How to cite: *Angew. Chem. Int. Ed.* **2025**, *64*, e202419188
doi.org/10.1002/anie.202419188

Nitrene Transfer

Introducing the Aziridination of Fluorinated Olefins by Metal-Catalyzed Nitrene Transfer

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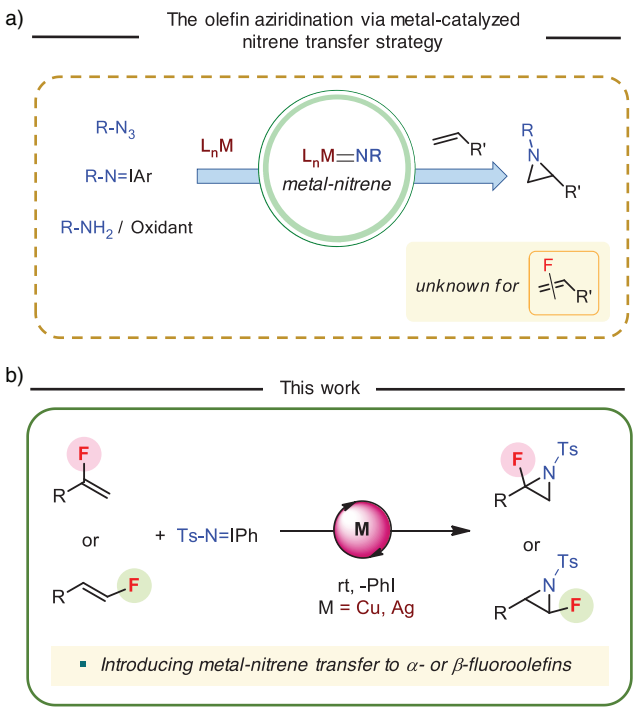
Abstract: After decades of development of the metal-catalyzed nitrene transfer reactions to olefins, examples involving the use of fluorinated olefins is yet unknown, despite the current importance of fluorocompounds. Herein we describe the use of copper- and silver-based catalysts for a general protocol that converts α- or β-fluoro olefins into the corresponding aziridines in high yields.

Albeit aziridines are known since 19th century, the chemistry of this class of compounds has developed at a low rate, compared, for example, with the more developed chemistry of epoxides.[1] Schomaker and co-workers have recently reviewed the field,[2] and have shown that nearly 30% of all contributions about aziridines have been published in the time frame 2011–2021. These data reflect the current interest of these heterocycles as well as the need for continuous research in the area, mainly due to the interesting features shown by the aziridine ring from both synthetic and medicinal point of views.[3–6]

Among the different strategies employed for the generation of aziridines, the catalytic addition of a nitrene moiety to a carbon–carbon double bond from the coordination sphere of a transition-metal complex is, by far, the most popular (Scheme 1a). With azides, iminoiodinanes or a mixture of amine/oxidant as nitrene precursors, a number of metal complexes have been reported as catalysts for the generation of aziridines.[1–5] Outstanding advances in the intra- or intermolecular aziridination reaction have allowed impressive values of chemo-, regio-, enantio- or diastereoselectivity in these transformations. In the search for new goals in the area, a literature survey revealed that the use of fluorinated olefins (referred to those with one or more fluorine atom directly bonded to the C=C bond) as starting materials for aziridination reaction via catalytic nitrene addition remains unreported, despite the interest of fluorinated compounds for pharma- and agricultural industry.[7,8] Actually, a recent revision about the synthetic methods for fluorinated three-membered rings by Charette and Jubault[9] demonstrated that there are no examples in which a fluoroolefin is directly converted into the corresponding fluoroaziridine.

Based on our background on the use of coinage metals for olefin aziridination using PhI=NTs as the nitrene source,[10,11] we herein report that the complexes $Tp^{Br3}Cu(NCMe)$ (**Cu_{cat}**) and $[Tp^{*,Br}Ag]_2$ (**Ag_{cat}**) efficiently catalyze the conversion of an array of α- or β-fluoro-olefins into the corresponding N-tosyl aziridines (Scheme 1d). With this strategy, highly electrophilic metal-nitrene intermediates are generated, capable of surpassing the low nucleophilicity of olefins containing



Scheme 1. a) Aziridination of olefins by metal-catalyzed nitrene transfer. b) Application to fluorinated olefins.

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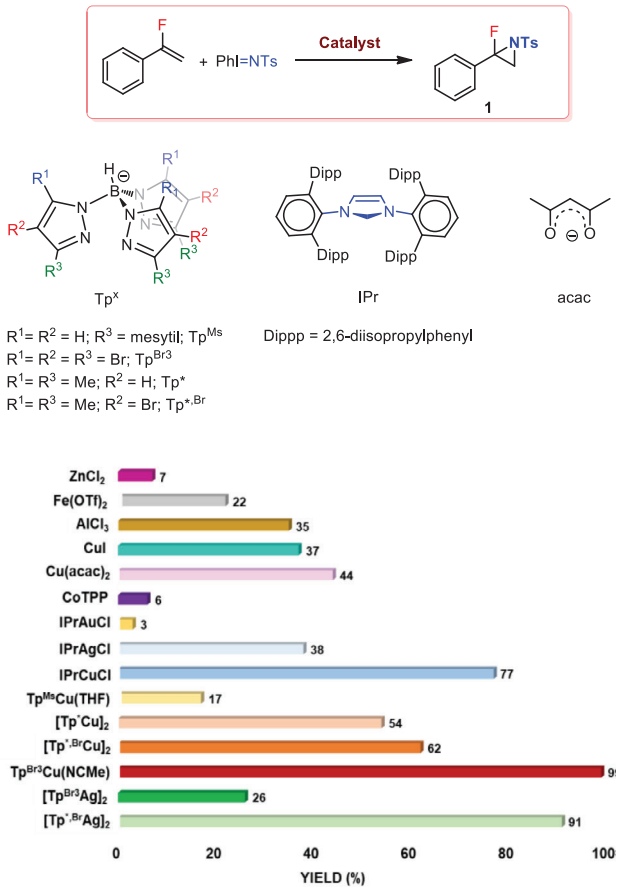
Additional supporting information can be found online in the Supporting Information section



Scheme 2. Catalyst screening for the reaction of α-fluorostyrene with PhI=NTs. Reaction conditions: [Cat.]:[PhINTs]:[α-fluorostyrene] = 1:20:100, r.t., DCM, 1.5 h. Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. The IPrMCl precatalysts were employed along with 1 equiv. of $NaBAr^F{}_4$ as halide scavenger. See Supporting Information for experimental details.

fluorine substituents. The reaction occurs with high yields and with a high degree of stereoselectivity.

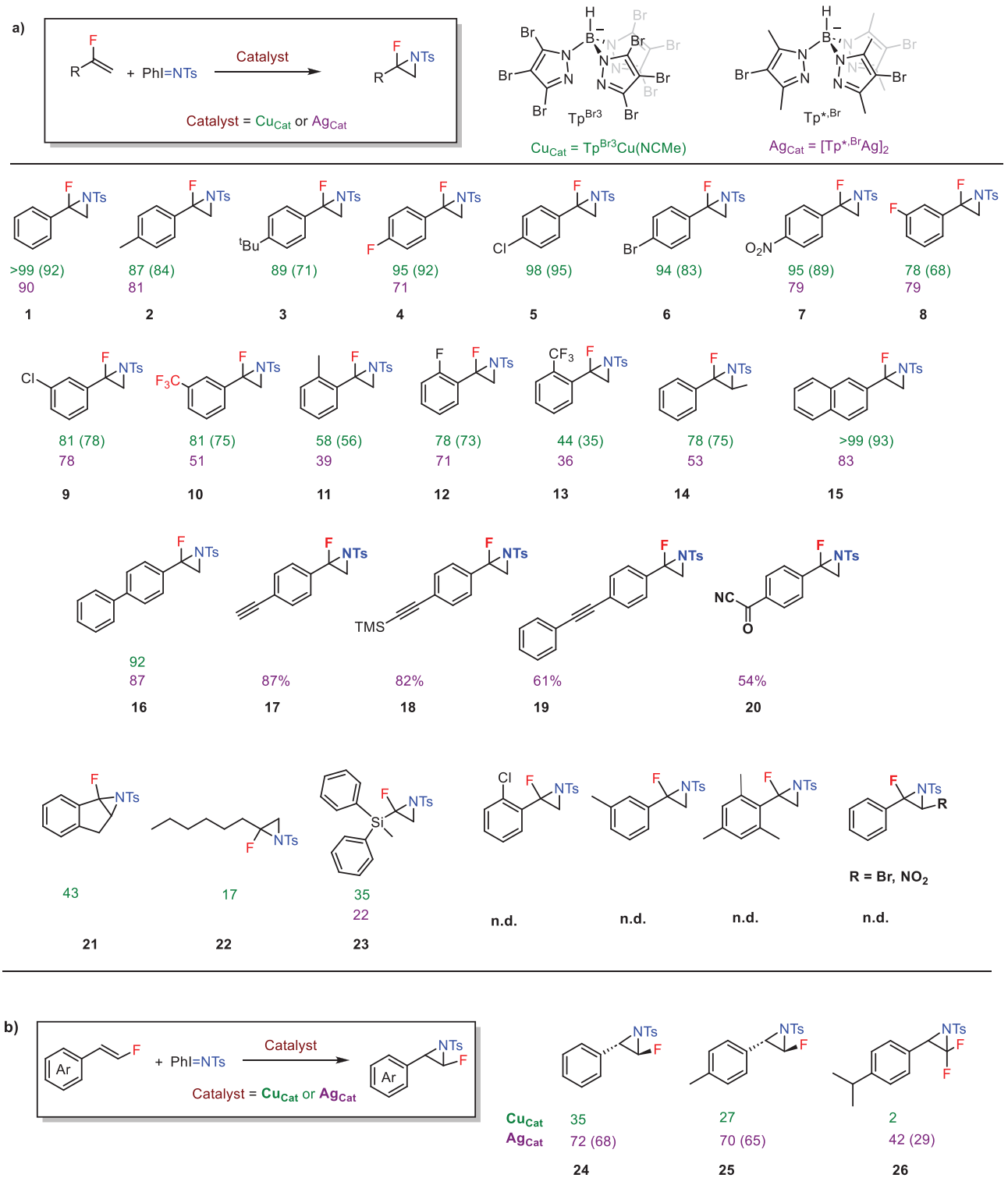
We first carried out a screening α-fluorostyrene as the model substrate (Scheme 2, optimized reaction conditions; see Supporting Information for details). Toward that end we tested a series of potential catalysts that have been previously described to promote the transfer of a nitrene group from PhI=NTs. It is the case of simple metal salts ($AlCl_3$, $Fe(OTf)_2$, $ZnCl_2$),[12] CuI, $Cu(acac)_2$ a cobalt-porphyrin complex,[13,14] and coinage metal derivatives bearing either IPr or trispyrazolylborate ligands.[15–18] Interestingly, all these candidates produced the desired aziridine **1**, albeit at variable extent. The Zn, Fe, and Al salts afforded **1** in 7–35% yield, whereas CuI or $Cu(acac)_2$, disclosed by Evans in his seminal work on olefin aziridination,[13] slightly improved those results. It is worth mentioning that the remaining nitrene precursor was converted into $TsNH_2$, in a non-desired, frequently observed decomposition route. The cobalt-porphyrin complex was no efficient at all with this substrate, despite the known capabilities for the aziridination of other olefins.[14] For the IPrMCl series, gold was nearly ineffective, the yields increasing up to 38% with silver and 77% with copper. This is the order of reactivity previously found for this family of catalysts for olefin aziridination,[15] although with this fluorinated olefin the gold catalyst is less effective.

The series of complexes with trispyrazolylborate ligands induced the formation of **1** from 17% with the Tp^{Ms}-containing catalyst to nearly quantitative with $Tp^{Br3}Cu(NCMe)$, with the Tp*-based catalyst providing an intermediate yield of 54%. It is worth mentioning that the Tp^xM cores are responsible of reacting with the nitrene precursor, either the binuclear species $[Tp^xM]_2$ or mononuclear adducts Tp^xML delivering the actual catalytic species Tp^xM.[19] Those three results illustrate the role of the Tp^x ligand in this transformation. The Tp*, $Tp^{*,Br}$ and Tp^{Br3} ligands are quite similar in terms of steric hindrance, as assessed by the very similar diastereoselectivity induced by them in the olefin cyclopropanation reaction.[20,21] As an additional evidence, the values for $\%V_{Bur}$ of the Tp^x ligand in the Tp*Cu and $Tp^{Br3}Cu$ cores are 54.7 and 56.2%, respectively.[22,23] Therefore, the difference in reactivity must be related to electronic effects. The values for the ν(CO) in the $Tp^xCu(CO)$ complexes are 2056 (Tp*), 2073 ($Tp^{*,Br}$) and 2107 cm^{-1} (Tp^{Br3}).[24] The lower electron density at the metal center in the latter enhances the electrophilicity of the copper–nitrene intermediate, thus favoring the aziridination reaction. On the contrary, the lower yield obtained with the Tp^{Ms}-based catalyst cannot be explained by such electronic effect, since the copper center displays a lower electron density compared with that of Tp* (ν(CO) for $Tp^{Ms}Cu(CO) = 2079\ cm^{-1}$).[24] In fact, the catalytic outcome is the result of a highly congested catalytic pocket for the Tp^{Ms} case: the $\%V_{Bur}$ for the Tp^{Ms} ligand in the $Tp^{Ms}Cu$ core is 71.8%, leading to a much reduced catalytic pocket that negatively affects the approach of the olefin to the copper-nitrene moiety.

For the silver catalyst, the $Tp^{*,Br}$-containing complex gave 91% yield into **1**, whereas the Tp^{Br3}-based catalyst only afforded 26% of the aziridine. Previous work from our laboratories have shown that the silver analogues (with the same Tp^x ligand) of the copper catalysts display higher electrophilicity, but for too electrophilic metal-nitrenes the decomposition pathway towards $TsNH_2$ is favored.[25]

The scope of this transformation includes 22 α-fluorinated olefins (see Supporting Information for their syntheses) that have been tested for the aziridination reaction under the optimized conditions with both $\mathbf{Cu_{cat}}$ and $\mathbf{Ag_{cat}}$ as catalysts. Scheme 3a shows the fluorinated aziridines obtained, which display variable stability. Whereas **1**–**20** can be isolated (via column chromatography or upon extraction with different organic solvents), **21**–**23** decomposed during workup (see Supporting Information).

The reaction outcome displays several trends that deserve some comments. Regarding the olefin substituent, the nature of the group located at the *para* position of the aryl ring has minor or none influence in the yields at a moderate extent. Electron-withdrawing groups provides ca 95% yield whereas with electron donating substituents yields are slightly lower (ca 88%). Substitution at *meta* position with electron withdrawing groups provide aziridines **8**–**10** in yields around 80%. *Ortho* substitution with Me, F or CF_3 originate a



Scheme 3. Substrate scope and limitations.a) Catalyst screening for the reaction of α-fluorinated olefins with PhI=NTs. Reaction conditions: [Cat]:[PhINTs]:[α-fluorinated olefins] = 1:20:100, r.t., DCM, 75 min. Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. Isolated yields in brackets. b) Aziridination of β-fluoroolefins. Reaction conditions: [Cat]:[PhINTs]:[β-fluoro-olefins] = 1:20:100, r.t., DCM, 75 min. Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. Isolated yield in brackets. See Supporting Information for experimental details.

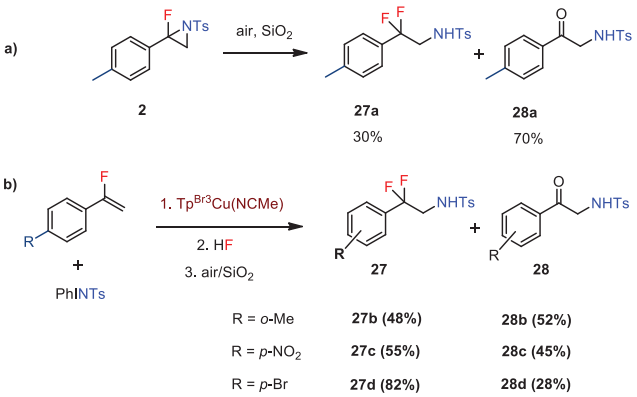
decrease in yields, that correlates with the bulkiness of the substituent. The same steric effect can explain the formation of **14** in 78%, with α-fluoro-β-methylstyrene as the olefin, compared with the quantitative yield found for **1** with α-fluorostyrene. Replacement of phenyl with naphthyl or biphenyl did not affect the very high yields (**15**–**16**). This procedure is tolerant with alkyne-substituents at the aryl ring (**17**–**19**), even with a TMS located at the acetyl end (**18**), providing a versatile reaction site for further derivatizations. The p-cyanocarbonyl derivative also verified the reaction with moderate yield (**20**). Aziridines **21**–**23** could only be detected at the end of the reaction in low to moderate yields: attempts to isolate them failed in all cases.

Limitations for this strategy are due to two different reasons. On one hand, the fluoro-olefins are not always stable. We have tried the synthesis of eight α-fluoro-monosubstituted olefins bearing benzyl, *p*-$EtCO_2$-C_6H_4, o-HOOC-$C_6H_4C_6F_5$, 3,5-difluorophenylyl or anthryl, as well as α-fluorostyrene with OMe at the β position, none of them being isolable in a pure form to run catalysis. Second, some fluoroolefins could be isolated but failed to react: it is the case of α-fluorostyrenes bearing chloro at *ortho* position, methyl at *meta* position or three methyl groups at 2,4,6 positions (mesityl). Analogously, the presence of Br or NO_2 at the olefin also led to inhibition of the aziridination reaction. Also, it is worth mentioning that the presence of N donors in the substrates containing amine or pyridine functionality leads to the corresponding N-N products, as previously reported.[26,27]

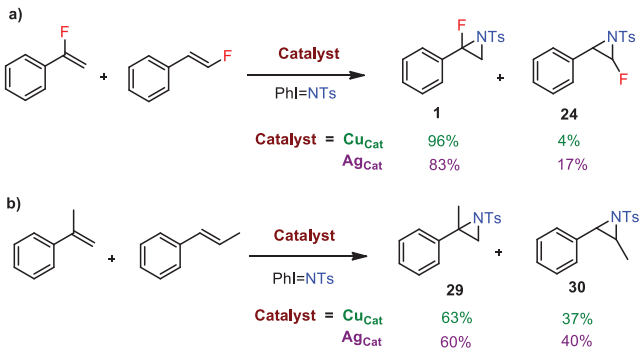
The location of the fluorine atom at the β position of the styrene brings new features. Scheme 3b shows three examples of such substrates, for which only the silver catalyst was effective at a significant extent, with copper providing none or low yields. The presence of Me (**25**) or iPr (**26**) at the *para* position influences the reaction outcome; however, given the distance of such position to the nitrene transfer region, it has to be related to electronic effects. In the three cases studied, the reaction takes place in a stereospecific manner.

Since we observed decomposition in some cases during purification process via chromatography, we have investigated the effect of silica gel/air/moisture (from air) on one isolated aziridine such as **2**. After 4 h of stirring, we could separate and characterized two products **27a** and **28a** (Scheme 4a), in a 30:70 ratio (yield based on initial aziridine > 95%). A visible glass deterioration of the Schlenk tube was associated to the formation of HF during the process. Then we decided to run the aziridination reaction of a several fluorostyrenes followed by addition of HF (10 equiv.) and silica gel, leaving the reaction mixture open to air for 24 h. In all cases, mixtures of **27b-d** and **28b-d** were obtained (Scheme 4b). The formation of β-difluoroamines **27** corresponds to a ring opening process, where the F adds to the carbon attached to the Ph ring whereas the H incorporates to the NTs moiety. The formation of these biologically relevant molecules had been disclosed with just one fluorine atom,[28–30] our system providing the first example for β-difluoroamines generated from aziridines.

Experiments with equimolar mixtures of α- and β-fluorostyrene have been carried out with both $\mathbf{Cu_{Cat}}$ and $\mathbf{Ag_{Cat}}$ (Scheme 5a), observing the major formation of the α-fluoro-derivative. When using the Me-analogues (Scheme 5b), again



Scheme 4. a) Decomposition of fluoroaziridines. b) Fluorostyrene aziridination followed by HF addition.

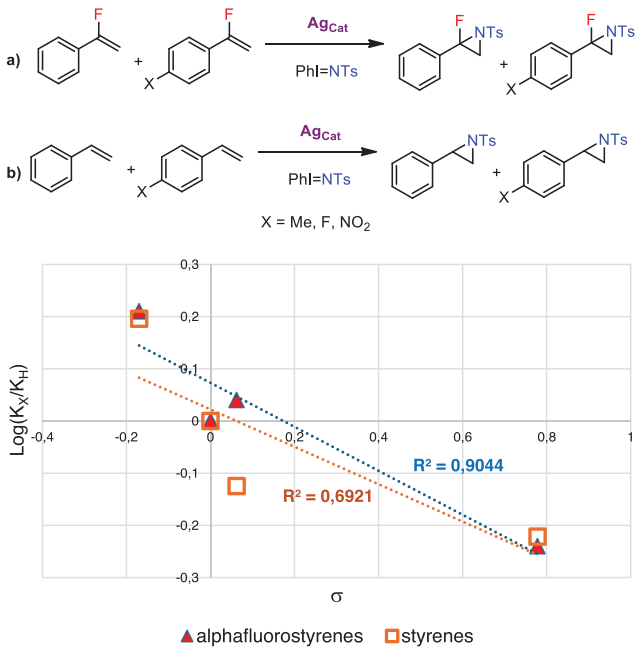


Scheme 5. a) Competition experiments with α- and β-fluorostyrenes. b) Competition experiments with α- and β-methylstyrenes. Reaction conditions: [Cat]:[PhINTs]:[α-olefin]:[β-olefin] = 1:20:50:50, r.t., DCM, 75 min. Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. See Supporting Information for experimental details.

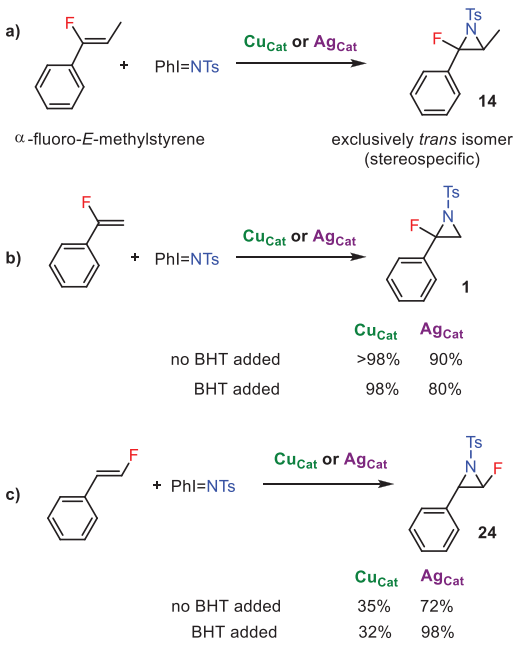
the α-methyl-derivative was obtained in higher yield, but not as much as with the fluorinated olefins.

A second set of competition experiments involves α-fluorostyrenes with substitutions at the *para* position of the phenyl ring, aiming at correlating the relative reactivity with Hammett equation $\log(K_X/K_H) = \rho.\sigma$, a frequent mechanistic test for aziridination reactions.[10,11,31,32] Scheme 6 displays the Hammett plot obtained with the silver catalyst, which also contains the results previously reported with non-fluorinated styrenes.[11] The former fits well using the σ_p scale ($\rho = -0.421$; $R^2 = 0.904$), whereas with styrenes lacking fluorine such fitting is quite poor ($R^2 = 0.692$). We and others[11,32] have demonstrated the need of a dual-parameter Hammett equation $\log(K_X/K_H) = \rho^+\sigma^+ + \rho^\bullet\sigma^\bullet$, involving polar and radical components to fit with the experimental values with non-fluorinated olefins. Interestingly, we now observed with fluorinated styrenes that the radical component is non-significant ($\sigma^+ = -0.418$; $\sigma^\bullet = +0.073$; see Supporting Information).

To gain more information towards a mechanistic proposal, α-fluoro-*E*-methyl-styrene was employed as the substrate. It is known that the initial geometry of the substituents at the double bond may change due to the formation of intermediates that allow rotation of the C–C bond before ring



Scheme 6. Hammett plots from competition experiments with *p*-substituted styrenes, comparing the fluorinated, a) and non-fluorinated b) olefins.



Scheme 7. a) Experiments to evaluate stereospecificity. b), c) Effect of radical inhibitors. Reaction conditions: [Cat]:[PhINTs]:[olefin] = 1:20:100, r.t., DCM, 75 min. Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. See Supporting Information for experimental details.

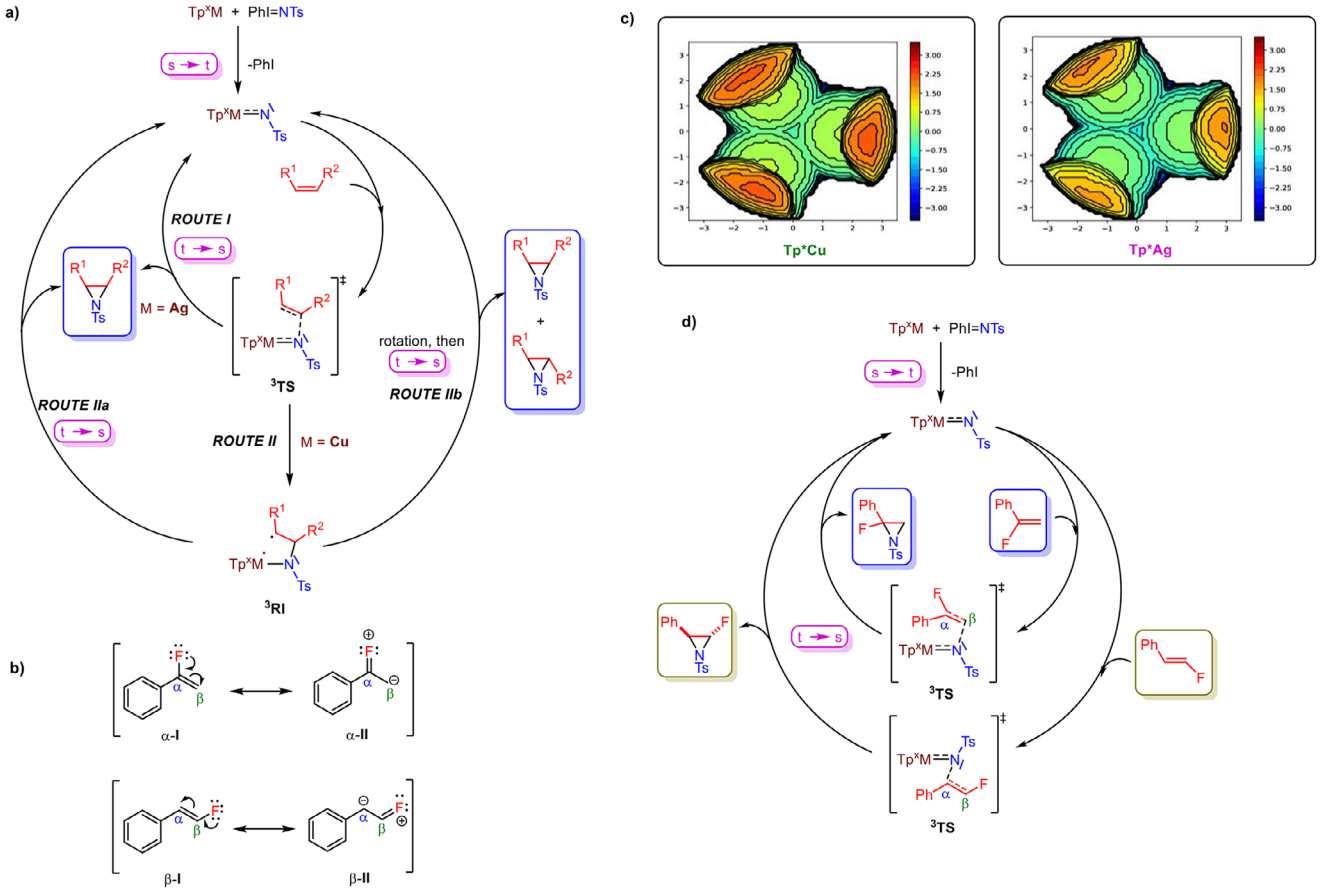
closing.[10,11,32] In our case, both the copper and silver catalysts did not induce such change in the geometry, the reaction being stereospecific since only the *trans* aziridine (referred to the initial *E* geometry of the Me and Ph substituents) was observed (Scheme 7a). The same is observed in the formation of **24** and **25** (Scheme 3), which employ E-*β*-fluorostyrenes. This is in agreement with previous similar experiments with this family of catalysts employing either *Z*- or *E*- olefins,[10,11] the relative geometry of the olefin being retained in the final aziridines.

A second set of experiments was performed upon adding BHT (2,6-di-*t*-butyl-4-hydroxytoluene) and comparing the reaction yields with those in the absence of such radical inhibitor. As shown in Scheme 7b-c, no effect of the additive was observed with the copper catalyst. For the silver case, the slight decreases observed are not relevant, compared with the strong effect usually reported for this type of control experiments.[11,32]

Our group has previously studied the general mechanism of the olefin aziridination reaction by Tp^{x}M units (M=Cu, Ag) for an array of olefins such as styrenes, dienes or dienols, based on mixed experimental and DFT data.[10,11] Scheme 8a contains a general view of such mechanism, which starts with the generation of metal-nitrene species in the triplet state (more stable than the singlet state). Interaction with the olefin involves a transition state ^{3}**TS** in which the first C–N bond is developed. From here, two possible routes were found by DFT calculations. On one hand, ^{3}**TS** may generate the aziridine in a one, concerted but asynchronous step (Route I). On the other, a radical intermediate ^{3}**RI** is formed from which the second C–N bond is formed. This intermediate may or not undergo C–C bond rotation and could originate loss of stereospecificity (Route IIb and IIa, respectively). In a general manner, we previously observed that Ag catalysis occurred via Route I and Cu catalysis throughout Route IIa or IIb. Experimental evidence for the presence of ^{3}**RI** stands on the observance of a decrease in the reaction yields when adding BHT and the loss of stereospecificity when using *E*- or *Z*- olefins as starting materials.

We have now applied this mechanism to the fluorinated olefins employed in this work. At variance with the styrenes or alkenes previously studied, the aziridination of these *α*- and *β*-fluorinated olefins with both metals is not influenced by the addition of BHT as radical inhibitor (Scheme 7b,c). In addition to that, the stereospecificity of the transformation is assessed with the use of *α*-fluoro-E-methyl-styrene, which only generates the *trans* aziridine (Scheme 7a). Therefore, the involvement of intermediates such as ^{3}**RI** can be discarded. Finally, the observance of a good fitting with Hammett equation without any radical parameter indicates that the reaction resembles that of the olefin cyclopropanation reaction with these catalysts, which is assumed to occur in a concerted manner.[21]

Having simplified the mechanism shown in Scheme 8a, there are still two questions to answer: i) *α*-fluorostyrene is much more reactive than *β*-fluorostyrene (Scheme 5a), and ii) copper is slightly more reactive than silver with *α*-fluorostyrenes whereas for the *β*-fluorostyrenes, silver is much more reactive than copper. It is well-known that fluorine displays –I and +M electronic effects, the former affecting at the electron density of the C=C bond in a similar manner for both *α*- and *β*- isomers. Therefore, the resonance forms derived from the +M effect are those relevant in this



Scheme 8. a) Mechanism previously proposed for Tp^{x}M-catalyzed olefin aziridination. b) Relevant resonance forms for α- and β-fluorostyrenes. c) Comparative of the topographic maps and buried volumes for Tp*M (M = Cu, Ag). d) Mechanistic picture for the aziridination of α- and β-fluorostyrenes.

transformation. As shown in Scheme 8b, resonance form **α–II** displays high electron density at β-carbon, which will be the reaction site with the metal-nitrene intermediate. The situation is reversed for β-fluorostyrene, for which resonance form **β–II** accumulates negative charge at the α carbon. The difference in the steric hindrance of both sites seems to govern this transformation, explaining that in the competition experiments (Scheme 5a), the reactivity of α-fluorostyrene is higher than that of β-fluorostyrene.

The use of α- and β-methyl-styrenes (Scheme 5b) originates a ca. 60:40 mixture of aziridines. At variance with the fluorostyrenes, the Me substituent enhances the nucleophilicity of the C=C double bond. The attack of the metal-nitrene takes place in both cases in the β-carbon,[32] which is less hindered for the α-methylstyrene.

This steric influence also explains the trends observed with the metals. The $\%V_{Bur}$ values (Scheme 8c) for the Tp* ligands in Tp*M complexes are 56.2 (M = Cu) and 48.5% (M = Ag).[22,23] Therefore, the remaining up to 100% corresponds to the available catalytic pocket that is higher for the silver case, as a consequence of the distinct ionic radii for Cu(I) and Ag(I) ($r_{Cu(I)} = 74$ pm, $r_{Ag(I)} = 114$ pm).[33] Thus, when comparing the reactivity of β-fluorostyrene with both catalysts (Scheme 3b), the yield of aziridine with the silver catalyst nearly doubles that with copper, as the result of the steric hindrance between the metal-nitrene intermediates and the α-carbon of the olefin.

With the α-fluoro-olefins, copper provides slightly higher yields. Since in this case the reaction site (the β-carbon of the olefin) is much less hindered, no steric effects are expected. We assume that the relatively lower yields with silver are due to a more favored decomposition pathway due to a higher electrophilicity of the silver-nitrene intermediate.

Scheme 8d shows the mechanistic picture for this transformation. The information collected with the fluorinated olefins points at the lack of any effect of radical intermediates for the fluorinated olefins: there is no significant effect of radical inhibitors, and the reaction is stereospecific with both metals. The metal–nitrene intermediates reacts with the fluoroolefins at a different carbon, the closing of the ring taking place in a concerted manner. The difference with the previous proposal is a consequence of the electronic effects of fluorine in the C=C bond. This is in line with the unique behavior that fluorine induces in many organic reactions.[34,35]

As a conclusion, we have developed the first catalytic system for the aziridination of fluorinated olefins using the metal-catalyzed nitrene transfer strategy, employing Tp^{x}M-based

catalysts (M = Cu, Ag). An array of α- or β-fluoroolefins have been converted into the corresponding aziridines with yields from moderate to excellent. The reactions are stereospecific and take place through a concerted addition of the olefin to the metal–nitrene intermediates.

Supporting Information

The authors have cited additional references within the Supporting Information.[32–40]

Acknowledgements

The authors thank to Ministerio de Ciencia e Innovación for Grants PID2020-113797RB-C21 and PID2023-146946NB-I00. The authors also thank Junta de Andalucía (P20-00348) and Universidad de Huelva (P.O. Feder UHU-202016). J.P.R. thanks Programa Garantía Juvenil. A.R. thanks Universidad de Sevilla for Proyecto de Recualificación REC-B19989-1 and -2. We also thank Prof. Tomás R. Belderrain for valuable discussions on fluorine NMR spectra.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Aziridination of fluoro-olefins · Copper/silver catalysis · Fluorinated aziridines · Nitrene transfer

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Manuscript received: October 05, 2024
Revised manuscript received: March 31, 2025
Accepted manuscript online: April 01, 2025
Version of record online: April 30, 2025