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Review of recent advances in nucleophilic C–F bond-forming reactions at sp^3 centers

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ABSTRACT

Because of the broad utility of organofluorine compounds, efficient nucleophilic fluorination reactions are of high synthetic value. This is because fluoride is generally less costly, more readily available as its positron-emitting isotope ($^{18}F^-$), and has a higher specific activity than its F^+ counterparts. New reactions for the construction of C–F bonds, that make use of contemporary chemical methods, have only lately begun to emerge. This review provides a brief summary of some of the recent disclosures in transition metal-catalyzed fluorination reactions at sp^3 -hybridized carbon centers with nucleophilic fluoride sources.

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Introduction

Organofluorine compounds play prominent roles in pharmaceuticals,^{1–8} medical imaging,^{9–14} material science,^{15–23} agrochemicals,²⁴ and other disciplines. Nevertheless, the breadth and scope of methods available for preparing fluorinated molecules by means of direct C–F bond-construction has lagged behind technologies for the molecular incorporation of other heteroatoms. Non-catalyzed transformations that rely on the use of stoichiometric fluorinating reagents, such as DAST and Deoxofluor for deoxyfluorination, have been known for some time. In contrast, fluorinations promoted by catalytic transition metals are comparatively less well-studied.

The purpose of this review is to summarize recent advances in the arena of catalytic C–F bond-formation at sp^3 carbon centers

using nucleophilic fluorinating reagents. Although there have been some reviews on this topic,^{25,26} in the intervening years since their publication, a significant number of new studies on this subject has appeared. Therefore, with a few exceptions, we will mostly restrict the contents of this summary to materials not covered previously. The field of transition metal-catalyzed fluorination reactions at sp^2 carbon centers have also experienced rapid growth;^{26,27} however, this topic is beyond the scope of the present manuscript. It is also not our intent to recap the many excellent fluorination reactions involving electrophilic F^+ reagents,^{28–38} non-catalytic systems, or enzymatic transformations.

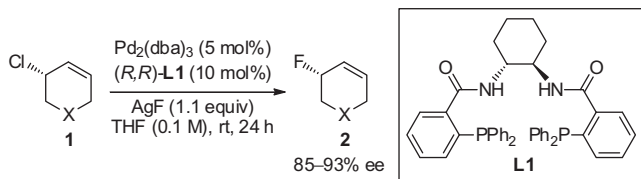
Allylic substitution

Brown and Gouverneur showed early on that allylic fluorides were competent substrates in allylic substitution reactions with malonate nucleophiles.³⁹ Importantly, they established a reactivity

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hierarchy in which fluoride was determined to be a more reactive leaving group than acetate, but less so than carbonate. This insight was critical to the development of transition metal-catalyzed allylic fluorination reactions because it revealed that judicious choice of leaving group is a necessary consideration if undesired substitution of the allylic fluoride products is to be avoided.



Scheme 1. Doyle's enantioselective fluorination.

Doyle and co-workers reported the first instance of a transition metal-catalyzed allylic substitution reaction by fluoride. They utilized cyclic allylic chlorides as electrophiles, with AgF as the source of nucleophilic fluoride (**Scheme 1**).⁴⁰ The reactions were catalyzed by Pd(0) complexes; and in the presence of chiral ligands **L1** popularized by Trost and others, desymmetrization products with high levels of enantiomeric excesses (ee) were obtained. The observation of net stereochemical retention in the products implicated a double inversion mechanism in which fluoride reacts with π -allyl Pd intermediates by means of outer-sphere attack. The authors followed this paper up with a publication detailing Pd-catalyzed enantioselective fluorination of *acyclic* allylic chlorides that furnished primarily branched compounds.⁴¹

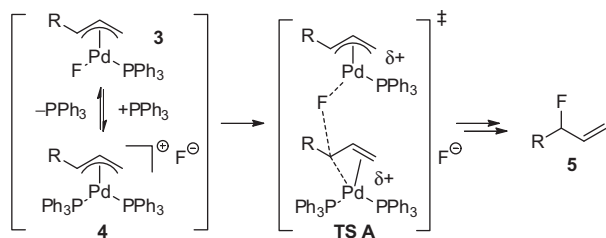
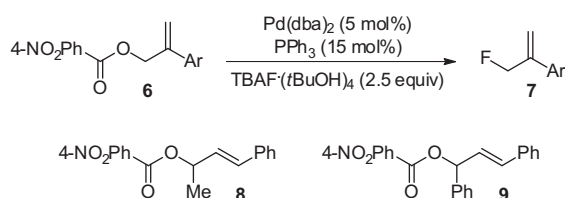


Figure 1. Proposed TS for Doyle's Pd-catalyzed fluorination.

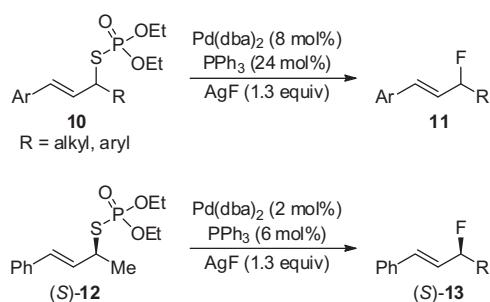
In a recent study utilizing a combination of computational methods and experiment validation, Doyle and Norrby elucidated a potential mechanistic pathway for the fluorination described above.⁴² As illustrated in **Figure 1**, the authors propose that the active fluorinating agent is the neutral Pd-fluoride complex **3** which is in equilibrium with cationic species **4**. The reaction is thought to proceed through a homobimetallic transition state **TS A**. Hard nucleophiles, such as Grignards and other organometallic reagents, typically engage in allylic substitution reactions by means of an inner-sphere mechanism (with net inversion of stereochemical configuration). The proposed association of fluoride with Pd, as in complex **3**, provides a rationale for why C–F bond formation occurs via outer-sphere attack with net retention of configuration.



Scheme 2. Brown and Gouverneur's allylic fluorination.

Following Doyle's disclosure, Brown and Gouverneur reported Pd-catalyzed fluorination reactions of allylic 4-nitrobenzoates (**Scheme 2**).⁴³ The fluorinating reagent that they used was TBAF·(tBuOH)₄ which is a convenient compound to handle due to its low hygroscopicity/basicity and good nucleophilicity. The authors then demonstrated for the first time that [¹⁸F] could be incorporated into molecules by means of Pd catalysis. Only substrates with leaving groups situated on primary carbons were suitable since the use of methyl substituted starting materials such as **8** resulted almost exclusively in elimination to give the corresponding diene. The use of chalcone derivative **9** gave no product.

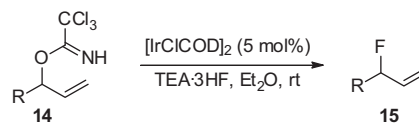
To address the challenges of elimination and reactivity associated with more highly substituted substrates,^{43,44} Wu and co-workers developed Pd-catalyzed allylic fluorination reactions of phosphorothioate esters **10** (**Scheme 3**).⁴⁵ Under their conditions,



Scheme 3. Wu's allylic fluorination of phosphorothioate esters and accompanying stereochemical studies.

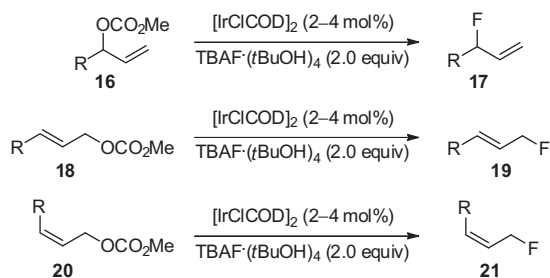
fluorination of various secondary electrophiles occurred smoothly with minimal formation of undesired dienes. Furthermore, the use of previously problematic chalcone-derived electrophiles now provided the desired product in good yield. Fluorination on a mixture of regioisomeric phosphorothioate esters resulted in a single regioisomeric product. Stereochemical studies with enantioenriched (*S*)-**12** proceeded with net retention of configuration at carbon. In analogy to Doyle's conclusions,^{40,42} Wu and co-workers similarly invoke an outer-sphere attack by fluoride to rationalize the observed stereochemical outcome.

The first non-Pd-promoted allylic fluorination reaction was described by Nguyen and co-workers (**Scheme 4**).⁴⁶ They reported that [IrClCOD]₂ catalyzes the fluorination of secondary allylic trichloroacetimidates with triethylamine·3HF (TEA·3HF) to furnish branched products. This methodology was also amenable to tertiary substrates; however, the resultant products readily decomposed during purification.⁴⁷ In contrast to Doyle^{40,42} and Wu's results,⁴⁵ under their conditions, the use of enantioenriched trichloroacetimidates (>95% ee) resulted in nearly racemic product (12% ee).



Scheme 4. Nguyen's Ir-catalyzed fluorination of trichloroacetimidates.

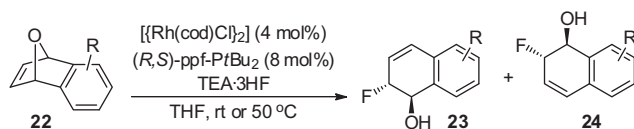
Gouverneur and Brown reported complementary Ir-catalyzed fluorinations of allylic carbonates that could provide either branched or linear (*E*)/(*Z*) fluorides in a stereospecific manner



Scheme 5. Gouverneur and Brown's stereospecific Ir-catalyzed fluorination of allylic methylcarbonates.

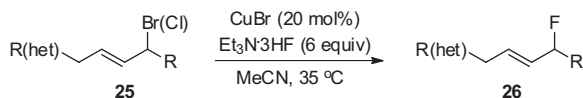
(Scheme 5).⁴⁸ Based on Nguyen's observations,⁴⁶ the successful fluorination of carbonates was unexpected, but ultimately attributed to the use of TBAF·(tBuOH)₄ as the fluoride source. Control experiments indicated that this reagent enhanced both rate and selectivity. ¹⁸O isotopic labeling studies support the intermediacy of an enyl–Ir complex rather than the corresponding η^3 -allyl species.

The Rh-catalyzed enantioselective fluorination of symmetrical oxabicyclic alkenes as well as regiodivergent resolution of racemic substrates to give allylic fluorohydrins was disclosed by Lautens and co-workers (Scheme 6).⁴⁹ The *trans* configuration of the fluorohydrins obtained suggested that fluoride participated in the substitution reaction by an S_N2'-like pathway. Such reactivity is more commonly observed with soft nucleophiles.



Scheme 6. Lautens' asymmetric ring-opening fluorination of oxabicyclic compounds.

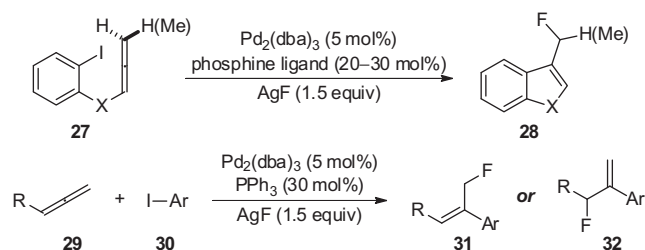
Szabó and co-workers developed (PPh₃)₃CuF as a stoichiometric fluorinating reagent for allylic chlorides.⁵⁰ A catalytic copper-promoted variant was reported by Liu (Scheme 7).⁵¹ Interestingly, this transformation only worked with secondary allylic bromides or chlorides as the use of primary substrates resulted in trace product formation. The requirement that a heteroatom be present was interpreted as evidence that coordination to copper throughout the reaction is an important mechanistic feature. Similar to Wu's observations,⁴⁵ these fluorinations were regioconvergent with respect to the allylic halide.



Scheme 7. Liu's Cu-catalyzed allylic fluorination.

Carbo-, iodo- and aminofluorination

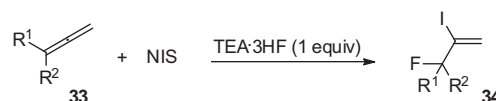
In 2013, Doyle disclosed the Pd-catalyzed carbofluorination between aryl halides and allenes using AgF as the nucleophilic fluorinating reagent (Scheme 8).⁵² Both intra- and intermolecular variants were described and resulted in the expected allylic fluorides in good yields. Mechanistic interrogations demonstrated that Ar–PdL_n–F complexes (generated from oxidative insertion, then halide metathesis) are kinetically viable intermediates. For instance, reactions with stoichiometric Ar–PdL_n–F in the absence



Scheme 8. Doyle's Pd-catalyzed carbofluorination.

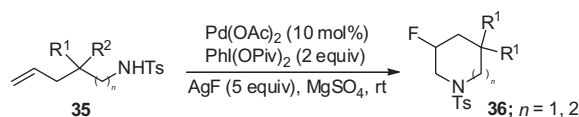
of AgF led to formation of the fluorinated products. These data, in combination with known difficulties of achieving reductive elimination with Pd^{II}–F to give C–F bonds, led the authors to speculate that fluorination is occurring via outer-sphere, bimetallic delivery of fluoride.

Transition metal-free iodo-fluorination of allenes (Scheme 9) was developed by Ma and Fu.⁵³ These reactions were promoted by *N*-iodosuccinimide (NIS) and TEA·3HF. Both monosubstituted and geminally disubstituted allenes were suitable substrates.



Scheme 9. Ma and Fu's iodo-fluorination.

Intramolecular aminofluorination of alkenes with nucleophilic fluoride has also been reported (Scheme 10).^{54,55} These reactions, reported by Liu, are catalyzed by Pd(OAc)₂ in the presence of stoichiometric I(III) oxidants and AgF as the fluorinating reagent. The formation of six- and seven-membered nitrogen heterocycles by *endo* cyclization is favored. The authors propose that the first step of the mechanism is intramolecular *trans* aminopalladation (potentially reversible). Oxidation of the resultant Pd(II) intermediate generates a Pd(IV)–F species, which would give the observed product upon reductive elimination. This step is believed to be kinetically competitive with S_N2'-like displacement of Pd(IV).



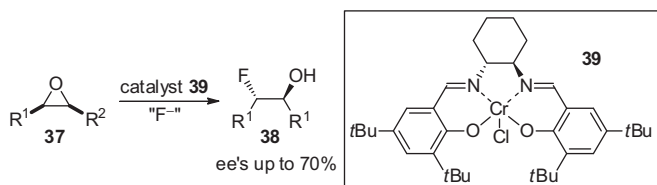
Scheme 10. Liu's aminofluorination of alkenes.

By swapping tosyl on nitrogen for a chelating protecting group, and in the presence of quinone-based oxidants and hexafluoroisopropanol (HFIP), Liu was able to generate complementary, regioisomeric *exo* products.⁵⁶

In two separate studies where Pd(OAc)₂ was replaced with BF₃·Et₂O, Meng, Li, and Zhang were able to achieve transition metal-free variants of Liu's aminofluorination.^{57,58}

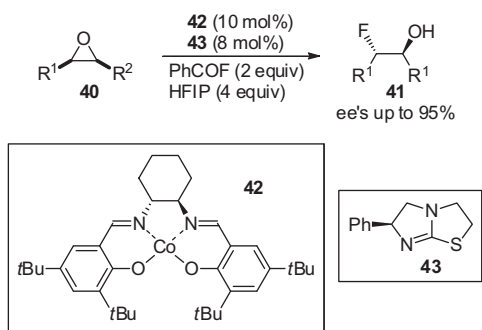
Ring-opening reactions of epoxides and aziridines

Some of the first enantioselective ring-opening reactions of *meso* epoxides by nucleophilic fluoride was reported by Haufe and co-workers (Scheme 11).^{59–61} Most of their early work relied on the use of chiral salen complex **39** as a Lewis acid to promote desymmetrization of *meso* epoxides or kinetic resolution of racemic starting materials. With a few exceptions, enantiomeric excesses obtained by these methods were generally no greater than 70% ee.



Scheme 11. Haufe's enantioselective epoxide ring-opening.

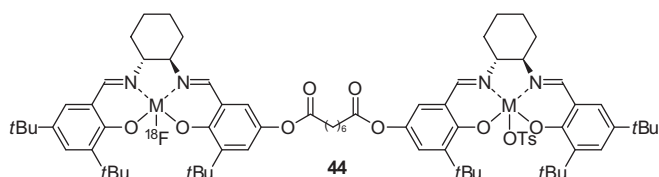
The moderate selectivities observed by Haufe could be attributed, in part, to the relatively fast background reactions as compared to the desired catalytic processes. To overcome these challenges, Doyle and co-workers implemented a strategy in which 'F⁻' was slowly generated in situ from an acyl fluoride, HFIP, and an amine co-catalyst **43** (Scheme 12).^{62,63} Cooperative enhancement in selectivity, as well as a pronounced matched/mismatched effect, were observed when either antipode of chiral (salen)Co complex **42** was utilized. Both desymmetrization of *meso* epoxides and kinetic resolution of racemic starting materials was carried out.



Scheme 12. Doyle's enantioselective epoxide ring-opening.

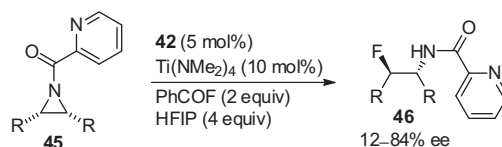
Subsequent mechanistic investigations led the authors to invoke a fluoride-bridged dimer as the resting state for the catalyst.⁶⁴ They concluded that the origin of cooperativity arises from the ability of the amine co-catalyst to facilitate dimer dissociation. The ultimate fluorinating species is proposed to be a monomeric Co–F complex. Insights gleaned from these data allowed the authors to design a dimeric salen(Co) catalyst which exhibited considerable rate enhancement when applied to epoxide ring-opening reactions with nucleophilic fluoride. Because of the relatively short half-life of ¹⁸F (~110 min), fluorination reactions used in the preparation of positron emission tomography (PET) tracers need to proceed very quickly. However, inherent difficulties associated with obtaining [¹⁸F]PhCOF precluded them from implementing this method with radiolabeled fluoride. Instead, the authors applied their methodology to the synthesis of the unlabeled PET tracer, F-MISO by rapid fluorination (5 min) of the corresponding racemic epoxide.

Guided by mechanistic insights from their initial studies, Doyle and co-workers were later able to carry out the syntheses of several radiolabeled [¹⁸F] fluorohydrin PET tracers using dimeric cobalt-based fluorinating agent **44**. This reagent was prepared by counterion metathesis of the corresponding bis-tosylate compound with [¹⁸F]⁻ generated by anion exchange column.⁶⁵



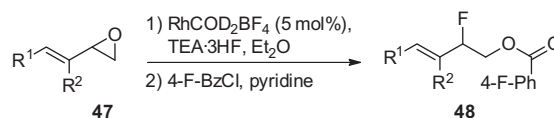
Using a modification of Doyle's method, Zhuravlev demonstrated the preparation of radiolabeled [¹⁸F]F-MISO.⁶⁶ In this case, [¹⁸F]HF gas was utilized as the fluorinated reagent.

Racemic⁶⁷ and enantioselective ring-opening transformations of *N*-picolinamide aziridines (Scheme 13) are also known.⁶⁸ In the latter case, an additional Lewis acid catalyst Ti(NMe₂)₄ was required in conjunction with salen(Co) **42**. Control reactions indicate that chelation of the co-catalyst to aziridine **45** is an important mechanistic feature since the use of substrates in which the picolinamide nitrogen was either absent or transposed to the meta position, resulted in little to no conversion.



Scheme 13. Doyle's enantioselective fluorination of *meso* aziridines.

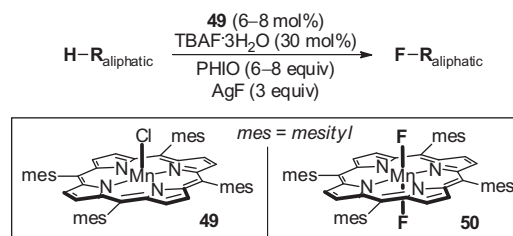
Very recently, Nguyen and co-workers established a rhodium-catalyzed method for the fluorination of vinyl epoxides to generate fluorohydrins (Scheme 14).⁶⁹ This method was amenable to mono- and 1,1-disubstituted epoxides. Control reactions demonstrated that although an uncatalyzed background reaction was operative, addition of the Rh catalyst had a substantial rate enhancing effect. In analogy to Lautens work,⁴⁹ these reactions proceeded with net inversion of stereochemistry with respect to the configuration of the starting epoxide.



Scheme 14. Nguyen's fluorination of vinyl epoxides.

Aliphatic, benzylic, allylic C–H activation

The first transition metal-catalyzed fluorination of unactivated, aliphatic C–H bonds with an 'F⁻' source was disclosed by Groves and co-workers (Scheme 15).^{70,71} These reactions were promoted by manganese porphyrin complexes **49** and provided products with moderate diastereoselectivity but good chemoselectivity for methylene C–H bonds. Late-stage fluorination of several structurally complex molecules was demonstrated. In this case, iodosylbenzene served as the stoichiometric oxidant while the requisite fluorinating agent(s) were a combination of AgF (3 equiv) plus catalytic TBAF·3H₂O (0.3 equiv).

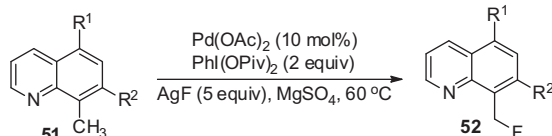


Scheme 15. Groves' fluorination of aliphatic C–H bonds.

Results obtained from deuterium kinetic isotope effect (KIE) studies identified C–H bond cleavage as the rate-limiting step. Experiments using cyclopropyl-based radical clocks supported the intermediacy of C-centered radical intermediates. The authors

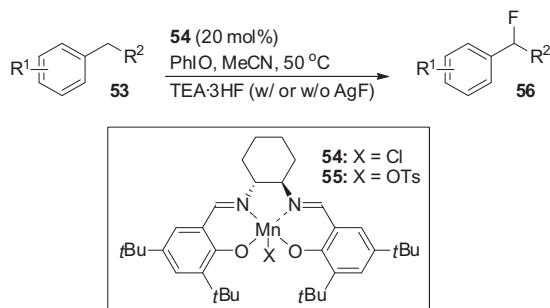
propose that the key fluorinating species is Mn(IV)(TMP) F_2 complex **50**, which was characterized by single-crystal X-ray analysis. To demonstrate that **50** is a viable fluorinating reagent, the authors successfully carried out the fluorination of cyclooctane with **49** (catalytic), iodosylbenzene, and stoichiometric **50** in lieu of AgF.

Oxidative fluorination of benzylic C–H bonds has also been described. Sanford and co-workers showed that 8-methylquinoline derivatives could be fluorinated with catalytic Pd(OAc) $_2$ using PhI(OPiv) $_2$ as the stoichiometric oxidant and AgF or CsF/AgOTf as fluorinating reagents.⁷² The authors suggest a mechanism in which PhI(OPiv) $_2$ serves as an oxidant for generating the Pd(IV)–F complex. Subsequent reductive elimination would result in C–F bond formation (see Scheme 16).



Scheme 16. Sanford's benzylic fluorination.

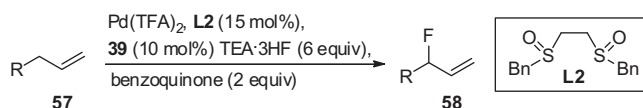
Groves then showed that salen(Mn) catalyst **54** could also effectively promote benzylic fluorination (Scheme 17).⁷³ PhIO and TEA·3HF (or KF) were used as terminal oxidant and source(s) of 'F $^-$ ', respectively. The reaction was compatible with several different functional groups including esters, halides, ethers, amides, and ketones.



Scheme 17. Groves' benzylic fluorination.

The utility of their methodology was highlighted by the late-state benzylic fluorination of ibuprofen methyl ester, celestolide, homophenylalanine, and a vitamin E analog. Under certain conditions, KF could be used as the fluoride source. The mechanism of the transformation is thought to be similar to that of their previously reported aliphatic fluorination method (Scheme 15).⁷⁰ Their work was followed up with the disclosure of conditions under which various radiolabeled benzylic fluorides could be prepared using [^{18}F] water and Mn(salen)OTs catalyst **55**. This method did not require vigorous drying and could be performed in air.⁷⁴

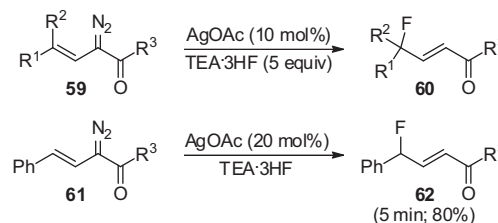
In a further variation, Doyle and co-workers showed that Pd(II)–sulfoxide complexes first developed by White⁷⁵ are competent catalysts for allylic fluorination by C–H activation (Scheme 18).⁷⁶ Salen(Cr) Lewis co-catalyst **39** was required; but in contrast to epoxide ring-openings with fluoride,⁶⁴ salen–M–F intermediates are not believed to be responsible for the delivery of F $^-$. Benzoquinone was identified as the most efficient oxidant. Branched allylic fluorides were formed in preference to the linear isomers.



Scheme 18. Doyle's allylic fluorination by C–H activation.

Fluorination of vinyl diazoacetates

Transition metal-stabilized vinyl carbenes possessing an adjacent carbonyl group are also appropriate electrophiles for nucleophilic fluorinations.⁷⁷ Davies and co-workers carried out such reactions with AgOAc on a diverse range of functionalized vinyl diazoacetates. Substituents at the olefin could be either aromatic or alkyl. Tertiary fluorides could be obtained with the use of trisubstituted substrates. When the method was applied to steroid derivatives, high diastereoselectivity was obtained (>20:1). In the case of **61**, complete fluorination occurred in 5 min (Scheme 19).



Scheme 19. Davies' fluorination of vinyl diazoacetates.

Conclusions and outlook

Despite the progress that has been made in the field of transition-metal catalyzed C–F bond construction at sp³ centers, much work remains to be accomplished. The numerous cross-disciplinary uses of fluorinated organic compounds have resulted in an ever-increasing demand for more efficient means of fluorine incorporation. It is our hope that this review will inspire the chemical community to continue expanding the frontiers of fluorination research.

Acknowledgments

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