationic polycyclizations, where the acids protonate olefins to initiate the reaction. A unique example is the cyclization of tosyl ynamines, which proceed through a ketiminium intermediate, reported by Evano (Figure 5).[8]
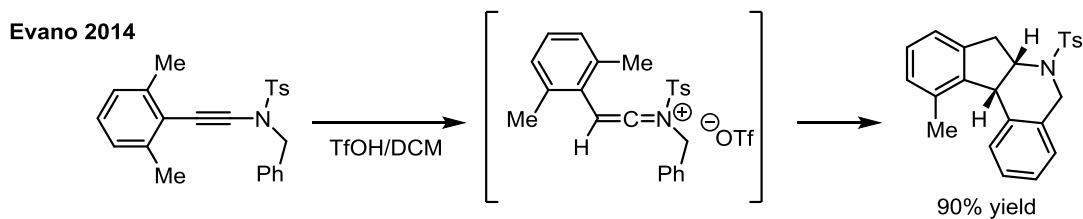
Figure 5: TfOH-promoted cyclization of ynamides.

Similar to the phosphoric acids, chiral sulfonic acids and sulfinimides have been synthesized and used as enantioselective catalysts. The basic structure of these catalysts is illustrated in Figure 6. These are significantly more acidic than their phosphorus counterparts, enabling them to activate unreactive substrates. Yamamoto reported a direct Mukaiyama aldol reaction with aldehydes; the disulfonimide catalyst gives nearly quantitative yield of the product but the corresponding phosphoric acid shows no reactivity (Figure 6, bottom).
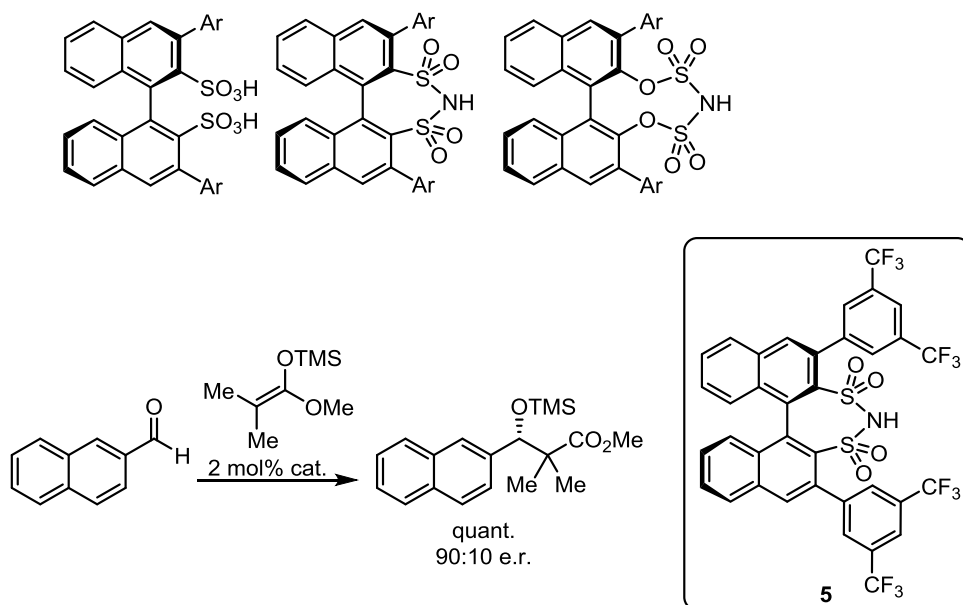
Figure 6: Chiral sulfonic acid derivatives and a Mukaiyama aldol reaction catalyzed by disulfonimide *5*.

A Survey of Organic Acids

Alcohols

In general, alcohols are only weakly acidic. Even extensively fluorinated alcohols such as hexafluoroisopropanol (HFIP) and nonafluoro-*t*-butanol are only slightly more acidic than acetic acid. HFIP is a strong hydrogen bond donor, and a very weak nucleophile, making it a good solvent for cationic reaction. For instance, the direct cyclization of **6** can be achieved under mild conditions using an HFIP/H$_2$O mixed solvent system.[9]
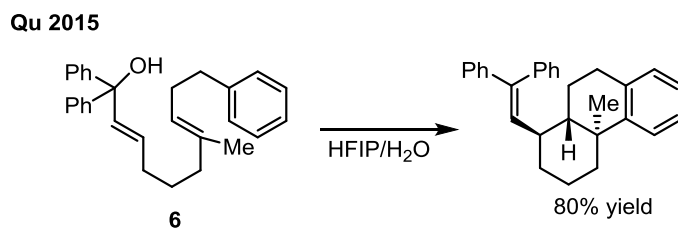
Figure 7: HFIP-promoted cationic cyclization of *6*.

The Kass group, inspired by the hydrogen bonding networks of enzymes, investigated polyols that would have a central hydroxyl group flanked by supporting hydrogen bonds. Upon

deprotonation, the oxyanion would be stabilized by the hydrogen bond network. In protic solvents, the solvent molecules themselves can arrange to coordinate to the oxyanion, negating the effect of the additional hydroxyl groups in Kass' molecules. On the other hand, in non-polar solvents the supporting hydrogen bond framework should drastically increase the acidity of the central O-H. Indeed, they found that **8** was 14 orders of magnitude more acidic than propanol (pK_a of 16.1 vs 30) in DMSO, and calculations extrapolated from their studies suggest that perfluorinated derivatives should be as acidic as HCl.[10] **8** has a pKa only slightly below phenol (18 in DMSO), though in the gas phase it is deprotonated by Br$^-$,[11] indicating it is a stronger acid than HBr. Further investigations found that perfluoropinacol **9**, a much simpler diol, has an impressively low pKa of 4.8 (DMSO),[12] comparable to 2,4-dinitrophenol. A related triol **10**, though possessing a slightly higher pKa, promoted the addition of *N*-methylindole to nitrostyrene more effectively.
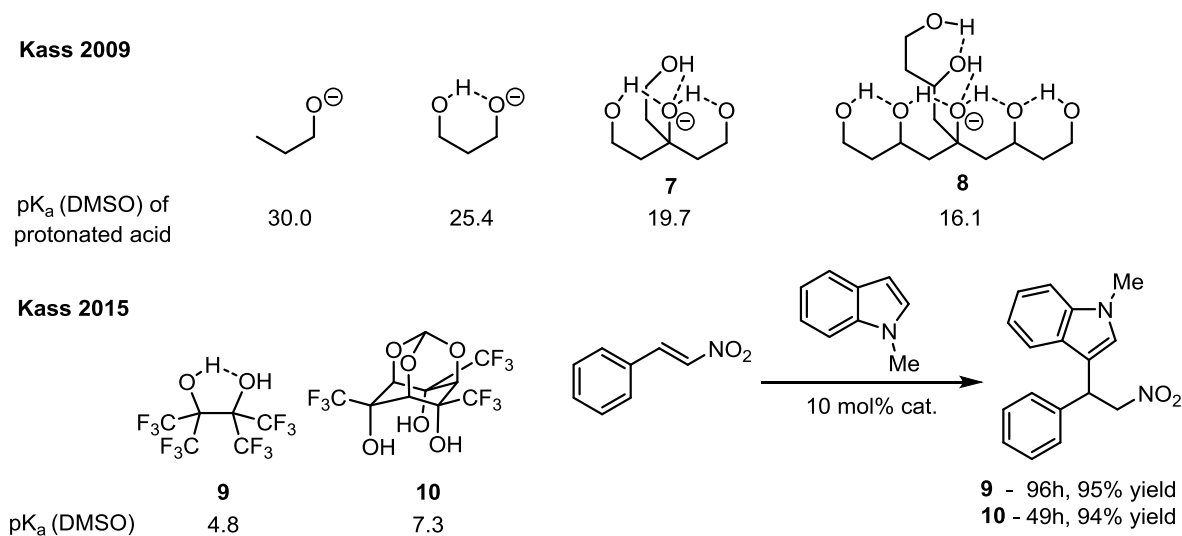
Figure 8: Strongly acidic alcohols stabilized by intramolecular hydrogen bond networks.

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Carboxylic acids

While intrinsically more acidic than alcohols, carboxylic acids are still comparably weak acids. As mentioned in a recent review by Seidel,[13] compared to the BINOL phosphoric acids, carboxylic acids have much less representation in organocatalysis research. This is likely a reflection of their lesser acidity, though reaction design often requires matching the acidity of the catalyst to substrate, offering a niche for these less acidic catalysts.

One of the most ubiquitous acids used to promote reactions is trifluoroacetic acid (TFA),[14] which is 10 orders of magnitude more acidic than acetic acid in MeCN, and approaches the acidity of HCl. The high level of acidity combined with its high volatility make it an attractive acid to use for deprotection of acid-labile groups such as Boc or MOM.

Several groups have approached catalyst design with the focus of increasing the acidity of the carboxylic functionality. Maruoka pioneered dicarboxylic acids built around the BINOL scaffold,[15] taking advantage of the well known chiral pocket to effect enantioselective transformations. The ability of the two carboxylic acids to form an intramolecular hydrogen bond drastically increases the acidity to only just above the BINOL phosphoric acids (~4 vs ~3 in DMSO).[16] Their first report described a Mannich reaction using diazoacetates as the nucleophile, giving the adducts in high yield and high e.r. A small change in the diazo nucleophile was found to drastically change the reaction outcome, giving the aziridine instead.[17] The carboxylic acid also displays unique selectivity, for instance in a three-component coupling reaction where the comparable phosphoric acid gave less selectivity (Figure 9, bottom).[18]
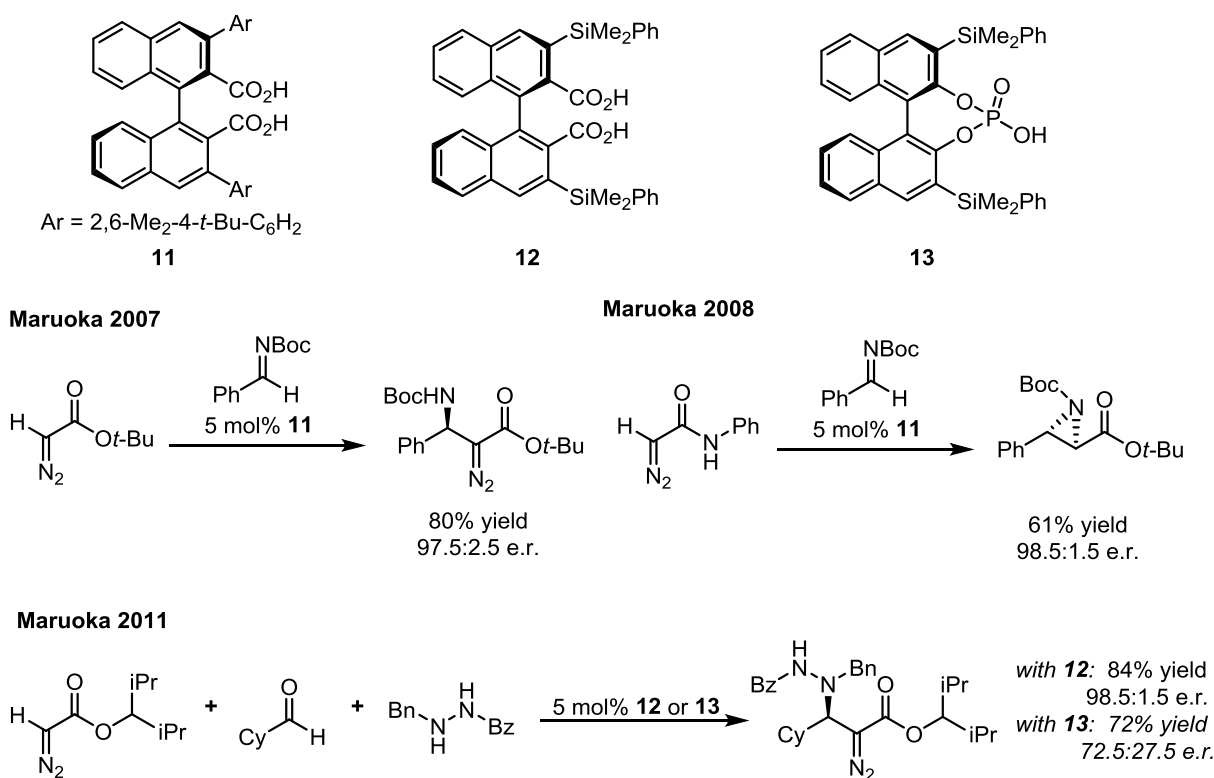
Figure 9: Binaphthyl dicarboxylic acid catalysts.

Yamamoto's concept[19] of increased Brønsted acidity using Lewis acid activation has also been applied. Mattson showed that an *ortho*-BPin group could increase the catalytic activity of benzoic acid in the addition of indole to nitroalkenes.[20] Cheng later measured the pKa of **14** to be 1.65 (DMSO), the same as methanesulfonic acid, showing the large acidity enhancement afforded by the intramolecular coordination of the carbonyl group to the boron atom. Maruoka furthered this concept by utilizing chiral diols to produce a chiral complex, applying this to their aziridination reaction to good effect.[21] The catalyst can be prepared *in situ* by mixing the boronic acid **15** and the diol **16**. This procedure allows for efficient screening of chiral diols in their optimization of the catalyst scaffold.

Mattson 2012

acidification by ortho-BPin

Maruoka 2013

Ar = 2-biphenyl
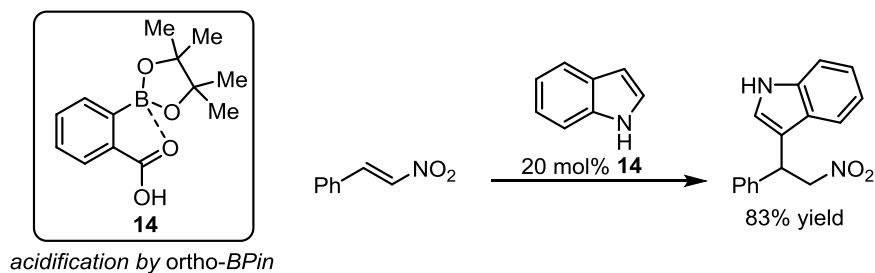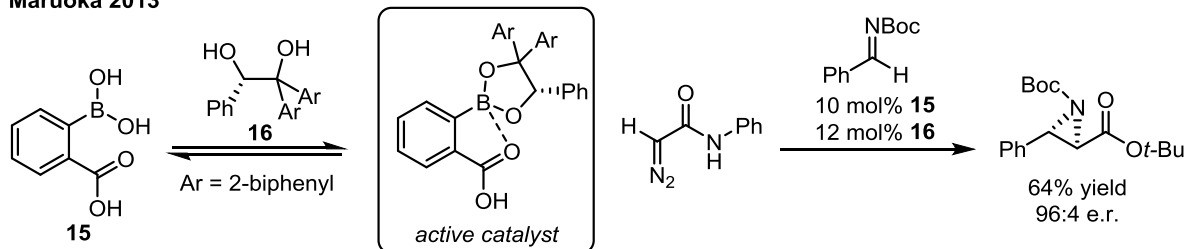
active catalyst

Figure 10: Boron-activated carboxylic acid catalysts.

Intramolecular hydrogen-bonding can also be used to activate carboxylic acids. Guo and Li have investigated carboxylic acids supported by two *ortho* hydrogen bond donors as lactone polymerization catalysts (Figure 11).[22] Another approach used by Seidel is to tether a thiourea to the carboxylic acid, allowing the carboxylate anion to be stabilized via intramolecular hydrogen bonding. Chiral catalysts developed in their group have been used to promote a number of reactions. Figure 12 depicts an enantioselective Pictet-Spengler reaction, giving the β-carboline products in high yield and high e.r.

Guo, Li 2016/2017
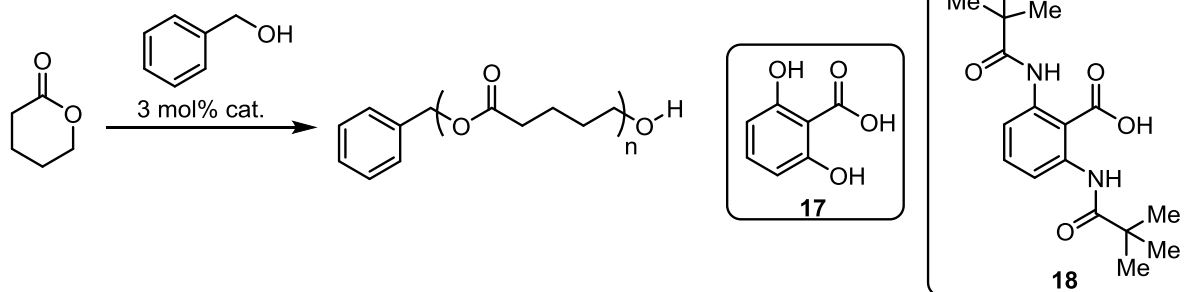
Figure 11: Activated carboxylic acid polymerization catalysts.

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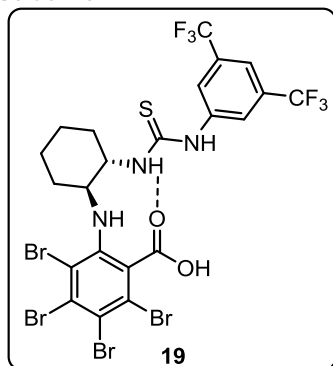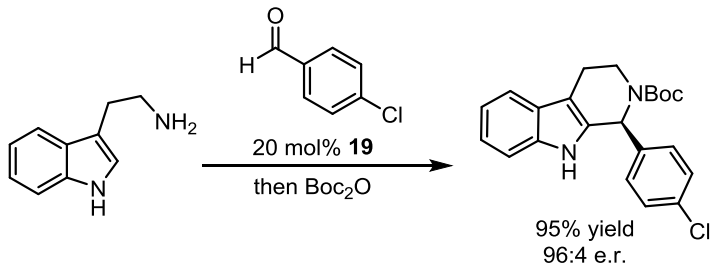
Figure 12: Enantioselective Pictet–Spengler reaction catalyzed by thiourea-activated carboxylic acid *19*.

C-H acids

Just like any other species, the substitution of the C–H bonds in methane with electron-withdrawing groups stabilizes the conjugate carbanion, leading to a much more acidic C-H bond. Methide species with three strongly acidifying groups can be extremely strong acids. For example, trinitromethane is nearly as acidic as HCl in water, with a pKa of ca. 0,[23] and the compound was described as early as 1899 by Hantszch.[24] Unsurprisingly, it also tends to form explosive salts. Research with trinitromethane has largely focused on its use as a feedstock for energetic materials as a convenient way to introduce -$C(NO_2)_3$ (Figure 13).[25]
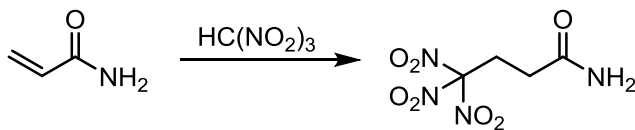
Figure 13: Conjugate addition of trinitromethane.

Tricyanomethane was also reported in 1899 by Hantzsch,[26] and salts of the methide anion have been studied extensively. The acid itself proved to be difficult to isolate in the pure form, or even as an anhydrous solution, limiting its usefulness as a Brønsted acid. It was only in 2015 that Kornath reported the characterization of the acid in anhydrous HF at -40 °C.[27] Initially, the

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compound was reported to be unstable above this temperature, but later work showed the inability to detect the proton resonance was due to extreme broadening of the signal.[28] The compound could conceivably exist as either the *C*- or *N*-protonated tautomer, and calculations suggested that protonation at the carbon would be thermodynamically preferred.[29] The vibrational specta obtained by Kronath agreed with the molecule being C_{3v} symmetric, confirming the protonation of central carbon. Upon repeated sublimation of an acidic water/ether solution, single crystals of the acid formed that were stable at room temperature, in stark contrast to the "anhydrous" solutions of the pure acid. The pK_a's of the nitro- and cyanomethanes have an interesting trend; while acetonitrile is less acidic than nitromethane, tricyanomethane is more acidic than trinitromethane, with Leito measuring a pKa of 5.1 in MeCN, about that of HBr (5.5).
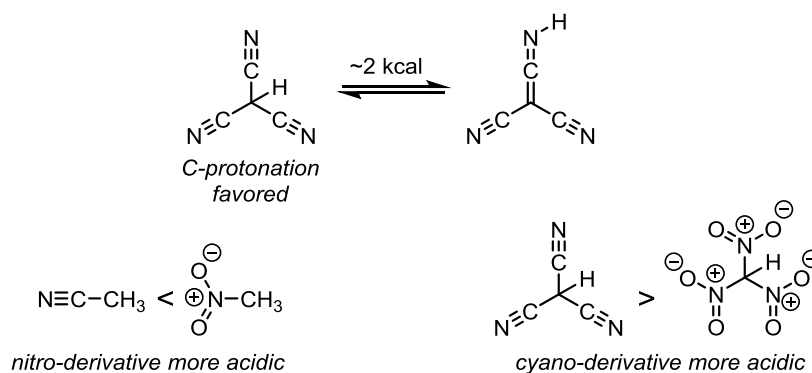
Figure 14: Trinitromethane and tricyanomethane are rarely-used Brønsted acids.

By far the most studied class of acidic methanes is the polysulfonylated methanes, as exemplified by Tf_2CH_2 (**20**) and Tf_3CH (**21**). **20** has a high acidity of -3.7 in MeCN. Both **20**[30] and **21**[31] can be synthesized by addition of repeated sulfonylation of MeMgBr with F_3CSO_2F. While these procedures are straightforward and yields are reasonable, the preparations suffer from CF_3SO_2F being a gas, making its use somewhat impractical. Waller reported a modified synthesis which uses triflic anhydride,[32] which Yamamoto later extended to synthesize other triflyl-substituted C-H acids, including a recyclable solid phase catalyst.[33] 1,1,3,3-

tetrakis(triflyl)propane (**22**), prepared by the condensation of formaldehyde, was found by Taguchi to be in equilibrium with bis(triflyl)ethene (**23**) and **20**.[34] Using this equilibrium to generate the reactive olefin *in situ*, nucleophilic addition of electron-rich arenes furnished the corresponding bis(triflyl)methane derivative. Variation of the arene nucleophile allows for the preparation of acids with multiple Tf$_2$CH- groups or zwitterionic ammonium derivatives.[35]

Seppelt 1987
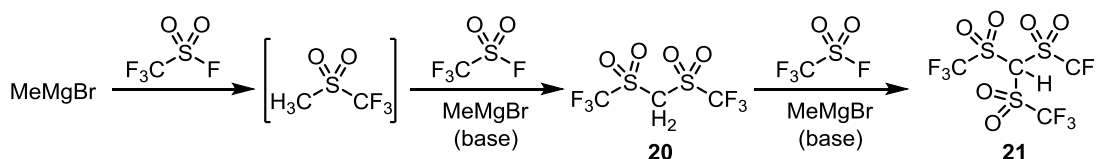
Waller 1999
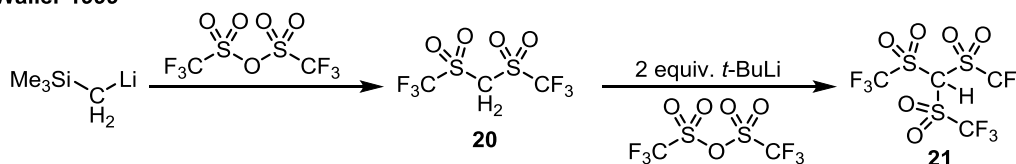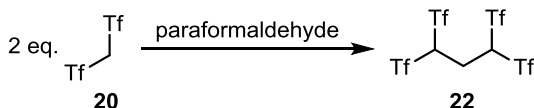
Barber, Koshar 1977   **Taguchi 2011**
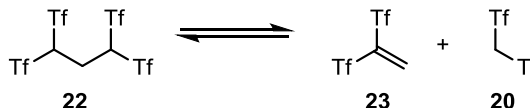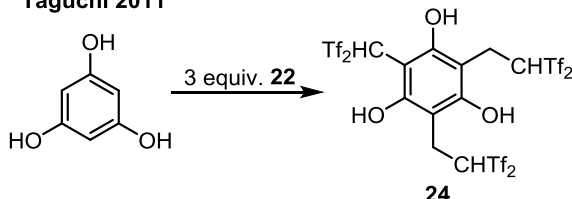
Taguchi 2011   **Taguchi 2013**
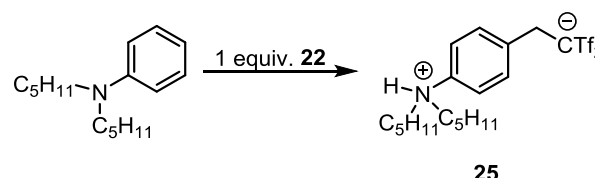
Figure 15: Synthetic methods to access triflylated C–H acids.

Early studies found **20** and **21** to be highly active and robust polymerization catalysts for epoxy resins. They also have served as ligands to create Lewis acidic metal salts, akin to metal triflates with greater Lewis acidity.

Yamamoto pioneered the use of these C-H acids as synthetically-useful acid catalysts, and their seminal publication showed the effectiveness of Tf$_3$CH for debenzylation of protected

alcohols, acids and amides.[36] They also developed a resin-supported solid phase catalyst **26** and demonstrated its utility across a range of acid-catalyzed reaction.[37] Matsumoto later demonstrated the unique effectiveness of the C-H acids for promoting sequential Mukaiyama-Michael reactions.[38]

Yamamoto 2000
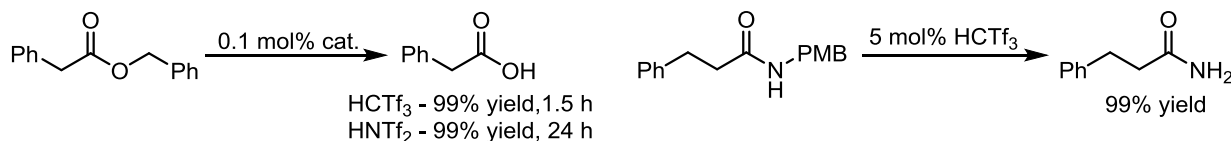
Yamamoto 2001
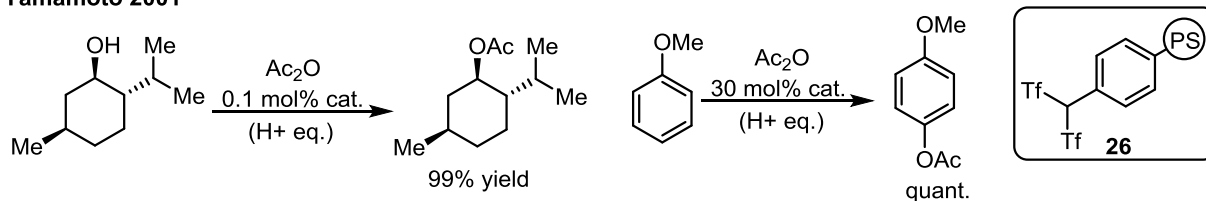
Matsumoto 2016
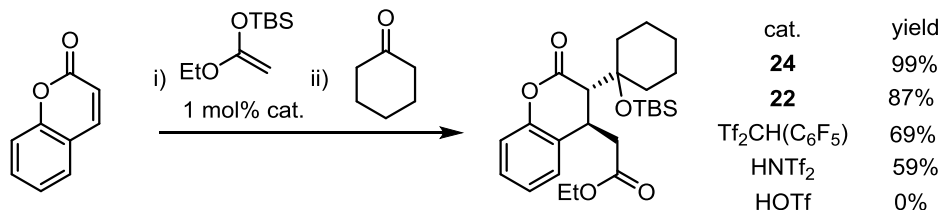
Figure 16: Catalysis using triflylated C–H acids.

Yamamoto has explored applications of these C–H acids in enantioselective synthesis. $Tf_2CHC_6F_5$ can be used to activate chiral oxazaborolidines via protonation of the nitrogen, drastically increasing the Lewis acidity of the boron atom.[37] These Brønsted-acid-enhanced Lewis acids can effect highly enantioselective Diels–Alder reactions between methacrylate and cyclopentadienes, and Yamamoto used this as a key step in their platensimycin synthesis.[39b] - Yamamoto also developed chiral BINOL-derived catalysts that were used in a Mukaiyama–Mannich reaction; the reactivity was high, although their highest reported e.r. was 88.5:11.5.

Yamamoto 2007

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Brønsted acid enhanced Lewis acidity

73% yield
99.5:0.5 e.r.

Yamamoto 2006

10 mol% **28**
1 equiv. ArOH

99% yield
88.5:11.5 e.r.

ArOH

28
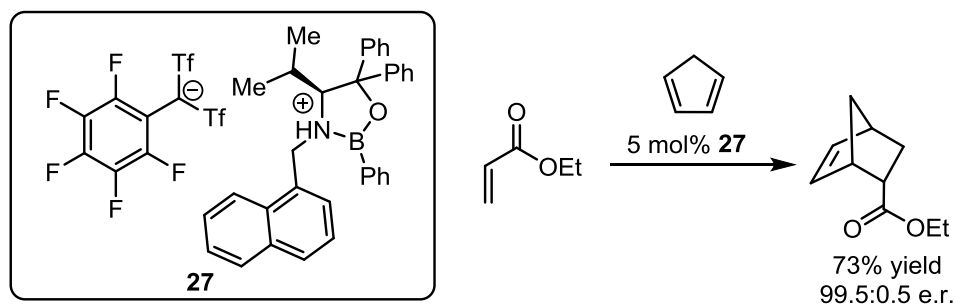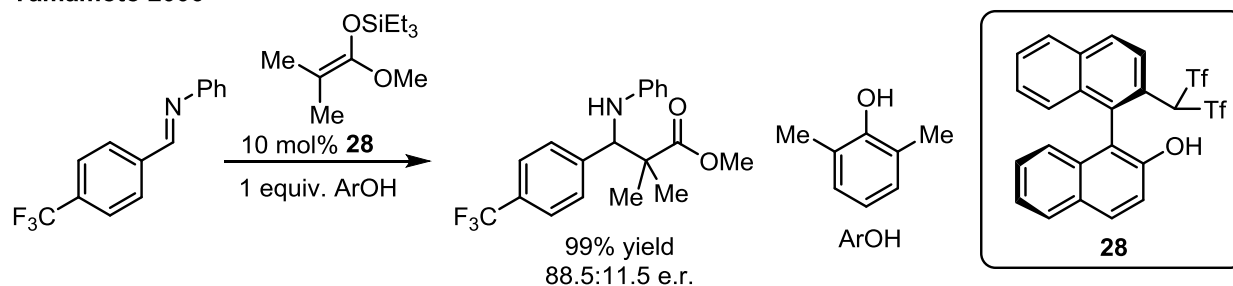
Figure 17: Enantioselective Diels–Alder and Mannich reactions using C–H acids.

Carbon is seemingly limited by its ability to make four bonds, and thus only a maximum of three stabilizing groups can be incorporated. A way around this problem is to create vinylogous acids with the anion spread across three carbon atoms and their five substituents. Cyanocarbons **29**[40] and **30**[41] were early such derivatives, being most often used for the formation of charge-transfer salts or coordination polymers. Though they have rarely been used as Brønsted acids, these polycyanopropenes are predicted to be extremely acidic in non-polar solvents,[42]

17 of page

17

Figure 18: Representative examples of tetracyanopropene derivatives and their syntheses.

List recently has pursued triflylpropenes as Brønsted acid catalysts. Tetrakis(triflyl)propene (TTP) **31** is straightforwardly synthesized from Tf_2CH_2 and the group was even able to obtain a crystal structure of the acid in its protonated state.[43] Reactivity comparisons to Tf_2NH or Tf_3CH show TTP to be a more active catalyst in a Hosomi–Sakurai allylation and a Friedel–Crafts acylation of chlorobenzene. List also developed axially chiral catalysts synthesized using the same methodology as TTP.[44] The triflylpropene catalyst **32** shows remarkably enhanced acidity and reactivity compared to the phosphoric acids or sulfonimides. The highly-enantioselective Diels–Alder reaction is catalyzed by the silyl species of the catalyst (See Chapter 3, pg 94)

Figure 19: A comparison study of acids with TTP, and List's axially-chiral C–H acid *32*.

<u>Conclusion</u>

Strong organic Brønsted acids have the potential to make wide-reaching impacts in chemistry. Their ability to promote reactions extends well beyond synthetic chemistry. Current acid catalysts show immense utility, though their syntheses point to a weakness that offers an avenue to be improved upon. One can note the heavy reliance on binaphthyl backbones to create chiral catalysts.

Carbon-based acids have been known for over a century, with many of the significant research advances coming in the last few decades. Even though the triflylmethides have demonstrated reactivity in a number of reactions, they remain underutilized in the broader

chemical community. While they are commercially available, they are quite expensive compared to triflic acid or triflimide. Furthermore, many of these species are difficult to derivatize due to their acidifying groups lacking any easy way to add functionality or a chiral environment. These drawbacks place significant limits to their potential uses. Thus, there is still a need for new frameworks to create strongly acid Brønsted acids, ideally that are easy to synthesize and are able to accommodate a large degree of modularity. With that as our goal, we sought to develop a platform centered around the cyclopentadiene scaffold. In the next chapter, we will examine this framework, and describe our efforts to realize these goals.

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Chapter 2: Stable Cyclopentadienes

Having explored the landscape of Brønsted acids, I will turn towards cyclopentadienes as a peculiar class of acidic compounds. The parent, unsubstituted cyclopentadiene is remarkably acidic for a hydrocarbon, with a pKa of 18 (DMSO), over 30 orders of magnitude more acidic than cyclopentane! This incredible amount of acidification of the C–H bond in cyclopentadiene reflects the great stability of the cyclopentadienide anion, its conjugate base. The aromatic π-system of the cyclopentadienide anion has 6 π electrons, corresponding to a Hückel aromatic system. The anion thus has a closed shell and the negative charge is delocalized around the ring giving it the high levels of stability observed. With additional substitution, even lower pKa's can be achieved, as in the case of pentacarboxycyclopentadienes (PCCPs), which will be the focus of this chapter.

Figure 1: The high acidity of cyclopentadienes.
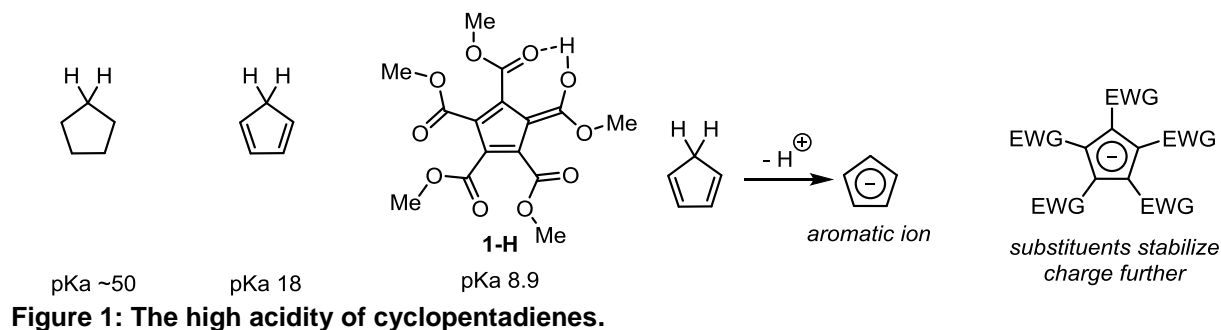
While cyclopentadiene is extremely acidic for a hydrocarbon, its pK_a is roughly that of phenol (18 in DMSO). Further, the acidic C–H bond is comparatively slow to undergo deprotonation, a common feature among carbon acids. This peculiar behavior - sluggish proton transfer - is a kinetic effect not tied to the acidity of the C–H bond. Deprotonation of carbon acids leads to anions with a vastly different electronic configuration; that is to say, the electron density is shifted in space upon deprotonation. Carbon is not a very electronegative element, and thus the stabilizing substitutents take up much of the negative charge. This "reorganization"

penalty is often invoked as leading to the slow kinetics of deprotonation. As with the species discussed in the previous chapter, its acidity can be increased via substitution of the ring with electron-withdrawing groups. In the main, cyano and carboxyl groups have been the most widely investigated.

Cyano-Substituted Cyclopentadienes

The polycyanated cyclopentadienes were the earliest examples of stabilized cyclopentadienes. The pentacyano derivative was first synthesized by Webster in 1965.[1] The synthesis begins with cyclization of the cyanated butadienide with acid, followed by decarboxylation to give the aminocyclopentadiene **2-Na**. The amine is then diazotized to **3** and the resulting zwitterionic diazo compound can then be reacted with copper cyanide to give the pentacyano-cyclopentadiene **4-Na**. Alternatively, **3** can be reduced with copper powder to give the less acidic tetracyanocyclopentadienide salt. Later work published in 1980 established tetracyanodithiin **5** as a more practicable starting material, itself being prepared straightforwardly from carbon disulfide and sodium cyanide.[2] Addition of methyl cyanoacetate gave **4-Na** via an interesting mechanism, which was first suggested due to the requirement for 2 equivalents of **5**. After the initial addition, a second molecule of **5** is needed to activate the liberated thiolate and allow for ring closure. This intermediate can then undergo decarboxylation and sulfur extrusion to provide the anion. Webster also showed that variation of the nucleophile provided access to other tetracyano anions, including (methoxycarbonyl)tetracyanocyclopentadiene and nitro-tetracyanocyclopentadiene. Mori improved upon this synthesis by incorporating a leaving group into the nucleophile, obviating the need for the second equivalent of **5** (Figure 2, bottom).[3] In addition, they found that use of tetracyanothiophene **6** was an even better electrophile for the

reaction. The reaction is quite general, with easily prepared tosylates offering a quick entry into many tetracyano derivatives, for instance the mono(carboxy)tetracyano **7-Na**.
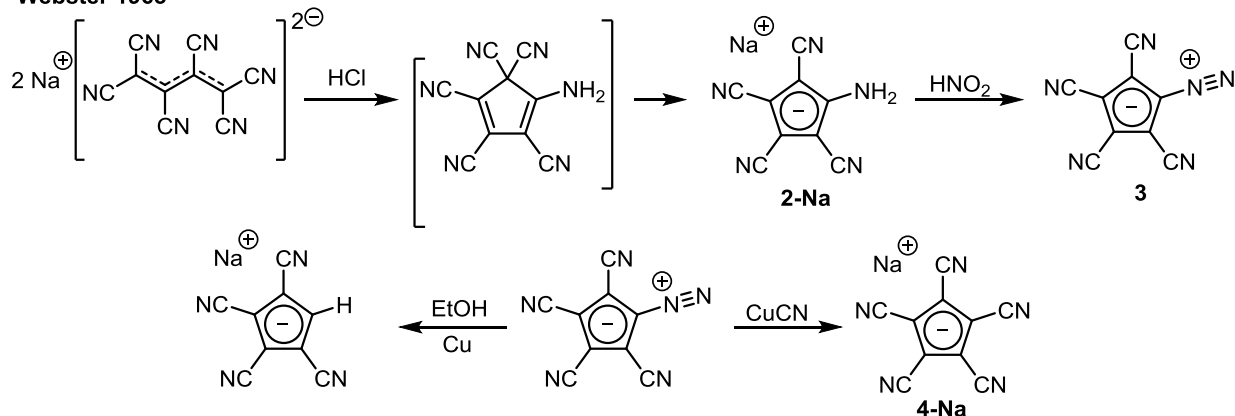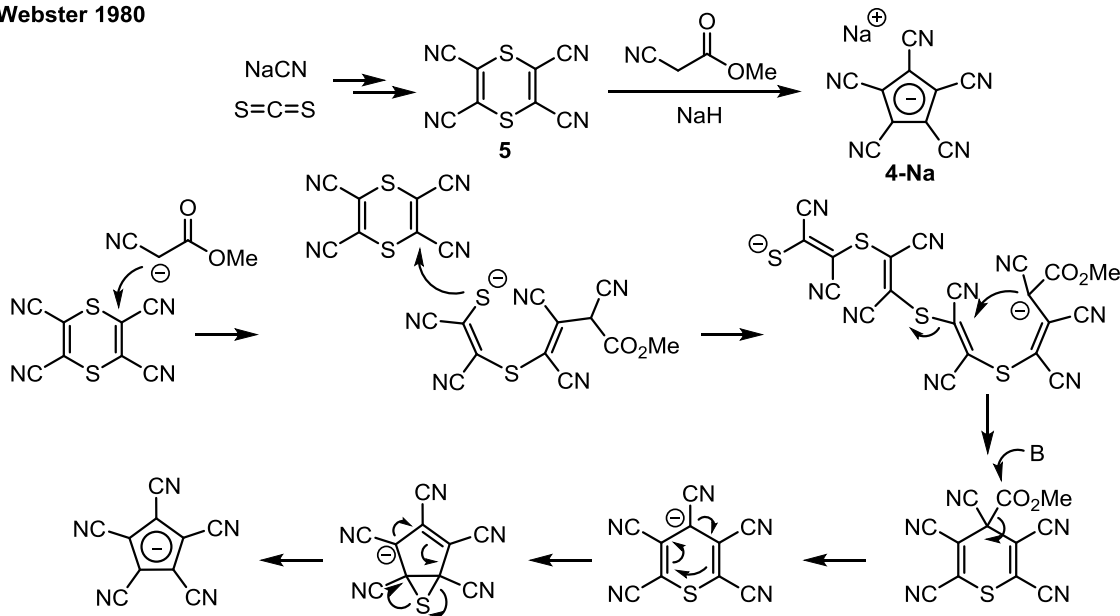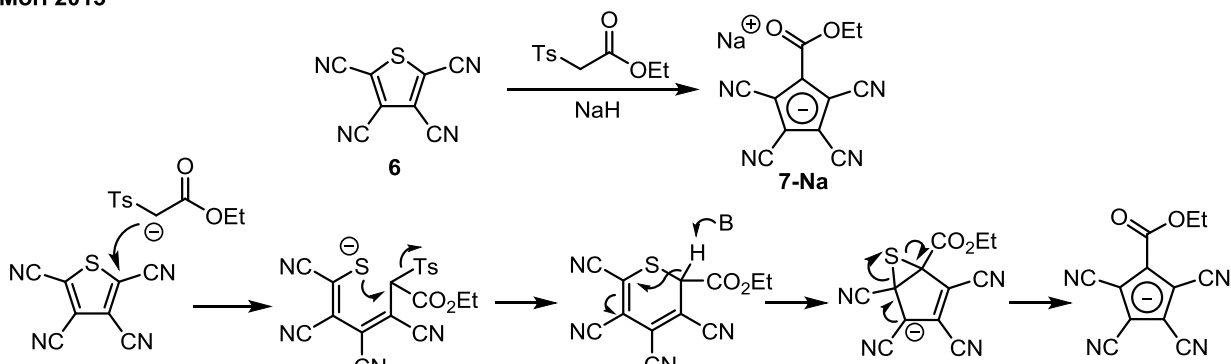
Figure 2: Syntheses of cyanated cyclopentadienes and their mechanisms.

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The initial attempts to protonate **4-Na** with $HClO_4$ in acetonitrile failed, leading to the conclusion that the compound is more acidic than $HClO_4$, with a pKa less than -2. The tetracyano was successfully protonated and was measured to have a pKa of 0 (MeCN), though the method for titration is not disclosed.[1,2] According to Leito's more recent spectrophotometric studies, the pKa of the tetracyano acid is -2.6 (MeCN).

The pentacyano anion was largely a curiosity, and only utilized sparingly as a counterion. It did, however, spark several computational studies, especially concerning its acidity. Despite the failed attempts to protonate the anion, it was calculated that the protonated cyclopentadiene should be an extremely strong acid. The first computational study was performed by Koppel[4] in 1996 using the PM3 semi-empirical method, and the researchers themselves conceded the values need extensive empirical corrections. Based on the deprotonation enthalpies, they predicted that the acidity should be very similar to $HClO_4$. Later work by Masić using more advanced functionals would corroborate the calculated gas phase values, and they further predicted a pKa of -20 (DMSO).[5] For comparison, the pKa for TfOH is predicted to be -14 and $HClO_4$ is -15.[6]
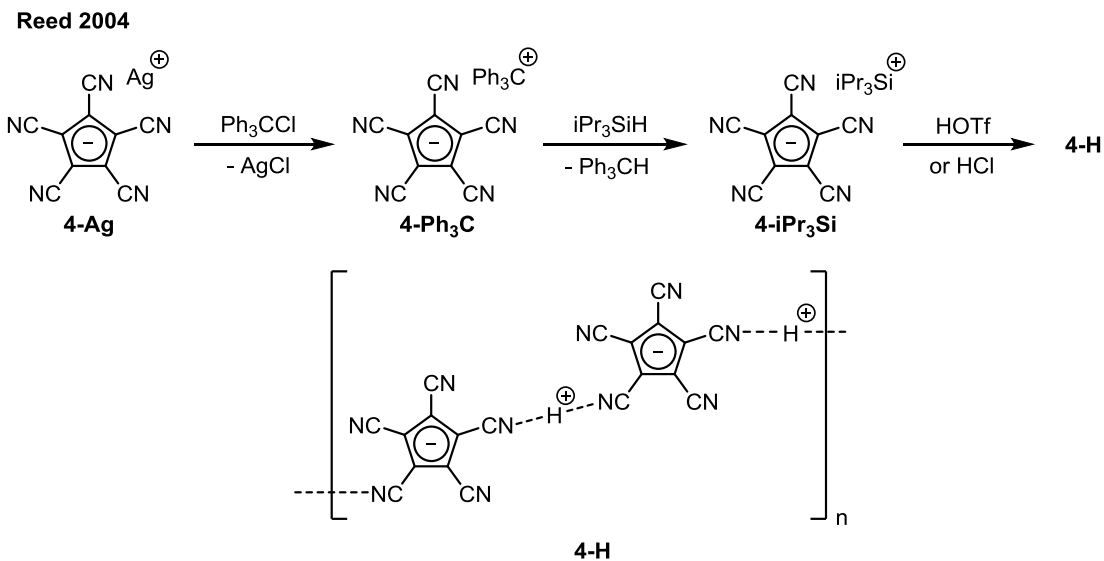
Figure 3: Protonation of *4* via consecutive cation exchanges.

In 2004, Reed utilized the same synthetic method for accessing the carborane superacids to protonate the pentacyano anion (Figure 3).[7] Formation of the TIPS species went smoothly, and the researchers were even able to obtain a crystal structure. The [29]Si-shift was similar to the shift of silylated acetonitrile (with a carborane anion as the counterion), suggesting the cyano groups of pentacyano are capable of fairly strong coordination to the Lewis acidic silicon center. The significance of this result will be discussed further in later chapters on silicon-based Lewis acid catalysis.

The "TIPS^{+}" of **4-iPr$_3$Si** was still capable of abstracting anions from acids (HCl or HOTf) to give the protonated form **4-H**. Protonation was accompanied by the immediate precipitation of the compound, likely through favorable formation of a polymeric hydrogen-bonded network as characterized by its IR spectra. Beyond this result, Reed noted that the acid was not able to protonate toluene, which would seem to contradict predictions of superacidity: acids stronger than $HClO_4$ should protonate toluene. The conclusion drawn was that the acidity of pentacyano is tempered by an extreme example of intramolecular hydrogen bonding making deprotonation less favorable. Computational work from Schaefer agreed with the characterization of the solid as a hydrogen-bonded polymer.[8]

Despite this result, there have been some reported uses of **4-H** as a Brønsted acid. Varanasi used the sulfonium salt as a photoacid generator in photolithography, noting the benefits of a non-fluorinated anion (Figure 4).[9] The most commonly used anions are fluorinated sulfonates, which have been shown to bioaccumulate and present toxicity concerns. Upon excitation with light, the sulfonium ion loses an aryl radical that recombines, yielding an extremely acidic proton due to the energy gained by rearomatization upon deprotonation. The

salts were successfully used to cleave protecting groups on a polymer to form a positive photoresist, showcasing the ability for the photoacid to generate the acidic for of the anion.
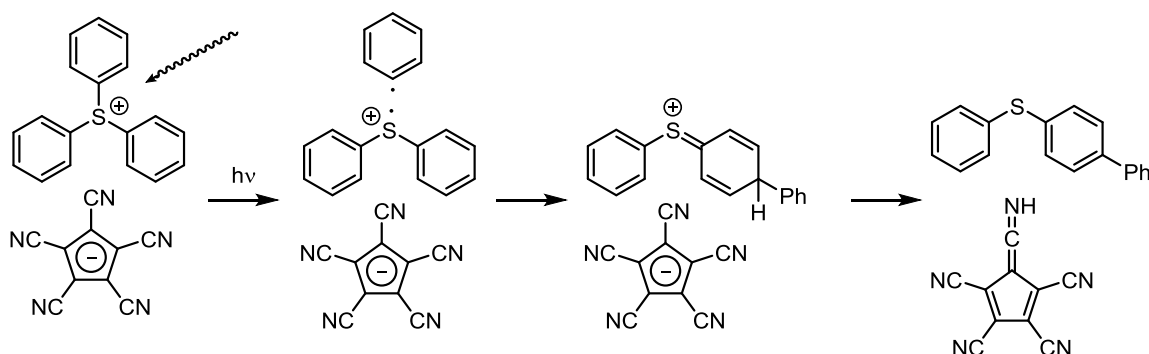
Figure 4: Use of *4* as the counterion in a sulfonium photoacid generator.

<u>Fluorinated Cyclopentadienes</u>

There are a few isolated reports of fluorinated derivatives of cyclopentadiene. The penta(trifluoromethyl) derivative was first reported in 1980 by Lamal,[10] and investigated further by Chambers (Figure 5, top).[11] Lamal's synthesis relied on the addition of 2-diazo-1,1,1-trifluoroethane to **8**, followed by reduction to give the bridged hydrazone **9**. Pyrolysis of **9** at 600 °C gave small amounts of the desired cyclopentadiene **10-H**. Chambers reported a more direct synthesis of **10-H** based on the fluorination and dimerization of perchlorobutadiene, though the yield remained modest.

Lamal reported that the compound was soluble in water, capable of etching glass and stronger than nitric acid. Titration with H_2SO_4 suggested a pKa of ~ -2 (H_2O). While not nearly as acidic as the cyano derivates mentioned above, **10-H** is stable and isolable in its protonated form; indeed, the acid can be distilled from sulfolane following protonation with H_2SO_4. Likely due to its troublesome synthesis, the chemistry of **10** has not been extensively explored.

The corresponding pentafluorophenyl derivatives have also been described. Becke describes the synthesis of **11-H** starting from the substituted acetylene,[12] though no characterization data is listed. The dimethylanilinium salt is described as a capable activator of

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Cp$_2$ZrCl$_2$, and thus is proposed as a possible replacement for MAO in olefin polymerizations. Deck reported the direct synthesis of tetrakis(C$_6$F$_5$) **12-Na** from the S$_N$Ar reaction of cyclopentadiene and hexafluorobenzene.[13] They then used the anion to prepare various piano-stool complexes of the bulky ligand. The group also reported the perfluorotolyl derivative using a modified procedure.[14] The reaction cleanly gives the tetrasubstituted product with no traces of the pentakis(aryl) product, possibly due to the unfavorable sterics of the fifth addition or the decreasing nucleophilicity of the anions with each additional aryl ring.
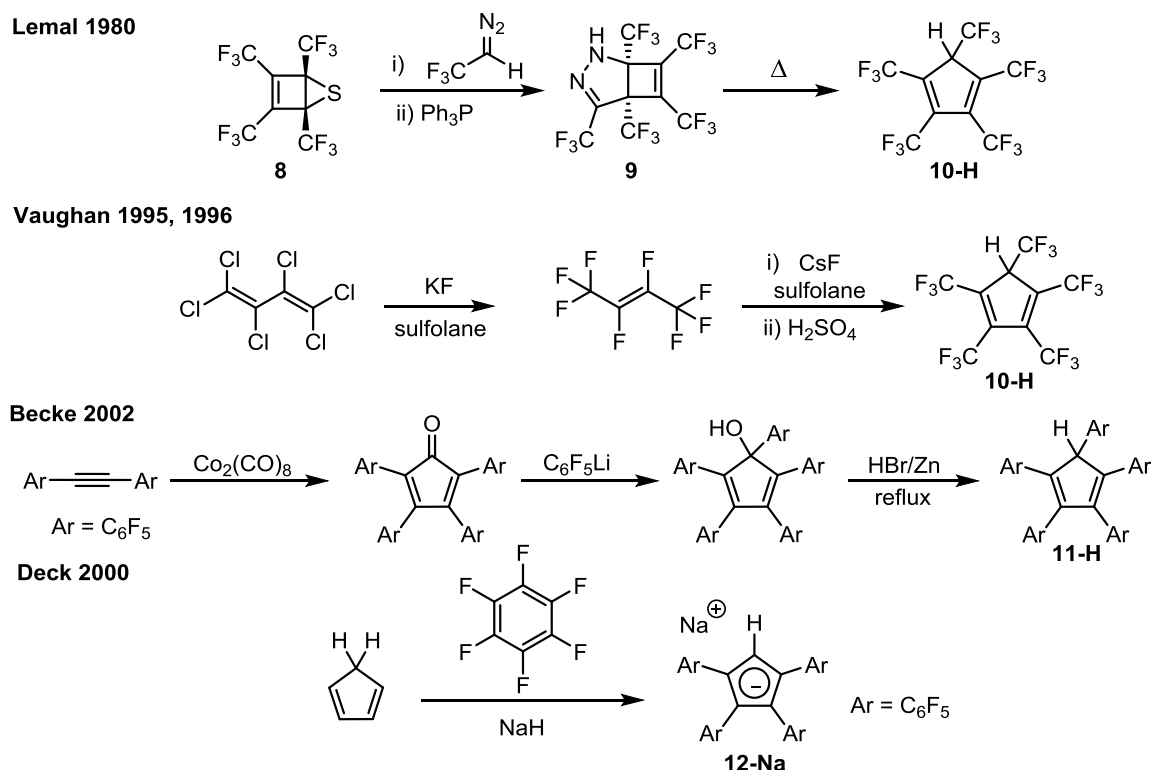
Figure 5: Syntheses of cyclopentadienes with fluorinated electron-withdrawing substituents.

On the basis of chemical reasoning, these should be very acidic due to the electron-withdrawing capabilities of the fluorinated phenyl substituents. An open question is to what extent does the inability for all four (or five) aryl rings to be conjugated simultaneously affect the stabilization of the anion. Notably, none of the reports make mention of the acidity of these

compounds. Further, there have been no pK_a determinations for these compounds, experimental or computational.

Carboxy-Substituted Cyclopentadienes

Initial Reports

The pentacarboxycyclopentadiene **1-H** was first described by Diels in 1942 as the product of base-promoted isomerization of the adduct of dimethyl acetylenedicarboxylate and dimethyl malonate.[15] Diels initially assigned the adduct as the incorrect hemi-ketal **13a** shown based on his mechanistic proposal and its ability to form a Diels–Alder adduct with maleic anhydride, though this product was likely the charge transfer salt and not a true adduct. The cyclopentadiene product was assigned correctly, though it was assumed to be *C*-protonated (**1a-H**) instead of the now known hydroxyfulvene tautomer. Spectra (IR, ^{1}H NMR spectroscopy) were later interpreted as supporting the hydroxyfulvene structure, and this was unambiguously confirmed by X-ray crystallography in 1981.[16]
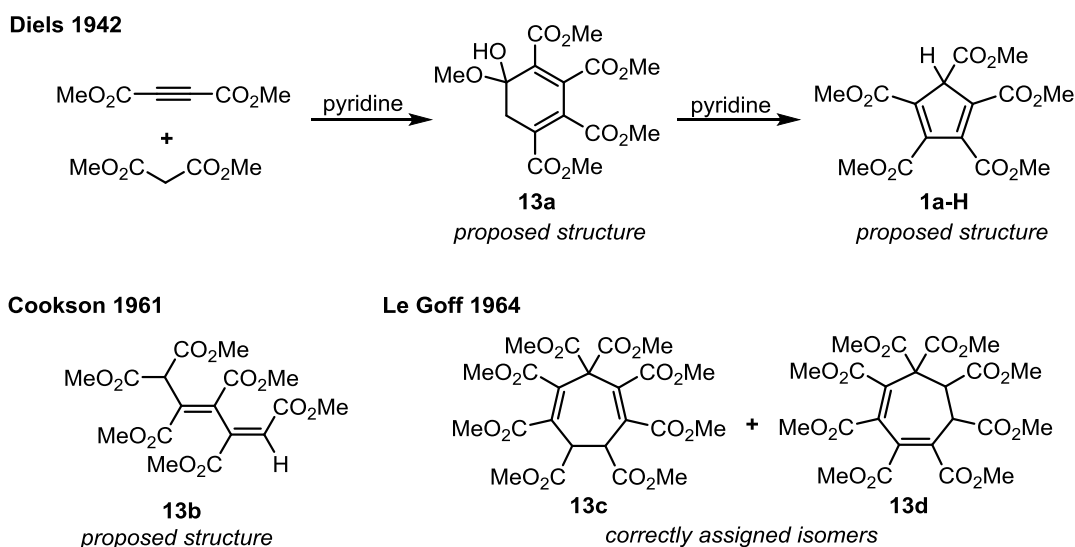
Figure 6: (top) Diels' original proposal for the synthesis of H[C$_5$(CO$_2$Me)$_5$] *1-H*. **(bottom)** Cookson's proposal for intermediate *13* and Le Goff's correct structure assignment, *13c* and *13d*.

Cookson revisited this synthesis in the 60's and first proposed the open chain isomer **13b**,[17] which would then undergo isomerization under the basic conditions to give **1-H**. In 1964, they reported elemental analyses and molecular weight measurements that supported a 3:1 adduct for **13** instead of the presumed 2:1 adduct that was resulting in the incorrect structure.[18] Contemporaneously, investigations by Le Goff[19] aided by ^{1}H NMR spectroscopy led to the proposed cycloheptadiene structures, **13c** and **13d**, that were later corroborated by Cookson.[20] Indeed, it has been firmly established that Le Goff's characterization is correct and the reaction gives a mixture of the constitutional isomers of the cycloheptadiene.

The formation of **13c/d** represents a triple Michael addition cascade - addition of malonate to acetylene, the product anion of which can then add to an additional molecule of acetylene. The linear product can then undergo proton exchange to give the malonate anion which closes the ring. Le Goff ingeniously used diethyl malonate to show that the malonate fragment is expelled, and no esters in the cyclopentadiene arise from the malonate starting material. They also note that 1 mol of carbon dioxide is evolved from the reactions, suggesting a decarboxylation step. The simplest mechanism would be a transannular Michael addition followed by a formal [2+2]-cycloreversion that expels the ethylene trimethylcarboxylate, which can then undergo the observed decarboxylation. Cookson noted that the reaction conducted at just below reflux produced the PCCP with no CO_2 evolution, indicating the decarboxylation takes place after formation of the product.
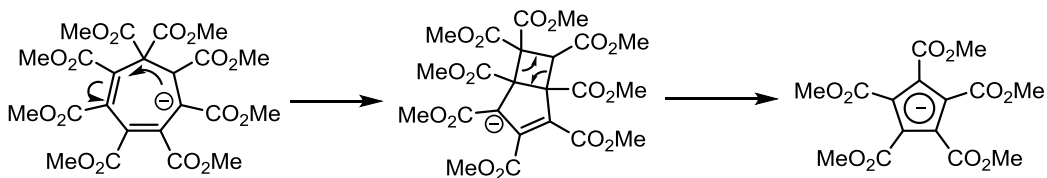
Figure 7: The mechanism for the ring contraction of *13* to form *1*.

The Chemistry of PCCPs

The subsequent chemical studies of PCCPs focused around the pentamethylcarboxy **1**, which was the sole representative for some time. Cookson performed several assays of the acidity of the **1-H**, showing that the water-soluble acid titrated as a strong acid, and appeared to be at least as strong an acid as HCl in aqueous solution. This observation was later confirmed by work performed by Dr. Chirag Gheewala, my colleague in the Lambert group, via determination of the pKa of **1-H** in MeCN.[21] His value of 8.89 (MeCN) is slightly more acidic that the reported value for HCl (10.6 in MeCN).

LeGoff and Cookson both independently showed the ring of **1** can be alkylated. Cookson demonstrated that **1** is methylated when mixed with diazomethane and Le Goff used MeI, which required activation by Ag_2O (Figure 8, top). By variation of the alkyl group, Warkentin showed that dealkylation could be effected if the alkyl group was sufficiently substituted to favor dissociation.[22] That is, given the likely S_N1-type mechanism, a sufficiently stable carbocation could be generated by ionization of the alklyated derivative and subsequently trapped. In their study, the rather stabilized benzhydryl group was necessary to see effective dealkylation; the benzyl-substituted derivative **17** rearranged at high temperature to **18**. These results directly impact our later work on alkylations (see Chapter 4).

The alkylated products were shown to be prone to decomposition, either by decarboxylation (as in the case of Cookson, forming the alkyl-tetracarboxy **15-Na**) or via 1,5-sigmatropic rearrangement of the carboxy group adjacent to the introduced alkyl group. These rearrangements have been studied extensively by several groups. This facile migration was also seen upon thermal decomposition of the dimerized species **19**, which was studied in the attempt

to characterize the neutral radical via homolytic cleavage of the dimer upon heating. The neutral radical was not observed by EPR spectroscopy under these conditions.
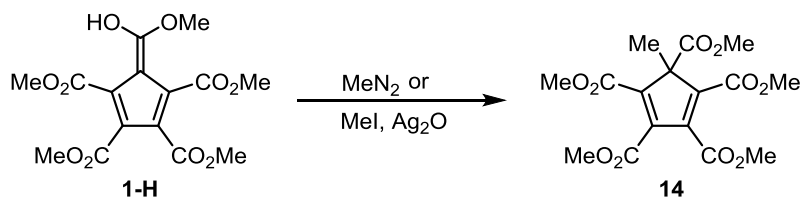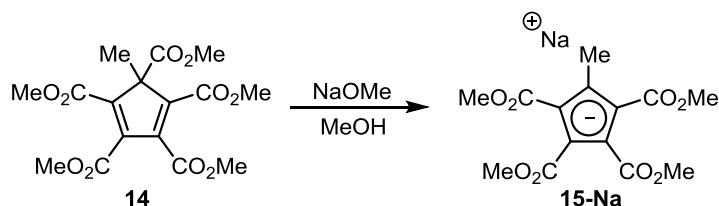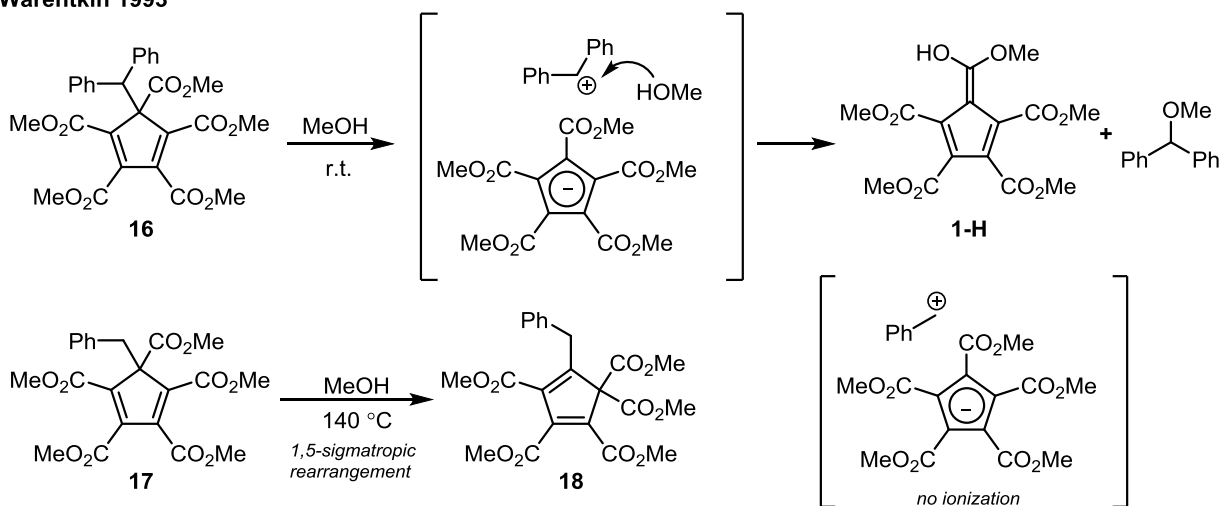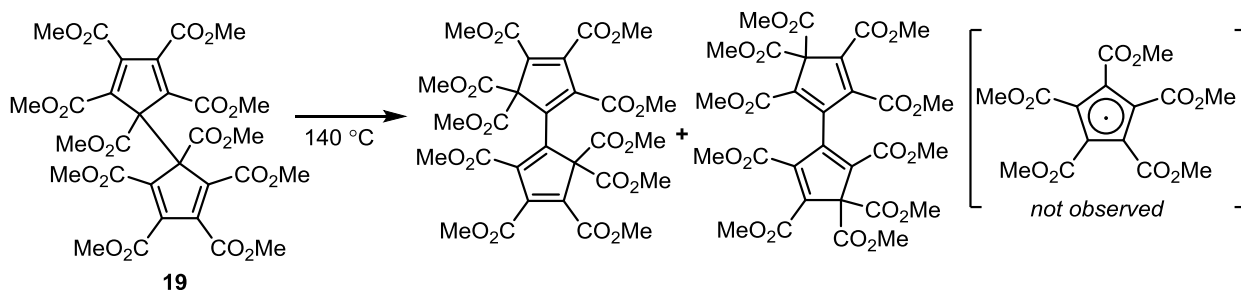
Figure 8: Studies of ring-alkylated PCCPs and their rearrangements.

Bruce extensively studied the coordination chemistry of **1** (along with some related compounds) and wrote a comprehensive review.[23] While an exhaustive description of all this

work is outside the purview of this chapter, some key aspects can be highlighted. The first is the notable tendency of the anion to form complexes via bidentate coordination through the carbonyl oxygens. The notable exceptions to this are complexes of Mn, Sn, and Rh (Figure 9). Despite this bidentate coordination, the anion is easily displaced, reflecting its weak basicity. The weak binding of PCCPs is further exemplified in the anionic nature of many complexes, with the PCCP acting solely as a counterion and not a ligand. In water, complexes tend to display absorbances of the aqua complexes.

The chemistry of the rhodium complexes of PCCPs has been studied by Williams.[24] These mixed, ferrocene-type complexes display η^5-bound PCCP with remarkable stability. To wit, subjecting the complex **20** to basic hydrolysis allows for the formation of the pentacarboxylic acid complex **21**. This result is astonishing given the PCCPs propensity for decarboxylation, as noted above. Presumably, the metal center is stabilizing the ligand, disfavoring the decarboxylation of the hydrolysis intermediates. Esterification of simple alkyl alcohols was accomplished via heating with acid; however, less reactive phenyl and thiopropyl esters could not be successfully formed. By utilizing cyanuric fluoride, the group was able to prepare the penta(acyl fluoride) derivative **23**, though characterization was unfortunately limited to ^{1}H-NMR spectroscopy. This acyl fluoride intermediate does undergo esterification catalyzed by DMAP to give the phenyl and thiopropyl esters, albeit in low yields of 16% and 33%, respectively.
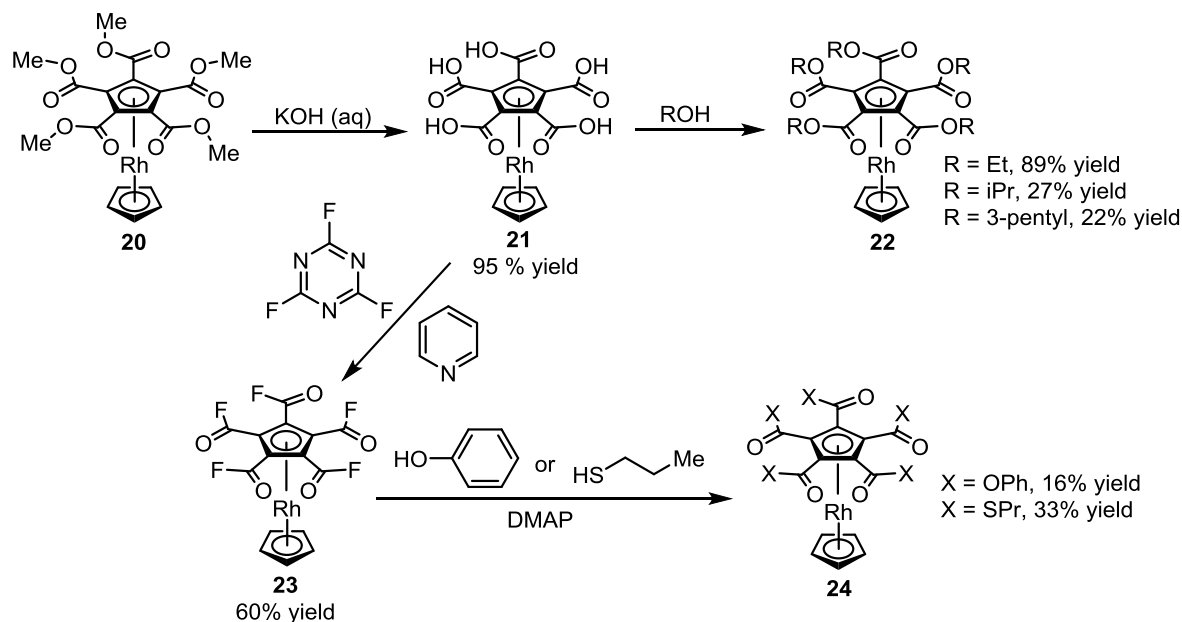
Figure 9: Functionalization of the esters of Rh-PCCP complex *20*.

Work in the Lambert Group

Research into the use of PCCPs in the Lambert group was initiated by Dr. Chirag Gheewala.[25] He developed conditions to effect the direct transesterification of the carbomethoxy groups of **1**, paving the way to new PCCPs. Extensive screening of transesterification catalysts was required to find practical conditions. The well known catalysts DMAP is completely ineffective, while N-methylimidazole (NMI) proved to be the optimal catalyst. Along with this work, amidation reactions were developed, though these will not be discussed.

With access to the chiral, menthol-derived PCCP **25-H**, Dr. Gheewala developed asymmetric Mukaiyama-Mannich and Mukaiyama-aldol reactions. The hydroxy substituents on the substrates proved to be necessary for high enantioinduction. Given the higher acidity of the PCCPs compared to the BINOL-phosphoric acids (14-12.5 in MeCN),[26] the reactions could be conducted at lower temperature and at low catalyst loadings. Later work resulted in the development of a formal hetero-Diels-Alder reaction utilizing oxocarbenium ions.[27] This

reaction required a new arylcyclohexanol-derived catalyst **26-H** that emerged from an extensive catalyst screening campaign. From this background, we will examine the synthesis of PCCPs in more detail.
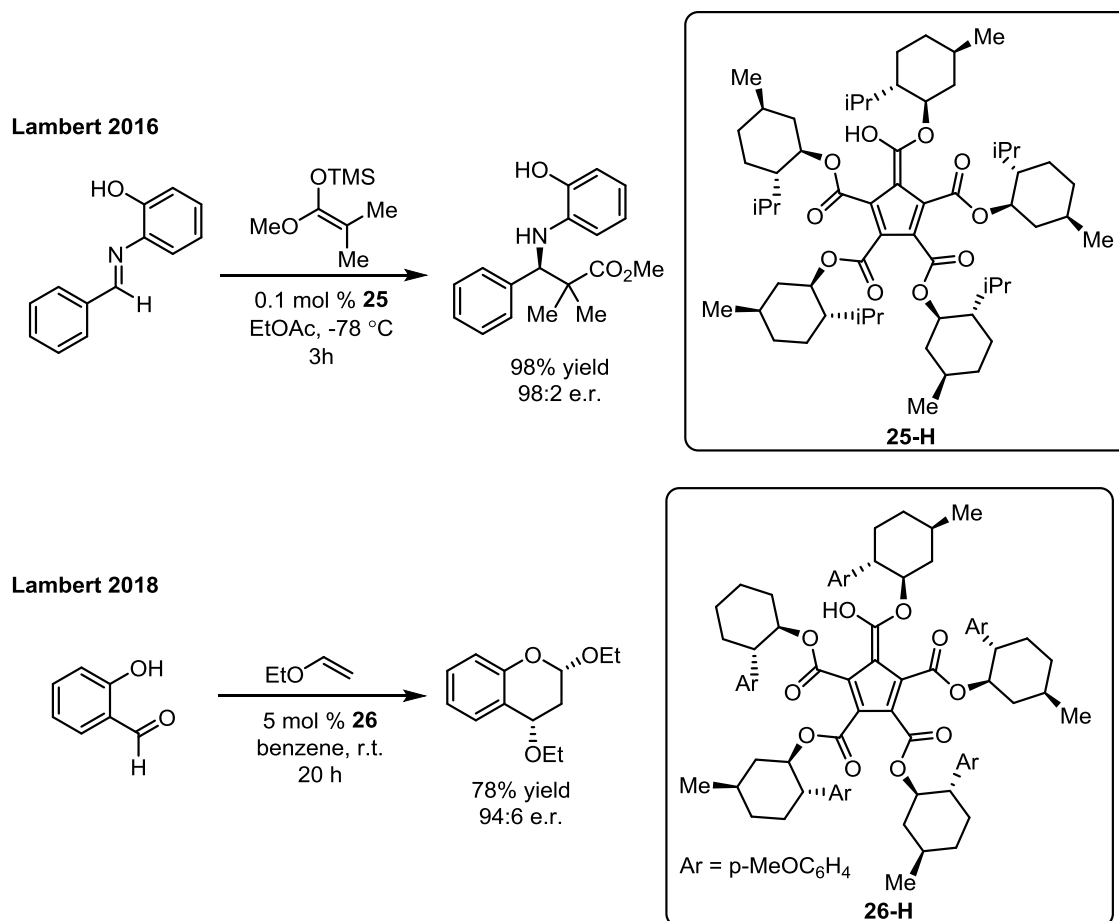
Figure 10: Enantioselective reactions using PCCP catalysts *25-H* and *26-H*.

Transesterification

The following discussion describes my own work concerning the transesterification of PCCPs. Before expounding on the successful transesterification reactions developed, I will point out the notable failure of some obvious strategies. Most significantly, use of acid catalysts proved to be completely ineffective. Heating the acid in ethanol, or a solution of the acid and an alcohol, only leads to decomposition via decarboxylation. Use of an exogenous acid such as *p-*

toluenesulfonic acid does not improve the reaction outcome. Further, several Lewis acidic transesterification catalysts were tested, with no positive results.

As mentioned, NMI was found to be the optimal transesterification catalyst. The reasons for this are not fully understood but clues from many experiments point to a confluence of factors. One of the main effects appears to be the protonation state of the PCCP. Utilizing the potassium salt **1-K**, or addition of exogenous base (NEt$_3$, forming **1-HNEt$_3$**), leads to no reaction, with the starting material being recovered unchanged. In addition, the use of a more basic transesterification catalyst (i.e. DMAP) gave no transesterification products. At the other end of the scale, 1,2,4-triazole has been reported as a very effective transesterification catalyst,[28] and is less basic than NMI. 1,2,4-Triazole does not deprotonate PCCP, and upon heating only decarboxylation is observed.

Our hypothesis is that complete deprotonation of the PCCP yields a species in which the carboxyl groups are unreactive towards nucleophilic addition. NMI does form a salt with **1-H** - in fact, it partially comes out of solution as an oil under the reaction conditions. However, the protonated NMI would be acidic enough to form a significant hydrogen-bonding interaction with the PCCP anion.

In line with this hypothesis, we noticed that protonation of the penta(phenyl)PCCP **27-Na** via washing with 1 M HCl lead to partial hydrolysis of the esters, leading to **28-H** (Figure 11). Speculating that upon protonation, the hydroxyfulvene of **27-H** is electrophilic enough to be attacked by water, we attempted to transesterify all five esters under acidic conditions. In CDCl$_3$ with 10 equivalents of benzyl alcohol and MsOH, **29-H** was formed after approximately three days at room temperature, highlighting the importance of the PCCP's protonation state. It can also be noted that the anionic penta(trifluoroethyl)PCCP is unreactive to our transesterification

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conditions, even though the TFE esters should be significantly more reactive. Unfortunately, the acid of TFE-derived PCCP could not be formed (*vide infra*), precluding further testing of this hypothesis.
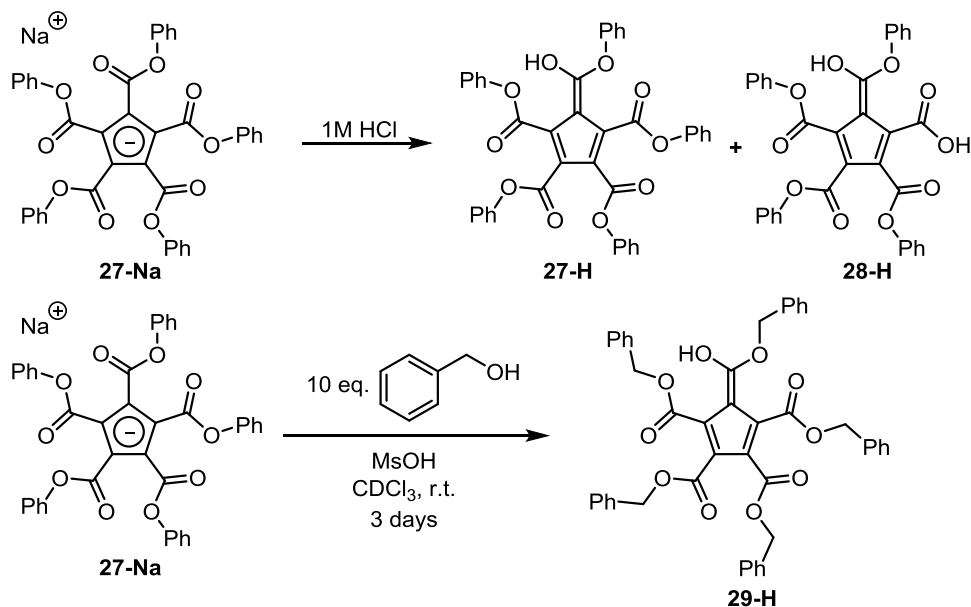
Figure 11: Lability of the phenyl esters of *27-H*, showing susceptibility to hydrolysis and transesterification.

With the conditions outlined in the seminal publication, we investigated the scope of this transformation (Figure 12). Overall, most alkyl alcohols were effectively installed utilizing this protocol. A variety of secondary alcohols could be used, even the very large cholesterol was effectively transesterified (leading to a product with a molecular weight of >2000). In the cases of hindered alcohols, transesterification was accompanied by decomposition of the product due to the lengthy reaction times required. To accelerate the reaction, an inert gas sweep was introduced to remove the toluene/methanol azeotrope, along with a cooled condenser to retain the majority of the refluxing toluene. The more efficient removal of the produced methanol pushes the reaction to completion via Le Chatelier's principle, as the transesterification is reversible. In addition, the reaction could be run under more dilute conditions, lessening the risk of solvent evaporation leading to a dry flask. The difference is considerable, especially on larger

scales. Using ~100 mg of **1-H** could previously take as long as a week, but the reaction could now be accomplished in approximately one day using the inert gas sweep set-up. These conditions allowed for the synthesis of the first PCCP containing a tertiary alcohol, using adamantanol, as well as the installation of the extremely bulky dicyclohexylmethyl ester.
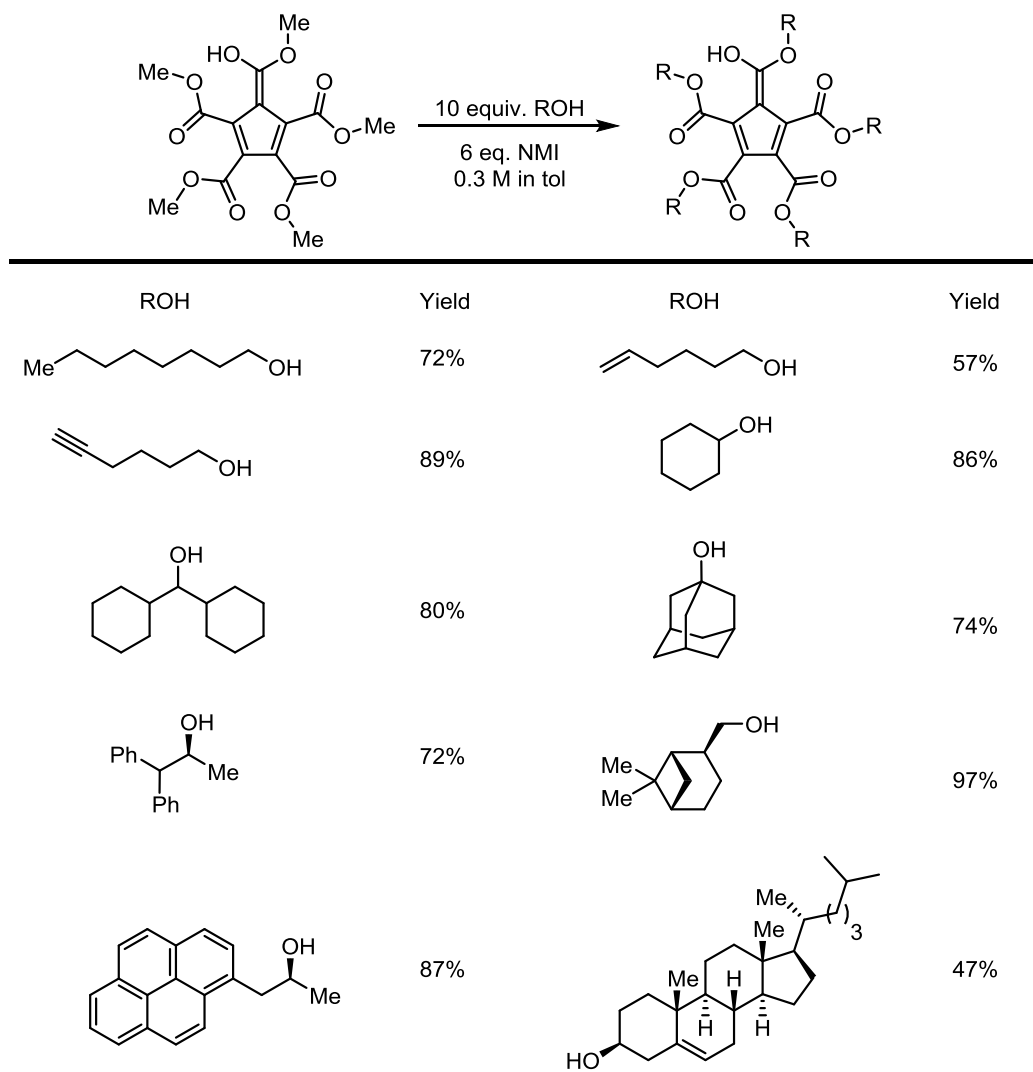
Figure 12: Scope of the transesterification of *1-H* with alkyl alcohols.

PCCP **30-H** is unique in that it is *C*-protonated: all the other PCCPs synthesized have the hydroxyfulvene struture when protonated. Upon examination of the ^{1}H NMR spectrum of the protonated product, the lack of the highly deshielded proton at δ ~20 ppm characteristic of the hydroxyfulvene was noted. Instead, the ring proton appears at δ 4.73 ppm, and the attached

carbon has a ^{13}C chemical shift of δ 61.7 ppm. Presumably, the great steric bulk of the dicyclohexylmethyl esters prevents the intramolecular hydrogen bond that favors the hydroxyfulvene tautomer, leading to the ring tautomer being thermodynamically favored. Rotation of one ester would cause immense steric clashing between the adjacent dicyclohexylmethyl ester groups, causing the five esters to only be able to adopt a geared conformation.
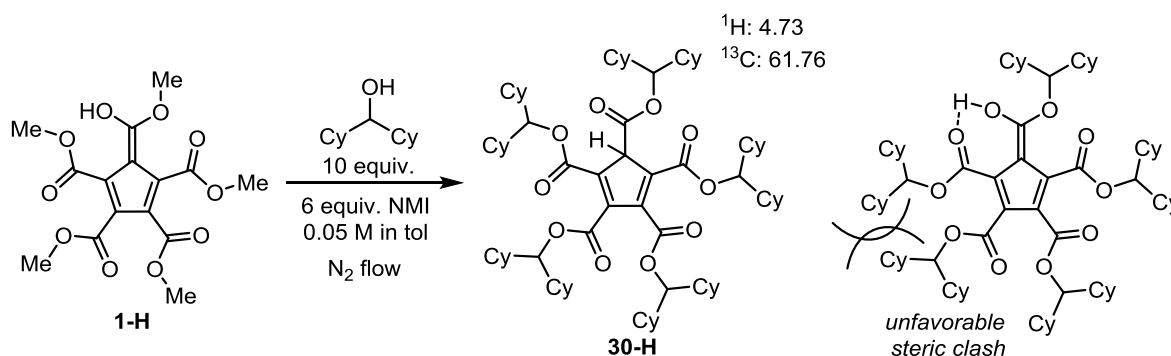
Figure 13: Dicyclohexylmethyl-derived PCCP *30-H* is ring-protonated.

Having developed more efficient conditions for the transesterification of **1-H**, we sought access to larger quantities of the successful menthyl catalyst **25-H**. As mentioned above, this chiral PCCP had prove effective in enantioselective catalysis developed by Dr. Gheewala. However, the purification of large amounts of the catalyst was tedious. The PCCP acids and salts are highly polar organic molecules that have the tendency to streak on silica gel; therefore, effective purification required comparatively large amounts of silica gel and solvent. While the laboratory routinely prepared **25-H**, scaling up the synthesis was rarely done on the multiple gram scale. The product was also often contaminated with minute amounts of highly colored impurities, which could not be removed by activated charcoal treatment.

Previous work suggested that the tetraalkylammonium salts of the PCCPs were quite well-behaved, microcrystalline solids, which is in stark contrast to the sodium salts that are often foams or sticky semisolids. Further, **25-H** is extremely soluble in most solvents, even cold

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hydrocarbons, preventing effective purification via recrystallization or precipitation. Quick screening of ammonium cations showed that the tetrabutylammonium salt **25-NBu₄** was easily formed and could be handled as a fine crystalline powder. Importantly, the sodium counterion of the PCCP was effectively exchanged for tetrabutylammonium cation by simply washing with a roughly equimolar amount of NBu₄Br in aqueous solution. Thus, the elements were in place to directly purify the PCCP from the reaction mixture.
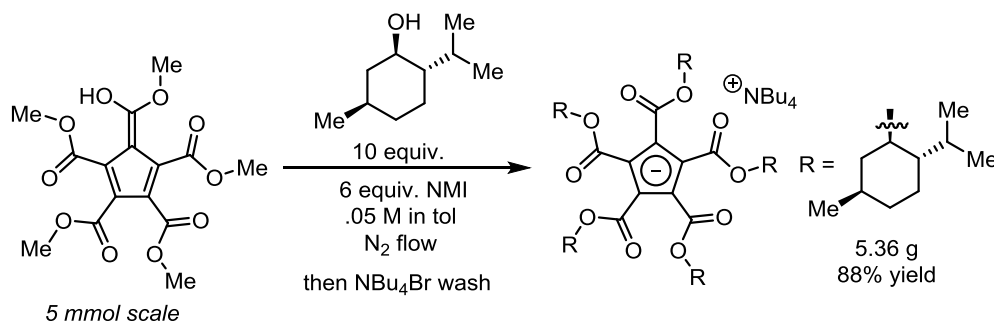
Figure 14: Multi-gram-scale synthesis of *25-NBu₄*.

The reaction design was tested at a 5 mmol scale. After completion of the reaction and routine work-up, the product is converted into the desired NBu₄ salt . Simple trituration of the crude product with hexanes and collection of the solid provides pure, microcrystalline **25-NBu₄** in 88% yield. The reaction has been performed multiple times on gram scales, and provides a robust, column-free approach to this useful chiral PCCP catalyst.

Failures of the Transesterification

During catalyst optimization studies, our group desired the phenethyl PCCP to test in reactions. Initially, synthesis proceeded as normal, with formation of intermediates with phenethyl esters can be seen via TLC and mass spectrometry (Figure 15). Unfortunately, as the reaction nears completion, large amounts of decarboxylated products are formed with the pentaester formed only in small amounts. An additional peak was seen in the mass spectrum, which has been assigned as the rearranged product **33**. Upon decarboxylation, the resulting anion

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traps the liberated phenethyl group to form the ring alkylated product. Attempts to reduce decarboxylation by lowering the reaction temperature only led to poor conversion of the starting material.
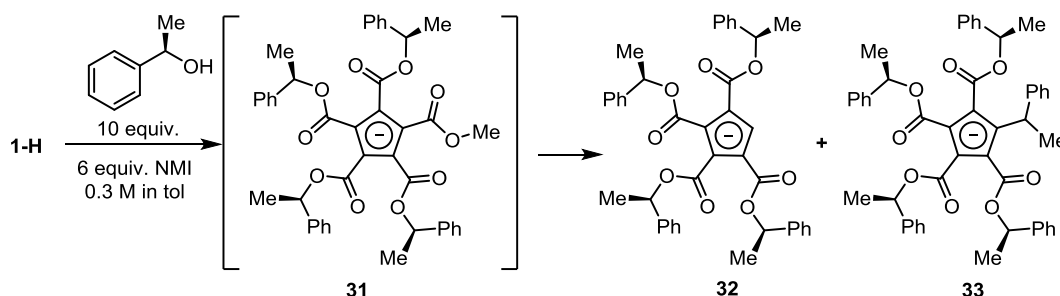
Figure 15: Decomposition during the attempted transesterification of *1-H* with *sec*-phenylethanol.

Another limitation was the inability to introduce electron-deficient alcohols into the PCCP. Neither phenol nor trifluroethanol produced detectable amounts of transesterification products under the conditions. It was noted that **1-H** dissolved in TFE gave small amounts of the mono(trifluoroethyl) ester. Heating for extended periods (~1 week) in a pressure tube led to further transesterification, but ultimately only a maximum of three trifluoroethyl esters were observed. Thus, a concerted effort was placed on accessing a greater variety of PCCPs.
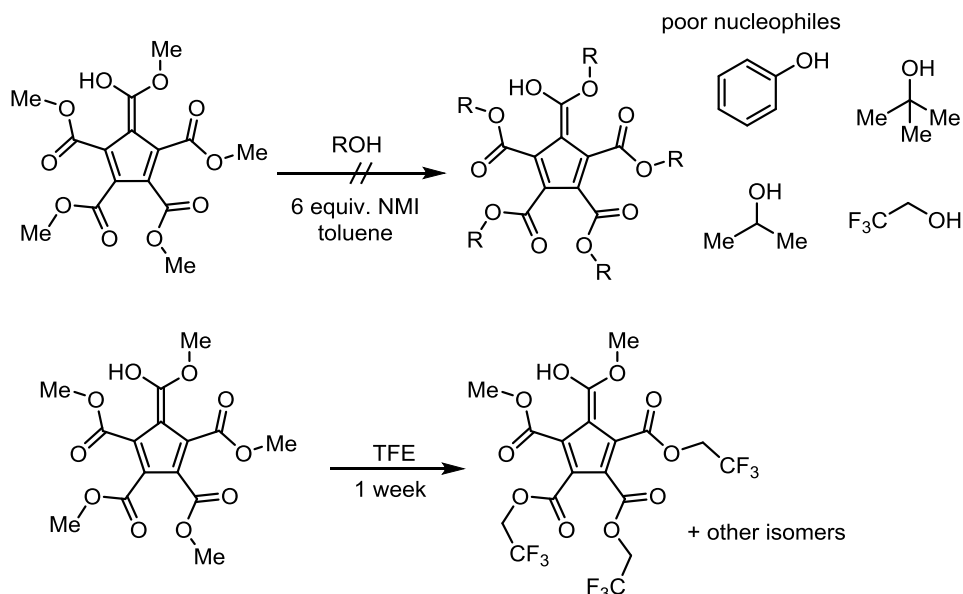
Figure 16: Unsuccessful transesterification attempts with poorly-nucleophilic alcohols.

Expanding the PCCP Library

De Novo Synthesis

Based on the synthesis of **1-H**, beginning with substituted precursors would lead to new PCCPs. The initial plan was to access a substituted PCCP that would be more amenable to undergo transesterification, thus allowing for easier synthesis of new PCCPs. We were particularly hopeful that a new strategy would enable the installation of alcohols that were incompatible with our transesterification conditions. Our first target was the penta(trifluoroethyl) PCCP **35**. Synthesis would begin with the malonate[29] and acetylenedicarboxylate,[30] which were prepared according to literature procedures. The acetylenedicarboxylate was particularly unstable and was used immediately without purification.
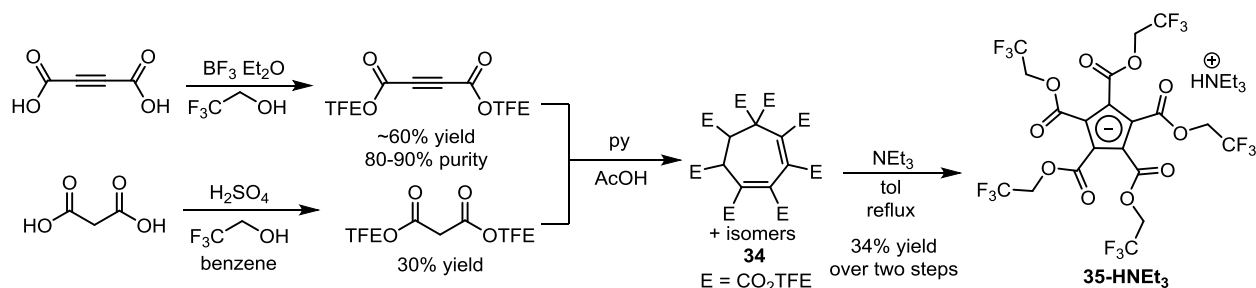
Figure 17: De-novo synthesis of trifluoroethyl PCCP *35*.

The conditions for the Le Goff synthesis were initially followed. Upon addition of HOAc/pyridine, the isomeric cycloheptadienes **34** are formed and can be isolated following column chromatography. In contrast to the methylcarboxy-derivative, these cycloheptadienes did not undergo ring contraction when heated in aqueous KOAc. Presumably, the extremely poor solubility of **34** in water prevented the significant deprotonation of the cycloheptadiene to initiate

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the reaction. By performing the reaction in toluene, with triethylamine as the base, cyclopentadiene salt **35-HNEt₃** was successfully formed in 34% yield over the two steps. Attempts to protonate the salt with aqueous acid, or concentrated sulfuric acid, did not lead to the desired acid form of **35-H**.

When transesterification was attempted with the salts of **35**, it was found they were incompetent substrates, only returning starting material. As previously observed, the anionic PCCPs proved to be completely unreactive in these conditions. The TFE esters are surprisingly robust, and are even stable to refluxing with amines, showing no amidation products. The increased electron density of the anion makes the esters less reactive, in addition to the negative charge disfavoring nucleophilic attack.

In light of these difficulties, a different approach was devised to form the penta(*t*-butyl) PCCP **37**. Here, acidic hydrolysis of the esters could be performed to give the pentaacid, which could then be activated to give a highly reactive intermediate for further transformations. The acetylene and malonate are both commercial compounds, and the cycloheptadiene **36** could be formed. Like the **34**, the *t*-butyl cycloheptadienes were negligibly soluble in aqueous solution, and the KOAc conditions failed to deliver the PCCP. Performing the reaction in toluene did not give product either, and this approach was abandoned.
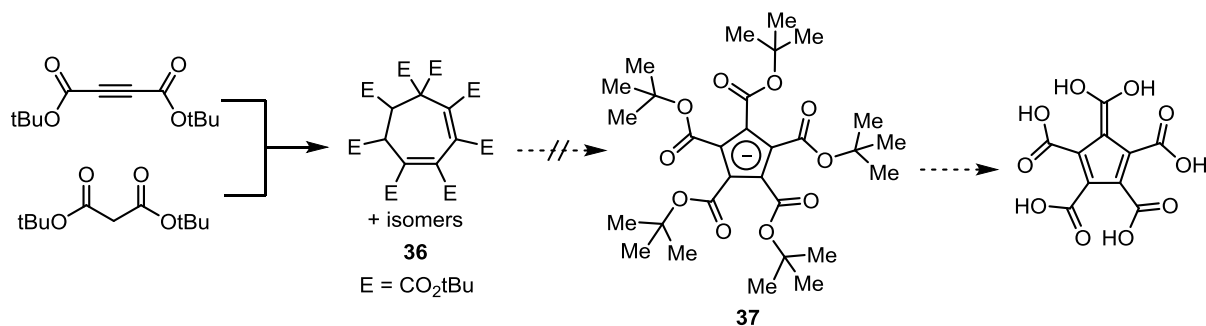
Figure 18: Attempted synthesis of *t*-butyl PCCP *37*.

Pentaacyl Chloride

Given the report by Williams describing their preparation of pentaacyl fluoride **23**, it seemed reasonable that one should be able to access the acyl halides, which could then undergo the desired esterification.

In the course of investigating the addition of sterically bulky alcohols, it was discovered that attempts to protonate the penta(adamantyl)PCCP **38** resulted in the partial dealkylation of the esters. A new peak at 16 ppm was observed in the ^{1}H NMR spectrum, and mass spectrometry led to the confirmation of the mono(carboxy) product **39-H** that presumably forms upon ionization of the ester. We further speculated that all five esters could be dealkylated under suitable conditions. Adventitiously, we found the esters of **39-NBu₄** could be directly converted into the acyl chlorides by treatment with thionyl chloride.[31] Upon quenching with EtOH, successful formation of the penta(ethyl) PCCP **41-H** was observed. With this successful proof of principle, we then focused on the direct conversion of the methyl esters of **1-H** into the acyl chloride **40**.
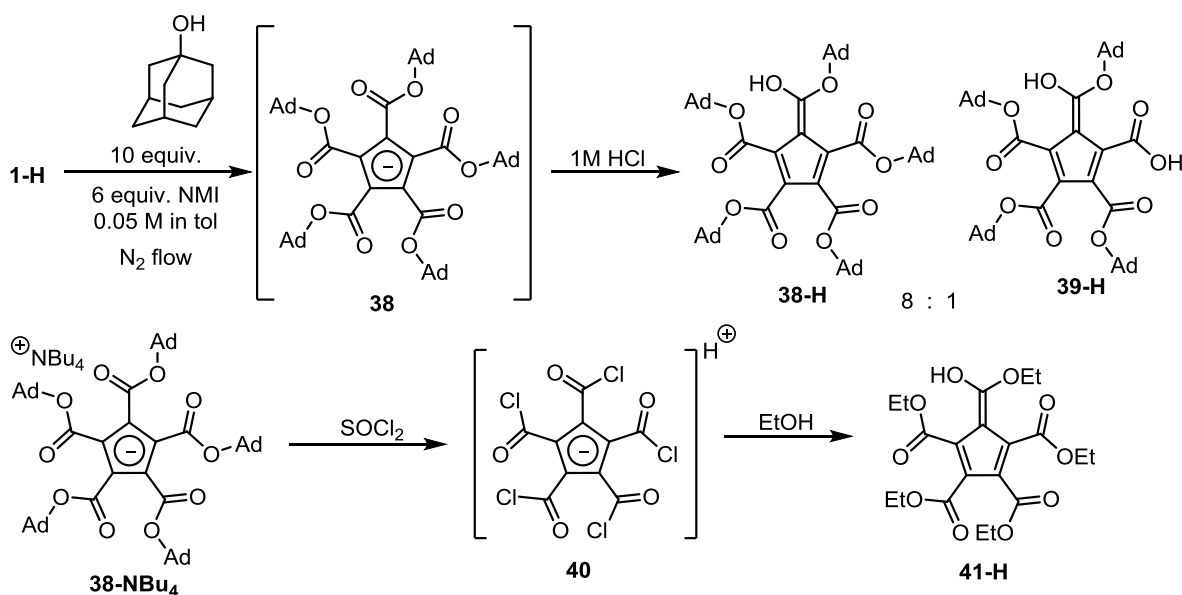
Figure 19: (top) Hydrolysis of the adamantyl-esters of *38* upon washing with acid. **(bottom)** In situ formation of the penta(acyl chloride) *40* using thionyl chloride.

Several researchers in our group tried various conditions to form acyl chlorides with **1-H**, with minimal success. For example, refluxing **1-H** in thionyl chloride only produces trace amounts of the monofunctionalized product upon quenching with an alcohol. Other reagents for preparing acyl halides (oxalyl chloride, PCl_5, PCl_2Ph_3, etc.) gave similar outcomes. It was eventually found that addition of DMF to the PCCP in $SOCl_2$ and refluxing overnight fully activated all five esters. Quenching with ethanol gave the desired penta(ethyl) **41-H**.

Presumably, the chloroiminium Vilsmeier reagent is formed and reacts with the esters.[32] The increased electrophilicity of the Vilsmeier reagent is required to engage the ester functionality. This intermediate can then be dealkylated in a Krapcho-type fashion[33] by chloride to give the activated ester, which is further reacted to give the acyl chloride. When the reaction is performed in a sealed tube, MeCl can be observed by ^1H and ^{13}C NMR spectroscopy, corroborating   this   mechanism.

The combination of DMF and $SOCl_2$ was found to be critical. Other activating agents known to give the chloroiminium chloride did not lead to full activation of all five esters. Further, other amides (DMA, NMP, etc.) in thionyl chloride were ineffective. Thus, the optimized conditions were determined to be refluxing for 16 hours, followed by removal of thionyl chloride via vacuum distillation. The crude pentaacyl chloride **40** was then dissolved in DCM and a solution of the alcohol added to give the desired PCCP.

Figure 20 shows the variety of alcohols that can be installed using this methodology. It is important to note that all of these PCCPs are inaccessible via transesterification. Benzylic alcohols work well, including the enantioenriched 1-phenylethanol and benzyl mandelate. In a few instances, modifications were required to form the desired esters. *t*-Butanol does react, but the HCl generated in the reaction then dealkylates the esters, giving a mixture of products with

variable numbers of free acids. Adding Na_2CO_3 effectively quenches the HCl, and the PCCP is formed in modest yield. In the case of electron deficient alcohols (phenol, TFE, etc.), the alcohols are not nucleophilic enough to engage the PCCP, and incomplete functionalization of the acyl chloride intermediate is seen. Again, Na_2CO_3 was found to be a suitable base, and the PCCPs are formed in low to moderate yield. The conditions were tested at a 5.0 mmol scale using L-ethyl lacate, and the product was obtained in 59% yield (2.55 g), showcasing the ability to generate significant amounts of these ions for further studies.
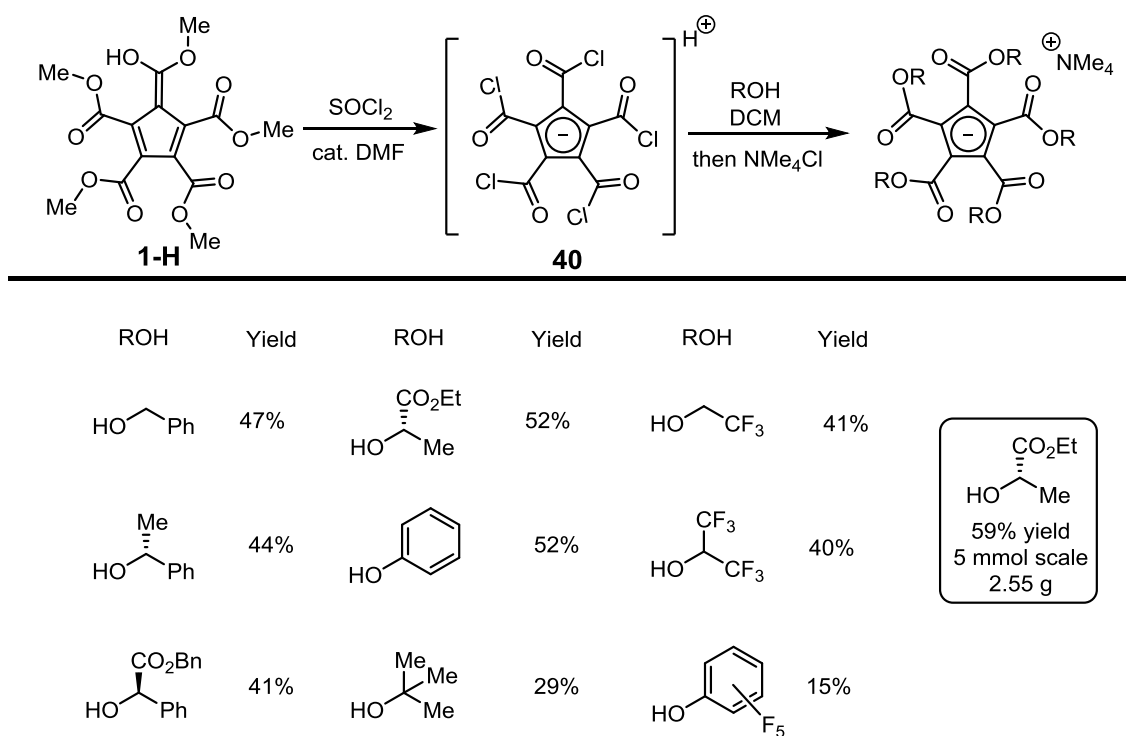
Figure 20: Scope of the addition of alcohols to *40*.

Despite the increased reactivity of the pentaacyl chloride intermediate **40**, there are still limitations to the nucleophile scope. In contrast to the report from Williams,[24] thiols were not successfully installed. Use of thiophenol and dodecylthiol gave mixtures of products with free carboxylic acids and anhydrides with only traces of the pentathioester. Variation of the reaction

temperature, addition of bases, and changing the solvent were unfruitful, and conditions could not be found for forming the desired product in reasonable yield.
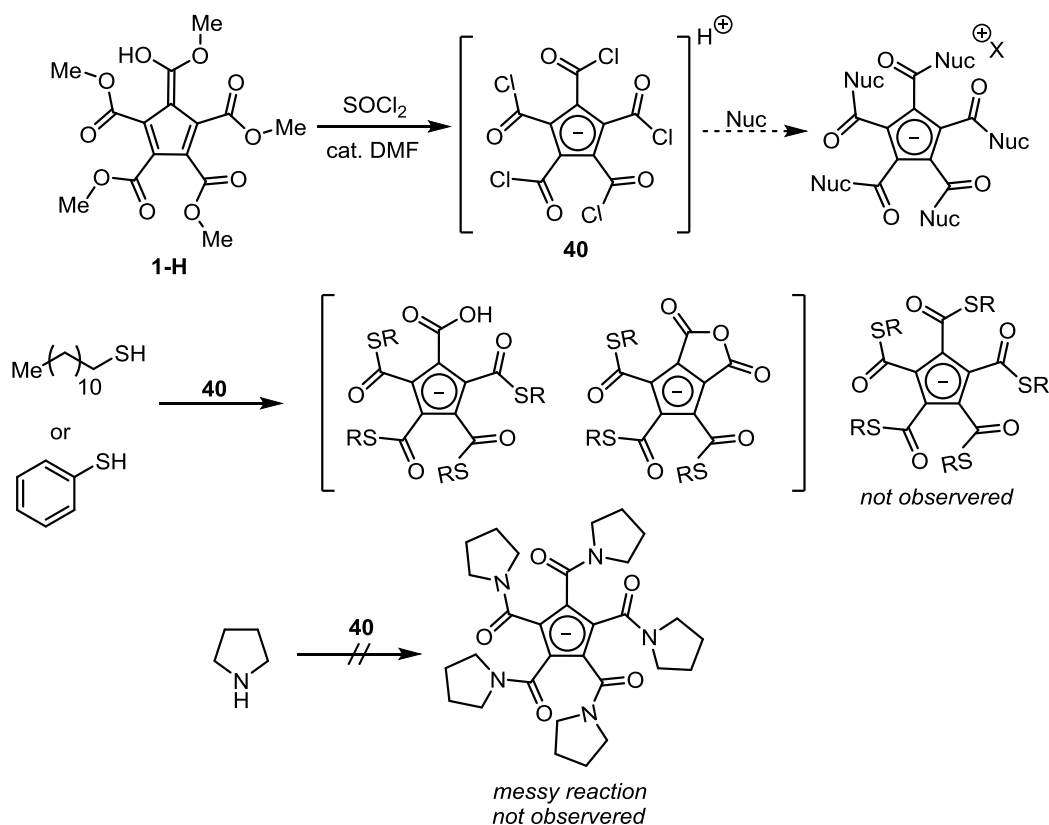
Figure 21: Attempted synthesis of thioesters and 3°-amides from acyl chloride *40*.

While Dr. Gheewala had shown that mono-, di- and penta-amide derivatives of PCCPs could be formed, the reactions were limited to primary amines. Therefore, secondary amines were targeted in an attempt to access new derivatives. After formation of the penta-acyl-chloride, slow addition of excess amine gave intractable mixtures of products with no trace of the desired pentaamide. While primary amines did give pentaamide products, the reaction gave lower yields than the previously published conditions (AlMe$_3$, excess amine). These conditions are preferable in most respects, and the use of the pentaacyl chloride did not provide any advantage.

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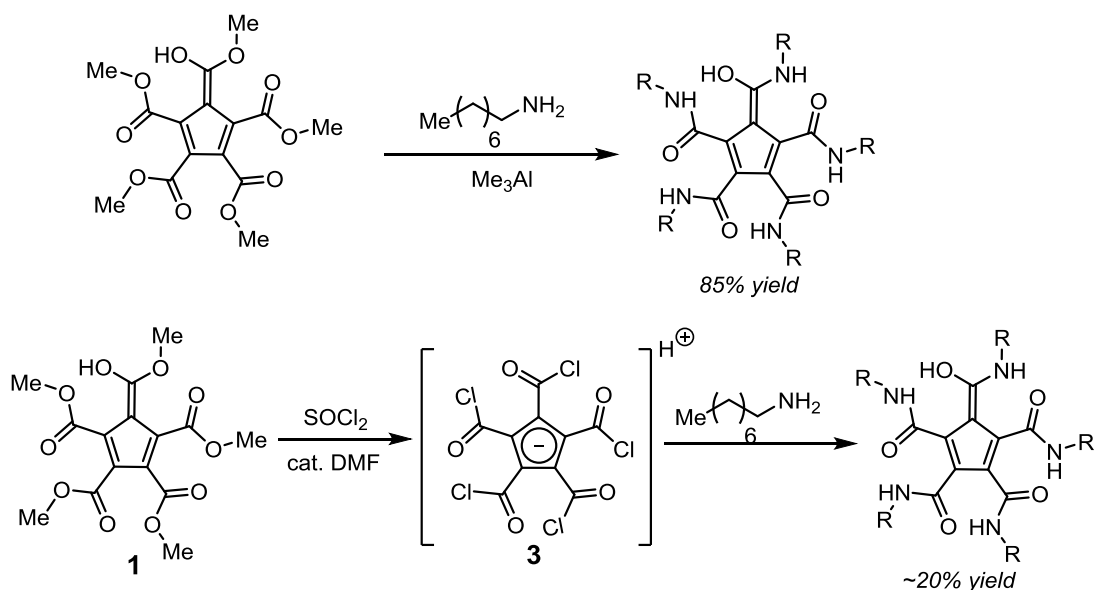
Figure 22: Comparison of penta(amide) formation using primary amines.

Lastly, the use of arenes as nucleophiles was attempted in the hopes of forming ketone products via consecutive Friedel–Crafts reactions. 1,3-Dimethylresorcinol was chosen as an electron-rich nucleophilic arene partner, and various reaction conditions tested. The acyl chloride **40** itself was unreactive towards the arene, even when reacted neat and at elevated temperatures. Therefore, Lewis acids were examined to promote the reaction. The classic Friedel–Crafts conditions use $AlCl_3$, but only rapid decomposition of the acyl chloride was observed upon addition of the Lewis acid. Eventually, reactions using $SnCl_4$ and $TiCl_4$ were found to give complicated mixtures but the desired product was observed by SFC-MS. Unfortunately, attempts to purify the products were unfruitful. Column chromatography gave indecipherable mixtures of products and the pentaarylated products were not successfully characterized. Thus, the formation of ketones via this method is not established. Attempts were made to use less electron-rich arenes as nucleophiles, but the same reaction conditions only decomposed the acyl chloride intermediate, with no evidence of acylation products.
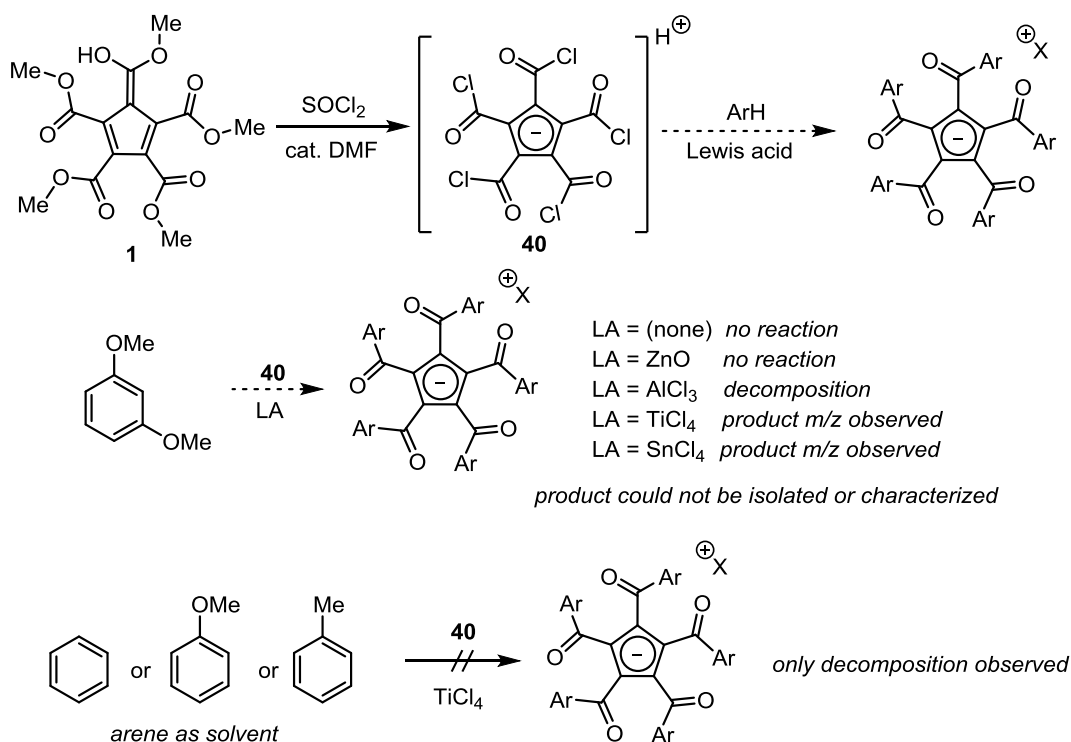
Figure 23: Attempted Friedel–Crafts reaction with acyl chloride *40*.

Conclusion

Exploration of the PCCP platform in the Lambert group has led to several strategies for accessing derivatives of this interesting class of compounds. Spurred on by interest in utilizing these anions in catalysis, we have placed a strong emphasis on diversification from readily accessible intermediates to aid in creation of libraries. Particularly, pentamethyl PCCP **1-H** represents an ideal starting material as it is easily prepared in large scale (>50 g). For most alkyl alcohols, the transesterification protocol works well, providing the PCCPs in good to excellent yields. In cases where transesterification is ineffective, the pentaacyl chloride **40** can be prepared, increasing the pool of potential nucleophiles. The combination of these two methods produces a wide range of substituted products, placing PCCPs on a good foundation for broad-based utility.

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Experimental Data

All reactions were performed open to the atmosphere, unless otherwise noted. Organic solutions were concentrated using a Buchi rotary evaporator. Methylene chloride, diethyl ether, benzene and toluene were dried using a J.C. Meyer solvent purification system. All other solvents and commercial reagents were used as provided. Flash column chromatography was performed employing 40-63 μm silica gel (SiliaFlash® P60 from Silicycle). Thin-layer chromatography (TLC) was performed on 250 μm glass-backed silica plates (SiliaPlateTM G TLC from Silicycle). ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ (except where noted) on Bruker DRX-300, DRX-400 or DRX-500 spectrometers as noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), integration, and assignment. All ^{1}H-NMR experiments were measured relative to the signals of tetramethylsilane (TMS, 0.00 ppm) or residual chloroform (7.26 ppm). Data for ^{13}C are reported in terms of chemical shift relative to deuterochloroform (77.16 ppm). Data for ^{19}F are reported in terms of chemical shift relative to hexafluorobenzene (-164.90 ppm). Optical rotations were measured using a Jasco DIP-1000 digital polarimeter. High-resolution mass spectra were obtained from the Columbia University Mass Spectrometry Facility on a Waters XEVO G2XS QToF mass spectrometer equipped with a UPC2 SFC inlet, electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, and atmospheric solids analysis probe (ASAP). Low-resolution mass spectrometry (LRMS) was performed on a Waters SQD2 quadrupole mass spectrometer equipped with a UPC2 SFC inlet and a dual ESI/APCI probe.

General Procedure for the Transesterification of PCCP 1

PCCP (1.0 equiv), alcohol (10 equiv), and *N*-methylimidazole (6.0 equiv) were dissolved in toluene (0.1 M) in a flame-dried two-neck round-bottom flask. A steady flow of N2 allowed for the removal of methanol . The reaction solution was refluxed for 48 hours while being monitored by SFC-MS. Upon completion, the reaction solution was cooled down to room temperature and concentrated *in vacuo*. The crude material was purified by silica gel column chromatography (0 → 5% MeOH/CH2Cl2). The purified material was subsequently washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), dried with anhydrous magnesium sulfate, and concentrated *in vacuo* to yield the title product. The transesterified PCCPs were stored in a sealed vial in the freezer.
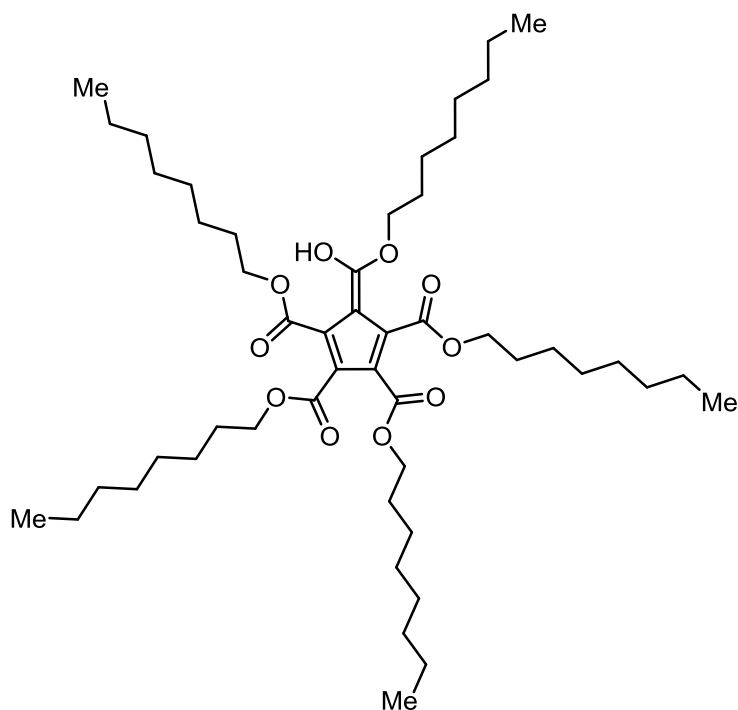
Pentakis(1-octyl) Cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate: The general procedure was followed using cyclopentadiene (0.100 g, 0.281 mmol, 1.0 equiv), 1-octanol (0.444 mL, 2.807 mmol, 10 equiv), and *N*-methylimidazole (0.134 mL, 1.684 mmol, 6.0 equiv) dissolved in 2.81 mL toluene (0.1 M). Upon completion of the reaction, the crude material was purified by

silica gel chromatography (0 → 5% MeOH/CH2Cl2), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO$_4$ to yield the title product as a brown viscous oil (0.170 g, 72% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 20.05 (s, 1H, **OH**), 4.66-3.87 (m, 10H, O**CH$_2$** x 5), 1.96-1.48 (m, 10H, OCH$_2$**CH$_2$** x 5), 1.48- 1.06 (m, 50H, OCH$_2$CH$_2$(**CH$_2$**)$_5$CH$_3$ x 5), 1.06-0.68 (m, 15H, **CH$_3$** x 5). ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.1, 167.5, 162.9, 134.1, 117.9, 106.5, 69.4, 65.8, 64.8, 32.0, 29.5, 29.4, 29.3, 28.9, 28.7, 28.5, 26.3, 26.0, 25.7, 22.8, 14.2. IR (thin film, cm$^-$^{1}) 2924, 2855, 1711, 1600, 1459, 1423, 1333, 1221, 1193, 1028, 760, 722, 622. HRMS (ESI-) exact mass calc'd for C50H85O10- [M-H+]- requires m/z 845.6148, found m/z 845.6138.
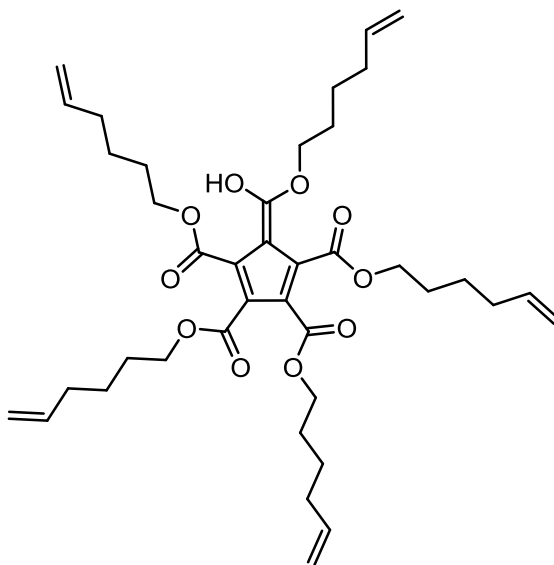
Pentakis(hex-5-en-1-yl) Cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate: The general procedure was followed using cyclopentadiene (0.100 g, 0.281 mmol, 1.0 equiv), 5-hexen-1-ol (0.337 mL, 2.807 mmol, 10 equiv), and *N*-methylimidazole (0.134 mL, 1.684 mmol, 6.0 equiv) dissolved in 2.81 mL toluene (0.1 M). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 5% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO$_4$ to yield the title product as a brown solid (0.112 g, 57% yield). 1H NMR (400 MHz, CDCl3) δ 20.00 (s, 1H, **OH**), 5.85-5.52 (m, 5H, H$_2$C=HC x 5), 5.06-

4.77 (m, 10H, H$_2$C=HC x 5), 4.44-3.92 (m, 10H, OC**H$_2$**), 2.15-1.10 (m, 30H, OCH$_2$(C**H$_2$**)**3**CH=CH$_2$ x 5). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.9, 167.3, 162.7, 138.3, 137.9, 133.9, 117.8, 115.3, 114.9, 106.4, 69.2, 65.5, 64.4, 33.4, 33.2, 29.7, 27.9, 25.4, 25.1, 24.8. IR (thin film, cm^{-1}) 3075, 2934, 2860, 1734, 1709, 1638, 1596, 1456, 1422, 1331, 1415, 1183, 1095, 1064, 993, 907. HRMS (ESI-) exact mass calc'd for C$_{40}$H$_{55}$O$_{10}$ - [M-H+]- requires m/z 695.3801, found m/z 695.3804.
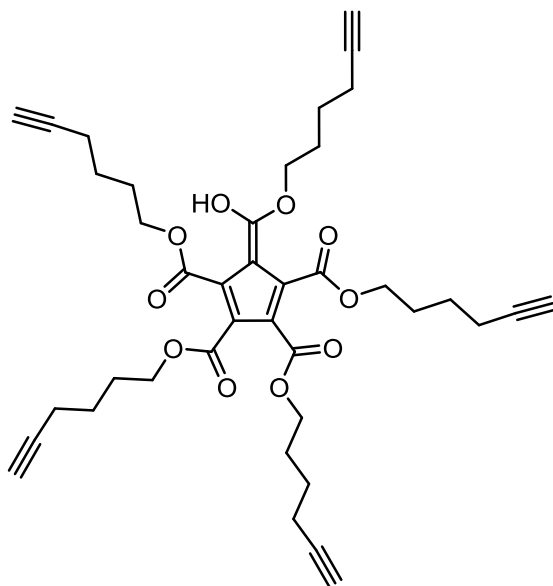
Pentakis(5-hexynyl) cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate:

The general procedure was followed using cyclopentadiene (0.089 g, 0.250 mmol, 1.0 equiv), 5-hexynol (0.275 mL, 2.50 mmol, 10 equiv), and *N*-methylimidazole (0.126 mL, 1.50 mmol, 6.0 equiv) dissolved in 5.0 mL toluene (0.05 M). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 5% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO$_4$ to yield the title product as a brown viscous oil (0.152 g, 59% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 20.06 (s, 1 H, OH), 4.45 (t, 4 H, OC**H$_2$**CH$_2$ x 2) 4.28 (t, 4 H, OC**H$_2$**CH$_2$ x2) (t, 2 H, OC**H$_2$**CH$_2$), 2.24 (m, 10 H, OCH$_2$C**H$_2$** x2), 2.02-1.54 (m, 25 H, **CH$_2$CH$_2$**CCH x 5) ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.0, 167.3, 162.7,

133.9, 117.8, 106.5, 84.0, 83.1, 69.4, 68.9, 28.8, 65.2, 64.1, 27.9, 27.6, 27.5, 25.1, 24.8, 24.4, 18.2, 18.1 IR (thin film, cm^{-1}) 3290. 2952, 2115. 1731, 1705, 1599, 1456, 1424, 1336, 1219, 1192, 1105, 1062, 1019, 921, 793, 761, 631. HRMS (ESI-) exact mass calc'd for $C_{40}F_{25}O_{10}$ - [M-H+]- requires *m/z* 685.3013, found *m/z* 685.3017.
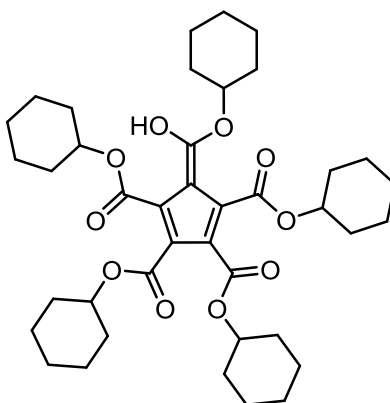
Pentakis(cyclohexyl) Cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate:

The general procedure was followed using cyclopentadiene (0.1580 g, 0.421 mmol, 1.0 equiv), cyclohexanol (0.445 mL, 4.21 mmol, 10 equiv), and *N*-methylimidazole (0.201 mL, 2.526 mmol, 6.0 equiv) dissolved in 4.21 mL toluene (0.1 M). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 5% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO$_4$ to yield the title product as a brown solid (0.253 g, 86% yield). ^{1}H NMR (400 MHz, CDCl$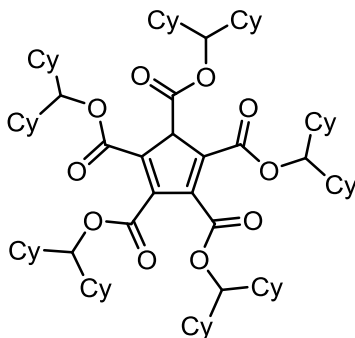_3$) δ 20.14 (s, 1H, O**H**), 5.25-4.45 (m, 5H, C**H**O), 2.23-0.60 (m, 50H, C**H$_2$** x 25). ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.7, 166.9, 162.5, 134.2, 118.4, 106.6, 79.3, 77.5, 74.0, 73.4, 32.0, 31.9, 31.6, 25.7, 25.6, 25.3, 24.4, 24.2, 24.0. IR (thin film, cm-1) 2932, 2856, 1733, 1702, 1590, 1452, 1415, 1357, 1313, 1212, 1188, 1124, 1007, 890. HRMS (ESI-) exact mass calc'd for $C_{40}H_{55}O_{10}$ - [M-H+]- requires m/z 695.3801, found m/z 695.3793.

Pentakis(dicyclohexylmethyl) cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate:

Following the general procedure using cyclopentadiene **2** (87 mg, .24 mmol), *N*-methylimidazole

(58 μL, 0.73 mmol) and dicyclohexylmethanol (470 mg, 2.4 mmol) dissolved in 20 mL of

toluene (0.01 M). Upon completion of the reaction, the crude material was purified by silica gel

chromatography (0 → 3% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (x3), dried with

Na$_2$SO$_4$ to give the product as a tan solid (230 mg, 80% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ

4.77 (t, 2H, CO$_2$C**H** x 2), 4.73 (t, 2 H, CO$_2$C**H** x 2), 4.70 (s, 1H, Cp C**H**), 4.45 (t, 1H, CO$_2$C**H**),

1.90 - 0.85 (m, 110H, alkyl C**H**) ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.3, 162.5, 161.5, 143.9, 84.5,

84.2, 83.9, 61.9, 39.1, 39.0, 38.9, 38.8, 38.6, 30.2, 30.1, 29.8, 28.0, 27.9, 27.8, 27.7, 27.6, 26.7,

26.7, 26.6-26.2 IR (thin film, cm^{-1}). 2923, 2851, 1727, 1622, 1590, 1447, 1407, 1322, 1236,

1189, 1091, 1065, 1045, 1008, 931, 891, 847. HRMS (ESI-) exact mass calc'd for C$_{75}$H$_{115}$O$_{10}$ -

[M-H+]- requires *m/z* 1175.8490, found *m/z* 1175.8491.

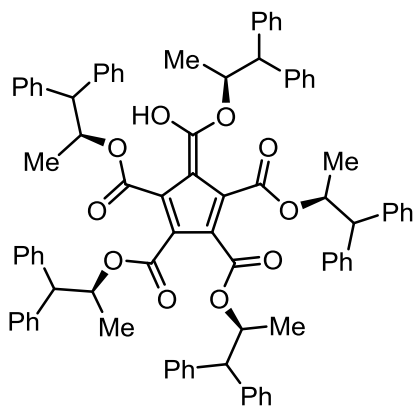**Pentakis((*S*)-1,1-diphenylpropan-2-yl) Cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate:**

The general procedure was followed using cyclopentadiene (0.118 g, 0.331 mmol, 1.0 equiv), (*S*)-1,1-diphenylpropan-2-ol (0.702 g, 3.312 mmol, 10 equiv), and *N*-methylimidazole (0.158 mL, 1.987 mmol, 6.0 equiv) dissolved in 3.31 mL toluene (0.1 M). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 8% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO4 to yield the title product as a brown solid (0.299 g, 72% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 19.66 (s, 1H, **OH**), 7.72-6.54 (m, 50H, Ar**H**), 6.02-5.10 (m, 5H, Ph2C**H** x 5), 4.60-3.37 (m, 5H, OC**H** x 5), 1.79-0.67 (m, 15H, CH$_3$ x 5). ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.3, 166.5, 162.5, 160.9, 160.8, 159.8, 142.2-140.3, 139.3, 134.9, 133.6, 130.4, 129.0-126.4, 118.7, 106.7, 78.6, 74.8, 74.4, 74.1, 73.9, 71.9, 59.5, 57.2, 57.1, 56.9, 56.6, 56.5, 56.4, 54.7, 29.8, 19.4, 19.2, 19.1, 19.0, 18.8, 18.5, 17.8. IR (thin film, cm^{-1}) 3027, 1731, 1598, 1494, 1452, 1406, 1321, 1238, 1046, 756, 700$[\alpha]_D^{23}$ = +4.92 (1.0 c, CHCl$_3$). HRMS (ESI-) exact mass calc'd for C$_{85}$H$_{75}$O$_{10}$ - [M-H+]- requires *m/z* 1255.5366, found *m/z* 1255.5364.
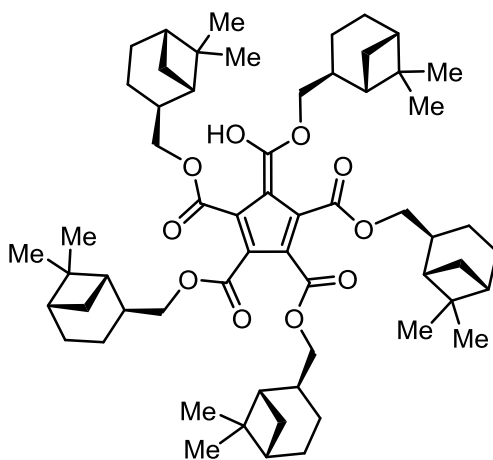
Pentakis((1*S*,2*S*)-6,6-Dimethylbicyclo[3.1.1]heptane-2-methanyl) Cyclopenta-1,3-diene-

1,2,3,4,5-pentacarboxylate: The general procedure was followed using cyclopentadiene (0.050 g, 0.140 mmol, 1.0 equiv), (1*S*,2*S*,5*S*)-(−)-Myrtanol (0.160 mL, 1.404 mmol, 10 equiv), and *N*-methylimidazole (0.064 mL, 0.842 mmol, 6.0 equiv) dissolved in 1.4 mL toluene (0.1 M). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 2% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO$_4$ to yield the title product as a tan solid (0.131 g, 97% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 20.04 (s, 1H, O**H**), 4.44-3.68 (m, 12H, OC**H$_2$**), 2.53-0.62 (m, 75H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.1, 167.4, 162.8, 134.0, 118.1, 106.5, 72.5, 69.2, 68.2, 42.65, 42.4, 42.1, 41.1, 41.0, 39.3, 34.6, 34.5, 34.2, 26.8, 26.7, 24.3, 24.0, 23.6, 23.5, 20.3, 18.5, 18.2. IR (thin film, cm^{-1}) 2913, 2868, 1734, 1597, 1460, 1418, 1332, 1211, 1185, 986, 753[α]$_D^{23}$ = −17.7 (1.0 c, CHCl$_3$). HRMS (ESI-) exact mass calc'd for C$_{60}$H$_{85}$O$_{10}$- [M-H+]- requires m/z 965.6148, found m/z 965.6143.
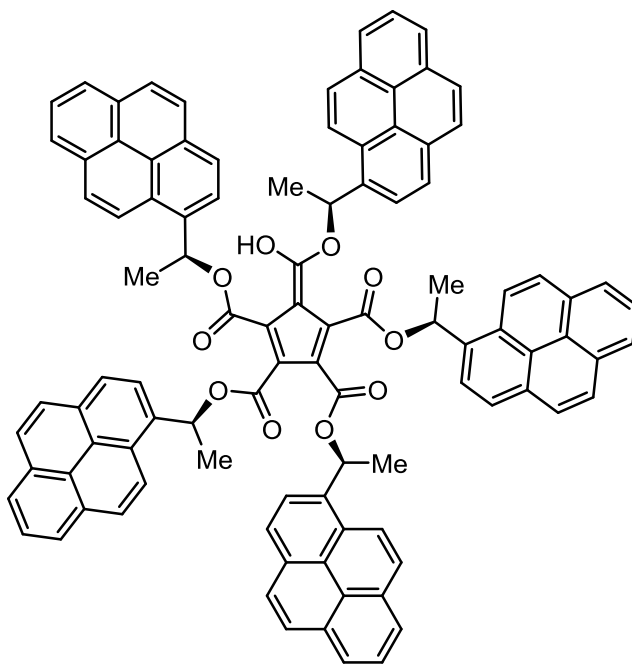

Pentakis((*S*)-1-(pyren-2-yl)propan-2-yl) Cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate:
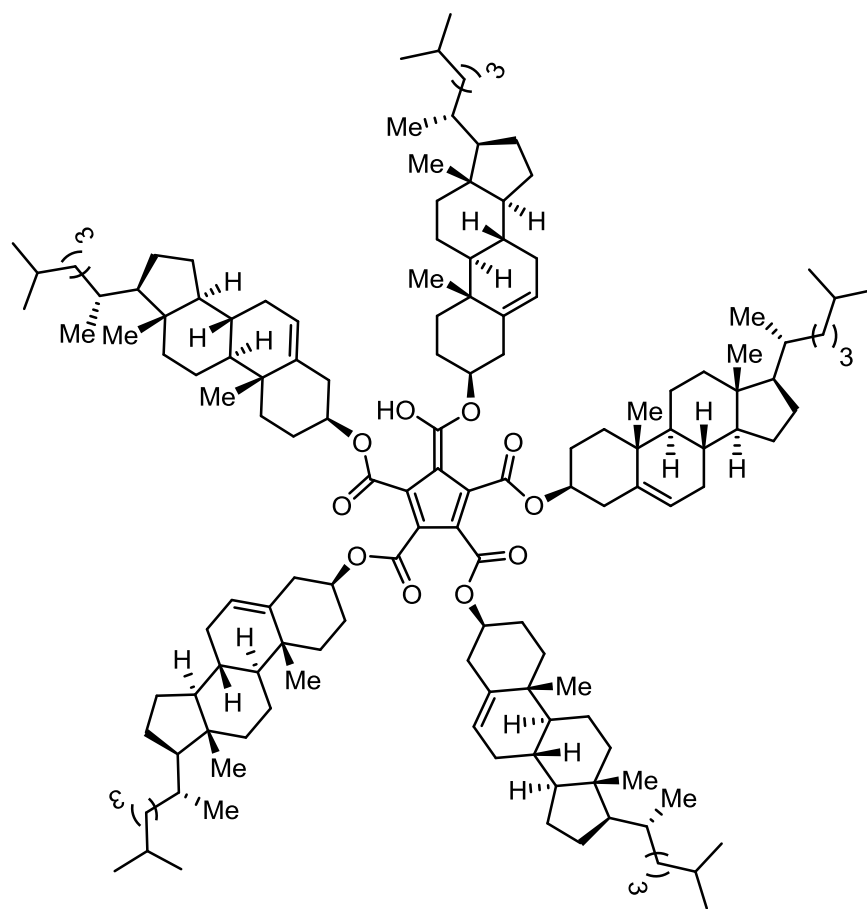
The general procedure was followed using cyclopentadiene (0.050 g, 0.140 mmol, 1.0 equiv), (*S*)-1-(pyren-2-yl)propan-2-ol (0.368 g, 1.403 mmol, 10 equiv), and *N*-methylimidazole (0.067

mL, 0.842 mmol, 6.0 equiv) dissolved in 1.40 mL toluene (0.1 M). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 5% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO$_4$ to yield the title product as a brown solid (0.184 g, 87% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 20.10 (s, 1H, OH), 9.02-7.42 (m, 45H, Ar**H**), 6.06-5.37 (m, 5H, C**H$_a$**H$_b$ x 5), 4.77-2.89 (m, 10H, [ROC**H** + CH$_a$**H$_b$**] x 5), 1.84-1.18 (m, 15H, C**H$_3$** x 5). ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.6, 167.5, 163.1, 134.5, 131.9, 131.3, 130.9, 130.7, 130.5, 130.0, 129.7, 128.6, 129.1, 128.9, 128.7, 128.5, 128.01, 127.96, 127.6, 127.4, 127.2, 127.1, 125.9, 125.7, 125.0, 124.8, 123.9, 122.8, 118.6, 107.0, 78.0, 73.7, 72.4, 40.1, 39.2, 29.8, 19.6, 19.5. IR (thin film, cm^{-1}) 2936, 2867, 1735, 1706, 1601, 1457, 1415, 1333, 1216, 1193, 1004, 758. $[\alpha]_D^{23}$= −2.45 (1.0 c, CHCl$_3$). HRMS (ESI-) exact mass calc'd for C$_{105}$H$_{77}$O$_{10}$ - [M-H+]- requires *m/z* 1495.5366, found *m/z* 1495.5376.

Pentakis((3β)-cholest-5-en-3-yl) Cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate: The general procedure was followed using cyclopentadiene (0.100 g, 0.281 mmol, 1.0 equiv), cholesterol (1.085 g, 2.807 mmol, 10 equiv), and *N*-methylimidazole (0.134 mL, 1.684 mmol, 6.0 equiv) dissolved in 2.81 mL toluene (0.1 M). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 5% MeOH/CH$_2$Cl$_2$), washed with 1 M HCl/CH$_2$Cl$_2$ (3 x), and dried with anhydrous MgSO4 to yield the title product as a brown solid (0.284g, 47% y). 1H NMR (500 MHz, CDCl3) δ 20.09 (s, 1H, O**H**), 5.55-5.19 (m, 5H, Vinylic H), 5.06-4.56 (m, 5H, OC**H** x 5), 2.71-0.44 (m, 220H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.4, 166.5, 162.1, 139.8, 138.8, 134.1, 123.6, 122.6, 122.4, 117.9, 106.4, 79.7, 75.1, 73.9, 56.7, 56.2, 50.1, 42.4, 39.8, 39.6, 38.5, 38.2, 37.7, 37.1, 36.8, 36.7, 36.6, 36.2, 35.8, 32.0, 31.9, 29.7, 29.4, 28.3, 28.0, 25.8, 24.3, 23.94, 23.86, 22.9, 22.6, 21.1, 19.4, 19.3, 18.8, 17.7, 14.2, 11.9. IR (thin

film, cm^{-1}) 2936, 2867, 1734, 1705, 1600, 1457, 1415, 1377, 1332, 1215, 1192, 1002, 756. $[\alpha]_D^{23}$ = −7.92 (1.0 c, CHCl$_3$). HRMS (ESI-) exact mass calc'd for C$_{145}$H$_{225}$O$_{10}$ - [M-H+]- requires m/z 2126.7103, found m/z 2127.7090.
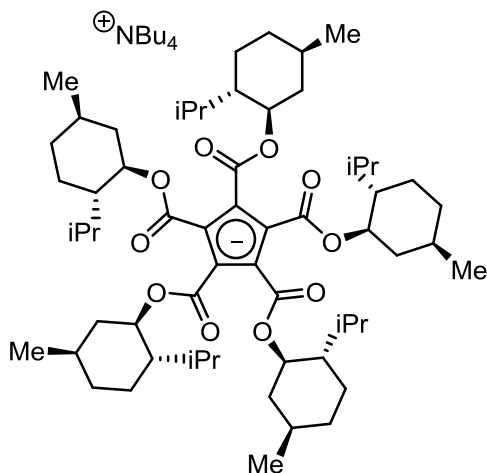
Large-Scale penta(menthyl)PCCP Synthesis:

To a three-necked flask, 1.78 g (5.00 mmol) of pentamethyl was dissolved in 100 mL of dry toluene. 7.81 g of (-)-menthol (50.0 mmol) were added and then finally 6.00 mL of N-methylimidazole (25.0 mmol) were added via syringe. A reflux condenser was added and the mixture heated at 110 °C with slow nitrogen flow from the two side-necks. After 72 h, the light brown mixture was cooled, and transferred to a separatory funnel with 100 mL of EtOAc. The organic layer was washed with 3 x 200 mL of 1 M HCl, then with 2 x 200 mL sat. NaHCO$_3$. Then 1.67 g of tetrabutylammonium chloride (6.00 mmol) was added and the organic shaken. This was washed with 2 x 100 mL of deionized water and then with 100 mL of brine. The organic layer was collected, dried and concentrated to give a tan solid. The crude product was triturated in ~150 mL of hot hexanes, then cooled, and placed in a -14 °C freezer overnight (Note: longer times will tend to also give needles of menthol). The product was collected via vacuum filtration and washed with cold (-14 °C) hexanes, yielding 4.80 g. The mother liquor

was concentrated, and triturated in ~50 mL of hot hexanes, then cooled and placed into a -14 °C freezer overnight. The solid was collected by filtration and washed with a minimum of cold hexanes. This solid was then suspended in ~5 mL of hexanes and cooled to -14 °C, then filtered to remove traces of menthol, yielding 560 mg. The two batches were combined to give 5.36 g of product. 88% yield

^{1}H NMR (500 MHz, CDCl$_3$) δ 4.73 (td, 5 H, COOC**H** x 5), 2.85 (m, 8 H, NC**H$_2$** x 4) 2.18-0.76 (m, 118 H, Alkyl **H**) ^{13}C NMR (125 MHz, CDCl$_3$) δ 167.2, 117.1, 72.6, 58.2, 46.7, 39.9, 34.6, 31.7, 25.1, 24.1, 23.3, 22.5, 21.5, 19.9, 17.0, 13.98 IR (thin film, cm^{-1}) 2953, 2931, 2869, 1705, 1679, 1655, 1481, 1451, 1685, 1268, 1191, 1177, 1097, 1079, 1038, 1013, 986, 918, 885, 838, 787 HRMS (ESI-) exact mass calc'd for C$_{60}$H$_{95}$O$_{10}$$^-$ [M-NBu$_4$$^+$]$^-$ requires *m/z* 975.6925, found *m/z* 975.6931.

General Procedure A:

175 mg (0.500 mmol) of pentamethyl was placed in a 25 mL flask under argon. This was dissolved in 2.00 mL of thionyl chloride and then 25 uL of DMF was added. A reflux condenser was attached and the solution heated at 60 °C for 16 h. The reaction was cooled and the thionyl chloride removed *in vacuo*. The yellow residue was dissolved in 4.00 mL of dry CH$_2$Cl$_2$ and used immediately thereafter.

2.50 mmol of alcohol (10 equivalents) was dissolved in 1.00 mL of dry CH$_2$Cl$_2$ in a flame-dried 2 dm vial under argon. To the stirred reaction mixture, the crude acyl chloride solution (2.00 mL, 0.250 mmol) was added over approximately 2 minutes. The solution was stirred for 20 minutes, then quenched by the addition of ~2 mL sat. NaHCO$_3$ solution. The mixture is then transferred to a separatory funnel and the flask washed with 10 mL CH$_2$Cl$_2$ and 10 mL of sat. NaHCO$_3$. The

organic layer was separated and the aqueous layer extracted with 2 x 5 mL of CH_2Cl_2. The organic layers were dried with Na_2SO_4 and purified by column chromatography. The collected products were converted to the tetramethylammonium salt by dissolving the material in CH_2Cl_2 and washing twice with aqueous NMe_4Cl, then once with deionized water. The organic layer was dried with Na_2SO_4 and the solvent removed to provide the desired product.

General Procedure B:

175 mg (0.500 mmol) of pentamethyl was placed in a 25 mL flask under argon. This was dissolved in 2.00 mL of thionyl chloride and then 25 uL of DMF are added. A reflux condenser was attached and the solution heated at 60 °C for 16 h. The reaction was cooled and the thionyl chloride removed in vacuo. The yellow residue was dissolved in 4.00 mL of dry DCM and used immediately thereafter.

2.50 mmol of alcohol (10 equivalents) was dissolved in 1.00 mL of dry DCM in a flame-dried 2 dm vial under argon. To this solution, 400 mg of anhydrous sodium carbonate was added. To the stirred reaction mixture, the crude acyl chloride solution (2.00 mL, 0.250 mmol) was added over approximated 2 minutes. The solution was stirred for the time indicated, then quenched by the slow addition of ~2 mL of deionized water. The mixture was then transferred to a separatory funnel, and the flask washed with 10 mL EtOAc and 10 mL of deionized water. The organic layer is separated and the aqueous layer extracted with 2 x 5 mL of EtOAc. The organic layers were dried with Na_2SO_4 and purified by column chromatography. The collected products were converted to the tetramethylammonium salt by dissolving the material in EtOAc and washing twice with aqueous NMe_4Cl, then once with deionized water. The organic layer was dried with Na_2SO_4 and the solvent removed to provide the desired product.
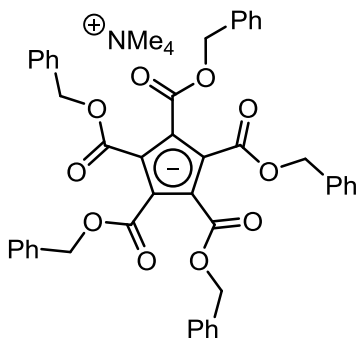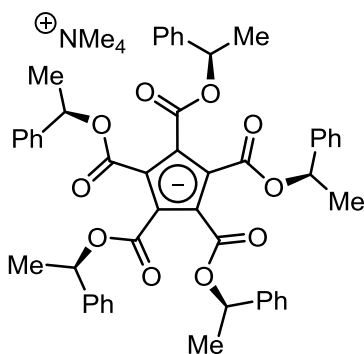
Pentakis(benzyl) cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethylammonium salt: Following General Procedure A, using benzyl alcohol (270 mg, 260 μL, 2.5 mmol). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 4% MeOH/CH$_2$Cl$_2$). The purified material was then washed with NMe$_4$Cl as described to give the product as a light brown semisolid. (96 mg, 47% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.22 (b s, 25 H, ArH x 5), 4.99 (s, 10 H, **CH$_2$**Ph x 5), 2.00 (s, 12 H, N(CH$_3$)$_4$) ^{13}C NMR (125 MHz, CDCl$_3$) 166.6, 136.8, 128.5, 128.5, 128.1, 117.0, 66.1, 54.9 IR (thin film, cm^{-1}) 3032, 2951, 1713, 1680, 1482, 1448, 1365, 1265, 1164, 1054, 1000, 945, 787, 746, 698 HRMS (ESI-) exact mass calc'd for, C$_{45}$H$_{35}$O$_{10}^-$ [M-NMe$_4^+$]$^-$ requires *m/z* 735.2330, found *m/z* 735.2225

Pentakis[(R)-1-phenylethyl)] cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethy-lammonium salt: Following General Procedure A, using (R)-1-phenylethanol (305 mg, 300 μL, 2.5 mmol). Upon completion of the reaction, the crude material was purified by silica gel

chromatography (0 → 2.5% MeOH/CH$_2$Cl$_2$). The purified material was then washed with NMe$_4$Cl as described to give the product as a light yellow solid (97 mg, 44% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ NMR 7.27 (m, 25 H, Ar**H**), 5.82 (q, 5H, **CH** x 5), 2.13 (s, 12H, N(**CH$_3$**)$_4$), 1.32 (d, 15 H, **CH$_3$** x 5) ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.4, 143.1, 128.3, 127.5, 126.4, 117.0, 72.1, 55.1, 21.9 . IR (thin film, cm^{-1}) 2981, 2931, 1728, 1692, 1453, 1165, 1052, 1029, 1009, 758, 699 $[a]_D^{23}$ = −103.9 (1.0 c, CHCl$_3$). HRMS (ESI-) exact mass calc'd for C$_{50}$H$_{45}$O$_{10}^-$ [M-NMe$_4^+$]$^-$ requires m/z 805.3013, found m/z 805.3016.

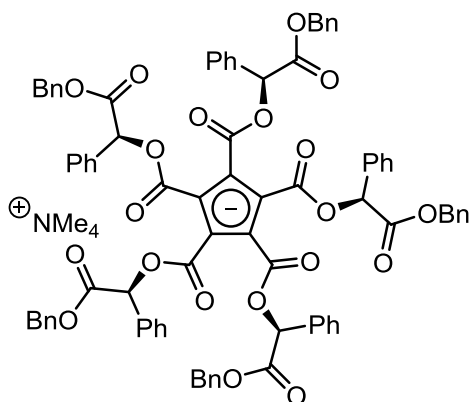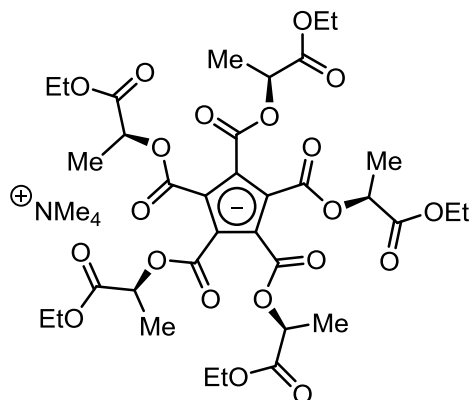**Pentakis[(S)-(benzyl)mandelyl] cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethylammonium salt**: Following General Procedure A, using (S)-benzyl mandelate (606 mg, 2.5 mmol). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 2% MeOH/CH$_2$Cl$_2$). The purified material was then washed with NMe$_4$Cl as described to give the product as a white solid (152 mg, 41% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27-7.07 (m, 50H, Ar**H**), 5.72 (s, 5H, C**H**Ph x 5) 5.07 (d, 5 H, C**H$_a$**H$_b$Ph x 5), 4.98, (d, 5 H, CH$_a$**H$_b$**Ph x 5) 2.71 (s, 12 H, N(**CH$_3$**)$_4$) ^{13}C NMR (125 MHz, CDCl$_3$) 169.5, 165.3, 135.9, 134.3, 128.6, 128.4, 128.0, 127.7, 127.5, 117.1, 74.5, 66.6, 56.0 IR (thin film, cm^{-1}) 3032, 17.31, 1699, 1482, 1451, 1253, 1148, 1081, 1047, 1028, 948, 748, 694 $[a]_D^{23}$ = +81.1 (1.0 c, CHCl$_3$)

HRMS (ESI-) exact mass calc'd for $C_{85}H_{65}O_{20}^-$ [M-NMe$_4^+$]$^-$ requires m/z 1405.4069, found m/z 1405.4076.

Pentakis[(S)-(ethyl)lactyl] cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethyl-ammonium salt: Following General Procedure A, using (S)-ethyl lactate (285 μL, 2.5 mmol). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 2.5% MeOH/CH$_2$Cl$_2$). The purified material was then washed with NMe$_4$Cl as described to give the product as a white solid (112 mg, 52% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.14 (**CH**CH$_3$ x 5) 4.11 (q, 10 H, **CH$_2$**CH$_3$ x 5) 2.91 (s, 12 H, N(**CH$_3$**)$_4$) 1.38 (d, 15 H, CHC**H$_3$** x 5), 1.24 (t, 15 H, CH$_2$C**H$_3$** x 5) ^{13}C NMR (125 MHz, CDCl$_3$) 171.9, 165.3, 117.2, 68.1, 60.8, 56.2, 16.8, 14.3 IR (thin film, cm^{-1}) 2987, 1740, 1462, 1378, 1269, 1173, 1132, 1096, 1047 $[a]_D^{23}$ = +82.7 (1.0 c, CHCl$_3$) HRMS (ESI-) exact mass calc'd for $C_{35}H_{45}O_{20}^-$ [M-NMe$_4^+$]$^-$ requires m/z 785.2504, found m/z 785.2505.

Large scale procedure was done following General Procedure A using cyclopentadiene (1.78 g, 5.0 mmol), (S)-ethyl lactate (5.73 mL, 50 mmol), thionyl chloride (12.0 mL), and DMF (0.25 mL). Upon completion of the reaction, the crude material was purified by silica gel

chromatography (0 →2.5% MeOH/CH2Cl2). The purified material was then washed with NMe4Cl as described to give the product as a white solid (2.52 g, 59% yield).
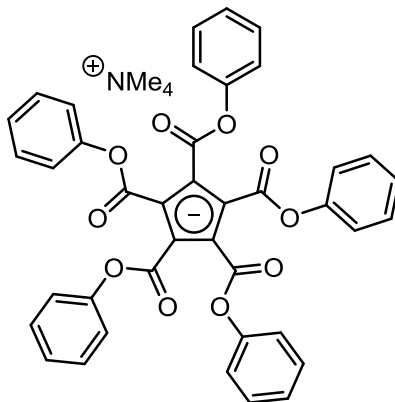
Pentakis(phenyl) cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethylammonium salt: Following General Procedure A, using phenol (235 mg, 2.5 mmol). Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 2.5% MeOH/CH$_2$Cl$_2$). The purified material was then washed with NMe$_4$Cl as described to give the product as a white solid (97 mg, 44% yield). (97 mg, 52% yield) ^{1}H NMR (500 MHz, CD$_3$CN) δ NMR 7.37 (t, 10 H, Ar**H**), 7.22 (t, 5 H, Ar**H**) 7.14 (d, 10 H, Ar**H**) 3.03 (s, 12 H, N(C**H$_3$**)$_4$) ^{13}C NMR (125 MHz, CD$_3$CN) δ 165.8, 152.7, 130.2, 126.3, 123.1, 118.5, 56.1 IR (thin film, cm^{-1}) 2924, 2859, 1707, 1593, 1552, 1480, 1448, 1380, 1267, 1163, 1066, 741, 690 HRMS (ESI-) exact mass calc'd for C$_{40}$H$_{25}$O$_{10}^-$ [M-NMe$_4^+$]$^-$ requires *m/z* 665.1448, found *m/z* 665.1451.
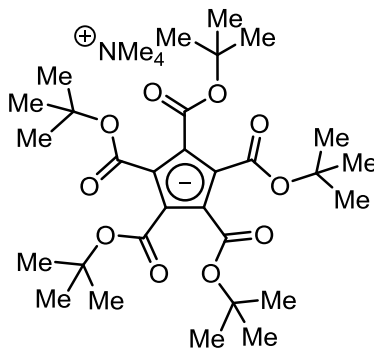
Pentakis[tert-butyl] cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethyl-ammonium salt: Following General Procedure B, using tert-butanol (235μL, 2.5 mmol). The reaction was stirred for 20 minutes. Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 2% MeOH/CH$_2$Cl$_2$). The purified material was then washed with NMe$_4$Cl as described to give the product as a white solid (76 mg, 29% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.74 (s, 12 H, N(C**H$_3$**)$_4$) 1.48 (s, 45 H, CC**H$_3$** x 5) ^{13}C NMR (125 MHz, CDCl$_3$) 167.4, 117.7, 79.0, 56.8, 28.4 IR (thin film, cm^{-1}) 2976, 2930, 1689, 1480, 1451, 1364, 1224, 1149 HRMS (ESI-) exact mass calc'd for C$_{30}$H$_{45}$O$_{10}$$^-$ [M-NMe$_4$$^+$]$^-$ requires *m/z* 565.3013, found *m/z* 565.3018.

Pentakis[2,2,2-trifluoroethyl] cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethyl-ammonium salt: Following General Procedure B, using 2,2,2-trifluoroethanol (182μL, 2.5 mmol). The reaction is stirred for 1 h. Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 1% MeOH/EtOAc). The purified material was then washed with NMe$_4$Cl as descri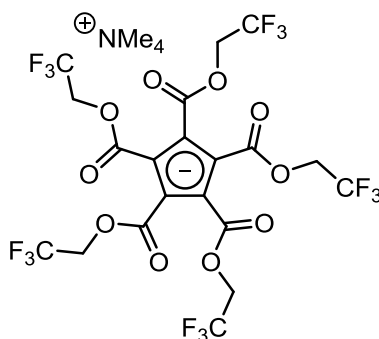bed to give the product as a white solid (79 mg, 41% yield). ^{1}H NMR (500 MHz, CD$_3$CN) δ 4.59 (q, 10 H, C**H$_2$**CF$_3$ x 5) 3.01 (s, 12 H, N(C**H$_3$**)$_4$) ^{13}C NMR (125 MHz, CD$_3$CN) 164.8, 124.7, 117.1, 61, 56.1 ^{19}F NMR (282 MHz, CD$_3$CN) -74.53 IR (thin film, cm^{-1}) 2975, 1738, 1693, 1485, 1451, 1410, 1277, 1254, 1142, 1079, 961 HRMS (ESI-) exact mass calc'd for C$_{20}$H$_{10}$F$_{15}$O$_{10}$$^-$ [M-NMe$_4$$^+$]$^-$ requires *m/z* 695.0034, found *m/z* 695.0039.
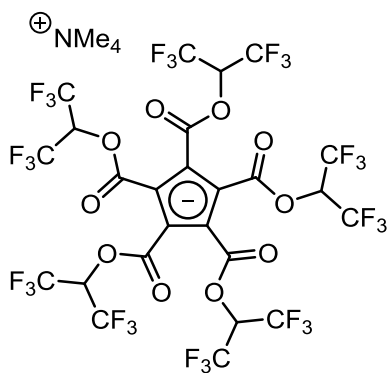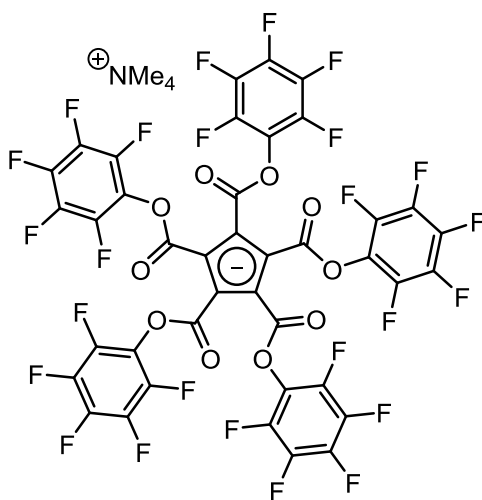
Pentakis[1,1,1,3,3,3-hexafluoro-2-propyl] cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethylammonium salt: Following General Procedure B, using 1,1,1,3,3,3-hexafluoro-2-propanol (263 μL, 2.5 mmol). The reaction is stirred for 16 h. Upon completion of the reaction, the crude material was purified by alumina chromatography, neutral Brockman grade 1 (10 → 60% MeOH/CH$_2$Cl$_2$). The purified material was then washed with NMe$_4$Cl as described to give the product as a yellow solid (109 mg, 40% yield). ^{1}H NMR (500 MHz, CD$_3$CN) δ 6.16 (m, 5 H, **CH**(CF$_3$)$_2$ x 5) 3.07 (t, 12 H, N(**CH$_3$**)$_4$) ^{13}C NMR (125 MHz, CD$_3$CN) 162.2, 120.4, 116.7, 67.5, 56.2 ^{19}F NMR (282 MHz, CD$_3$CN) -73.79 IR (thin film, cm^{-1}) 2972, 1751, 1483, 1387, 1354, 1285, 1233, 1203, 1112, 1081, 910, 690 HRMS (ESI-) exact mass calc'd for C$_{25}$H$_5$F$_{30}$O$_{10}^-$ [M-NMe$_4^+$]$^-$ requires *m/z* 1034.9403, found *m/z* 1034.9419.

Pentakis[2,3,4,5,6-pentafluorophenyl] cyclopenta-1,3-diene-1,2,3,4,5-pentacarboxylate tetramethylammonium salt: Following General Procedure B, using 2,3,4,5,6-pentafluorophenol (460 mg, 2.5 mmol). The reaction is stirred for 48 h. Upon completion of the reaction, the crude material was purified by silica gel chromatography (0 → 2% MeOH/EtOAc). The purified material was then washed with NMe_4Cl as described to give the product as a green oil (42 mg, 15% yield). ^1H NMR (500 MHz, CD_3CN) 3.06 (s, 12 H, $N(CH_3)_4$) ^{13}C NMR (125 MHz, CD_3CN) 161.5, 142.5, 140.4, 139.0, 126.2, 117.5, 56.2 ^{19}F NMR (282 MHz, CD_3CN) -165.3, -161.2, -154.3 IR (thin film, cm^{-1}) 1741, 1520, 1485, 1485, 1115, 996 HRMS (ESI-) exact mass calc'd for $C_{40}F_{25}O_{10}^-$ [M-NMe_4^+]$^-$ requires *m/z* 1114.9092, found *m/z* 1115.9105.

Chapter 3: An Overview of Electrophilic Silicon

Silicon, being right below carbon in Group 14 on the periodic table, faithfully displays the properties we are taught as students to expect of it. It tends to form four coordinate compounds and adopt the tetrahedral geometry characteristic of carbon. Prima facie, one's naïve chemical intuition should lead to a good understanding of silicon chemistry. However, it does not take long for this illusion to be shattered by the many contrasts between silicon and carbon chemistry: the tendency for silicon to form hypervalent compounds and the extreme nature of the silicon-fluorine bond being prime examples. We will be concerned with the astonishing difference between the stability of trityl (Ph_3C^+) and triphenylsilyl (Ph_3Si^+) cations. This chapter will explore the history of electrophilic silicon species, the pursuit of a true silylium species, and the use of silicon Lewis acids in organic synthesis.

Differences between C and Si

To illustrate the fundamental differences between carbon and silicon, we will consider the pair of compounds Ph_3C^+ and Ph_3Si^+. The trityl cation is a rather stable species producing a characteristic, deep yellow color. Many trityl salts have been produced and isolated, and truly ionic examples have been definitively characterized. Indeed, the ease of ionization is one of its most recognizable features: a trityl group can be introduced as an effective protecting group that is easily removed by acid. The Ph_3Si^+ cation, by contrast, shows a voracious hunger for electron density, and crystal structures nearly always show it coordinated to its counterion or solvent molecules.

Our chemical precepts would predict that the Ph_3Si^+ should be more stable than Ph_3C^+. Silicon is a more electropositive element, and with its larger size and greater polarizability, it should be able to better stabilize the positive charge than carbon.

Many factors come together to explain the strong electrophilicity of silylium ions, and why it is particularly difficult to synthesize fully ionized silylium salts, as illustrated in Figure 1. The two main differences between carbon and silicon - silicon's greater size and greater electopositivity - are largely responsible. The electronegativity difference means Si–C bonds are slightly polarized ($Si^{\delta+}- C^{\delta-}$), leading to localization of the positive charge on the silicon center. In addition, the mechanisms employed to stabilize carbocations do not work well for silyliums. While the charge in Ph_3C^+ is delocalized into the phenyl rings (though not all three at once due to the impossibility of all three being fully planar simultaneously), the Si(3p)-C(2p) overlap is poor due to the difference in orbital size and the increased Si-C bond length. This lack of π-bonding leads to ready deformation of the idealized trigonal planar structure, opening the silicon atom to coordination. Thus, the conclusion is that Ph_3Si^+ is more stable but counterintuitively more readily accepts electron density to form complexes.

good p_π-p_π overlap   *poor p_π-p_π overlap*   *polarized bonds*   *easily distorted geometry*
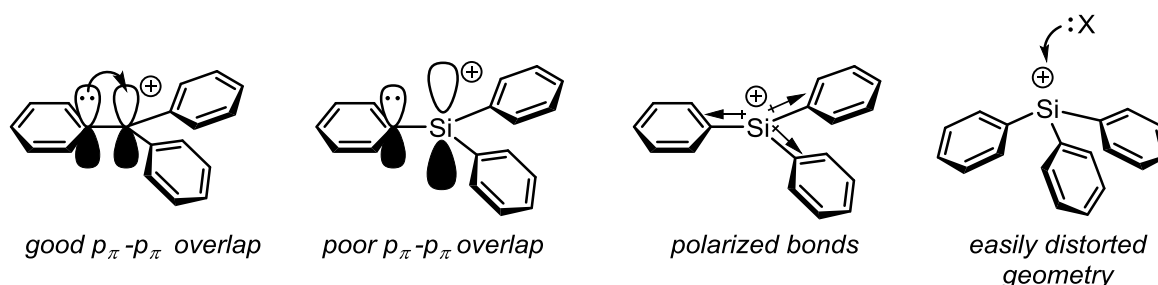
Figure 1: Differences between Ph_3C^+ and Ph_3Si^+.

The Silylium Problem

The inability to form a compound with an uncoordinated R_3Si^+ fragment lead to what Reed characterized as the silylium problem.[1] Many of the "non-coordinating" anions known to chemists have been shown to coordinate strongly when the "silylium" compounds are formed; for instance, Olah showed that triphenylsilyl perchlorate exists as the covalent *O*-bound silyl ester (Figure 2).[2] Often the silicon atom is reactive enough that decomposition occurs resulting from abstraction of fluoride or oxo species. An interesting example comes from the well-known fluorinated borates, where etrakis(3,5-bis(trifluoromethyl)phenyl)borate decomposes[3] while the tetrakis-(pentafluorophenyl)borate (TPFPB) can form stable compounds with silicon counterions.
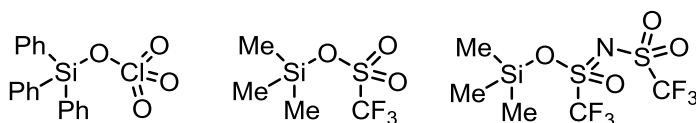
Figure 2: Most silyl species are covalently bound, even anions of very strong acids.

In fact, TPFPB was used to form **1,** the first claimed free silylium Et_3Si^+, where the silicon was proposed to be three-coordinate (Figure 3, top left).[4] This claim prompted considerable debate from chemists in the field. The main disagreement was to what extent should one call the "Et_3Si" moiety of **1** a free silylium ion. The crystal structure showed a coordinated toluene molecule, though the bond between the silicon and carbon is significantly elongated compared to typical Si-C bond. Further, the ^{29}Si shift of 85 ppm was well short of the ~300 ppm predicted for a completely cationic silicon center. The end result of this debate was that **1** represented an intermediate species between a σ- and π-complex of the Et_3Si^+ and toluene, with a significant portion of the positive charge being shifted to the arene.

Reed would go on to pioneer carborane anions as an answer to the silylium problem. The stability of carboranes are unmatched as anions. The negative charge is highly delocalized across

the cage-like structure due to the aromaticity of the molecule, and the addition of electron-withdrawing halides offers further stability. Besides being one of the strongest acids known in the chemical zoo, the extreme nature of the anion led to the isolation of a freer silylium **2**[5] (in fact, it was through the silylium salt that access to the carborane acid was achieved).

The extent to which **2** was ionized was shown both via ^{29}Si NMR spectroscopy and the pyramidalization of the silyl group in the crystal structure. While the chemical shift (δ 115 ppm) is still far upfield from the calculated gas phase value of free R_3Si^+, calculations show the ^{29}Si chemical shift is extremely sensitive to any electron density, even at fairly lengthy distances. In this case, one of the bromides on the carborane provides enough electron density to significantly shield the cationic silicon center.
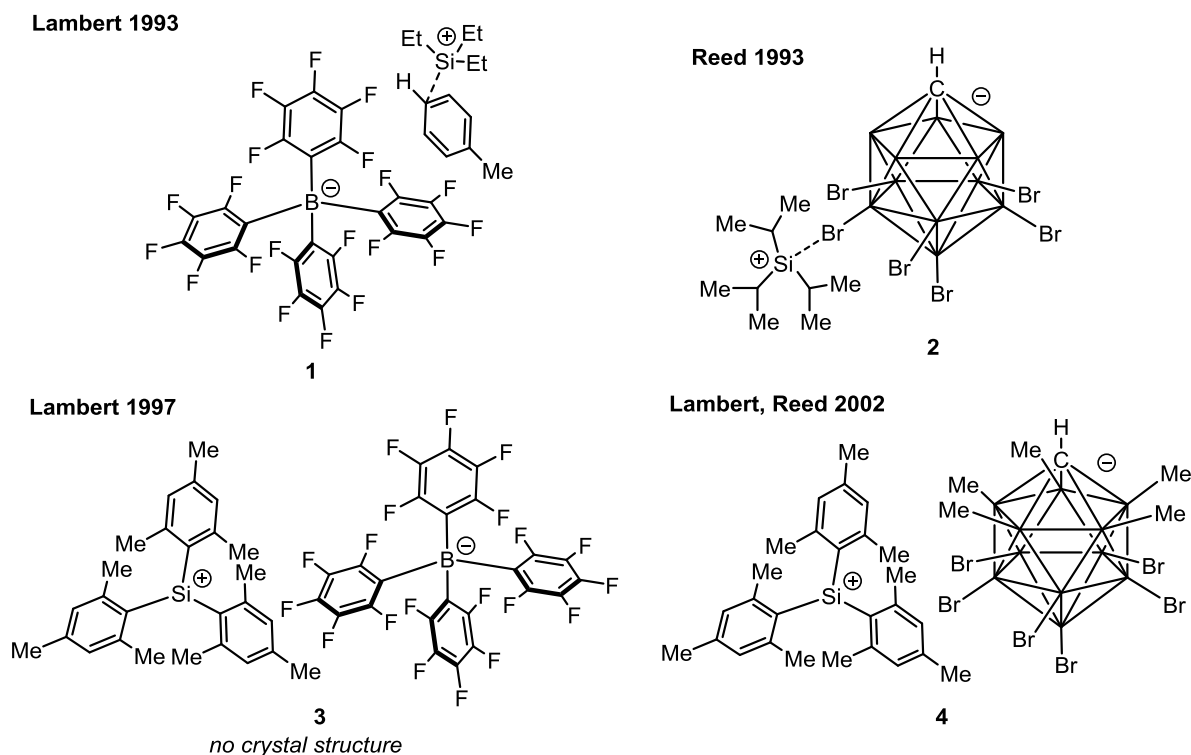
**Figure 3: Examples of highly-cationic silylium salts.**

The fact that both **1** and **2** show significant coordination led to a change in focus to manipulating the substitution at the silicon to achieve a free silylium. The bulky tris(mesityl)silyl

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group, with its ortho-methyls blocking access to the silicon center, proved to be crucial. Lambert first prepared the TPFPB salt **3** with a ^{29}Si chemical shift of δ 225.5 ppm,[6] and comparison to computations suggested it to be ionic, though they were unable to obtain a crystal structure. True confirmation came with the more crystaline carborane salt **4**, which has a solid state ^{29}Si chemical shift of δ 226.7 ppm.[7] The lasting impact of this scientific debate was to demonstrate the surprising difficulty in obtaining a truly free silylium species. The consensus seems to have settled on the fact that in solution the Si^+ will be quenched to some significant degree, either by solvent or the counterion. However, that very fact can be exploited to great effect to produce interesting chemistry.

Lewis Acid Catalysis

From the discussion above, there is an obvious basis for the use of silicon as a Lewis acid. Lewis acidity is defined as the ability for a chemical species to accept electron density. This is an alternative acidity to Brønsted acidity that was discussed earlier. Lewis acidity can be understood in terms of filling an incomplete valence shell; in this case, the three-coordinate silicon accepts two electrons to reach the eight required for a closed shell. Silicon is a rather electropositive element - with a Pauling electronegativity of 1.9 - and is a third row element, which limits the ability for π-type interactions to stabilize the positive charge. Thus, much of the charge is localized on the Si atom. These descriptions offer the foundation to understand the potent Lewis acidity of silylium species. We can then apply this reactivity towards the activation of chemical species, as represented by the equilibrium in Figure 4, and describe it in the same manner as Brønsted acids were in Chapter 1. In fact, Brønsted acids can be imagined as a specific category of Lewis acids where H^+ is the Lewis acidic species. Therefore, the same

description can be used to characterize the interactions of a Lewis acid with a substrate. By accepting electron density, the HOMO of the substrate is lowered, and it becomes more electrophilic and more reactive towards nucleophiles (*vide infra*, pg 89).
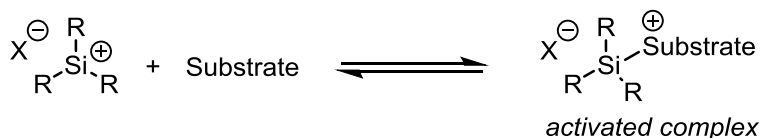
Figure 4: Activation of a generic substrate with a silylium salt.

One important aspect, if not the most important aspect, is turnover of the catalytic species. All forms of catalysis must reform the initial reactive catalyst, and often this is made more difficult by product inhibition. For silicon-based catalysts, turnover is especially problematic due to the strong bonds silicon makes, for instance with oxygen or fluorine. Creative strategies to mitigate this will be discussed, but it should be noted that the common approach is to ignore this issue altogether. That is, the reactions are designed to *not be catalytic in the silicon species*. Silicon-containing nucleophiles such as silanes, silylketene acetals or silyl enol ethers can be used which lose "R_3Si^+" during the reaction to close the catalytic cycle. These same molecules can also be used as an exogenous silyl source (or "fuel") that do not take part in the reaction to be incorporated into the product; instead, they only serve to react with a catalytic intermediate to generate the required silylium.

Borane-Silane reductions

An interesting class of reactions are silane reductions catalyzed by strong boron Lewis acids, with tris(pentafluorophenyl)borane (BCF) being the most common. Conceivably, direct activation of the substrate by the boron could occur followed by nucleophic hydride addition of the silane. What has been found by mechanistic studies points to an initial equilibrium between the borane and silane to give a silylium borohydride. The electrophilic silylium then coordinates

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to the substrate, thereby activating the substrate towards accepting the relatively poorly nucleophilic borohydride. This important mechanistic detail connects the following reactions together, with the silicon-substrate interaction being key to the observed reactivity. Thus, these systems deserved to be considered as full-fledged members of electrophilic silicon reactions.

The reduction of carbonyls was first described in 1996 by Piers using triphenylsilane (Figure 5).[8] Interestingly, esters were reduced more quickly than aldehydes yet in competition experiments aldehydes are reduced preferentially. This result suggested complexation of the "Ph_3Si^+" was key for activation of the substrate, and that the BCF-substrate adduct was not the active intermediate. Further studies confirmed the transient formation of the silylium borohydride.[9,10] A corroborating experiment was performed that showed the inability for BCF to reduce carbonyls with iPr$_3$SiH, presumably because the hydride is too sterically hindered to be abstracted by the borane to form the active silyl borohydride complex.

Piers 1996, 2000
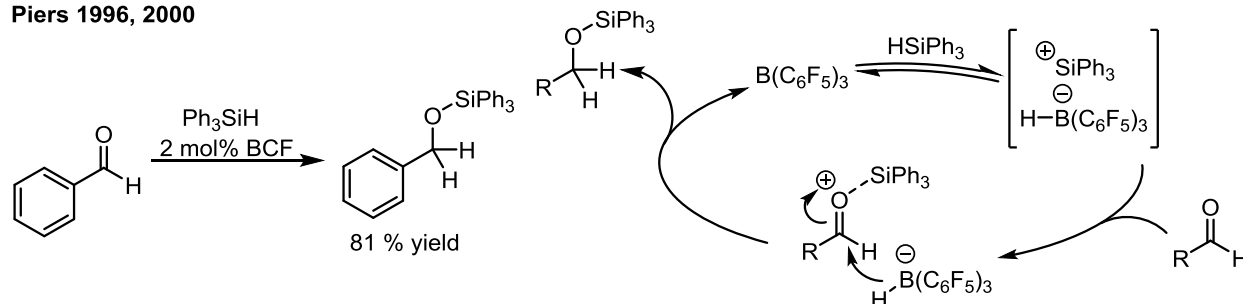
Figure 5: Piers' hydrosilylation and its mechanism, showing initial activation of the silane by BCF.

The system is extremely versatile. Ketones and aldehydes can be reduced to the corresponding alcohols with 1 equivalent of silane; they can be further deoxygenated with excess silane. Esters are reduced to protected acetals, which can be hydrolysed to obtain the aldehydes. Gevorgian later showed that the carboxylates can be fully reduced to the alkanes directly with the use of Et$_3$SiH (Figure 6, top left).[11] While imines are also reduced, the process is mechanistically distinct,[12] with the BCF-imine adduct being reduced by the silane directly.

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This methodology has been extended to various substrates. Rosenberg showed 1,2-diketones can be reduced to either the syn- or anti-diols depending on the silane used.[13] α,β-Unsaturated ketones undergo clean conjugate reduction to the silylenol ether (Figure 6, top right).[14] With excess silane, cyclopentenone substrates are quickly hydrosilated to the α-silyl silylether; cyclohexenones require heating and extended reaction times. As an alternative to much harsher and nucleophilic reductants such as diisobutylaluminum hydride or lithium aluminum hydride, BCF can be used to reduce amides to the amine,[15] albeit at elevated temperatures. Gagné recently reported alkyl-B(C$_6$F$_5$)$_2$ Lewis acids as a more active catalysts capable of performing the amide reduction at room temperature.[16] By showing that the BCF-silane system can promote amidations, as well as selectively reduce amides in the presence of carboxylic acids, Fu created a one-step *N*-alkylation using carboxylic acids.[17] The selectivity for amide reduction likely arises from the greater coordination ability of the amide product over the carboxylic acid.
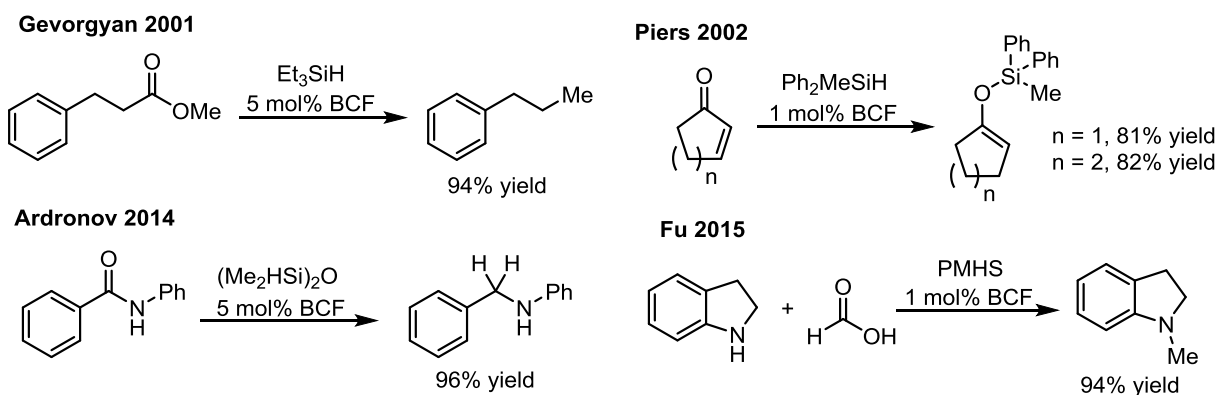
Figure 6: Silane reductions of carbonyls catalyzed by B(C$_6$F$_5$)$_3$.

The reductive deoxygenation of alcohols has been extensively studied by Gagné (Figure 7). In excess silane, sugars and other polyols can be fully reduced to the corresponding alkane.[18] Under more controlled conditions, polyols can be sequentially silylated and reduced,[19] with primary alcohols being reduced selectively. Further reduction of the secondary alcohols then

occurred with either retention or inversion of the stereocenter dependent on the structure of the sugar used. Mechanistic studies showed the selectivity arises from the formation of cyclic silyloxonium intermediates. Morandi developed a useful twist on this reaction, using diphenylsilane to form a cyclic siloxane, followed by addition of triethylsilane to cleave the primary C-O bond (Figure 7 bottom).[20]

Gagné further showed the utility of borane reduction in the late-stage reduction of natural products.[21] Using a family of four "super-electrophilic" boranes (Figure 7 box), various reductive transformations could be selectively performed in the context of complex, polyfuctional molecules, such as dihydroartemisinin (Figure 7, middle) and 10-deacetoxybaccatin.
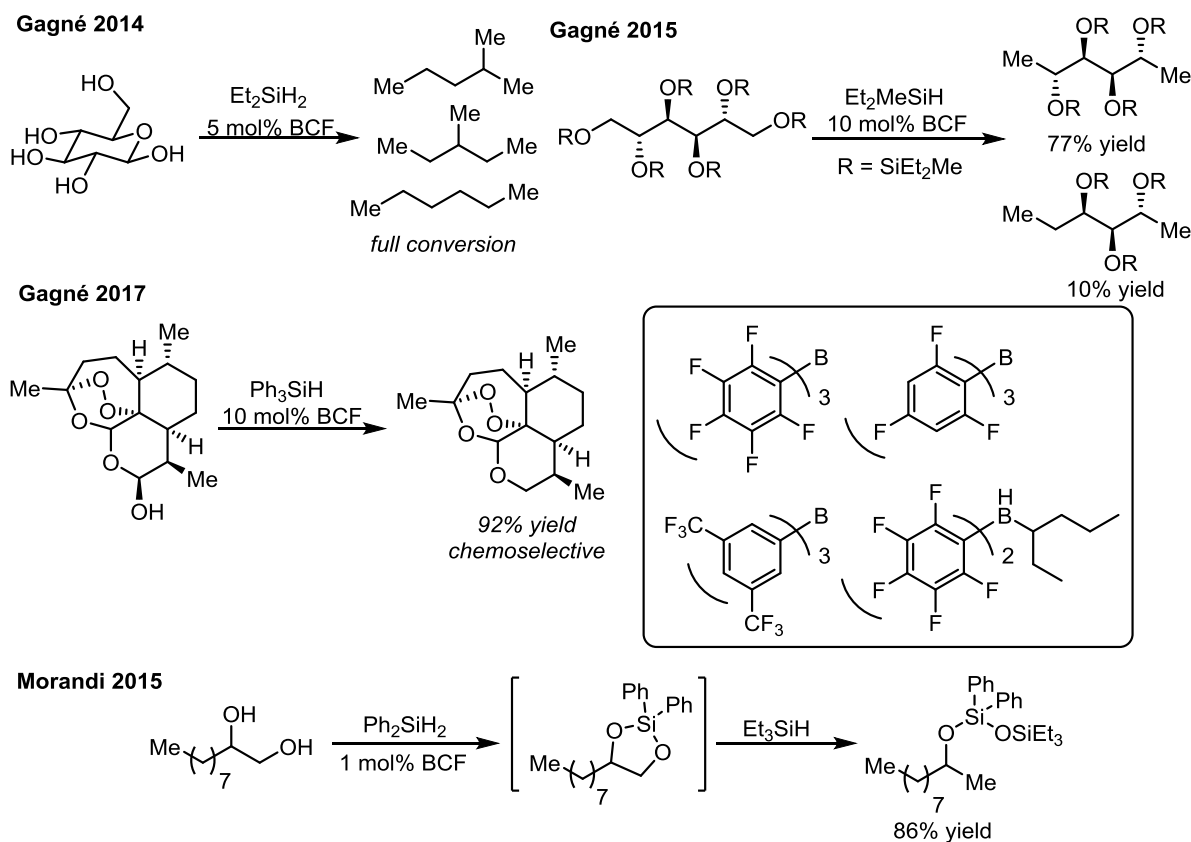
Figure 7: Reduction of C–O bonds with silanes catalyzed by B(C$_6$F$_5$)$_3$.
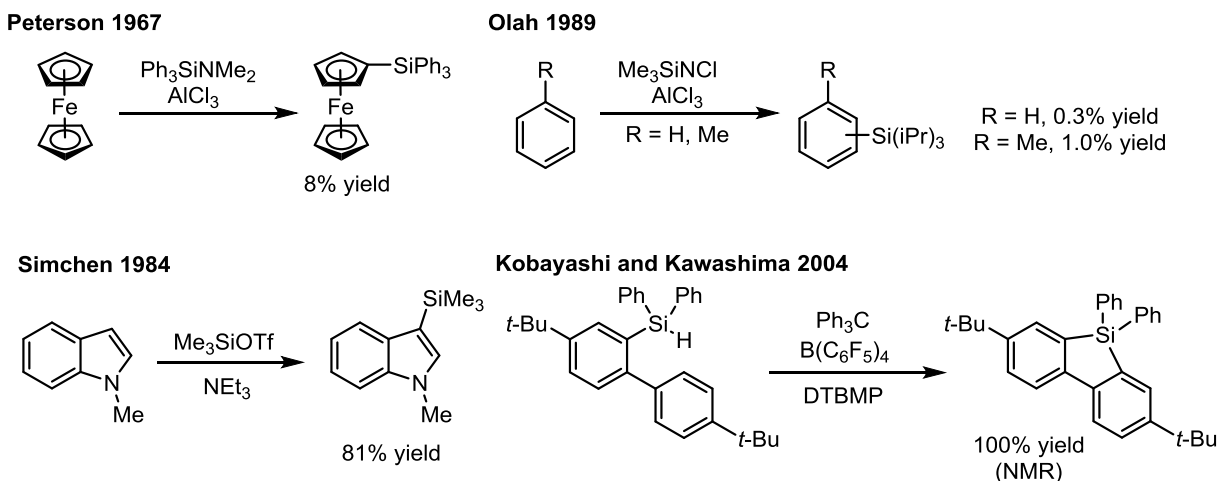
Silylations

While the discussion of the last section detailed the effectiveness of BCF/silane systems for reduction of carbon-heteroatom bonds, reactions designed to form C-Si bonds are comparatively rare. In 2002, Gevorgyan developed the catalytic hydrosilylation of alkene using BCF (Figure 8).[22] The protocol worked well for styrenyl and aliphatic olefins, and a variety of silanes could be sucessfully activated, giving the products in high yields. Quinolines and pyridines can be reduced, then subsequently hydrosilyated to form the 3-silyl heterocycles[23] in good yields. Electrophilic silylation of arenes is somewhat more difficult. Ingleson investigated the silylation of thiophenes, achieving modest to good yields of the silylated products, though reduction of the arene was competetitive, giving a mixture of products.[24]

Gevorgyan 2002

Ingleson 2014
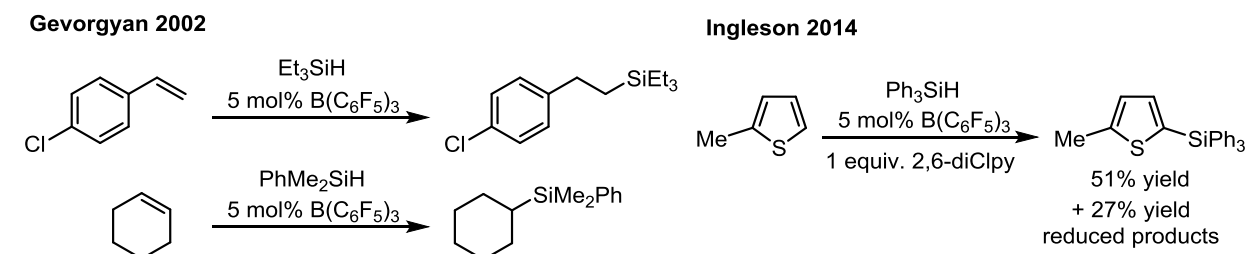
Figure 8: Catalytic C–H silylations catalyzed by B(C₆F₅)₃.

The first sila-Friedel–Crafts reaction was reported by Peterson, using $AlCl_3$ to activate silyl chlorides with ferrocene as the nucleophile (Figure 9, top left).[25] They successfully isolated the silylferrocenes, albeit in modest yields. When less nucleophilic benzene or toluene are used, only trace silylarene is formed due to the very slow rate of silylation.[26] Work by Simchen demonstrated that Me_3SiOTf is electrophilic enough to silylate electron-rich indoles and pyrroles using stoichiometric triethylsilane to absorb the liberated proton (Figure 9, bottom left).[27] Addition of the amine is essential for preventing protodesilylation of the desired product. Kobayashi and Kawashima described the intramolecular sila-Friedel–Crafts of arylsilanes to form dibenzosiloles[28] via oxidation with an equivalent of $Ph_3CB(C_6F_5)_4$ with a bulky pyridine

base to deprotonate the arenium intermediate (Figure 9, bottom right). Notably, these methods all

rely on stoichiometric amounts of activators to produce the highly reactive silicon electrophile.

Figure 9: Stoichiometric Friedel–Crafts silylation of arenes.

Kawashima and Mochida later described the autocatalytic cyclization of alkynes and

benzylsilanes (Figure 10, top).[29] After initial abstraction of hydride from the silane, the alkyne

nucleophile intercepts the silylium. Subsequent cyclization and 1,3-hydride shift produces a

carbocation that can abstract hydride from another silane, continuing the cycle. While the yields

are modest, the system achieves up to 25 turnovers. Oestreich made a significant advance by

utilizing Brookhart's acid to catalyze the silylation of indoles and anilines (Figure 10, bottom).[30]

The acid is strong enough to protonate silanes, producing the silylium and hydrogen, while the

reverse protodesilylation is controlled enough to provide good yields of products with a catalyst

loading of only 1 mol%.

Mochida and Kawashima 2014
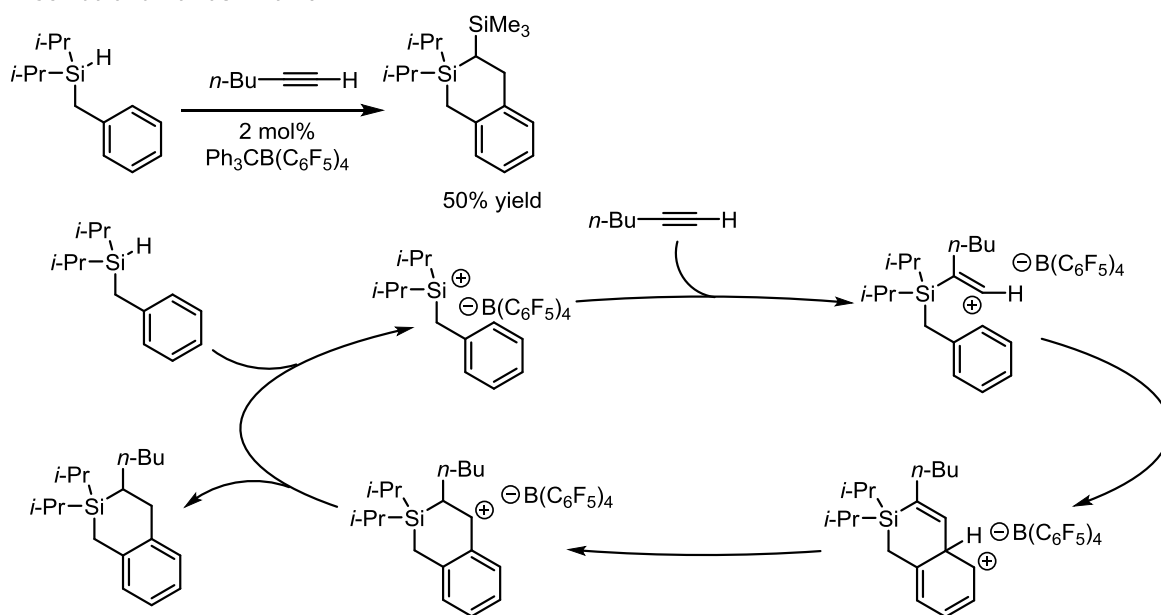
Oestreich 2016
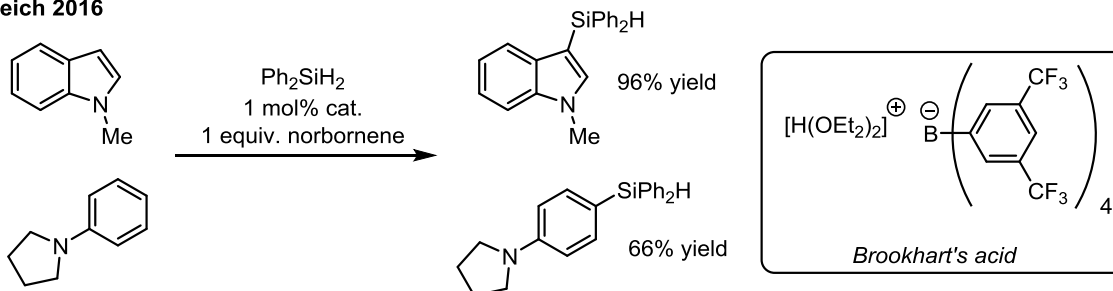
Figure 10: C–H silylation via catalytic activation of silanes.

Polymerizations

Being a strong Lewis acid makes silyl cations an obvious choice for Lewis acid catalyzed polymerizations. Not long after the TPFPB anion was introduced by Lambert as a stabilizing anion for silyliums,[31] Olah reported its use in the ring-opening polymerization of siloxanes, lactones and THF.[32] Reed utilized the silyl carborane as a Lewis acid for the ring opening polymerization of chlorophosphazenes.[33] The polymerization of methyl methacrylate with dimethyl silyl ketene acetal catalyzed by $HNTf_2$ reported by Kakuchi likely involves $TMS-NTf_2$ formation and polymerization via silyl group transfer (Figure 11, lower middle).[34] This mechanism is fairly general and often shows up in the polymerization of such silyl nucleophiles.

A unique strategy was developed by Chen whereby the oxidizing reactivity (hydride affinity) of R_3Si^+ is used to access the silylium species of the "pre-monomer" (Figure 11, bottom). This is intercepted by a silyl ketene acetal (SKA) in a Michael addition, after which the silyl cation can dissociate and oxidize another SKA molecule, propagating the polymerization. Each Mukaiyama–Michael addition produces a new SKA with an additional monomer incorporated into the growing chain.
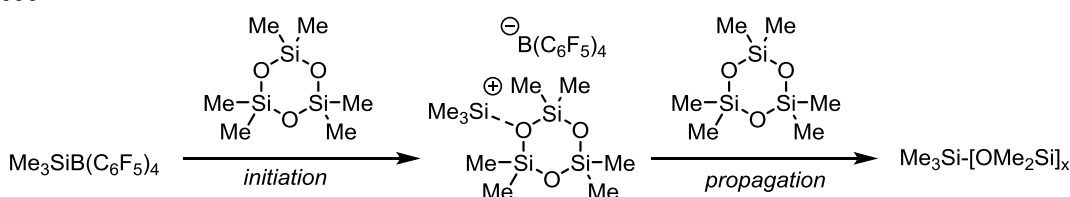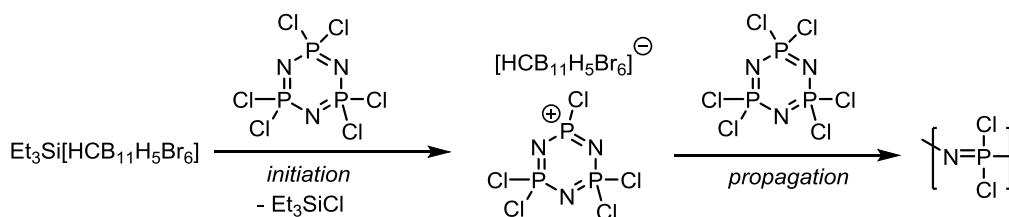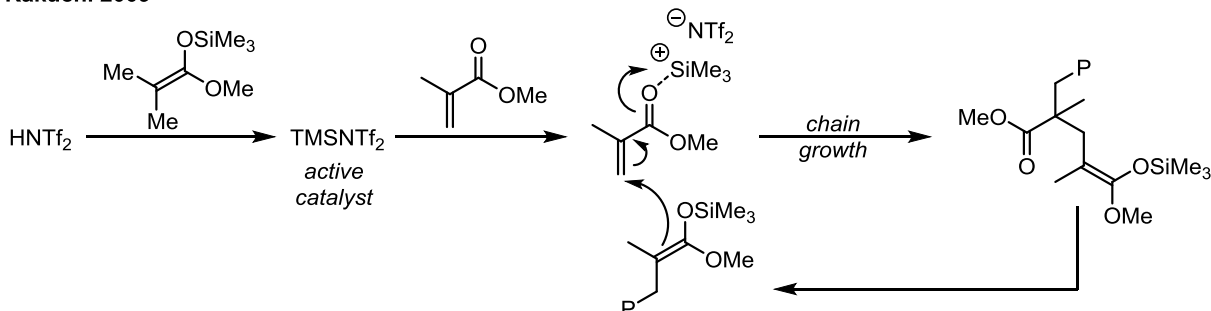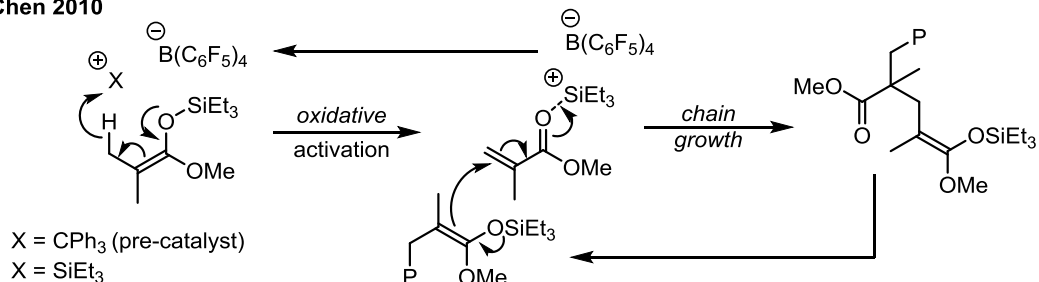

Figure 11: Polymerizations initiated by electrophilic silicon activation of the monomer.

Halide Activation

A major area of silylium catalysis is the generation of reactive intermediates via the abstraction of a halide atom. The principle that is leveraged is the thermodynamic sink that the strong Si-X bond provides, in the case of Si-F it is one of the strongest single bonds in chemistry. This enthalpic driving force allows for the generation of highly reactive cations, even giving access to phenonium cations. The strength and specificity of the silicon and fluorine interaction leads to unique chemoselectivity, which is a hallmark of silicon Lewis acids and adds to their utility.

The generation of such highly reactive cations requires a stable and non-coordinating anion to stabilize the species. The anion should not quench the Lewis acidic silicon atom, which needs to be electrophilic enough to interact strongly with the pro-electrophile, and thus the extremely stable carborane anions are often used.

Seigel reported the cyclodehydrofluorination of aryl fluorides using silyl carboranes (Figure 12, top).[35] While the reaction could be successfully performed with various silyl groups, the optimized system used dimethylmesitylsilylium. The catalytic cycle consists of abstraction of the fluoride, followed by attack of the phenonium by an arene π-nucleophile. The liberated carborane acid then protodesilylates dimethyldimesitylsilane, giving mesitylene and diMeMesSi$^+$, regenerating the active silyl species. Further studies provided direct proof of the phenonium intermediate postulated by the fluoride abstraction mechanism.[36] Nelson later showed that the use of silyl-stabilized phenoniums enabled intermolecular variation of this reaction (Figure 12, bottom left).[37] In addition, C-H insertion into alkanes could be performed, making it a direct arylation of alkanes, a highly sought after and difficult reaction. Most impressively, the reaction could be performed using methane to give the methylated arene.
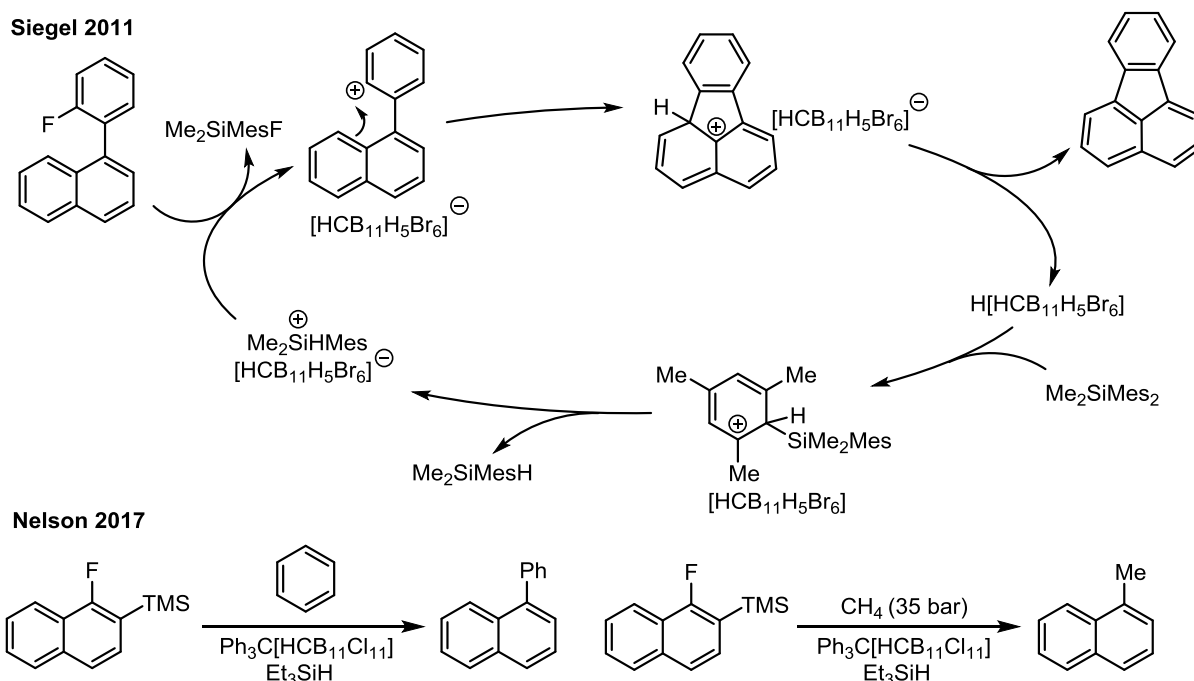
Figure 12: Activation of aryl fluoride bonds towards arylations using silylium carborane salts.

Ozerov used a similar system for the hydrodefluorination of perfluoroalkanes,[38] with high turnover numbers (>2500) seen in some cases (Figure 13, left), a testament to the chemical robustness of the carborane anion. Triethylsilane provides the hydride for the reduction of the activated alkyl group and acts as a source for silylium cations. The reaction was later extended to other halides,[39] with the expected finding that lighter halides react faster (i.e. F > Cl > Br). Interestingly, this is reversed in the specific case of $C_6F_5CX_3$, where the trichloromethyl reacts faster than the trifluoromethyl derivative (Figure 13, right). Here, the competition is not simply fluoride versus chloride abstraction, because two different cations are being formed ($C_6F_5CF_2^+$ vs $C_6F_5Cl_2^+$). Given the first halide abstraction is rate-determining and the observed preference of fluoride abstraction over chloride abstraction, the inversion of the rate of consumption in favor of $C_6F_5CCl_3$ suggests the rate difference arises due to preferential formation of the $C_6F_5Cl_2^+$ intermediate.
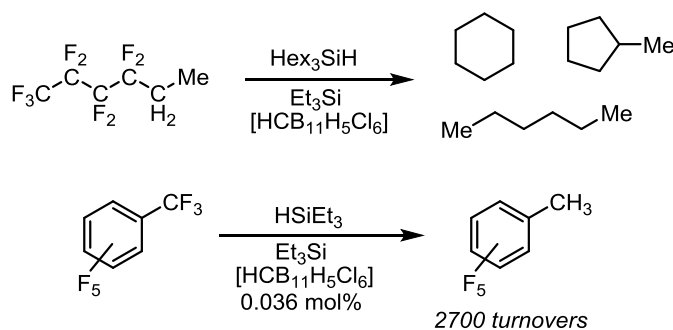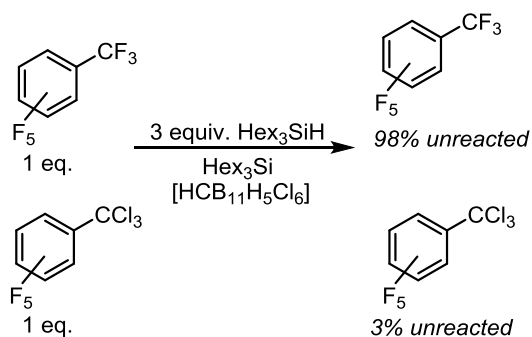
Figure 13: Hydrodefluorination of C–X bonds.

When activating -CF$_3$ groups, one often encounters difficulties in mono-activation, that is forming products corresponding to -CF$_2$X. The inability to stop after the first substitution is due to the C-F bond strengths of the intermediates; the CF$_3$ has the strongest C–F bond and thus each subsequent fluoride is easier to activate. A creative solution to this problem developed by Hosoya[40] is to perform the halide abstraction intramolecularly - the single equivalent of silylium is generated and quickly abstracts the fluoride from the adjacent CF$_3$ group (Figure 14, top). The cationic intermediate can then be intercepted by various allylsilanes to give the *gem*-difluoro products in good yield. Grimme and Stephan created a related FLP system where the cationic CF$_2^+$ is stabilized by an adjacent phosphors (Figure 14 bottom).[41] This lead to the development of a *ortho*-Si,P-FLP, with the phosphine intramolecularly stabilizing the silylium. After hydride abstraction, the cation could used to stoichiometrically mono-activate PhCF$_3$ and PhCHF$_2$.
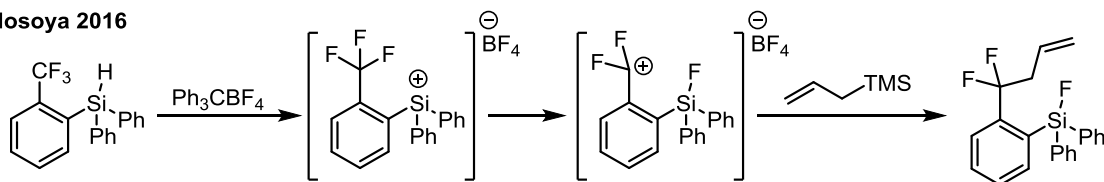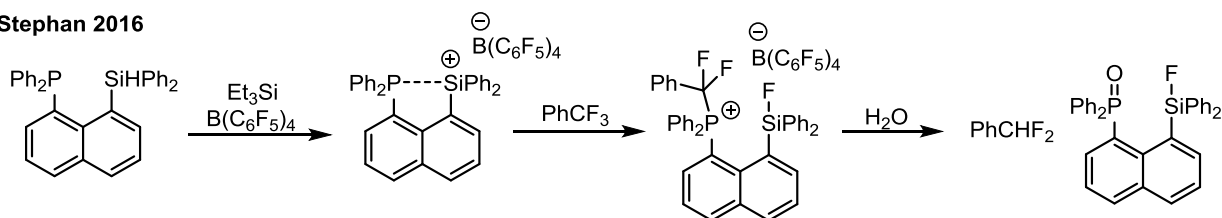

Figure 14: Monoactivation of CF$_3$ groups using designed silyl cations.

Cycloadditions

For cycloadditions, we will consider the canonical Diels–Alder reaction. The [4+2]-cycloaddition occurs via the overlap of orbitals on the diene and dienophile as shown in Figure 15. In the so-called normal electron demand Diels–Alder, the HOMO of the electron-rich diene interacts with the LUMO of the dieneophile. This is "normal" as unfunctionalized dienes are more electron-rich than unfunctionalized dienophiles. The reverse can also be used as a reaction design, i.e. the HOMO on the dienophile and the LUMO on the diene interact in an inverse electron demand Diels–Alder, though the reactions are generally more difficult. As discussed above, Lewis acid catalysis functions by lowering the LUMO of the reactant to increase the rate of the reaction. Thus, the strategy for catalysis focuses on activation of the dieneophile.
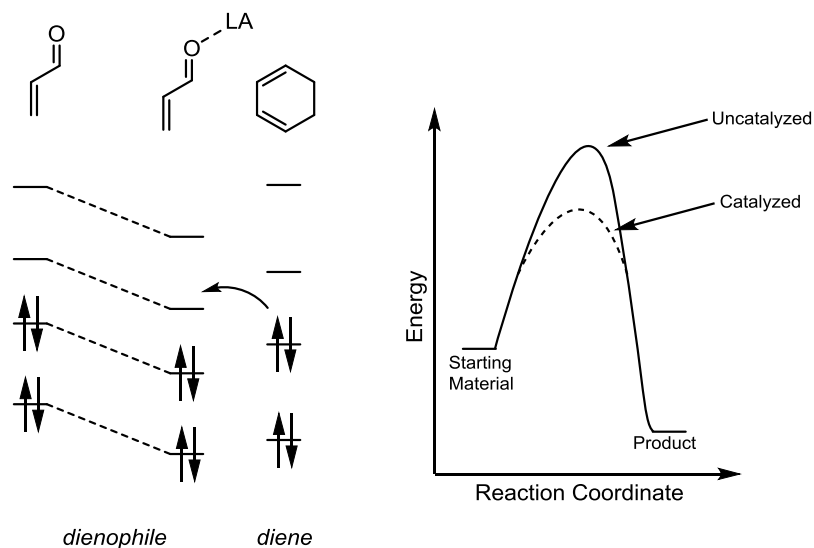
dienophile   *diene*

**Figure 15: FMO description of the activation of dienophiles with a Lewis acid and the effect on the energy of the reaction.**

To have a handle to activate the dienophile, α,β-unsaturated substrates are often used. Gassman studied the ionization of protected carbonyls, and an early example of catalysis used triethyl orthoacrylate as the dienophile (Figure 16).[42] TMSOTf ionized the orthoester to the

oxocarbenium, which could then be captured by dienes in good yield. However, high loadings of TMSOTf were required, and the usual conditions require 50 mol%.

Gassman 1988
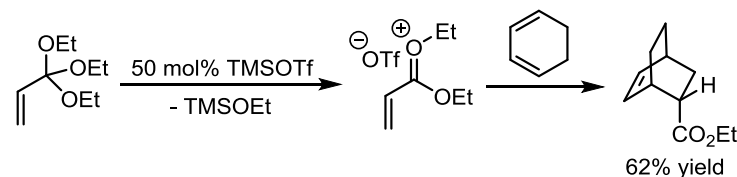
Figure 16: Gassman's activation of unsaturated orthoesters.

Silyl triflates only weakly coordinate to carbonyl compounds, and thus the Gassman strategy requires the use of acetals (or equivalent groups). This can be overcome by using more reactive substrates. For instance, TBSOTf can catalyze the addition of dimethyl acrylamide and an activated cyclohexadiene (Figure 17, top left).[43] The greater basicity of the acrylamide increases the strength of silicon-carbonyl coordination. Using methyl acrylate with the same cyclohexadiene gives no reaction.[44] For direct activation of esters for Diels–Alder reactions, more electrophilic silicon catalysts are required. Ghosez found that the reaction between methyl acrylate and cyclopentadiene is efficiently catalyzed by TMSNTf$_2$, while TMSOTf only gives trace product (Figure 17, right). Sawamura later showed the even more electrophilic B(C$_6$F$_5$)$_4$ silylium is a active catalyst for the Diels–Alder reaction,[45] as shown in the comparison with silyl triflimide (Figure 17, bottom left).
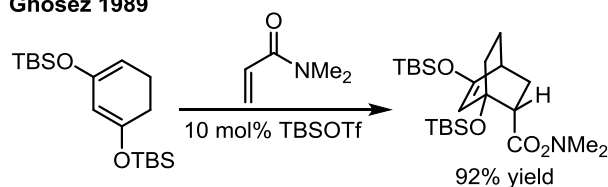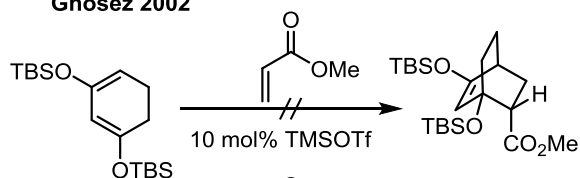
Figure 17: Silyl-catalyzed Diels–Alder reactions.

90

Oestreich extensively investigated the ferrocene-stabilized silyliums (e.g. **5**), using $B(C_6F_5)_4$ as the counterion, and their catalytic efficiency in promoting Diels-Alder reactions 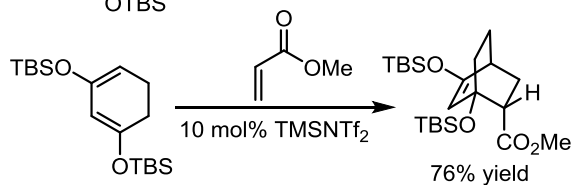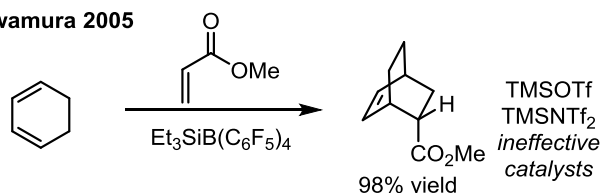(Figure 18). While the iron center appears to stabilize the cationic silicon, this silicon center remains highly catalytically active, with the reaction working even at low temperatures with a catalyst loading of 1 mol%. Oestreich speculated that the silylium is tuned for high reactivity: the catalyst's steric environment allows for a stable cation that can still effectively coordinate the substrate while preventing product inhibition of the catalyst. When looking at different silylium catalysts, the reactivity could not be correlated to either the silicon shift or the NMR shifts of Lewis base adducts (Et$_3$PO, d5-pyridine, etc.),[46] hinting at the confluence of multiple factors in making an effective catalyst.
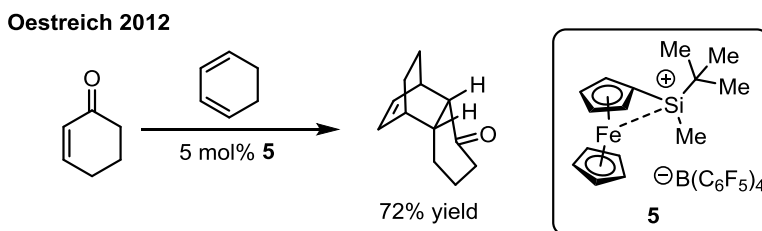
Figure 18: Diels–Alder catalyzed by a ferrocene-stabilized silylium.

Enantioselctive Reactions with Silicon Lewis Acids

This short section will attempt to highlight significant developments in enantioselective reactions using silicon Lewis acids. The strategy of activating silicon centers with highly electron-withdrawing substituents is most germane to the work in this thesis, and discussion will be focused on these examples. Two other notable strategies have been developed: activation of weak Lewis acids with a Lewis base and using the increased Lewis acidity of strained silacycles.

Despite the fact that catalytic enantioselective Diels–Alder reactions are known with other catalyst systems, most famously the oxazaborolidines, enantioselective silicon-based catalysis has been challenging to develop (Figure 19). Using chiral-binapthyl silylium **6** with

vinyl oxazolidinone gave the Diels-Alder adduct in high yield, but with only a 10% ee.[47] Ghosez investigated chiral silyl triflimides,[48] with a best result of 59% ee at -100 °C in DCM using the *trans*-cyclohexane catalyst **7**. Oestreich has pursued a series of chiral silyliums using an intermolecular thioether donor to stabilize the cation.[49] The catalysts are able to activate less reactive substrates, for example chalcones can be reacted with cyclohexadiene. The optimal catalyst **8** gave a best result of 59% ee with the naphthyl-derived chalcone shown. Leighton reported the first example of a silicon-catalyzed Diels–Alder with high enantioinduction.[50] Using strain-induced Lewis acidity enhancement as a design principle, the activated silyl chloride catalyst **9** was synthesized. The silyl chloride itself was Lewis acidic enough to promote the reaction between cyclopentadiene and methyl methacrylate with an impressive 94% ee.
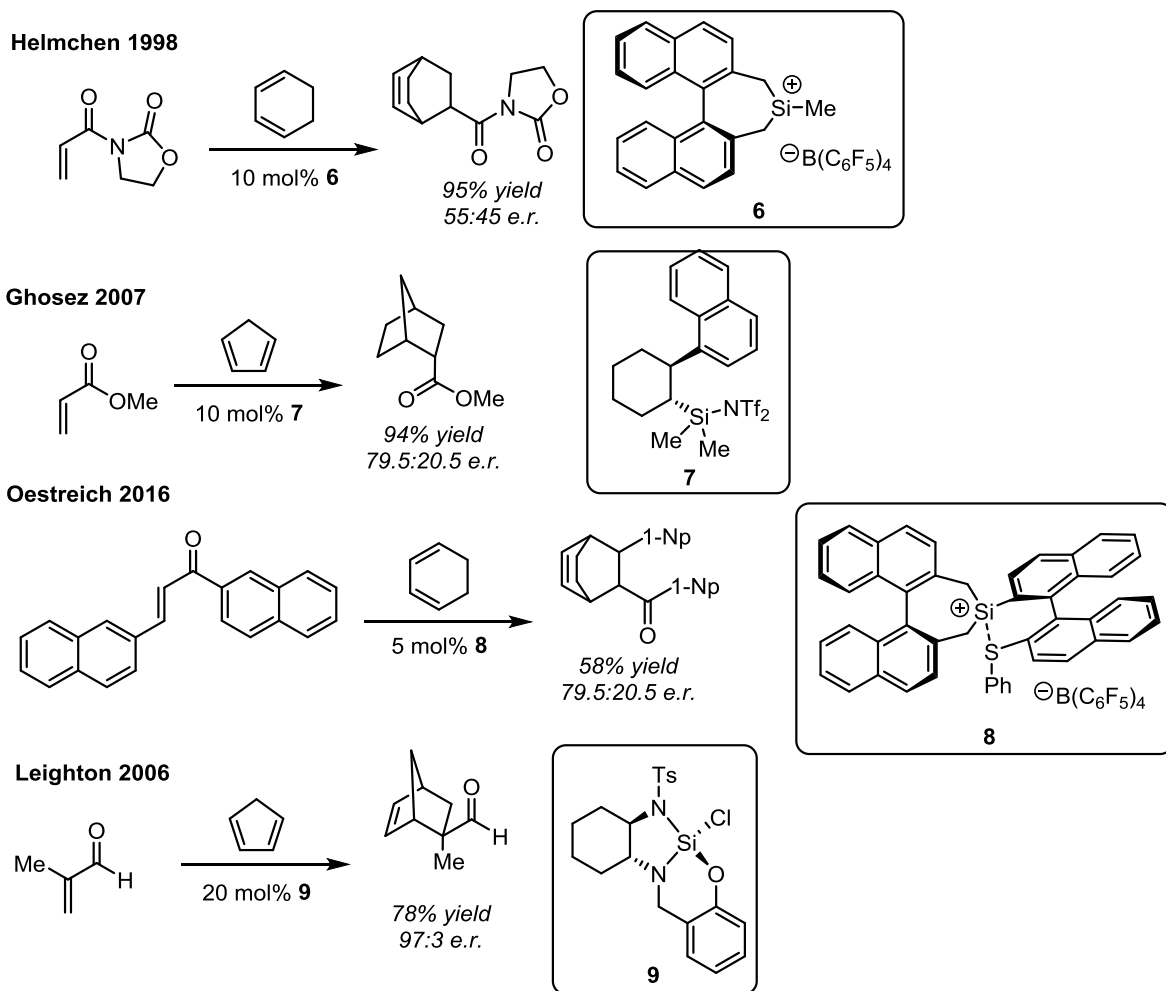
Figure 19: Progression of enantioselective Diels–Alder reactions.

Another approach is to induce enantioselectivity through the use of a chiral anion supporting the silylium species in asymmetric counterion directed catalysis (ACDC). Examples of ACDC have been reported with trityl cation catalysis. For silicon Lewis acids, one difficulty has been generating anions that are weakly coordinating to give the desired reactivity. The commonly encountered BINOL-derived phosphoric acids generally do not yield active silylium catalysts. Thus, the development of chiral, weakly coordinating anions (or equivalently, extremely acidic Brønsted acids) is an active area of research.

Attempts to use chiral derivatives of fluorinated borates has been largely unsuccessful. Both List and Oestreich reported routes to access the binapthyl-functionalized fluorinated borate

10 (Figure 20). Unfortunately, both groups reported minimal enantioinduction in Mukaiyama aldol and Diels–Alder reactions when used as the trityl salt. Further, Oestreich reported that the attempted hydride abstraction using the trityl salt led to decomposition, perhaps due to the electron-rich binapthyl functionality of **10** being incompatible with the strongly electrophilic silicon cation.

The extensive library of binaphthyl catalysts developed by List has really been the vanguard for enantioselective catalysis. As reported in 2016, the sulfonylated propene motif for generating highly acidic *carbon acids* was key for an enantioselective silylium catalyst.[51] The need for an extremely weakly-coordinating anion was necessary as cinnamates are fairly unreactive dienophiles. The large phenanthrene substitution provide a sterically demanding chiral pocket for good enantioinduction. In addition, the cinnamate substrates were optimized with bulky fluorenyl esters to yield the cycloadducts with high e.r.'s, demonstrating the many elements that need to work in concert for silylium catalysis to succeed.
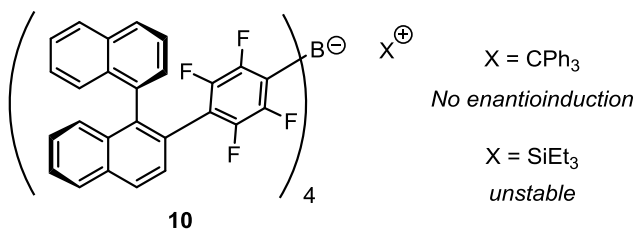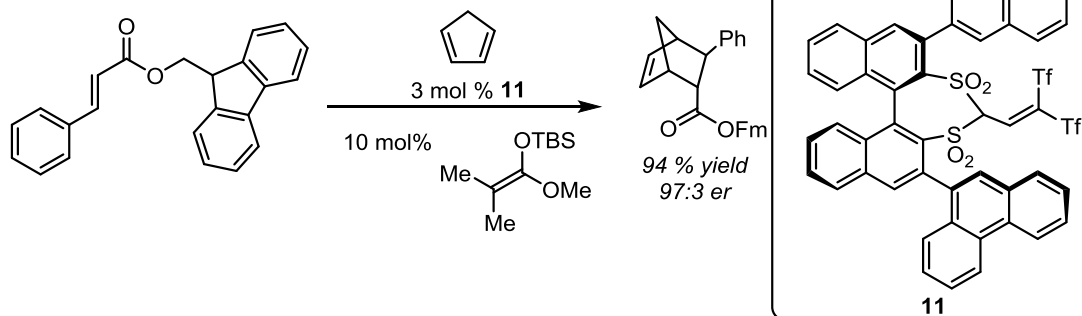
Figure 20: Enantioselective Diels–Alder reaction using chiral anions.

Finally, another strategy developed for enantioselective silicon-based catalysis is the use

of hydrogen-bond donors to activate a weak Lewis acid via coordination to the anion. This leads

to an increase in the Lewis acidity of the silicon center while simultaneously introducing

chirality through the neutral ligand bound to the anion. Jacobsen reported the highly

enantioselective [4+3]-cycloaddition using squaramide **12** as the anion abstractor (Figure 21).[52]

Their mechanistic studies confirmed that the formation of the oxyallyl cation was rate-limiting,

with the subsequent cycloaddition step being enantio-determining.
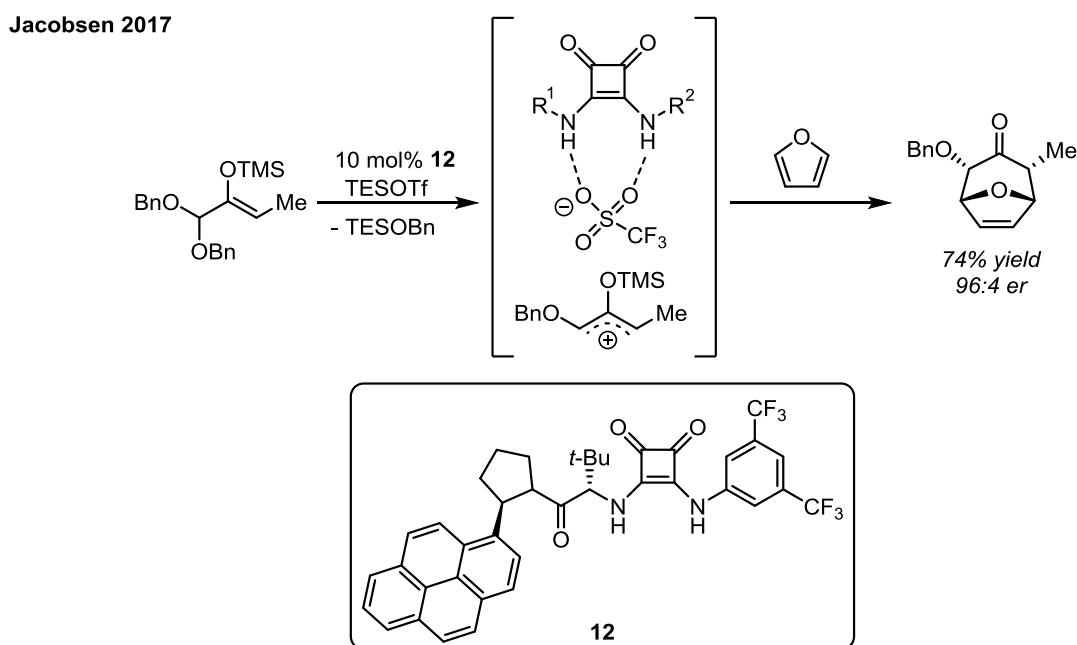
Figure 21: Anion-binding strategy for activating silyl triflates in enantioselective [4+3]-cycloadditions.

Conclusion

The unique nature of the silylium cation presents both difficulties and immense

opportunities for catalysis. Due to its extreme electrophilicity, the cation is sensitive to electron

density and coordinating solvents, oftentimes with decomposition of the solvent or its

counterion. On the other hand, when paired with very weakly coordinating anions (e.g.

carboranes), the high reactivity can be translated into powerful transformations. The examples

highlighted in this chapter show that high levels of reactivity can be achieved, along with chemoselectivity unique to silicon. Many groups have attempted to bring this chemistry into the realm of enantioselective catalysis, and the limited number of successful examples points to both the difficulty in transmitting chirality through the silylium cation and the ingeniuity that has been brought to bear to solve these problems.

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Chapter 4: Silylated Cyclopentadienes

After establishing a route to access the highly stabilized PCCPs highlighted in Chapter 2, we became interested in taking advantage of the predicted increase in reactivity. As briefly covered in that chapter, simple protonation of these anions proved challenging, and they would likely suffer from limited stability in their protonated state, as hinted at by the hydrolysis of the penta(phenyl)PCCP. The insolubility of pentacyanocyclopentadiene noted by Reed[1] further dissuaded us from tackling the protonation of the mono(carboxy)tetracyanocyclopentadienes. Taking a cue from Reed's pioneering work, our focus shifted towards the silyl derivatives as a practical way of generating reactive species using these anions. Given the expected stability of these anions, the corresponding silyl species would be expected to be exceedingly electrophilic. It turn, the potent Lewis acidity would enable these compounds to be used as Lewis acid catalysts. Our efforts towards these ends are detailed in this chapter.

After our initial investigations, we set our sights on a halide-activation strategy, which ultimately resulted in the development of alkylation strategies utilizing benzyl bromides. The second half of this chapter will discuss related methodologies involving the activation of benzylic substrates before describing the system we developed with silyl cyclopentadienide species.[2]

Anion Synthesis

As covered in Chapter 2, our ability to access more stable cyclopentadienes was enabled by the development of an ester-activation strategy for derivatizing PCCP **4-H** with $SOCl_2$. Trifluoroethanol is ~6 orders of magnitude more acidic than ethanol (DMSO),[3] and our anion

should gain a considerable acidity enhancement with the TFE esters. Thus, our initial studies were performed using the penta(trifluoroethyl)PCCP, which could be synthesized in reasonable yield and was more easily purified than the corresponding HFIP-derived PCCP. Further refinement of the synthesis allowed for preparation of significant quantities of the NMe_4^+ salt (>500 mg) without necessitating column chromatography via trituration in ether to purify the crude reaction mixture.

During the course of testing for reactivity, we wanted to have a set of catalysts to test the effects of the anions' stability on the observed reactivity. To this end, mono(carboxy)tetracyano-cyclopentadienes (e.g., **1**) were also targeted as potential catalysts. In 2013, Mori reported an innovative synthesis of these cyanated cyclopentadienes (Figure 1).[4] Earlier syntheses of the $C_5(CN)_5$ anion required two equivalents of tetracyanodithiin[5] because one equivalent was used to activate the thiolate generated after nucleophilic attack and ring-opening. Activation was required to reform the ring, after which sulfur extrusion could take place and furnish the desired cycopentadiene. By incorporating a leaving group into the acetate fragment, ring closure can directly occur by displacement of the sulfonyl group, obviating the need of excess dithiin. Furthermore, a variety of acetate-derivates could be used, allowing them to generate a number of novel cyanated anions.
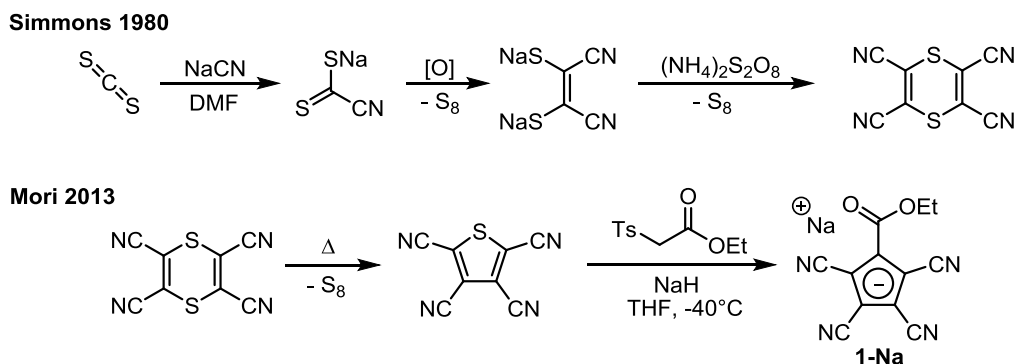

Figure 1: Simmons' synthesis of tetracyanodithiin and Mori's synthesis of cyanated cyclopentadienes.

While Mori's work showed that using tetracyanothiophene gave better yields of the cyclopentadienes, we found that it was more expedient to use the dithiin, which gave only marginally lower yields while reducing the material loss from the preparation of the thiophene. Additionally, in our hands, the described precipitation of dithiin was operationally difficult and did not yield pure dithiin. Purification of the dithiin by Soxhlet extraction, as described by Reed, removed most of the sulfur contamination and markedly improved the following reaction.

For our studies, we synthesized three mono(carboxy)tetracyanocyclopentadienides with variation of the ester moiety. The dicyclohexylmethyl (**2**) was chosen to probe the effect of a sterically encumbered ester and hexafluoroisopropyl (**3**) to test whether the anion could be influenced by an electron-deficient ester. The synthesis of tosylated acetates is straightforward and generally high yielding (Figure 2). Esterification of bromoacetyl bromide gives the bromoacetate, which can be purified if desired. Displacement of the bromide with sodium toluenesulfinate in DMF usually proceeded quantitatively and the products did not require further purification. The syntheses generally followed the procedure of Mori without difficulty, with the exception of the hexafluoroisopropyl derivative.

After esterification, the bromide was volatile and removal of solvent at higher pressures (~120 torr) was required to limit product loss. In addition, conducting the substitution reaction in DMF lead to many biproducts, potentially due to dimethylamine present in the DMF. Switching the solvent to DMSO greatly mitigated the impurities, and the product could be obtained after a simple silica gel plug. Finally, when the acetate was added to dithiin, impurities formed that were inseparable on silica gel. Ultimately, alternative purification conditions were developed using acidic alumina to give pure **3**.
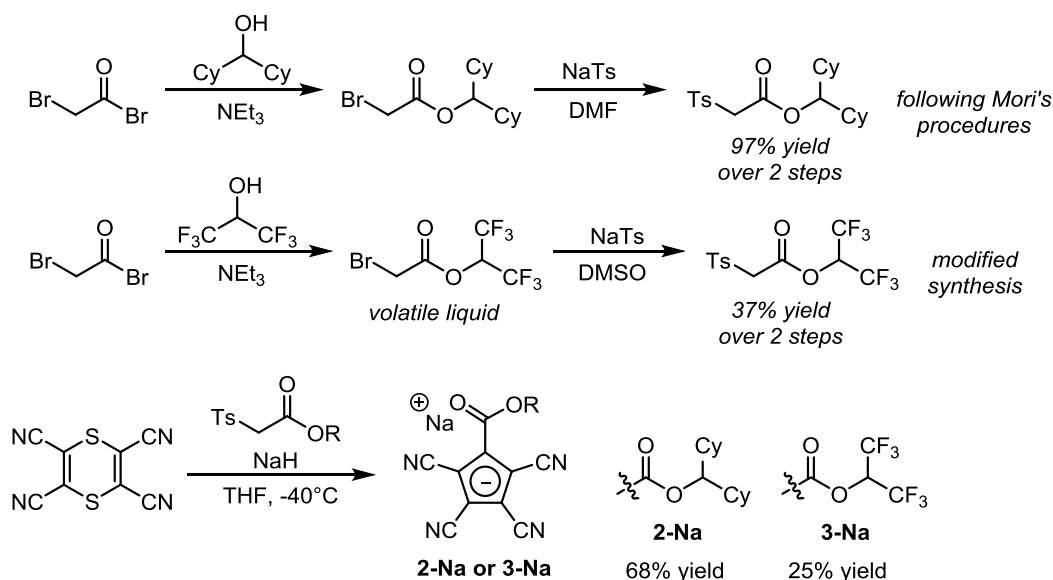
**Figure 2: Synthesis of new cyanocyclopentadiene salts.**

To generate the desired silylium salts, the Ag-PCCP complexes needed to be synthesized. The pentamethyl silver salt **4-Ag** was prepared as previously described using AgOAc.[6] The procedure described by Le Goff and Cookson using Ag_2O also worked but was found to be less practical.[7] For the trifluoroethyl derivative, it was found that the salt metathesis could be achieved by using AgOTf, with the choice of Et_2O as the solvent proving crucial to precipitate NMe_4OTf (Figure 3). While the **5-NMe₄** itself is only marginally soluble in ether, it is soluble enough to undergo the metathesis and the equilibrium ultimately yields the **5-Ag**. This strategy generally worked for the PCCP NMe₄ salts it was attempted with, and **4-Ag** could be also be prepared by this route. We also sought to probe the effect of a highly-sterically-encumbered anion, and examined using PCCP **6**. In this case, **6-NMe₄** is completely insoluble in ether and no metathesis occurs. After examination of other metathesis conditions, we could not cleanly isolate **6-Ag** and ultimately we chose not to pursue **6-Ag** for our subsequent studies.
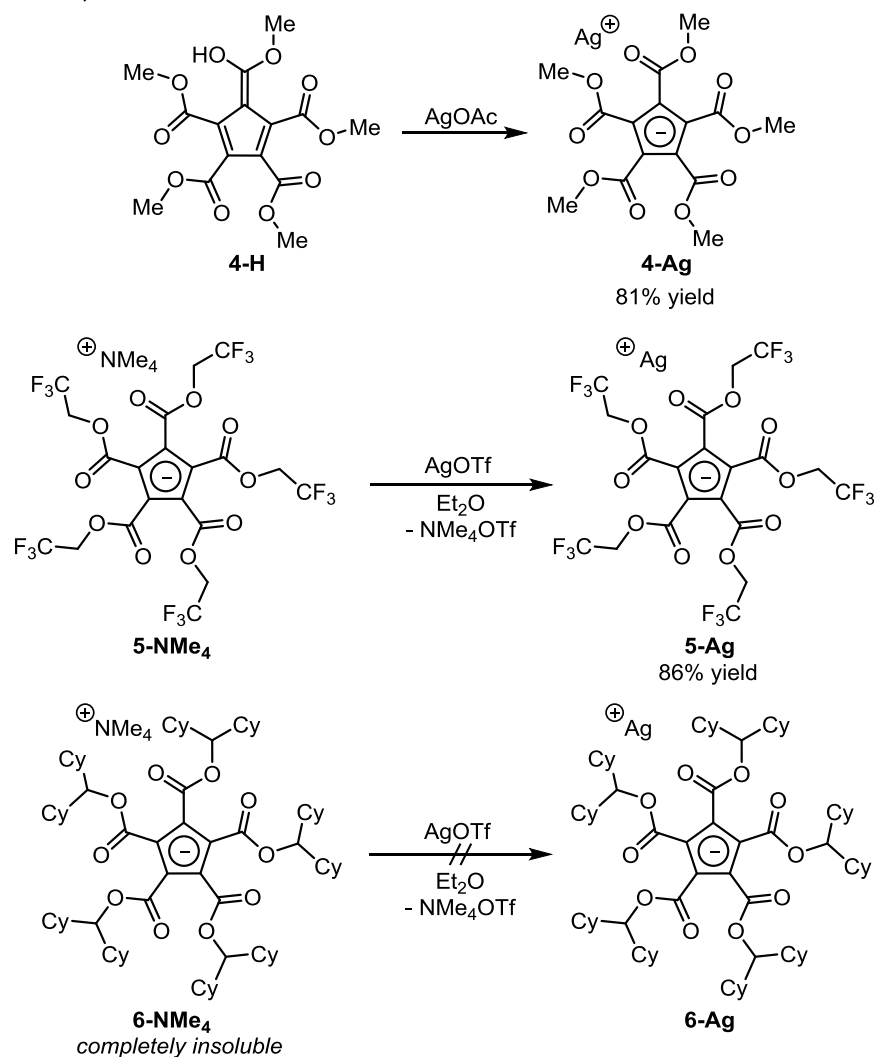
Figure 3: Salt metathesis of PCCP anions.

For the tetracyanocyclopentadienes, modified conditions used by Reed for $C_5(CN)_5$ were found to be generalizable (Figure 4). Addition of an aqueous $AgNO_3$ solution to a solution of the sodium salt in acetone leads to precipitation of the Ag cyclopentadienide. The substituted monocarboxy anions we synthesized behaved similarly, and the Ag salts precipitate from solution, though occasionally as fine powders that were difficult to filter.
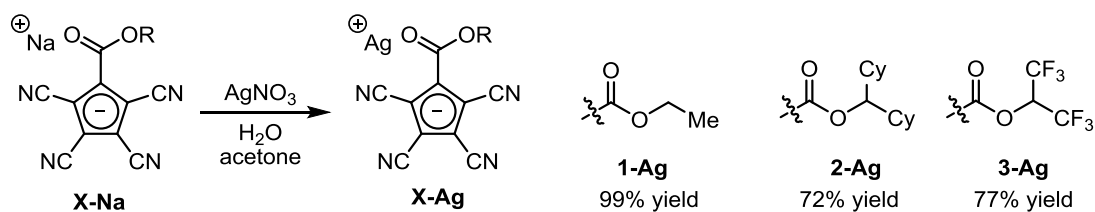
Figure 4: Preparation of silver cyclopentadienide salts.

With the silver salts in hand, synthesis of the silylium salts commenced. Mixing the silver salts with trityl chloride in MeCN immediately produced a bright yellow solution, indicating the presence of Ph_3C^+. The formation of the trityl salt was generally quantitative, as judged by ^{1}H-NMR and the amount of AgCl collected. Filtration through glass-fiber filter paper and evaporation of the MeCN gave the trityl salts as deeply colored solids. These salts are quite moisture sensitive, rapidly discoloring when exposed to air. Therefore, these preparations were carefully performed in a glove box with rigorously dried materials. The trityl salts of the monocarboxytetracyanocyclopentadienes are qualitatively more robust than the PCCP salts, perhaps due to stronger coordination to the Si (*vide infra*).
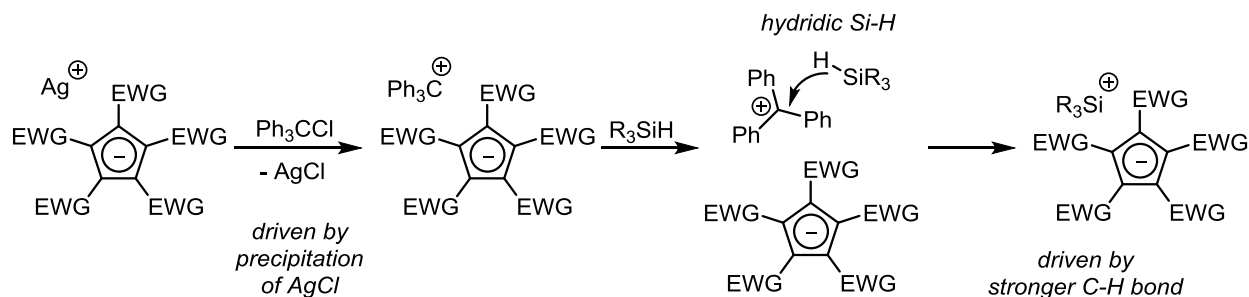
Figure 5: Salt metathesis followed by silane reduction to yield silylated cyclopentadienides.

Preparation of the silylium salts was straightforward, as addition of a silane reduced the trityl cation, giving Ph_3CH and a colorless solution of the $R_3SiPCCP$. However, characterization proved challenging. Initial tests in $CDCl_3$ gave inconclusive results and observation of the characteristic ^{29}Si chemical shift by direct detect 1D-NMR spectroscopy was never achieved. Silylium species are known to decompose in halogenated solvents via halide abstraction, and

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HCl present in the solvent may also quench the silylium by forming R_3SiCl and the protonated anion. In addition, the low abundance of ^{29}Si can make detection difficult due to low signal-to-noise ratios.

Ultimately, the silylium species could be characterized by ^{1}H-^{29}Si HMBC NMR spectroscopy, taking advantage of the greater detection sensitivity afforded by ^{1}H-NMR spectroscopy. Several alternative solvents were tried before settling on $d4$-1,2-dichlorobenzene[8] for its solubilizing ability while remaining non-coordinating. Different silanes can be used to give different silylium salts, and Et_3SiH, Ph_3SiH and t-$BuMe_2SiH$ were all competent reductants. iPr_3SiH was chosen for the stability of salts produced, ease of handling (e.g. Me_3SiH is a gas), and for direct comparison with other iPr_3Si-X species in the literature. Figure 6 shows the ^{29}Si chemical shifts observed for various cyclo-pentadienide counterions.
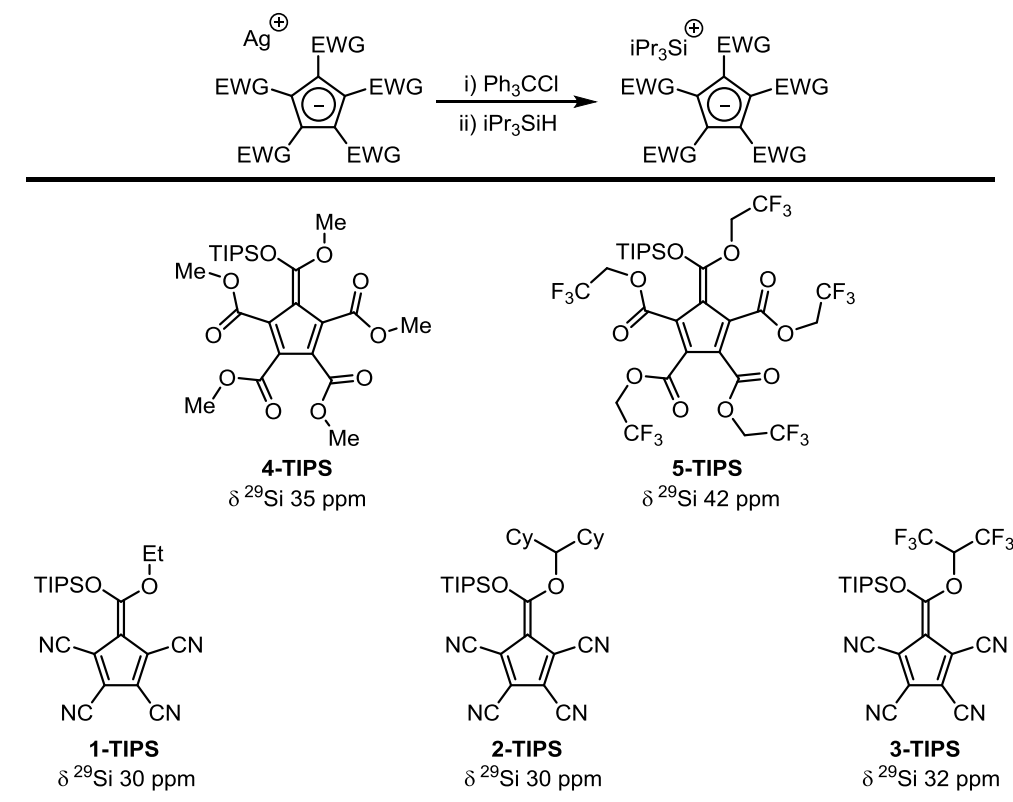

Figure 6: ^{29}Si-shifts measured by ^{1}H-^{29}Si HMBC.

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Comparing the different silylium salts, **5-TIPS** is approximately 7 ppm more downfield than **4-TIPS** (δ 42 ppm compared to δ 35 ppm). The former is similar to that reported for iPr$_3$SiOTf (δ 40 ppm),[9] suggesting a potential parallel between the two anions. The more electron-deficient trifluorocarboxy groups stabilize the resulting cyclopentadienide anion, leading to a more electrophilic silicon center reflected in the silicon shift. Surprisingly, the shift for **1-TIPS** is upfield at δ 30 ppm. This is only moderately affected by modifications to the ester functionality, with the dicyclohexyl derivative showing identical ^{29}Si shift, and the hexafluoroisopropyl only 2 ppm downfield. These shifts are similar to the observed resonance for silylated acetonitrile (δ 37 ppm, CD$_2$Cl$_2$),[10] with extremely weakly coordinating carborane as the supporting anion. The cationic silicon center has been shown to be very sensitive to electron density, with calculations showing dramatic upfield shifts when an atom approaches, even well outside the van der Waals radius.[7] The cyano groups may also be coordinated to the silicon, instead of the carbonyl oxygen (Figure 7). Interpretation of this result as an indication of a less electrophilic silylium source is unwarranted, and reactivity data confirms these species are more active catalysts, as would be expected from the greater stability of the anions.
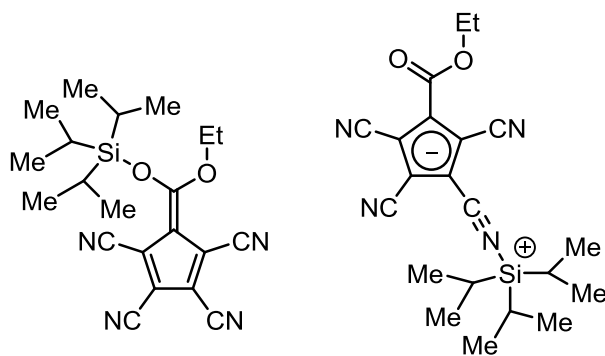

Figure 7: Possible coordination modes of the iPr$_3$Si$^+$ to the *1* anion.

<u>Reactivity Studies</u>

Oestreich's work with ferrocene-based silylium provides a thorough characterization of the differences between silylium and proton-based catalysis through the use of various Diels–

Alder reactions as test cases (Figure 8).[11] Briefly, Brønsted acids tend to decompose the starting

materials in contrast to the effective catalysis seen for their catalysts (e.g. **7**). We attempted to

use these reactions similarly as a benchmark for our own silyl species. Unfortunately, under

various reaction conditions, no reactivity was seen, even when using highly-reactive

cyclopentadiene as a substrate. Potentially, the silylated cyclopentadienes were themselves

reacting with the dienophile; reactions with similar highly-electron-deficient cyclopentadienes

have been reported. In addition, MS analysis of the reaction mixture contained a peak

corresponding to the *m/z* of the cycloadduct **8**, offering support for this interpretation of the lack

of reactivity. An alternative way of assessing the catalytic activity of these species was required.
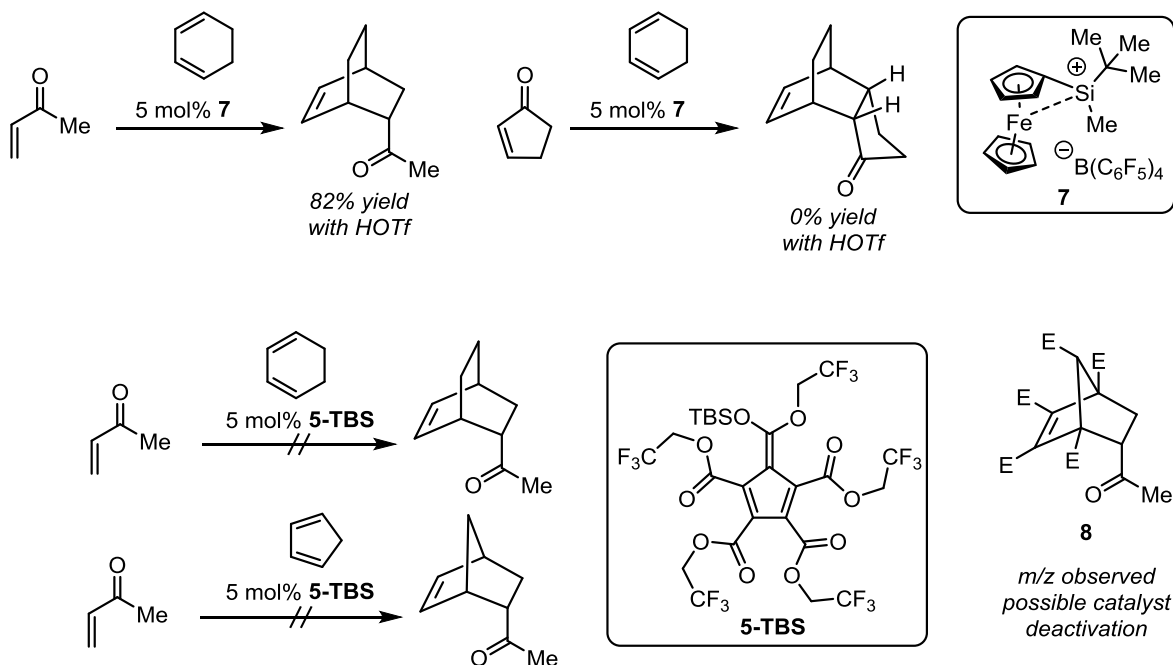

Figure 8: Oestreich's comparison of Brønsted acids and silicon Lewis acids, and attempted use of
***5-TBS* as a catalyst for Diels–Alder reactions.**

We then turned to the Hosomi–Sakurai allylation of aldehydes as a test reaction.[12]

Benzaldehydes with more electron-withdrawing substituents are less reactive under our catalytic

conditions. Electron-deficient aldehydes coordinate less strongly to the Lewis acid, leading to

less activation of the carbonyl. 4-(Trifluoromethyl)benzaldehyde was found to be an ideal substrate as it clearly demonstrated the difference between our anions and could be readily monitored by ^{1}H and ^{19}F NMR spectroscopy. The conditions and data for these NMR spectroscopy studies is shown in Figure 9. *tert*-Butyldimethylsilane was chosen as an easily handled silane to prepare the precatalyst. **4-TBS** showed no catalytic activity, even at extended reaction times. In contrast, **5-TBS** showed significantly increased reactivity, giving 90% yield in 6 hours.
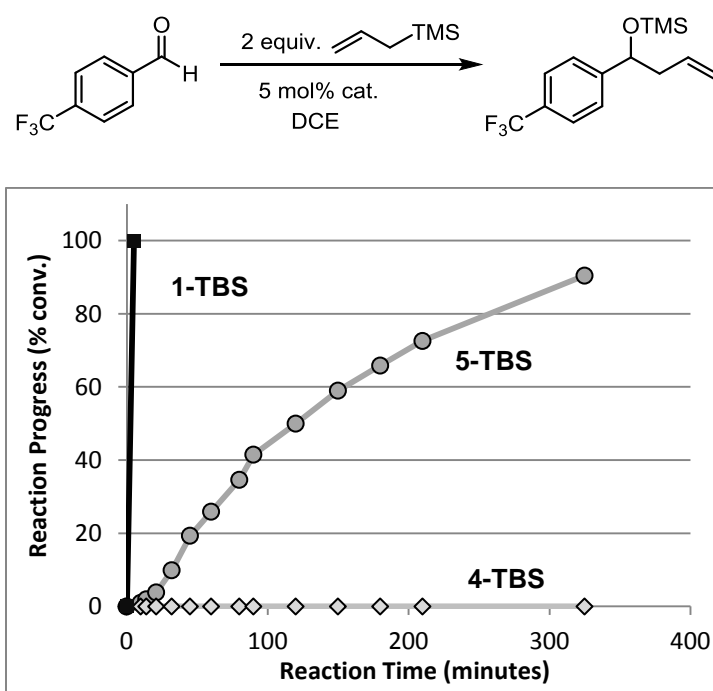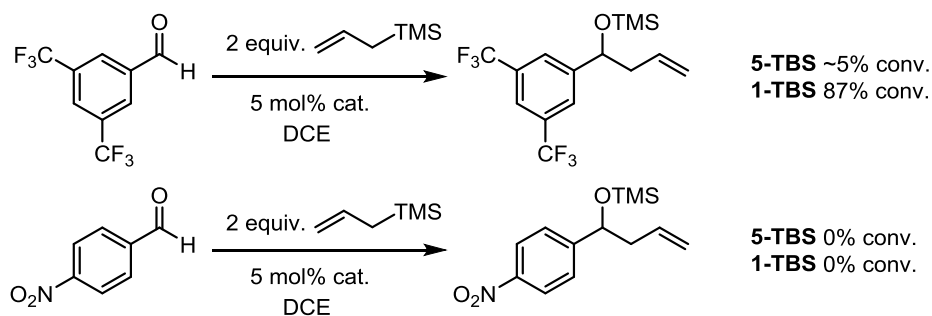

Figure 9: Hosomi–Sakurai allylation as a benchmark reaction, showing *1-TBS* as the most active precatalyst.

As a control, no reaction was seen in the absence of catalyst or using TMSOTf. The inability of TMSOTf to promote the reaction is in agreement with previous reports, though the dichotomy with **5-TBS** is interesting. While one might conclude that **5-TBS** is a stronger Lewis acid than TMSOTf, the mechanism of the allylation has been shown to be influenced by coordination of the allylsilane leading to a stronger nucleophile. The PCCP anion, with its

multiple carbonyl groups, could plausibly interact with both silyl groups simultaneously, mediating the reaction through a complex between the aldehyde and allylsilane.

When the reaction is performed with **1-TBS**, the reaction is complete before NMR analysis can be performed (<5 minutes). The increased reactivity can plausibly be explained as a confluence of the expected higher Lewis acidity of the silyl group and the greater coordinating ability of the cyano groups. As shown by the ^{29}Si shift, the anion has the potential to coordinate significantly more than the PCCPs. The additive effect leads to the high observed reaction rate. The catalyst was also able to activate the more electron-poor 3,5-bis(CF$_3$)benzaldehyde, while **5-TBS** only gave trace yield of product. No reactivity was seen with 4-nitrobenzaldehyde, which may be due to the even less activated carbonyl or competitive binding of the nitro group.


Figure 10: Further Hosomi–Sakurai allylations.

Upon close inspection of the reaction progress for the allylation with **5-TBS**, there is a potential induction period seen in the early stages of the reaction (see graph in Figure 9). We speculated this could be due to the lower reactivity of **5-TBS** compared to **5-TMS** as a catalyst, which is further corroborated by comparison studies (*vide infra*). The induction period would then represent the first initial turnover of the catalys, which is injected into the reaction mixture as **5-TBS**, before the liberation of **5-TMS** from the addition of allylTMS. As the reaction progresses, the catalyst becomes the more reactive TMS derivative, leading to the increased rate. To test this hypothesis, the reaction was performed using allyl(*tert*-butyl)dimethylsilane so as to

obviate the effect of the silane shuffling. The reaction displays no induction period, though the reaction itself is significantly slower. Overall, this supports the idea that the formation of **5-TMS** as the active catalyst leads to a slight but noticeable induction period.

Benzyl Halide Activation

After these initial demonstrations of reactivity, our attention turned to utilizing these silcon Lewis acids in further bond-forming reactions. As mentioned in the previous chapter, several examples of silicon-based activation of fluoride have been developed, taking advantage of silicon's particular affinity for fluoride. This was a clear starting point for further development of our silicon Lewis acids. We initially targeted substrates with ionizable fluorides reported by Nelson[13] and Paquin,[14] with the hope of forming a cationic intermediate that would be subsequently trapped by a nucleophile to give addition products (Figure 11). In the first instance, Nelson reported the addition of arenes to the β-silyl-stabilized phenonium cation using silylium carborane salts. In the second, Paquin relies on a β-fluoride elimination of a palladium catalyst to activate the substrate. Attempts were made to activate these fluorides with **1-TBS** in the presence of allylTMS as a nucleophile. Unfortunately, the silicon was was not electrophilic enough to abstract the fluoride; no conversion of the substrates was observed and unreacted starting material was recovered. Alteration of the nucleophile to more nucleophilic silyl ketene acetals and silyl enol ethers did not change the outcome, and neither did changing the precatalyst by altering the silane used (e.g. using **1-TES**).
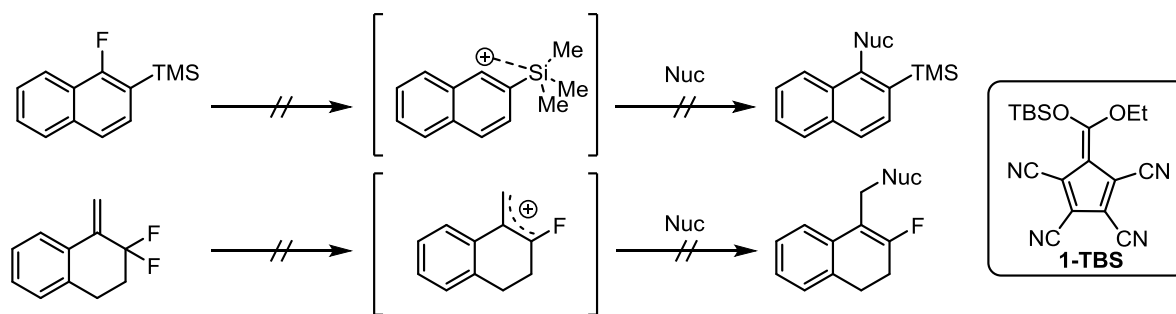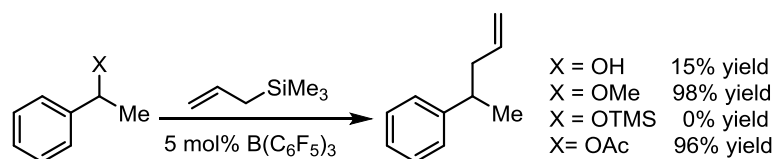
Figure 11: Attempted activation of fluorides by *1-TBS*.
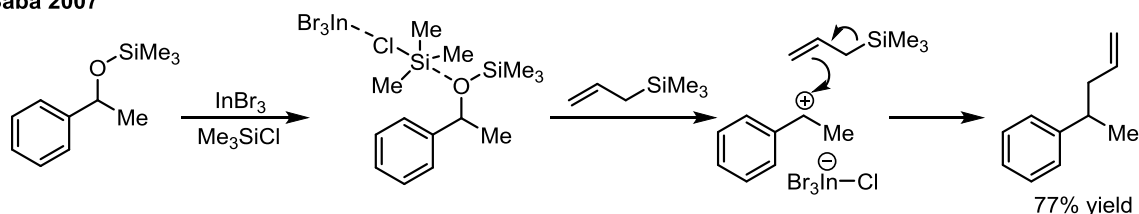
Undeterred by these failures, we shifted our focus shifted to more easily ionized benzyl halides as substrates. Ionization of benzylic functional groups to give the corresponding carbocation is a well-precedented strategy for functionalization of substrates. Halides, alcohols, acetates and other groups provide a reactive handle which are turned into very good leaving groups via interaction with the Lewis acid catalyst

Much reaction development has been done towards activating alcohols (or alcohol derivatives), which can be easily ionized by Brønsted or Lewis acids. A recent review[15] listed Lewis acids based on 30 different elements, a testament to the diverse array of catalysts developed for this reaction. Gevorgyan demonstrated $B(C_6F_5)_3$ as an effective catalyst for activating oxygen functionality in benzylic allylations using allylsilanes.[16] While methyl ethers and acetates are good substrates, TMS ethers are completely unreactive. Baba described the indium halide activation of trimethylsilyl chloride, resulting in a more electrophilic silicon species that activates alcohols, acetates and silyl ethers.[17] The $InBr_3$ or $InCl_3$ itself does not effectively promote the reaction in the absence of the silyl chloride. Recently, Paquin has found that the deoxyfluorination reagent XtalFluor could be used to promote S_N1 reactions, and that allyltrimethylsilane effectively traps the intermediate cation, giving the allylated products.[18]
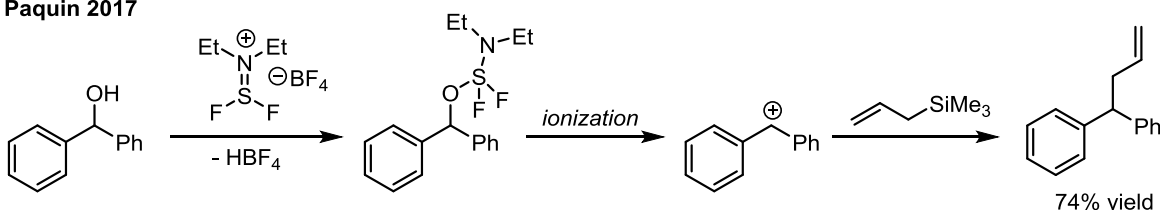
Gevorgyan 2001

X = OH   15% yield
X = OMe   98% yield
X = OTMS   0% yield
X= OAc   96% yield

Baba 2007

77% yield

Paquin 2017

74% yield

Figure 12: Activation of benzylic alcohol derivatives.

There are fewer reports of catalytic activation towards the allylation of benzyl halides, though one can note that direct nucleophilic allylation using allylmagnesium or allylzinc reagents is relatively common. Classically, activation with metal halides is a commonly-used method; for instance, the allyation of sec-phenyethyl chloride can be accomplished using $ZnCl_2$ and $TiCl_4$ as reported by Mayr and Faust, respectively (Figure 13). There are fewer examples describing allylations with main group catalysts.
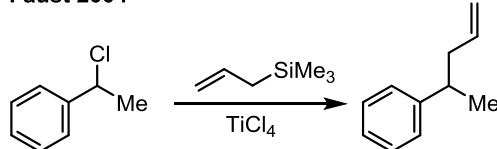
Classical Friedel-Crafts Arylation

Mayr 1994

20 mol% $ZnCl_2$
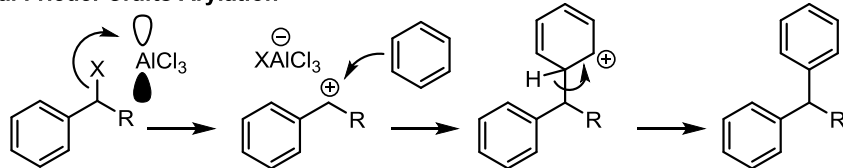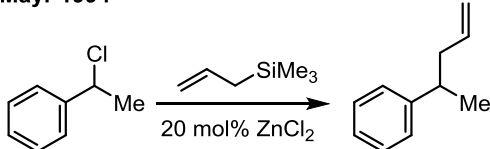
Faust 2004

$TiCl_4$

Figure 13: Activation of benzylic halides with metal Lewis acids.

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Tian reported a single example of benzylic bromide allylation with allyltrimethylsilane as the nucleophile.[19] Using HNTf$_2$ as a precatalyst, with TMSNTf$_2$ being the likely active species, allyldiphenylmethane was obtained in a modest 53% yield. They speculated that the yield was adversely affected by product degradation from the TMSBr produced in the reaction. Stephan has developed electrophilic phosphonium cations, supported by B(C$_6$F$_5$)$_4$, as potent Lewis acids.[20] They showcased this reactivity in the activation of benzylic fluorides, which could be effectively allylated by allylTMS with catalyst loadings of only 1 mol%. The phosphonium performs the fluoride abstraction with subsequent production of Me$_3$SiF after the addition of the allylsilane. Finally, Hosoya designed the aforementioned *o*-(trifluoromethyl)phenylsilane for the selective mono-allylation of the CF$_3$ group via intramolecular fluoride abstraction.[21] Notably, this is not catalytic, but requires stoichiometric Ph$_3$CBF$_4$ to generate the silylium.

For our purposes, we were interested in testing the capability of our silyl cyclopentadienides in these reaction manifolds. As stated above, there are only a handful of examples of halide activation using main-group elements. In addition, the fact that the mono(carboxy)tetracyano-cyclopentadienide anion is relatively strongly bound to the silicon might allow us to influence the reaction, offering a handle for chemoselectivity and potential enantioselectivity in future studies. Thus, the allylation of benzyl bromides offered a way to probe the reactivity of these silyl Lewis acids.
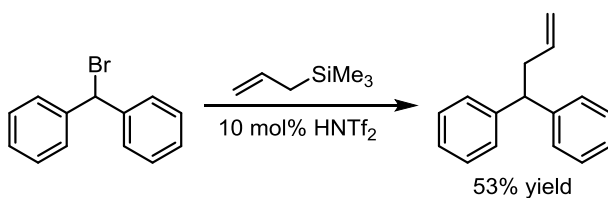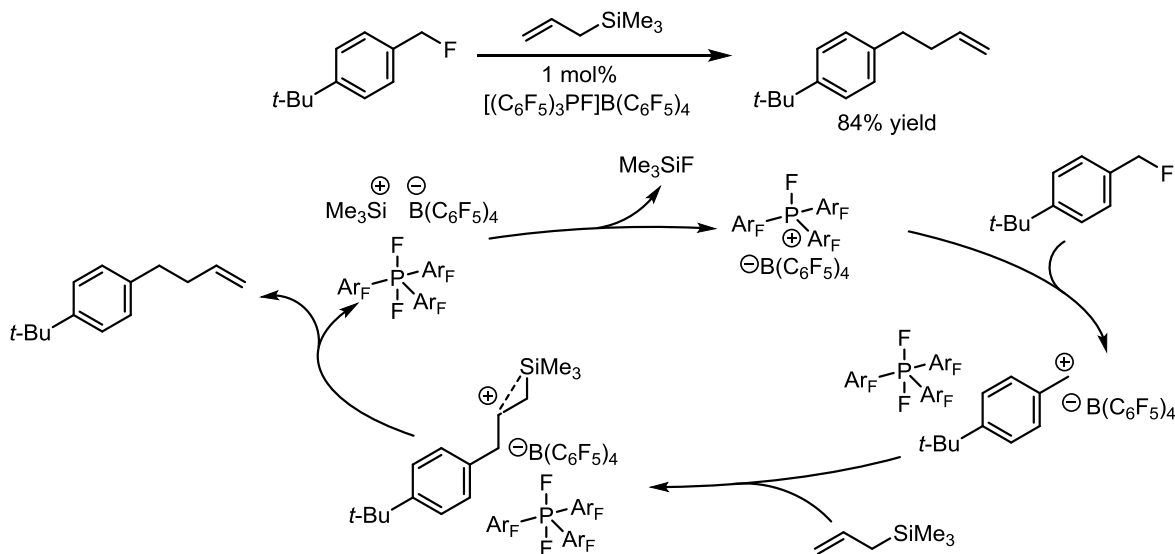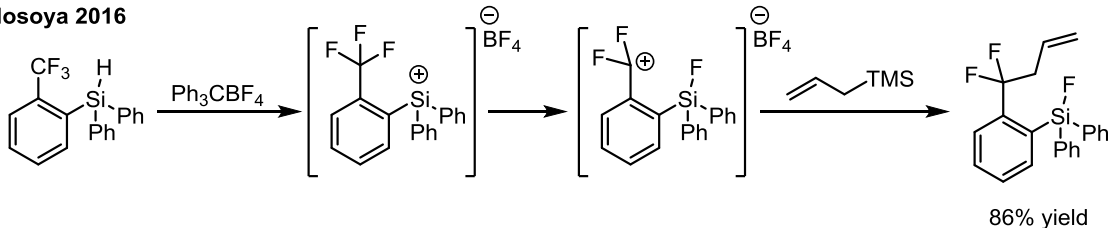
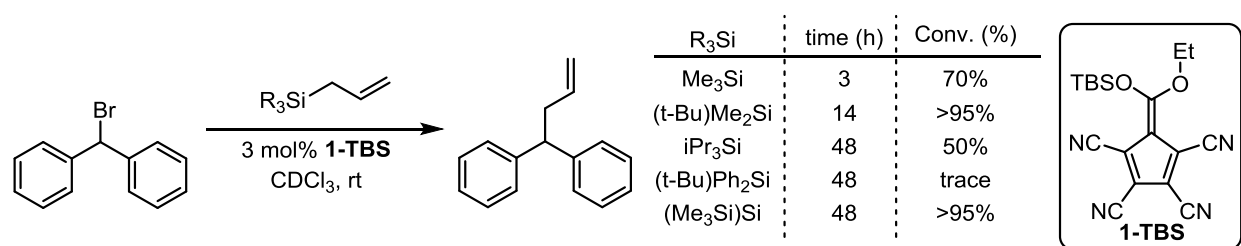**Figure 14: Benzyl halide activation using strong main group Lewis acids.**

We began by using **1-TBS**, as it was the most reactive in our previous studies, with bromodiphenylmethane. In DCE at room temperature, the allylated product was produced with 70% conversion the bromide as measured by ^{1}H NMR spectroscopy. Increasing the reaction temperature to 50 °C gave full consumption of the starting material, and the product could be isolated in 89% yield, while lowering the temperature to 0 °C was detrimental, giving only 50% conversion. Use of neither **4-TBS** nor **5-TBS** led to formation of the allylated product, even at elevated temperatures.

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Figure 15 shows the range of proelectrophiles tested to probe the effect of the leaving group. The use of the phenethyl substrates gave a better range of reactivity, in addition to ease of synthesis of the starting materials. As expected, the fluoride, acetate and methyl ether substrates were the most reactive, in accordance with Lewis acid activation of the benzylic functionality. For the other halides, bromide was more productive than either the chloride or iodide, which only gave low conversions after 3 hrs. The availability, and ease of synthesis, of benzylic bromides made them the best choice for further studies.

X	Conv. (%)
AcO	>95%
MeO	>95%
F	>95%
Cl	15%
Br	67%
I	20%
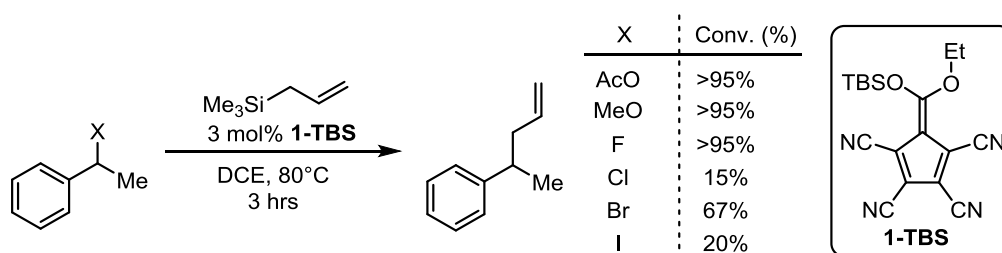
Figure 15: Leaving group comparison using 1-phenylethyl substrate.

Variation of the allylsilane allowed us to examine the effect of the silylium itself on the reaction (Figure 16). A general trend of decreasing reactivity with increased steric encumbrance about the silicon center is evident, with TMS being the most reactive and TBDPS being the least reactive. At the simplest level, these results accord with our expectation that a more stable silicon cation should lead to a less reactive catalyst. In addition, the increasing steric bulk of the silylium would make interaction with the substrate less favorable, contributing to the decrease in reactivty. However, one must consider that the nucleophile is also being altered in these reactions, with the more substituted allylsilane being less nucleophilic and more difficult for the catalyst to activate towards nucleophilic attack. The convolution of these multiple factors makes it difficult to point to a singlular cause, though the negative effect of steric bulk on the initial rate is clear.

| R$_3$Si	time (h)	Conv. (%)
Me$_3$Si	3	70%
(t-Bu)Me$_2$Si	14	>95%
iPr$_3$Si	48	50%
(t-Bu)Ph$_2$Si	48	trace
(Me$_3$Si)Si	48	>95%

Figure 16: Comparison between allylsilanes.

While the trimethylsilyl system gave the fastest initial rate and gave the highest reactivity, it also was prone to decomposition of the catalyst. For the test substrate, catalyst decomposition led to incomplete conversion, with no further conversion beyond 70% seen after 3 hours. In contrast, the extremely bulky supersilyl group was quite slow, but eventually reached full completion after 2 days. Intermediate between these two was *tert*-butydimethylsilyl, which is less reactive than the trimethylsilyl but only takes 14 hours to reach completion. This comparison highlights the balance of factors required for effective catalysis with these highly reactive cations. It also echoes the conclusions reached by Oestriech when developing their ferrocene-stabilized silylium catalysts, i.e. the required addition of a bulky *tert*-butyl group to lend stability to their catalyst.

Having established conditions for the allation catalyzed by **1-TBS**, we examined the scope of the benzylic bromide, which is shown in Figure 17. Benzhydryl substrates in general were good substrates. Adding electron-withdrawing substituents requires higher reactions temperatures of 80 °C, and in the case of *p*-CF$_3$-benzhydryl bromide incomplete conversion was seen with a diminished yield obtained. Oxygenated functionality was tolerated, which illustrates the selective activation of the benzylic bromide. However, an acetyl substituent was not tolerated. Monobenzylic bromides generally required higher temperatures, but were capable substrates. The *p*-methoxy and 2-naphthyl substrates gave increased yields as expected for more easily ionized substrates. Cyclic bromides were good substrates, though in the case of

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benzosuberyl, the reaction produced a significant amount of the elimination product. Tertiary bromides were the most difficult substrates for our system. 1-phenyl-2-bromopropane gave 48% yield, with the remainder being elimination to alpha-methylstyrene, the increase in elimination likely resulting from the greater number of alpha protons. Allylation of 1-bromoadamantane produced a mixture of the olefin isomers in 30% yield.

The mechanism of the allylation is shown below in Figure 18. First, the bromide is abstracted by the electrophilic silyl catalyst to give R_3SiBr and the carbenium cyclopentadienide salt. The intermediate displays enough carbocation character to be intercepted by the allylsilane. Desilylation of the adduct gives the desired product and releases the silyl cyclopentadienide, completing the catalytic cycle. Because the *tert*-butyldimethylsilyl salt is used as the precatalyst, the catalyst must enter the cycle by an initial production of TBS-Br before giving the more reactive **1-TMS** catalyst, similar to the Hosomi-Sakurai allylation above.
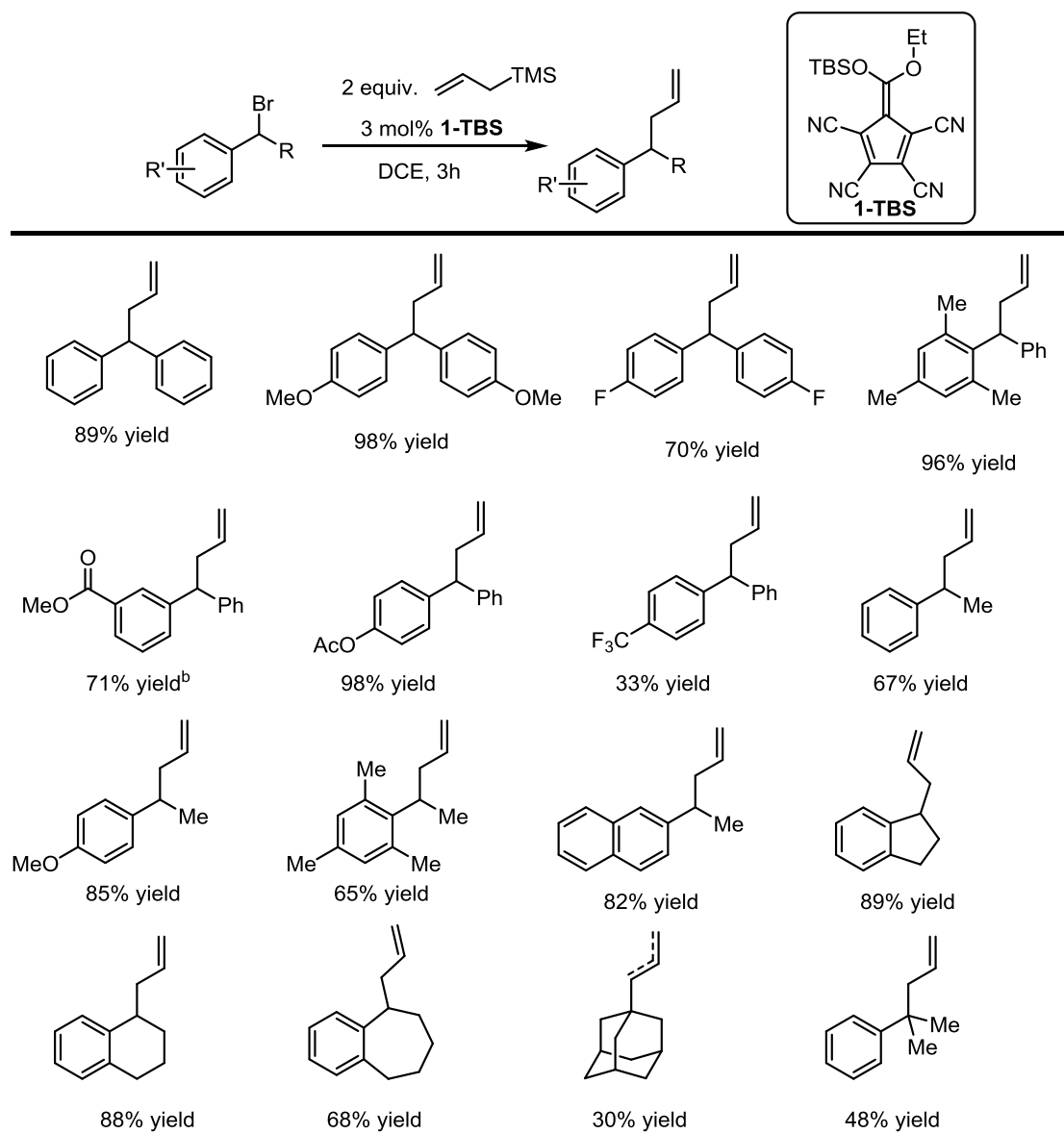
Figure 17: Substrate scope for the allylation of benzyl halides catalyzed by *1-TBS*.
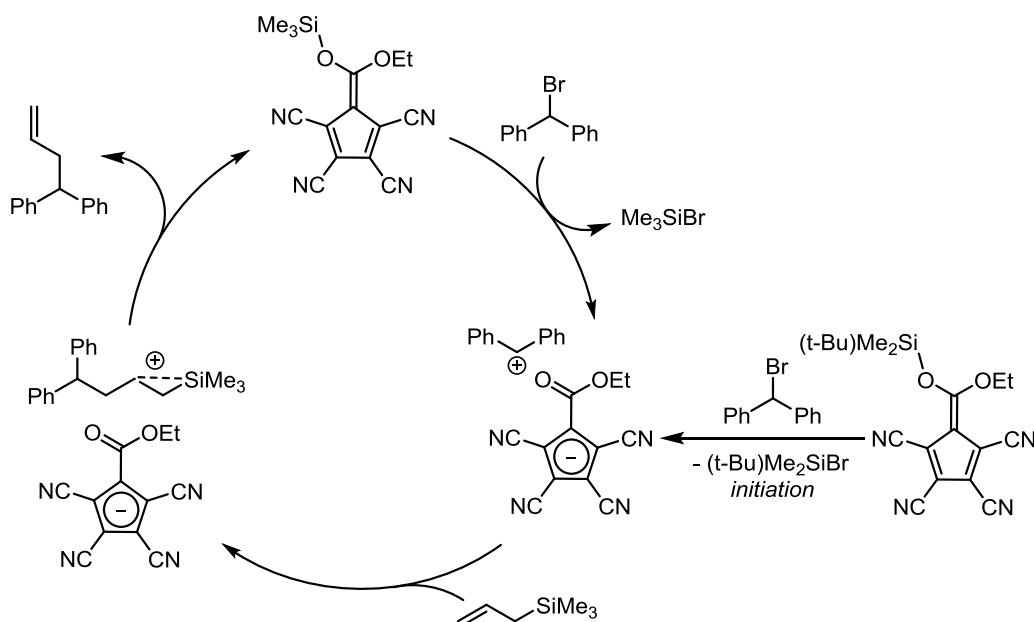
Figure 18: Proposed mechanism for the allylation of benzyl halides.

Having demonstrated the ability of **1-TBS** to act as a precatalyst for generating reactive cationic intermediates, we turned to expanding the range of nucleophiles that could be used in this catalytic manifold. It should be expected that other silyl nucleophiles (e.g., silyl ketene acetals, silyl acetylenes, etc.) would be competent partners in this reaction. On the other hand, using non-silyl nucleophiles - for example, arenes - would require a slightly different catalytic cycle, as the silyl cyclopentadiene is not formed following the addition step. Instead, the protonated species is produced upon rearomatization of the adduct, as depicted in the catalytic cycle in Figure 19. Protodesilylation of a suitable sacrificial silyl source could be used to regenerate the catalytic silyl cyclopentadiene.[22] For this manifold to be viable, the addition of the desired nucleophile must outcompete the addition of the silyl source. We found allyl-trimethylsilane was a viable source of Me_3Si^+, provided a sufficiently nucleophilic arene is used as the nucleophile.
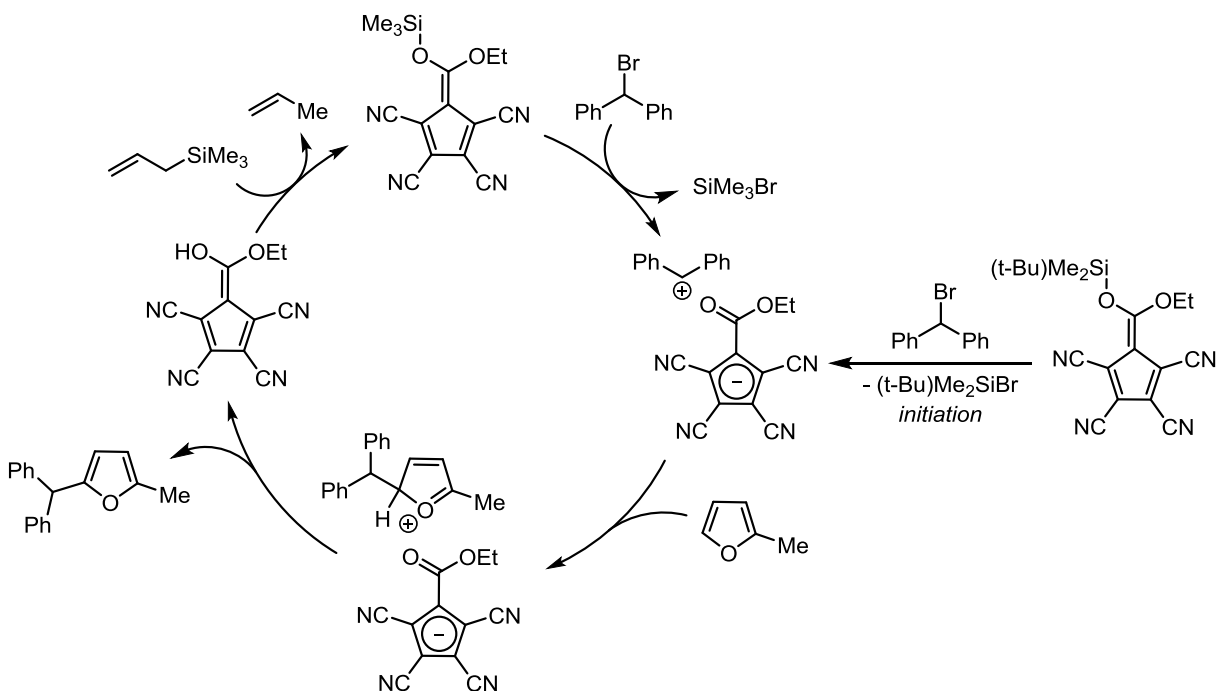
Figure 19: Proposed mechanism for the alkylation of arenes using allylsilane as a Si⁺ fuel.

We explored the scope of arenes using bromodiphenylmethane as the pro-electrophile, the results of which are shown in Figure 20. *N*-alkyl indoles are generally good substrates, with *N*-methyl, *N*-benzyl and *N*-allylindole all being alkylated in good yield. Unsubstituted indole was a viable substrate, albeit in reduced yield. Substitution of the 2- and 3-positions was tolerated, giving the 1,2,3-trialkylindole products in high yield. Other electron-rich arenes also could be effectively alkylated. 1,3-dimethoxybenzene was productively alkylated, though a small amount of dialkylation was also observed and the product was obtained as 8:1 mixture. 2-Methylfuran was nearly quantitatively alkylated exclusively at the 5-position. Pyrroles were somewhat less productive, with 1,2,5-trimethylpyrrole giving 55% yield, and 1-phenylpyrrole effectively alkylated but as a 4:1 mixture of the 2- and 3-position products.
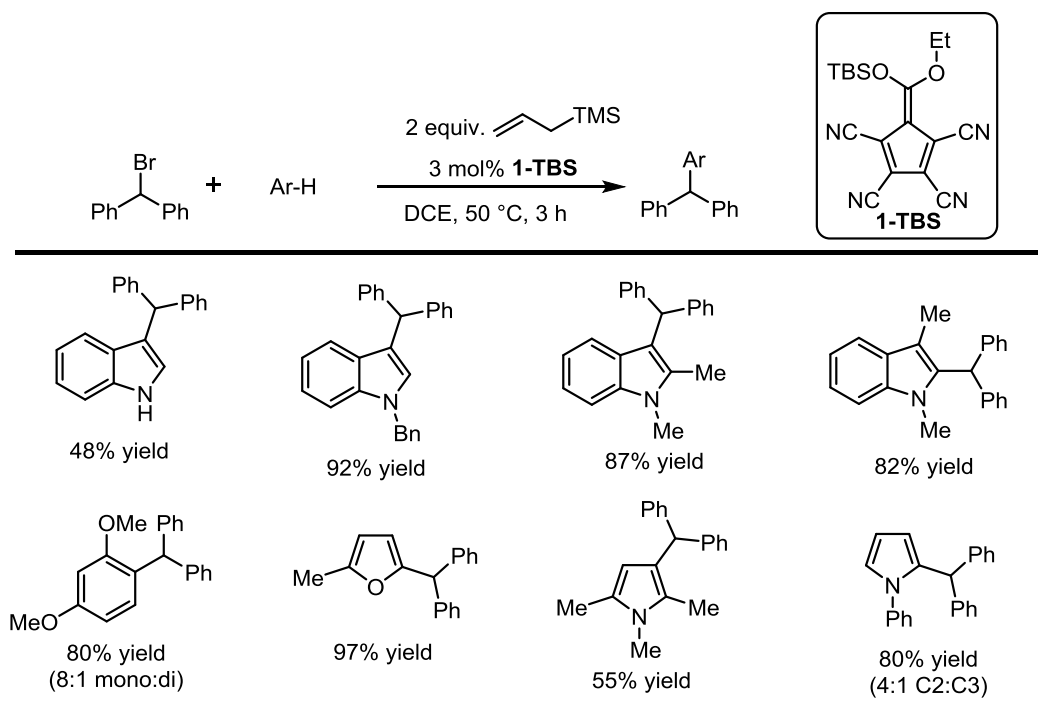
Figure 20: Allylation of arenes using *1-TBS*.

As noted above, the arene must outcompete addition of the allyltrimethylsilane to the carbocationic intermediate. While 1,3-dimethoxybenzene is successfully alkylated, anisole or 1-methoxynaphthalene are not nucleophilic enough and allylation is observed instead (Figure 21). Attempts to use less nucleophilic silane sources such as vinyltrimethylsilane were unsuccessful as no catalytic turnover was seen. Another limitation is the use of indoles with electron-withdrawing *N*-substituents. This deactivates the indole, rending it less nucleophilic; for instance, *N*-tosylindole remains unreacted. With more Lewis basic functionality, such as the *N*-Boc or *N*-acetylindole substrates, the *N*-substituent is reactive under the catalytic conditions and deprotection or degradation is observed.
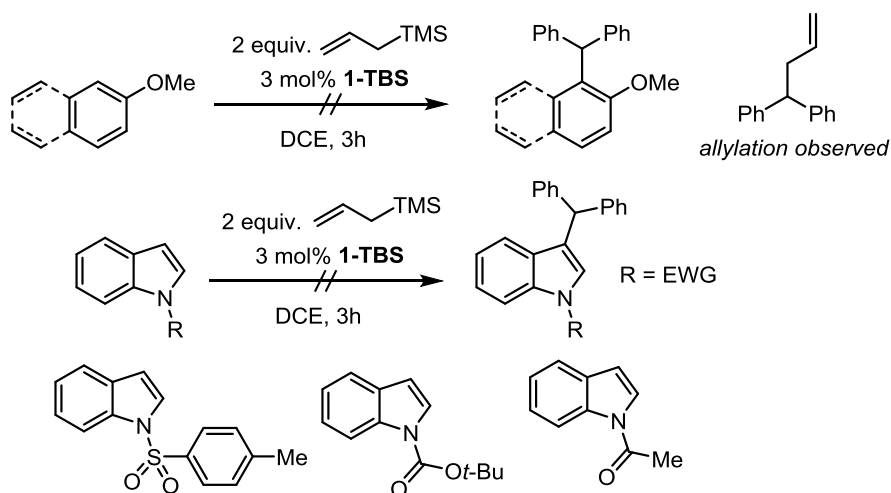
Figure 21: Non-productive substrates

Conclusion

Through investigating the reactivity of stable cyclopentadiene anions, we established routes to silylated cyclopentadienes via salt metathesis. The iPr$_3$Si$^+$ derivatives were characterized, with their ^{29}Si shifts placing them as covalently bound Lewis acidic silicon species. They exist in the range of the silyl triflates but display unique reactivity, as shown by a comparison in catalyzing a Hosomi-Sakurai allylation. We further developed the alkylation of benzylic bromides using the cyanated species **1-TBS**, and showed the successful use of non-silyl arenes as nucleophiles by exploiting an allylsilane as a sacrificial silyl source.

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[22] Stephan utilized a similar mechanism in their arylation methodology (Ref. 20). They use triethylsilane, which is protonated by $HB(C_6F_5)_4$ to produce $Et_3SiB(C_6F_5)_4$.

Experimental Data

General Information

All reactions were performed in a glovebox or using standard air-free techniques. Organic solutions were concentrated using a Buchi rotary evaporator. Methylene chloride, diethyl ether, benzene and toluene were dried using a J.C. Meyer solvent purification system and stored over activated 3Å molecular sieves. Deuterated solvents were stored over activated 3Å molecular sieves. All other solvents were purchased as anhydrous and used as received. All other commercial reagents were used as provided. Flash column chromatography was performed employing 40-63 μm silica gel (SiliaFlash® P60 from Silicycle). Thin-layer chromatography (TLC) was performed on 250 μm glass-backed silica plates (SiliaPlate™ G TLC from Silicycle). ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-300, DRX-400 or DRX-500 spectrometers as noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q =quartet, p = pentet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), integration, and assignment. All ^{1}H-NMR experiments were measured relative to the signals of tetramethylsilane (TMS 0.00 ppm) or residual solvent (chloroform 7.26 ppm, methanol 3.31 ppm, acetonitrile 1.94 ppm). Data for ^{13}C are reported in terms of chemical shift relative to the deuterated solvent (chloroform: 77.16 ppm, methanol: 49.00 ppm, acetonitrile: 118.26 ppm). High-resolution mass spectra were obtained from the Columbia University Mass Spectrometry Facility on a Waters XEVO G2XSQToF mass spectrometer equipped with a UPC2 SFC inlet, electrospray ionization (ESI) probe, atmospheric pressure chemical ionization (APCI) probe, and atmospheric solids analysis probe (ASAP). IR spectra were collected on a Perkin Elmer Spectrum Two FT-IR spectrometer.

1. Substrate Synthesis

Bromide synthesis general procedure: To a solution of the benzylic alcohol (1 eq.) in dry benzene (5 mL per mmol of alcohol substrate) was added acetyl bromide (1.5 eq.). The reaction was allowed to stand overnight. The reaction was quenched by slow addition into a beaker of with 15 mL of cold (0 °C) saturated $NaHCO_3$. The mixture was extracted with 2 portions of ether (2 mL per mL of benzene used) and the ethereal extracts washed with brine. The organic layer was then dried with $MgSO_4$ and then the solvent removed to give the desired bromide. Some bromides were then purified as specified.
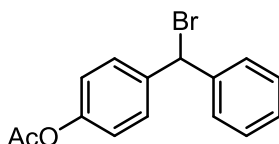
1-phenyl-4'-acetoxybenzyl bromide: Reaction done with 177 mg of alcohol (0.73 mmol). Yield: 193 mg (0.63 mmol, 87% yield)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.47 (m, 4 H, Ar**H**), 7.38-7.27 (m, 3 H, Ar**H**), 7.07 (m, 2H, Ar**H**), 6.29 (s, 1 H, C**H**BrAr$_2$), 2.30 (s, 3 H, C**H$_3$**CO$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 169.4, 150.3, 140.8, 138.7, 129.7, 128.7, 128.5, 128.3, 121.7, 54.7, 21.3. IR (thin film, cm^{-1}) 3064, 3028, 1759, 1604, 1503, 1493, 1451, 1368, 1191, 1166, 1017, 911, 862, 748, 696. HRMS (ASAP$^+$) exact mass calc'd for C$_{15}$H$_{14}$O$_2$Br [M+H]$^+$, requires *m/z* 305.0177, found *m/z* 305.0169.
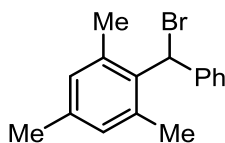
2-(1-bromo-1-phenylmethyl)mesitylen: Reaction done with 453 mg of alcohol (2.00 mmol). Crude product was purified by column chromatography (hexanes). Yield: 428 mg (1.48 mmol, 74% yield)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42-7.38 (m, 2H, Ar**H**), 7.31-7.21 (m, 3H, Ar**H**), 6.90-6.85 (overlapping s, 3H, Mes**H** and C**H**Ar$_2$), 2.29 (s, 3H, *p*-MesC**H$_3$**), 2.21 (br s, 6H, *o*-MesC**H$_3$**). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 139.9, 138.3, 134.7, 130.4 (br), 128.5, 128.4, 127.9, 127.2, 52.4, 21.1, 20.9. IR (thin film, cm^{-1}) 3031, 2968, 2917, 2858, 1609, 1492, 1444, 1377, 1163, 1030, 843, 791, 755, 727, 695, 670, 614. HRMS (ASAP$^+$) exact mass calc'd for C$_{16}$H$_{16}$Br [M+H]$^+$, requires *m/z* 287.0435, found *m/z* 287.0437.
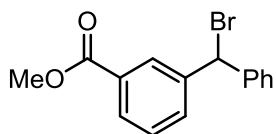
3'-(methoxycarbonyl)benzyl bromide: Reaction done with 121 mg of alcohol (0.50 mmol). Crude product was purified by column chromatography with silica gel (5-15% EtOAc/hexanes) Yield: 112 mg (0.37 mmol, 73% yield)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.18 (s, 1 H, Ar**H**), 7.99 (d, 1 H, Ar**H**), 7.69 (d, 1 H, Ar**H**), 7.50-7.28 (m, 6H, Ar**H**), 6.33 (s, 1 H, C**H**Br), 3.94 (s, 3 H, C**H$_3$**CO$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 166.7, 141.7, 140.7, 133.0, 130.7, 129.6, 129.4, 128.9, 128.8, 128.5, 128.4, 54.5, 52.4. IR (thin film, cm^{-1}) 3031, 2950, 2825, 1720, 1607, 1433, 1286, 1197, 1175, 1106, 1084, 750, 699. HRMS (ASAP$^+$) exact mass calc'd for C$_{15}$H$_{14}$O$_2$Br [M+H]$^+$, requires *m/z* 305.0177, found *m/z* 305.0175.
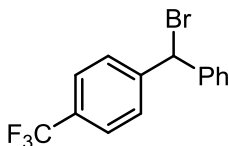
1-phenyl-4-(trifluoromethyl)benzyl bromide: Reaction done with 126 mg of alcohol (0.50 mmol). Yield: 129 mg (0.41 mmol, 82% yield)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62 (m, 4 H, CF$_3$Ar**H**), 7.49-7.31 (m, 5 H, Ar**H**), 6.31 (s, 1 H, C**H**Ar$_2$). ^{13}C{^{1}H,^{19}F} NMR NMR (101 MHz, CDCl$_3$) δ 145.1, 140.3, 130.3, 129.0, 128.9, 128.6, 128.5, 125.7, 124.0, 53.9. IR (thin film, cm^{-1}) 2978, 2934, 1780, 1596, 1388, 1360, 1324, 1306, 1278, 1268, 1225, 1202, 1190, 1161, 1106, 1083, 948, 910, 895, 811, 747, 691. HRMS (ASAP$^+$) exact mass calc'd for C$_{14}$H$_9$F$_3$Br [M+H]$^+$, requires *m/z* 312.9840, found *m/z* 312.9836.
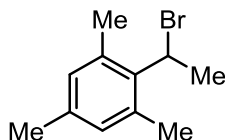
2-(1-bromoethyl)mesitylene: Reaction done with 328 mg of alcohol (2.0 mmol). Crude product was purified by column chromatography with silica gel (hexanes). Yield: 285 mg (1.26 mmol, 63% yield)

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.88 (s, 1 H, Ar**H**), 6.84 (s, 1 H, Ar**H**), 5.75 (q, 1 H, C**H**BrCH$_3$), 2.61 (s, 3 H, *o*-C**H$_{3a}$**Ar), 2.38 (s, 3 H, *o*-C**H$_{3b}$**Ar), 2.27 (s, 3H, *p*-CH3Ar), (d, 3H, CHBrC**H$_3$**). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 138.3, 137.9, 135.5, 135.3, 131.8, 129.3, 46.7, 25.3, 21.4, 20.9, 20.7. IR (thin film, cm^{-1}) 3011, 2968, 2918, 1862, 1610, 1450, 1376, 1216, 1189, 1075, 1044, 1030, 975, 850, 721, 616. HRMS (ASAP$^+$) exact mass calc'd for C$_{11}$H$_{14}$Br [M+H]$^+$, requires *m/z* 225.0279, found *m/z* 225.0275

2. **Catalyst Preparation:**
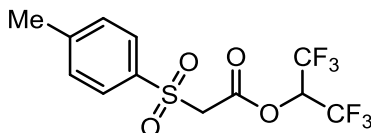
Hexafluoroisopropyl 2-tosylacetate: 2.10 mL of HFIP (20 mmol) was added to 15 mL of dry DCM, along with 1.74 mL (20 mmol) of bromoacetyl bromide. The solution was cooled to 0 °C on an ice bath. Then 2.00 mL of pyridine (25 mmol) in 10 mL of dry DCM was added and the reaction stirred for 1 hr at 0 °C. The reaction was then allowed to warm to r.t. and stirred for an additional 2 hr. The slightly yellow reaction mixture was quenched with 1 M HCl and the aqueous mixture extracted three times with 20 mL of DCM. The organic extracts were washed with sat. $NaHCO_3$, dried with Na_2SO_4 and the solvent removed carefully at ~120 torr. The crude product (~12 mmol from NMR analysis) is the desired bromoacetate with small amounts of HFIP and DCM and was used without further purification.

The bromoacetate was dissolved in 30 mL of DMSO and sodium p-toluenesulfinate (5.34 g, 30 mmol) was added. The reaction was stirred at r.t. overnight. The mixture was diluted with 120 mL of water and extracted 4 times with 30 mL of Et_2O. The combined ethereal extracts were washed 3 times with water and once with brine. The organic layer was then dried with Na_2SO_4 and then the solvent removed via rotovap. The crude product was dissolved in 10 mL of DCM passed through a short silica plug, eluting with ~100 mL of DCM and collecting ~50 mL of product-containing solution. The solvent was removed via rotovap and the solid dried on hi-vac, yielding 2.69 g (7.38 mmol, 37% yield over two steps) of desired product.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.82 (d, 2 H, Ar**H**), 7.39 (d, 2 H, Ar**H**), 5.68 (m, 1 H, **CH**(CF$_3$)$_2$), 4.28 (s, 2 H, **CH$_2$**Ts), 2.47 (s, 3 H, Ar**CH$_3$**). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 160.1, 146.3, 135.2, 130.3, 128.7, 120.0 (J$_{CF}$ = 286 Hz), 67.5 (J$_{CF}$ = 35 Hz), 60.1, 21.9. IR (thin film, cm^{-1}) 2978, 2934, 1780, 1596, 1388, 1360, 1324, 1306, 1278, 1268, 1225, 1202, 1190, 1161, 1106, 1083, 948, 910, 895, 811, 747, 691. HRMS (ASAP$^+$) exact mass calc'd for C$_{12}$H$_{11}$O$_4$F$_6$S [M+H]$^+$, requires *m/z* 365.0282, found *m/z* 365.0271
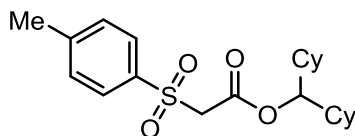
Dicyclohexylmethyl 2-tosylacetate: To a flame-dried 100mL round bottom flask under an argon atmosphere was added 40 mL of dry DCM, 392 mg of dicyclohexylmethanol (2.0 mmol), and 350 µL of Hünig's base (2.0 mmol). The solution was cooled to 0 °C in an ice bath and 175 µL of bromoacetyl bromide (2.0 mmol) was added slowly dropwise over 30 minutes. The reaction was stirred at 0 °C for 1 hr, then at r.t. for 1 hr. The reaction was then cooled to 0 °C and quenched with sat. NH$_4$Cl. The layers were separated and the aqueous layer was extracted 3 times with 10 mL of DCM. The combined organic layers were washed successively with 1M HCl and sat. NaHCO$_3$, dried with Na$_2$SO$_4$ and concentrated to give the crude bromoacetate which was used without purification.

The bromoacetate was dissolved 20 mL of DMF and 713 mg of sodium p-toluenesulfinate (4.0 mmol) added. The reaction was stirred for 4 h. The mixture was diluted with 50 mL of water and extracted 4 times with 20 mL of Et$_2$O. The combined ethereal extracts were washed 3 times with water and once with sat. NaCl. The organic layer was then dried with MgSO$_4$ and then the

solvent removed via rotovap to give 760mg (1.94 mmol, 97% yield over 2 steps) of the desired product.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83 (d, 2 H, Ar**H**), 7.36 (d, 2 H, Ar**H**), 4.61 (t, 1 H, C**H**Cy$_2$), 4.13 (s, 2 H, C**H$_2$**Ts), 2.45 (s, 3 H, ArC**H$_3$**), 1.78-1.46 (m, 12 H), 1.29-0.82 (m, 10 H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 162.6, 145.4, 136.1, 129.9, 128.8, 84.5, 60.8, 38.3, 29.8, 27.4, 26.4, 26.3, 26.1, 21.9. IR (thin film, cm^{-1}) 2995, 2918, 2849, 1734, 1598, 1449, 1327, 1323, 1290, 1147, 1129, 1088, 1061, 970, 939, 898, 886, 807, 726, 641. HRMS (ESI$^-$) exact mass calc'd for C$_{22}$H$_{31}$O$_4$S [M-H]$^-$, requires m/z 391.1943, found m/z 391.1952
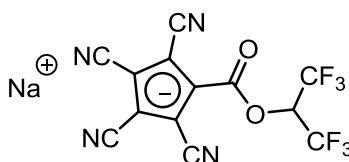
Sodium tetracyano(hexafluoroisopropoxycarbonyl)cyclopentadienide: To a flame-dried, 6-dram vial was added the tosylacetate (364 mg, 1.0 mmol) and 5 mL of dry THF. The solution was cooled to 0 °C in an ice bath and 60% sodium hydride (120 mg, 3.0 mmol) was added in one portion. The mixture was stirred at 0 °C for 30 min, then allowed to warm to r.t. and stirred for an additional 30 min. Then a solution of tetracyanodithiin (220 mg, 1.0 mmol) in 5 mL of dry THF was added over approximately 10 minutes. The dark red mixture was then heated at 60 °C for 3 hr. The reaction was then quenched slowly (CAUTION: vigorous gas evolution) with brine (~ 15 mL). The mixture was diluted with 20 mL of EtOAc and 40 mL of brine and the layers separated. The aqueous layer was further extracted two times with 20 mL of EtOAc. The organic

layers were washed once with brine, then dried with Na_2SO_4, and the solvent removed via rotovap. The crude product was purified via column chromatography with acidic alumina (10–30% MeCN/EtOAc) to give 96 mg (0.25 mmol, 25% yield) of desired product as a yellow-orange solid.

^{1}H NMR (400 MHz, CD$_3$CN) δ 6.30 (m, 1 H, C**H**(CF$_3$)$_2$). ^{13}C{^{1}H,^{19}F} NMR (101 MHz, CD$_3$CN) δ 158.5, 121.8, 118.5, 114.9, 114.6, 105.1, 102.7, 67.2. IR (thin film, cm^{-1}) 2972, 2929, 2855, 2781, 2227, 1732, 1631, 1563, 1473, 1381, 1292, 1240, 1198, 1105, 1057, 904, 681. HRMS (ESI$^-$) exact mass calc'd for C$_{13}$HF$_6$N$_4$O$_2$ [M-Na]$^-$, requires m/z 359.0004, found m/z 359.0010.
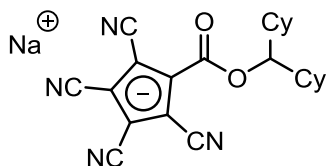
Sodium tetracyano(dicyclohexylmethoxycarbonyl)cyclopentadienide: To a flame-dried, 6-dram vial was added 60% sodium hydride (120 mg, 3.0 mmol) and 3 mL of dry THF and the mixture was cooled to 0 °C in an ice bath. A solution of the tosylacetate (393 mg, 1.0 mmol) in 2 mL of dry THF was added slowly dropwise. The mixture became very viscous, and 5 mL of dry THF were added to aid stirring. The mixture was stirred at 0 °C for 40 min. Then a solution of tetracyanodithiin (216 mg, 1.0 mmol) in 4 mL of dry THF was added over approximately 5 mins, during which the reaction became dark red. The mixture was stirred at 0 °C for 1 hr and then allowed to warm to r.t. and stirred for an additional 1 hr. The reaction was then quenched slowly (CAUTION: vigorous gas evolution) with brine. The mixture was poured into a separatory funnel, diluted with 20 mL of EtOAc and 20 mL of brine and the layers separated. The aqueous layer was further extracted three times with 20 mL of EtOAc. The organic layers were washed twice with brine, then dried with Na_2SO_4, and the solvent removed via rotovap. The crude

product was purified via column chromatography with silica gel (0–1% MeCN/EtOAc) to give 278 mg (0.68 mmol, 68% yield) of desired product.

^{1}H NMR (500 MHz, CD$_3$CN) δ 4.82 (t, 1 H, C**H**Cy$_2$), 1.77-1.56 (m, 12H, alkyl CH), 1.34-0.98 (m, 10H, alkyl H). ^{13}C{^{1}H} NMR (126 MHz, CD$_3$CN) δ 162.3, 124.1, 116.0, 115.2, 103.6, 101.0, 82.8, 39.2, 30.5, 28.4, 27.1, 26.9, 26.7. IR (thin film, cm^{-1}) 2928, 2851, 2221, 1689, 1471, 1448, 1274, 1131, 1096, 933, 894, 783. HRMS (ESI$^-$) exact mass calc'd for C$_{23}$H$_{23}$O$_2$N$_4$ [M-Na]$^-$, requires *m/z* 387.1821, found *m/z* 387.1832
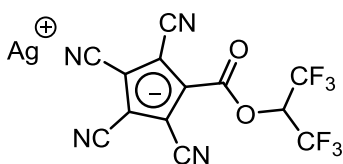
Silver tetracyano(hexafluoroisopropoxycarbonyl)cyclopentadienide: Na salt (38 mg, 0.10 mmol) was dissolved in 1.0 mL of acetone in a 2-dram vial wrapped in tin foil. To this, a solution of AgNO$_3$ (68 mg, 0.40 mmol) in 0.50 mL of water was added and the reaction stirred overnight. The solution was then filtered and the tan solid washed with water. The solid was collected and dried on hi-vac to give 36 mg (0.077 mmol, 77% yield) of the desired product.

^{1}H NMR (400 MHz, CD$_3$CN) δ 6.30 (m, 1 H, C**H**(CF$_3$)$_2$). ^{13}C{^{1}H,^{19}F} NMR (101 MHz, CD$_3$CN) δ 158.5, 121.7, 118.6, 114.9, 114.5, 105.1, 102.6, 67.2. IR (thin film, cm^{-1}) 2933, 2853, 2236, 2222, 1739, 1476, 1362, 1241, 1193, 1102, 1059, 924, 892, 766, 716, 686. HRMS (ASAP$^+$) exact mass calc'd for C$_{13}$HF$_6$N$_4$O$_2$, requires *m/z* 359.0004, found *m/z* 359.0007
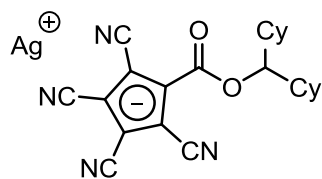
Silver tetracyano(dicyclohexylmethoxycarbonyl)cyclopentadienide: Na salt (113 mg, 0.28 mmol) was dissolved in 2.5 mL of acetone in a 2-dram vial wrapped in tin foil. To this, a solution of AgNO₃ (148 mg, .87 mmol) in 0.50 mL of water was added and the reaction stirred for 3 days. The very fine precipitate was collected over celite. The brown solid was then dissolved in MeCN and the solution collected. The MeCN was removed via rotovap and the material dried on hi vac to give 98 mg (0.20 mmol, 72% yield) of the desired product.

^{1}H NMR (500 MHz, CD₃CN) δ 4.82 (t, 1 H, C**H**Cy₂), 1.77-1.57 (m, 12H, alkyl CH), 1.34-0.98 (m, 10H, alkyl H). ^{13}C{^{1}H} NMR (126 MHz, CD₃CN) δ 162.2, 124.2, 116.0, 115.2, 103.6, 101.0, 82.8, 39.2, 30.5, 28.4, 27.1, 26.9, 26.7. IR (thin film, cm⁻¹). 2925, 2851, 2224, 1708, 1474, 1447, 1254, 1117, 1094, 1065, 961, 934, 893. HRMS (ESI⁻) exact mass calc'd for C₂₃H₂₃O₂N₄ [M-Ag]⁻, requires *m/z* 387.1821, found *m/z* 387.1825.
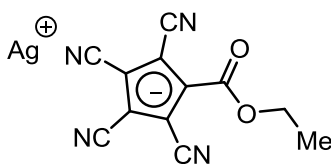
Silver tetracyano(ethoxycarbonyl)cyclopentadienide: Sodium tetracyano(ethoxycarbonyl)-yclopentadienide[1] (92 mg, 0.32 mmol) was dissolved in 2.0 mL of acetone in a 6-dram vial wrapped in tin foil. To this, a solution of AgNO₃ (82 mg, 0.482 mmol) in 0.50 mL of water was added and the reaction stirred overnight. The solution was then filtered and the tan solid washed

with water and then washed with acetone. The solid was collected and dried on hi-vac to give

110 mg (0.32 mmol, 99% yield) of the desired product.

^{1}H NMR (500 MHz, CD$_3$CN) δ 4.30 (q, 2 H, C**H$_2$**CH$_3$), 1.33 (t, 3H, CH$_2$C**H$_3$**). ^{13}C{^{1}H} NMR (126 MHz, CD$_3$CN) δ 161.9, 124.1, 115.9, 115.1, 103.5, 100.9, 61.5, 14.4. IR (thin film, cm^{-1}) 2982, 2772, 2239, 2217, 1712, 1702, 1482, 1468, 1445, 1386, 1261, 1135, 1107, 1012, 780, 653. HRMS (ESI$^-$) exact mass calc'd for C$_{12}$H$_5$O$_2$N$_4$ [M-Ag]$^-$, requires m/z 237.0413, found m/z 237.0412.
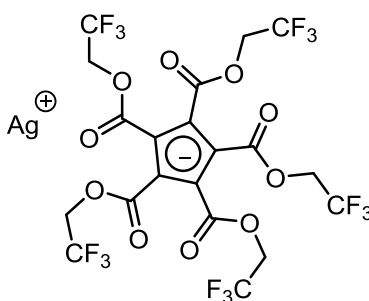
Silver penta(trifluoroethoxycarbonyl)cyclopentadienide: NMe$_4$ penta(trifluoroethoxy-carbonyl)cyclopentadienide[2] (140 mg, 0.18 mmol) was added to a solution of AgOTf (70.0 mg, 0.27 mmol) in 2 mL of diethyl ether in a 2-dram vial wrapped in tin foil. The reaction was stirred overnight. The mixture was then cooled to −14 °C in a freezer and filtered. The solution was then washed with water, dried with Na$_2$SO$_4$ and evaporated to give 125 mg (0.16 mmol, 86% yield) of the desired product as an off-white solid.

^{1}H NMR (400 MHz, CD$_3$CN) δ 4.59 (q, 10 H, C**H$_2$**CF$_3$). ^{13}C{^{1}H} NMR (101 MHz, CD$_3$CN) δ 164.69, 124.71, 117.03, 60.92. IR (thin film, cm^{-1}). 2975, 1695, 1661, 1446, 1413, 1277, 1256, 1149, 1047, 958, 650, 628. HRMS (ESI$^-$) exact mass calc'd for C$_{20}$H$_{10}$O$_{10}$F$_{15}$ [M-Ag]$^-$, requires m/z 695.0034, found m/z 695.0042

Triisopropylsilyl synthesis general procedure: The silver salt (0.01 mmol) was added to a 1-dram vial with 200 μL of dry acetonitrile and trityl chloride (2.78mg, 0.01 mmol). The mixture immediately turned yellow-orange and a white precipitate was generated. The mixture was stirred for 5 minutes and then filtered. The acetonitrile was removed in vacuo. The material was then washed with 450 μL of pentane/benzene (2:1) and then dried on high vac. The trityl salt was used immediately thereafter.

The trityl salt was dissolved in 600 μL of d_4-1,2-dichlorobenzene. 1 eq. of triisopropylsilane (2.0 μL, 0.01 mmol) was added and the mixture became colorless over the course of several minutes (5-15 minutes). ^{1}H,^{29}Si-HMBC spectra were collected with a delay optimized for 6 Hz coupling.

Triisopropylsilyl penta(methoxycarbonyl)cyclopentadienide (5a): [29]Si δ 35 ppm

Triisopropylsilyl penta(trifluoroethoxycarbonyl)cyclopentadienide (5b): [29]Si δ 42 ppm

Triisopropylsilyl tetracyano(ethoxycarbonyl)cyclopentadienide (6a): [29]Si δ 30 ppm

Triisopropylsilyl tetracyano(dicyclohexylmethoxycarbonyl)cyclopentadienide (6b):
[29]Si δ 30 ppm

**Triisopropylsilyl tetracyano(hexafluoroisopropoxycarbonyl)cyclopentadienide (6c):**
[29]Si δ 32 ppm

3. Catalytic Reactions

Tert-butyldimethylsilyl (Ethoxycarbonyl)tetracyanocyclopentadienide: Silver salt (5.1 mg, 0.015 mmol) was dissolved in 200 μL of dry acetonitrile in a flame-dried 1-dram vial. Trityl chloride (4.2 mg, 0.015 mmol) was added and the mixture turned bright yellow-orange with a white precipitate. The mixture was stirred for 5 minutes and then filtered. The vial was washed with 200 μL of acetonitrile and then the solvent removed in vacuo. The crude trityl salt was then dissolved in 1000 μL of dry DCE. To this, tert-butyldimethylsilane (2.5 μL, 0.015 mmol) was added and the solution quickly became colorless. This solution was then used immediately for reactions.

Allylation general procedure: The bromide (0.1 mmol) and allyltrimethylsilane (0.2 mmol) were added to a flame-dried 2-dram vial with 800 μL of dry DCE under an atmosphere of argon. A solution of the catalyst (200 μL, 0.003 mmol) was added and the reaction heated at the specified temperature. After 3 hours, the reaction was quenched with triethylamine and purified.
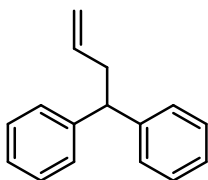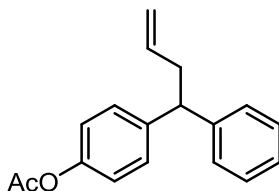

4,4-diphenyl-1-butene: Reaction was conducted at 50 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 2% CH_2Cl_2/hexanes). The product was collected as a colorless oil (19 mg, 89% yield). Spectra of the product were consistent with previous reports[3]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.31-7.09 (m, 10 H, Ar**H**), 5.72 (m, 1 H, C**H**=CH$_2$), 5.03 (m, 1 H, CH=C**H$_a$**H$_b$), 4.94 (m, 1 H, CH=CH$_a$**H$_b$**), 4.01 (t, 1 H, Ph$_2$C**H**), 2.82 (m, 1 H, C**H$_2$**CH=CH$_2$)
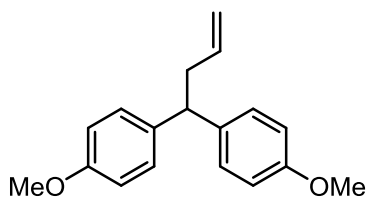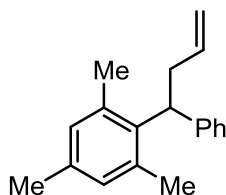
4,4-bis(4-methoxyphenyl)-1-butene: Reaction was conducted at 50 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (10 → 20% CH_2Cl_2/hexanes). The product was collected as a colorless oil (26 mg, 98% yield). Spectra of the product were consistent with previous reports[3]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19-7.14 (m, 4 H, Ar**H**), 6.87-6.83 (m, 4 H, Ar**H**), 5.75 (m, 1 H, C**H**=CH$_2$), 5.05 (m, 1 H, CH=C**H$_a$**H$_b$), 4.97 (m, 1 H, CH=CH$_a$**H$_b$**), 3.95 (t, 1 H, Ar$_2$C**H**), 3.80 (s, 6 H, C**H$_3$**O), 2.83-2.75 (m, 2 H, C**H$_2$**CH=CH$_2$)
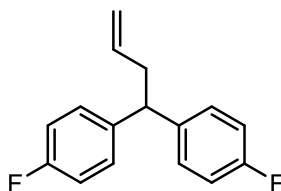
4,4-bis(4-fluorophenyl)-1-butene: Reaction was conducted at 50 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (hexanes). The product was collected as a colorless oil (17 mg, 70% yield). Spectra of the product were consistent with previous reports[4]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19-7.08 (m, 4 H, ArH), 7.01-6.89 (m, 4 H, ArH), 5.69 (m, 1 H, CH=C**H$_2$**), 5.06-4.89 (m, 2 H, CH=C**H$_2$**), 3.99 (t, 1 H, Ar$_2$C**H**), 2.79-2.72 (m, 2 H, C**H$_2$**CH=CH$_2$)
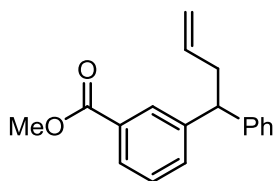
1-acetyl-4-(1-phenylbut-3-enyl)benzene: Reaction was conducted at 50 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 5% EtOAc/hexanes). The product was collected as a colorless oil (26 mg, 98% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.18 (m, 7H, Ar**H**), 7.02 (m, 2 H, Ar**H**), 5.73 (m, 1 H, C**H**=CH$_2$), 5.06 (m, 1 H, CH=C**H$_a$**H$_b$), 4.98 (m, 1 H, CH=CH$_a$**H$_b$**), 4.04 (t, 1 H, ArArC**H**CH$_2$), 2.83 (td, 2 H, ArArCHC**H$_2$**), 2.30 (s, 3H, C**H$_3$**CO$_2$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 169.5, 148.9, 144.1, 142.1, 136.6, 128.8, 128.5, 128.0, 126.3, 121.4, 116.5, 50.7, 40.0, 21.2. IR (thin film, cm^{-1}) 3064, 3029, 2921, 1760, 1752, 1506, 1369, 1018, 909, 731, 699. HRMS (ASAP$^+$) exact mass calc'd for C$_{18}$H$_{19}$O$_2$ [M+H]$^+$, requires *m/z* 267.1385, found *m/z* 267.1395
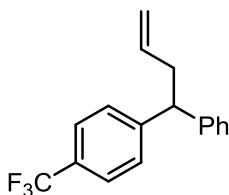

2-(1-phenylbut-3-enyl)mesitylene: Reaction was conducted at 50 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (hexanes). The product was collected as a colorless oil (24 mg, 96% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38-7.16 (m, 5 H, ArH), 6.87 (s, 2 H, ArH), 5.81 (m, 1 H, C**H**=CH2), 5.81 (m, 1 H, C**H**=CH$_2$), 5.16 (m, 1 H, CH=C**H$_a$**H$_b$), 5.01 (m, 1 H, CH=CH$_a$**H$_b$**), 4.67 (t, 1 H, ArArC**H**CH$_2$), 3.15 (m, 1 H, ArArCHC**H$_a$**H$_b$), 2.85 (m,

1 H, ArArCHCH**a**H**b**) 2.32 (s, 3 H, *p*-ArCH**3**), 2.20 (br s, 6 H, *o*-ArCH**3**). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 144.1, 138.1, 137.3, 136.9, 135.5, 129.9, 128.1, 127.2, 125.5, 115.7, 43.4, 35.8, 21.4, 20.8. IR (thin film, cm^{-1}) 3064, 3013, 2978, 2920, 2862, 1639, 1611, 1601, 1495, 1447, 1031, 995, 909, 848, 765, 731, 696, 650, 629. HRMS (ASAP$^+$) exact mass calc'd for C$_{19}$H$_{23}$ [M+H]$^+$, requires *m/z* 251.1800, found *m/z* 251.1786

methyl 3-(1-phenylbut-3-enyl)benzoate: Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 10% CH$_2$Cl$_2$/hexanes). The product was collected as a colorless oil (19 mg, 71% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (s, 1 H, Ar**H**), 7.87 (m, 1 H, Ar**H**), 7.46-7.15 (m, 7H, Ar**H**) 5.71 (m, 1 H, C**H**=CH$_2$), 5.04 (m, 1 H, CH=CH**a**H**b**), 4.96 (m, 1 H, CH=CH**a**H**b**), 4.08 (t, 1H, C**H**Ar$_2$), 3.91 (s, 3H, C**H3**CO$_2$), 2.85 (t, 1 H, Ar$_2$CHC**H2**). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 167.3, 145.0, 144.0, 136.5, 132.8, 130.4, 129.2, 128.7, 128.6, 128.0, 127.7, 126.6, 116.8, 52.2, 51.2, 39.9. IR (thin film, cm^{-1}) 3064, 3028, 2951, 2843, 1718, 1643, 1602, 1587, 1496, 1445, 1433, 1279, 1196, 1106, 1084, 993, 915, 748, 702. HRMS (ASAP$^+$) exact mass calc'd for C$_{18}$H$_{19}$O$_2$ [M+H]$^+$, requires *m/z* 267.1385, found *m/z* 267.1392
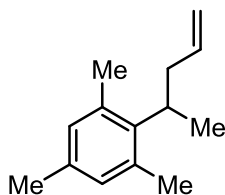
4-phenyl-4-(4-trifluoromethylphenyl)-1-butene: Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 2% CH_2Cl_2/hexanes). The product was collected as a colorless oil (9.2 mg, 33% yield). Spectra of the product were consistent with previous reports[3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, 2 H, CF3-Ar**H**), 7.38-7.17 (m, 7 H, Ar**H**), 5.70 (m, 1 H, C**H**=CH$_2$), 5.09-4.93 (m, 1 H, CH=C**H$_2$**), 4.07 (t, 1H, C**H**Ar$_2$), 2.91-2.75 (m, 2 H, C**H$_2$**CH=CH$_2$)
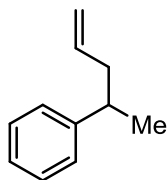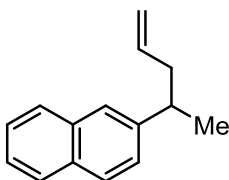

4-phenyl-1-pentene: Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (pentane). The product was collected as a colorless oil (9.4 mg, 64% yield). Spectra of the product were consistent with previous reports[5]. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.33-7.14 (m, 10 H, Ar**H**), 5.72 (m, 1 H, C**H**=CH$_2$), 5.03-4.92 (m, 2 H, CH=C**H$_2$**), 2.79 (m, Ar$_2$C**H**), 2.44-2.35 (m, 1 H, C**H$_a$**H$_b$CH=CH$_2$), 2.33-2.24 (m, 1 H, CH$_a$**H$_b$**CH=CH$_2$), 1.26 (d, 3 H, CHC**H$_3$**)
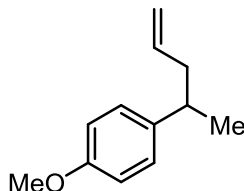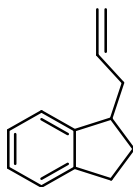
4-(4-methoxyphenyl)pent-1-ene: Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 20% CH_2Cl_2/hexanes). The product was collected as a colorless oil (15 mg, 85% yield). Spectra of the product were consistent with previous reports[5]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.09 (m, 2 H, Ar**H**), 6.87-6.82 (m, 2 H, Ar**H**), 5.75-5.66 (m, 1 H, C**H**=CH$_2$), 5.02-4.92 (m, 2 H, CH=C**H$_2$**), 3.79 (s, 3 H, C**H$_3$**O), 2.75 (m, 1 H, ArC**H**(allyl)CH$_3$), 2.39-2.31 (m, 1 H, C**H$_a$**CH$_b$CH=CH$_2$), 2.30-2.22 (m, 1 H, CH$_a$C**H$_b$**CH=CH$_2$), 1.23 (s, 3 H, ArCH(allyl)C**H$_3$**)
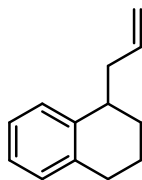

2-(1-methylbut-3-enyl)mesitylene: Reaction was conducted at 50 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (hexanes). The product was collected as a colorless oil (12 mg, 65% yield). Spectra of the product were consistent with previous reports[6]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (s, 2 H, Ar**H**), 5.80-5.69 (m, 1 H, C**H**=CH$_2$), 5.04 (m, 1 H, CH=C**H$_a$**H$_b$), 4.95 (m, 1 H, CH=CH$_a$**H$_b$**), 3.29 (m, 1 H, ArC**H**(allyl)CH$_3$), 2.47 (m, 2 H, C**H$_2$**CH=CH overlapped), 2.36 (s br, 6 H, o-ArC**H$_3$**), 2.25 (s, 3 H, p-ArC**H$_3$**), 1.31 (d, 3 H, ArCH(allyl)C**H$_3$**)

2-(1-methylbut-3-enyl)naphthalene: Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 2% CH_2Cl_2/hexanes). The product was collected as a colorless oil (16 mg, 82% yield). Spectra of the product were consistent with previous reports[5]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.35 (m, 7 H, Ar**H**), 5.77 (m, 1 H, CH=C**H₂**), 5.11-4.94 (m, 2 H, CH=C**H₂**), 2.99 (m, 1 H, ArC**H**CH₃), 2.57-2.36 (m, 2 H, C**H₂**CH=CH₂), 1.36 (d, 1 H, ArC**H**C**H₃**)
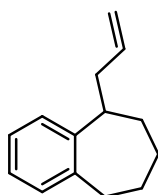

1-allylindane : Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (pentane). The product was collected as a colorless oil (17 mg, 89% yield). Spectra of the product were consistent with previous reports[7]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.12 (m, 4 H, Ar**H**), 5.87 (m, 1 H, C**H**=CH₂), 5.14-5.02 (m, 2 H, CH=C**H₂**), 3.22 (m, 1 H, ArC**H**(allyl)), 2.98-2.80 (m, 2 H, ArC**H₂**), 2.58 (m, 1 H, alkyl**H**), 2.30-2.20 (m, 2 H, alkyl H), 1.80-1.70 (m, 1 H, alkyl H)
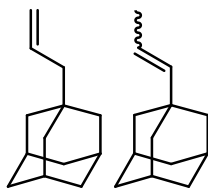

1,2,3,4-tetrahydro-1-allylnaphthalene : Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The

crude material was purified via column chromatography (pentane). The product was collected as a colorless oil (18 mg, 88% yield). Spectra of the product were consistent with previous reports[5].

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.25-7.06 (m, 4 H, Ar**H**), 5.86 (m, 1 H, C**H**=CH$_2$), 5.12-5.02 (m, 2 H, CH=C**H$_2$**), 2.93-2.71 (m, 3 H, alkyl H), 2.55-2.47 (m, 1 H, X), 2.39-2.30 (m, 1 H, X), 1.90-1.68 (m, 4 H, alkyl H)
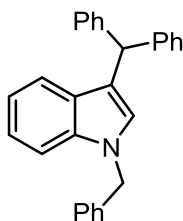

1-allylbenzosuberan: Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (pentane). The product was collected as a colorless oil (4:1 product:elimination) (16 mg, 68% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.23-7.10 (m, 4 H, Ar**H**), 5.87 (m, 1 H, C**H**=CH$_2$), 5.11 (m, 1 H, CH=C**H$_a$**H$_b$), 5.06 (m, 1 H, CH=CH$_a$**H$_b$**), 2.89 (m, 1 H, ArC**H**(allyl)CH$_2$), 2.92-2.85 (m, 2 H, ArC**H$_2$**CH$_2$), 2.63 (m, 1 H, CH$_2$=CHC**H$_a$**CH$_b$), 2.46 (m, 1 H, CH$_2$=CHCH$_a$C**H$_b$**), 2.46-1.42 (m, 6 H, alkyl H) ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) 145.4, 142.8, 138.0, 129.7 (2 peaks overlapping), 126.1, 126.0, 116.1, 37.8, 36.3, 36.2, 32.7, 32.6, 28. IR (thin film, cm^{-1}) 3074, 3017, 2920, 2851, 1640, 1490, 1448, 994, 909, 781, 755, 745. HRMS (ASAP$^+$) exact mass calc'd for C$_{14}$H$_{19}$ [M+H]$^+$, requires *m/z* 187.1487, found *m/z* 187.1490
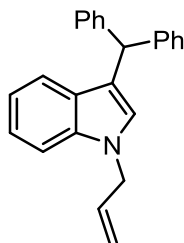
1-allyladamantane and 1-(1-propenyl)adamantane: Reaction was conducted at 80 °C. Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (hexanes). The products were collected as a colorless oil as a 2:1 mixture (**25a**:**25b**). (5.3 mg, 30% combined yield). Spectra of the products were consistent with previous reports[5,8]. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.82 (m, 1 H, C**H**=CH$_2$), 5.05-4.95 (m, 2 H, CH=C**H$_2$**), 1.98-1.42 (m, 17 H, alkylH and C**H$_2$**CH=CH$_2$) **25b:** 5.31-5.19 (m, 2 H, C**H**=C**H**CH$_3$), 1.98-1.42 (m, 18 H, alkyl**H** and CH=CHC**H$_3$**),

Aryl nucleophile scope general procedure: Diphenylmethyl bromide (0.1 mmol), allyltrimethylsilane (0.2 mmol) and the corresponding arene (0.2 mmol) was added to a flame-dried 2-dram vial with 800 μL of dry DCE under an atmosphere of argon. A solution of the catalyst (200 μL, 0.003 mmol) was added and the reaction heated at 50 °C. After 3 hours, the reaction was quenched with triethylamine and purified.
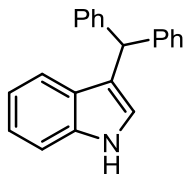

N-benzyl-3-benzhydrylindole: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column
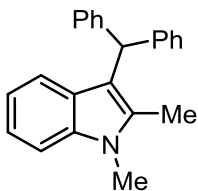
chromatography (10 → 20% CH$_2$Cl$_2$/hexanes). The product was collected as a colorless oil (34 mg, 92% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36-7.21 (m, 15 H, ArH), 7.15 (t, 1 H, ArH), 7.09 (m, 2 H, ArH), 7.00 (m, 1 H, ArH), 6.57 (s, 1 H, indole C2-H), 5.27 (s, 2 H, N-C**H$_2$**Ph). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 144.1, 137.9, 137.2, 129.1, 128.8, 128.5, 128.4, 127.8, 127.6, 126.5, 126.3, 122.0, 120.3, 119.2, 119.1, 109.9, 50.1, 49.0. IR (thin film, cm^{-1}) 3059, 3027, 1711, 1658, 1614, 1600, 1494, 1466, 1454, 1355, 1278, 1176, 1077, 1030, 740, 698. HRMS (ASAP$^+$) exact mass calc'd for C$_{28}$H$_{24}$N [M+H]$^+$, requires *m/z* 374.1090, found *m/z* 374.1904
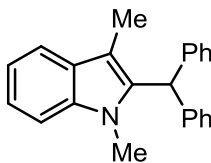

N-allyl-3-benzhydrylindole: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (10 → 20% CH$_2$Cl$_2$/hexanes). The product was collected as a colorless oil (28 mg, 87% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38-7.19 (m, 13 H, ArH), 7.02 (t, 1 H, ArH), 6.52 (s, 1 H, indole C$_2$-H), 5.99 (m, 1 H, C**H**=CH$_2$), 5.73 (s, 1 H, Ar$_3$CH), 5.20 (m, 1 H, CH=CH$_a$**H$_b$**), 5.10 (m, 1 H, CH=CH$_a$**H$_b$**), 4.68 (m, 2 H, N-C**H$_2$**CHCH$_2$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 144.2, 137.0, 133.8, 129.1, 128.4, 127.9, 127.8, 126.3, 121.8, 120.2, 119.1, 118.8, 117.1, 109.70, 49.9, 48.9. IR (thin film, cm^{-1}) 3058, 3025, 2924, 2858, 1600, 1549, 1493, 1466, 1449, 1389, 1333, 1191, 1078, 1031, 1014, 990, 920, 738, 698. HRMS (ASAP$^+$) exact mass calc'd for C$_{24}$H$_{22}$N [M+H]$^+$, requires *m/z* 324.1752, found *m/z* 324.1747.
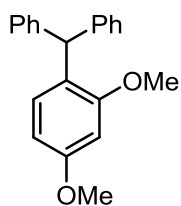
3-benzhydrylindole: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (10 → 30% CH_2Cl_2/hexanes). The product was collected as a colorless oil (14 mg, 48% yield). Spectra of the product were consistent with previous reports[9]. NMR (500 MHz, CDCl$_3$) δ 7.90 (s br, 1 H, indole N**H**), 7.36-7.11 (m, 13 H, Ar**H**), 7.02-6.95 (m, 1 H, Ar**H**), 6.55 (s, 1 H, indole C2-**H**), 5.67 (s, 1 H, Ph$_2$C**H**)

3-benzhydryl-1,2-dimethylindole: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 5% CH_2Cl_2/hexanes). The product was collected as a colorless oil (27 mg, 87% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36-7.19 (m, 11 H, ArH), 7.13 (t, 1 H, ArH), 7.02 (d, 1 H, ArH), 6.91 (t, 1 H, ArH), 5.80 (s, 1 H, Ar$_3$C**H**), 3.68 (m, 3 H, N-C**H$_3$**), 2.28 (s, 3 H, indole C2-C**H$_3$**). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 144.21, 136.83, 134.00, 129.28, 128.27, 127.55, 126.11, 120.42, 119.73, 118.88, 113.61, 108.63, 48.18, 29.65, 10.87. IR (thin film, cm^{-1}) 3058, 3024, 2925, 2854, 1601, 1494, 1470, 1447, 1367, 1333, 1031, 739, 699. HRMS (ASAP$^+$) exact mass calc'd for C$_{23}$H$_{22}$N [M+H]$^+$, requires *m/z* 312.1752, found *m/z* 312.1758.
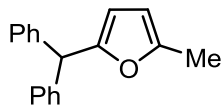
2-benzhydryl-1,3-dimethylindole: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 5% CH_2Cl_2/hexanes). The product was collected as a white solid (26 mg, 84% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58-7.53 (m, 1 H, ArH), 7.36-7.10 (m, 13 H, ArH), 5.94 (s, 1 H, ArC**H**Ph$_2$), 3.52 (s, 1 H, NC**H$_3$**), 1.88 (s, 3 H, indole C3-C**H$_3$**) ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 141.3, 136.7, 136.6, 129.3, 128.8, 128.5, 126.6, 121.2, 118.7, 118.3, 108.9, 108.6, 48.3, 30.5, 9.1. IR (thin film, cm^{-1}) 3026, 2939, 2867, 1601, 1494, 1473, 1448, 1363, 1327, 1238, 1077, 1029, 1013, 770, 745, 723, 697, 671. HRMS (ASAP$^+$) exact mass calc'd for $C_{23}H_{22}N$ [M+H]$^+$, requires *m/z* 312.1752, found *m/z* 312.1751
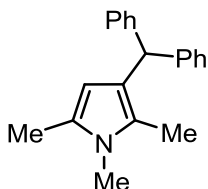

4-benzhydryl-1,3-dimethoxybenzene: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (10 → 20% CH_2Cl_2/hexanes). The product was collected as a colorless oil and as an 8:1 mixture of the mono- and di-alkylated products (26 mg, 80% yield). Spectra of the product were consistent with previous reports[10]. ^{1}H NMR (500 MHz, CDCl$_3$) δ

7.32-7.08 (m, 10 H, Ar**H**), 6.77 (d, 1 H, ArH), 6.49 (d, 1 H, Ar**H**), 6.42 (dd, 1 H, Ar**H**), 5.86 (s, 1 H, Ph$_2$C**H**), 3.81 (s, 3 H, C**H$_3$**O), 3.72 (s, 3 H, C**H$_3$**O)

4-benzhydryl-1,3-dimethoxybenzene: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 5% EtOAc/hexanes). The product was collected as a colorless oil. (24 mg, 97% yield). Spectra of the product were consistent with previous reports[10]. ^{1}H NMR (500 MHz, CDCl$_3$) 7.31-7.14 (m, 10 H, Ar**H**), 5.88-5.85 (m, 1H, furan**H**), 5.74 (d, 1 H, furan**H**), 5.39 (s, 1 H, Ph$_2$C**H**), 2.24 (s, 3H, C**H$_3$**)

3-benzhydryl-1,2,5-trimethylpyrrole: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 5% EtOAc/Hexanes buffered with 1% NEt$_3$). The product was collected as a colorless oil (15 mg, 55% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30-7.18 (m, 10 H, Ar**H**), 5.47 (s, 1 H, C**H**Ph$_2$), 5.34 (s, 1 H, pyrrole Ar**H**), 3.39 (s, 3 H, NC**H$_3$**), 2.17 (s, 3 H, 5-pyrrole C**H$_3$**), 2.07 (s, 3 H, 2-pyrrole C**H$_3$**). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 145.6, 129.2, 129.0, 128.0, 127.9, 125.6, 120.4, 48.9, 30.2, 12.5, 10.3. IR (thin film, cm^{-1}) 3023, 2919, 2857, 1599, 1493, 1448, 1395, 1347, 1032, 763, 741, 700 HRMS (ASAP$^+$) exact mass calc'd for C$_{20}$H$_{22}$N [M+H]$^+$, requires m/z 276.1752, found m/z 276.1740.
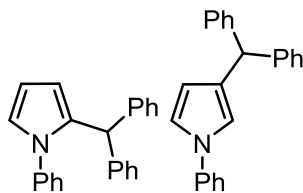
2-benzhydryl-1-phenylpyrrole: Upon completion of the reaction, the reaction was quenched with the addition of triethylamine and concentrated. The crude material was purified via column chromatography (0 → 10% CH_2Cl_2/hexanes). The product was collected as a colorless solid as a mixture (4:1) of the 2- and 3-benzhydrylpyrroles (25 mg, 81% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.40-7.00 (m, 16 H, ArH + pyrrole C2-H minor), 6.77 (dd, 1 H, pyrrole C5-H major), 6.63 (m, 1 H, pyrrole C-5H minor), 6.22 (t, 1 H, pyrrole C4-H major), 6.13 (dd, 1 H, pyrrole C4-minor), 5.82 (dd, 1 H, pyrrole C-2 major), 5.40 (s, 1 H, Ph$_2$**CH** minor), 5.30 (s, 1 H, Ph$_2$**CH** major) ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ (major) 143.3, 140.2, 135.9, 129.6, 129.1, 128.9, 128.3, 127.0, 126.4, 122.5, 110.2, 107.9, 49.3 (minor) 145.0, 140.8, 129.4, 128.4, 127.5, 126.3, 125.4, 120.1, 119.4, 118.5, 111.6, 50.3 (one peak unobserved). IR (thin film, cm^{-1}) 3084, 3063, 3026, 1600, 1500, 1452, 1325, 1079, 1032, 766, 697. HRMS (ASAP$^+$) exact mass calc'd for $C_{23}H_{20}N$ [M+H]$^+$, requires *m/z* 310.1596, found *m/z* 310.1594.

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