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Fluorine Chemistry

Catalytic HF Shuttling between Fluoroalkanes and Alkynes**

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Abstract: In this paper, we report $BF_3{\cdot}OEt_2$ as a catalyst to shuttle equivalents of HF from a fluoroalkane to an alkyne. Reactions of terminal and internal aliphatic alkynes led to formation of difluoroalkane products, while diarylalkynes can be selectively converted into fluoroalkenes. The method tolerates numerous sensitive functional groups including halogen, protected amine, ester and thiophene substituents. Mechanistic studies (DFT, probe experiments) suggest the catalyst is involved in both the defluorination and fluorination steps, with BF_3 acting as a Lewis acid and OEt_2 a weak Lewis base that mediates proton transfer. In certain cases, the interconversion of fluoroalkene and difluoroalkane products was found to be reversible. The new catalytic system was applied to demonstrate proof-of-concept recycling of poly(vinylidene difluoride).

Due to their applications in pharmaceuticals, agrochemicals, materials, and next generation refrigerants, there is a growing demand for organofluorine compounds.[1–3] This demand has stimulated widespread interest in synthetic methods for fluorination. For example, the addition of HF to unsaturated substrates represents a simple and atom-efficient approach to construct organofluorines.[4–13] Despite finding broad use, the approach has its drawbacks; HF is a corrosive and toxic gas and high concentrations can be fatal in contact with skin. Although milder and easier to handle reagents such as pyridinium poly(hydrogen fluoride) or triethylamine trihydrofluoride have been developed, they do not entirely mitigate the risk.[14]

In recent years, we[15,16] and others have begun developing new catalytic approaches that allow the recycling of the fluorine content of organofluorine compounds. These methods hold promise as a first step toward a circular economy of fluorine, while also obviating the need to handle HF. Our long-term aim is to establish reversible processes such that fluorine content can be moved from one molecule to another without significant energy input. Related approaches have already emerged for shuttling HCl or HBr between substrates. In 2020, Morandi and co-workers reported the iridium chloride catalyzed hydrobromination and hydrochlorination of internal alkynes through HBr or HCl shuttling from bromo- or chloroalkanes (Figure 1).[17] More recently, the same group documented a rhodium-catalysed transfer hydroiodination of terminal alkynes.[18] Oestreich and co-workers have reported a Lewis-acid catalysed decarboxylative transfer hydrochlorination of alkynes.[19] Expansion of these methods to organofluorine compounds is non-trivial. Carbon–fluorine bond strengths are extremely high,[20] oxidative addition of sp^3 C–F bonds to transition metals is essentially unknown,[21] and in cases that defluorination does occur the resulting metal fluoride can be too thermodynamically stable to engage in catalysis.[22–24] Here we report $BF_3{\cdot}OEt_2$ as an efficient catalyst for the HF shuttling between fluoroalkanes and alkynes to form an alkene and a difluoroalkane. We show that there is an aspect of reversibility to this reaction and that difluoroalkane products can be converted back into fluoroalkene intermediates. This discovery was leveraged to use poly(vinylidene difluoride) (PVDF) as an HF donor, allowing the recycling of its fluorine content.

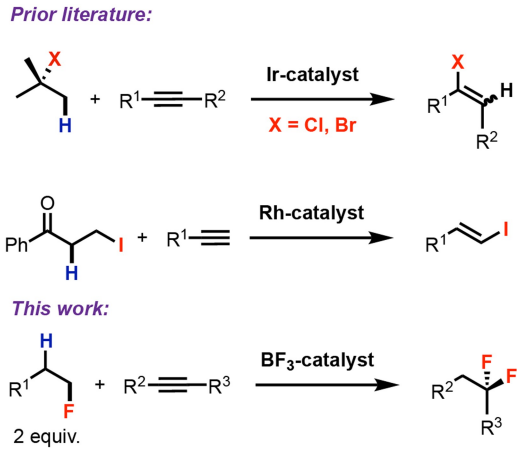


Figure 1. Catalytic methods for HX (X = I, Br, Cl, F) shuttling and transfer between haloalkanes and alkynes

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Lewis acidic group 13 compounds have been reported as both reagents and catalysts for the hydrofluorination of internal alkynes[25] and the defluorination of fluoroalkanes,[26–28] and represented a logical starting point for the development of an HF shuttle catalyst. Very recently, $BF_3{\cdot}OEt_2$ has been reported as a catalyst for the homologation of fluoroalkanes with diazoesters,[29] and the intramolecular fluorocarbamoylation of alkynes.[30] Upon revision of this work,[31] a Lewis-acidic heterogeneous catalyst was reported for HF shuttling between fluoroalkanes and alkynes.[32]

Initially, a series of group 13 Lewis acid catalysts and group 15/16 bases were screened for the reaction of 1-fluorohexane with a small array of alkynes. $BF_3{\cdot}OEt_2$ in combination with weak Lewis-bases such as 2,6-dichloropyridine or triphenylphosphine proved active for HF shuttling in modest yields. Ultimately, it was discovered that the Lewis-base was unnecessary for product formation, and that aliphatic alkynes gave the simplest product distributions. Focusing on these substrates, we optimized the reaction temperature, solvent, reaction time, catalyst loading and absolute concentration for formation of the difluoroalkane product. Under the optimized conditions 1-fluoroheptane (2 equiv.) and 1-dodecyne (1 equiv.) react to form a mixture of internal heptene isomers (**1a**, 79 %) and 2,2-difluorododecane (**2b**, 76 %) catalyzed by 10 mol % $BF_3{\cdot}OEt_2$ in $CHCl_3$ at 80 °C (Figure 2). A control reaction that omitted the 1-fluoroheptane gave <2 % yield of the product. The

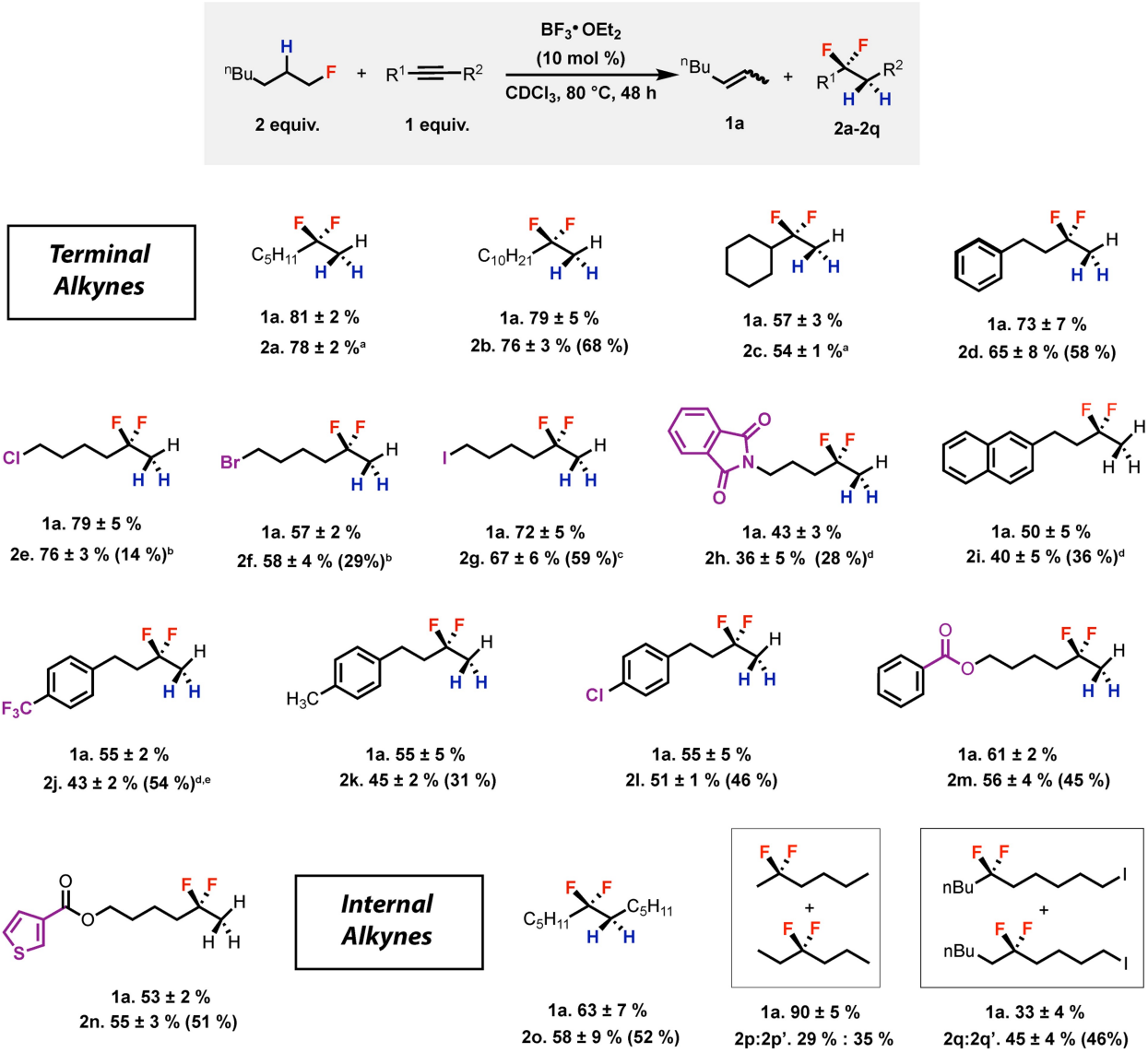


Figure 2. Reaction scope under optimised conditions. Difluoroalkane yield monitored by quantitative ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. Alkene yields were monitored by ^{1}H NMR spectroscopy using fluorobenzene as an internal standard. Reactions were performed in triplicate and errors based on standard deviation with a 99% confidence level. Isolated yields provided in parenthesis. [a]product could not be isolated. [b]low recovery due to volatility. [c] isolated product contaminated with n-pentane which was not fully removed due to volatility of **2g**. [d]isolated products contain small amounts of grease entrained from work-up procedure. [e]isolated yield was obtained using 20 mol% $BF_3{\cdot}OEt_2$.

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formation of internal heptene isomers likely arises from alkene isomerisation under the catalytic conditions. To confirm this possibility, the catalytic reaction mixture was spiked with 1-hexene, upon heating to 80 °C for 48 h the terminal alkene additive was entirely consumed generating a mixture of internal isomers. Catalyst poisoning experiments were conducted by added stoichiometric quantities of methyl benzoate, thiophene, and furan, to the standard catalytic procedure. Yields of **1a** and **2b** ranged from 30–75 % and 30–72 % respectively in the presence of these additives, and in no case was catalysis completely inhibited. In contrast, addition of pyridine completely shut down the catalytic reactions.

Using 1-fluoroheptane as the HF donor, a range of terminal alkynes could be employed in the HF shuttling reaction to afford respective products with moderate to good yields (**2a**–**2n**). Remarkably, substrates with potentially sensitive functional groups were tolerated, including halogens (**2e**–**2g**), and a phthalimido group (**2h**). The reaction is also selective for a single sp^3 C–F moiety, as the trifluoromethyl group can be carried through unscathed (**2j**) with similar yields to the methylated analogue (**2k**). Coordinating groups including a benzoate ester (**2m**), a thiophene ring system (**2n**) also delivered the gem difluoro products in moderate to good yields. Internal alkynes also proved effective acceptors in HF shuttle catalysis with modest yields (**2o**–**2q**). Both 6-dodecyne and 2-hexyne lead to the corresponding difluorinated products, with the latter unsymmetrical alkyne leading to formation of a near 1:1 mixture of isomers with functionalisation at the 2- and 3-position (**2p** and **2p'**). Similar selectivity was observed with remotely iodo-substituted alkynes (**2q** and **2q'**).

During the catalytic reactions E/Z-fluoroalkenes could be observed as reaction intermediates by ^{1}H and ^{19}F NMR spectroscopy. It was assumed that the formation of the difluoroalkane products occurs by two sequential HF shuttling events, the first of which generates a mixture fluoroalkene isomers. Independent synthesis of (*Z*)-6-fluorododec-6-ene and exposure to the catalytic conditions resulted in formation of **2o** in 60 % yield alongside (*E*)-6-fluorododec-6-ene in 8 % yield, confirming the *Z*-fluoroalkene as a potential intermediate.

Further to this observation, the scope of shuttle catalysis could be expanded to allow the preparation of fluoroalkenes directly. In a 1:1 reaction of 1-fluoroheptane with diaryl-substituted alkynes, the fluoroalkene intermediates were formed in good yields and stable enough to be isolated. It proved essential to perform these reactions in fluorinated ethylene propylene (FEP) tubes to reduce the side products from ketone formation assumed to derive from adventitious water. Mixtures of *E:Z* stereoisomers of fluoroalkenes derived from diphenylacetylene (**3a**), along with fluorinated (**3b**–**c**) and ester-substituted analogues (**3d**) could all be obtained under these conditions (Figure 3a). Fluoroalkenes could also be prepared by exploiting the partial reversibility of HF shuttle catalysis (Figure 3b). The reaction of the 1,1-difluoroalkane with dodec-6-yne resulted in formation of **3e** as a mixture of *Z:E* isomers in 81 % yield (Figure 3c). The result demonstrates that difluorinated alkanes themselves are viable donors in HF shuttle catalysis.

Based on these findings, further reactions were attempted using PVDF as an HF donor. Among many applications, PVDF is used as an electrical insulator and binding agent in Li-ion batteries and is an attractive target for chemical recycling.[33] Reaction of a commercial sample of powdered PVDF (Sigma Aldrich, $M_w \approx 534{,}000$) with but-3-yn-1-ylbenzene at 180 °C for 8 h. in cumene with 1 equiv. of $BF_3 \cdot OEt_2$ led to the formation of a mixture of **2d**, **3e** and **3f** in 80–88 % combined yield. Although not currently catalytic, this result holds great promise for recycling of PVDF through its direct use as a source of HF.

To gain further insight into the mechanism of HF shuttling, a series of density functional theory (DFT) calculations were conducted (Figure 4). To reduce potential issues with the conformational flexibility of medium-length hydrocarbon chains, the reaction of fluoroethane with 1-propyne was considered as a model.

Broadly the pathway can be divided into defluorination and fluorination stages. In the first stage, defluorination of fluoroethane with $BF_3 \cdot OEt_2$ is calculated to proceed by three possible pathways: two involve explicit solvent involvement and the third occurs with dissociation of OEt_2. Addition of $BF_3 \cdot OEt_2$ to fluoroethane is calculated to lead to endergonic formation of **Int-1**, a weakly associated complex. Elimination of HF from **Int-1** can occur in a concerted fashion, via **TS-1-syn** (37.0 kcal mol^{-1}) or **TS-1-anti** (34.6 kcal mol^{-1}) leading to formation of ethane and $HBF_4 \cdot OEt_2$ (**Int-2**). In these transition states BF_3 plays a role of Lewis-acid, coordinating and polarizing the carbon–fluorine bond, Et_2O plays the role of a weak base. The two transition states differ in geometry with the lower energy stationary point **TS-1-anti** possessing a favorable anti-periplanar arrangement of the H and F atoms involved in HF elimination. Such a conformation is expected to be energetically favorable based on effective orbital overlap. An alternative pathway involving dissociation of $BF_3 \cdot OEt_2$ was ultimately found to be more feasible. Dissociation of $BF_3 \cdot OEt_2$ into $BF_3 + OEt_2$ is calculated to be mildly exergonic at 80 °C in $CHCl_3$, subsequent weak coordination to fluoroethane forms **Int-1'** which can eliminate HF by **TS-1'** (28.2 kcal mol^{-1}). This is again a concerted transition state, but one which omits an explicit role of Et_2O solvent. BF_3 plays the role of both Lewis acid and base, with the lone-pair on one of the fluorine atoms accepting a proton. Subsequent re-association with OEt_2 leads to **Int-2**.

The second stage of the mechanism involves fluorination of the alkyne with $HBF_4 \cdot OEt_2$. From **Int-2**, $HBF_4 \cdot OEt_2$ delivers a proton to the terminal position of 1-propyne and a fluoride to the internal position via **TS-2** (27.6 kcal mol^{-1}) leading to the formation of 2-fluoroprop-1-ene and reforming $BF_3 \cdot OEt_2$. While again the calculations suggest a concerted process, **TS-2** is highly asynchronous and resembles protonation of alkyne, with very little C–F bond formation. Investigation of the IRC associated with this step reveals that C–H bond formation occurs on the way to the transition state, and C–F bond formation after the transition state is traversed. **TS-2** results in the syn-addition of HF

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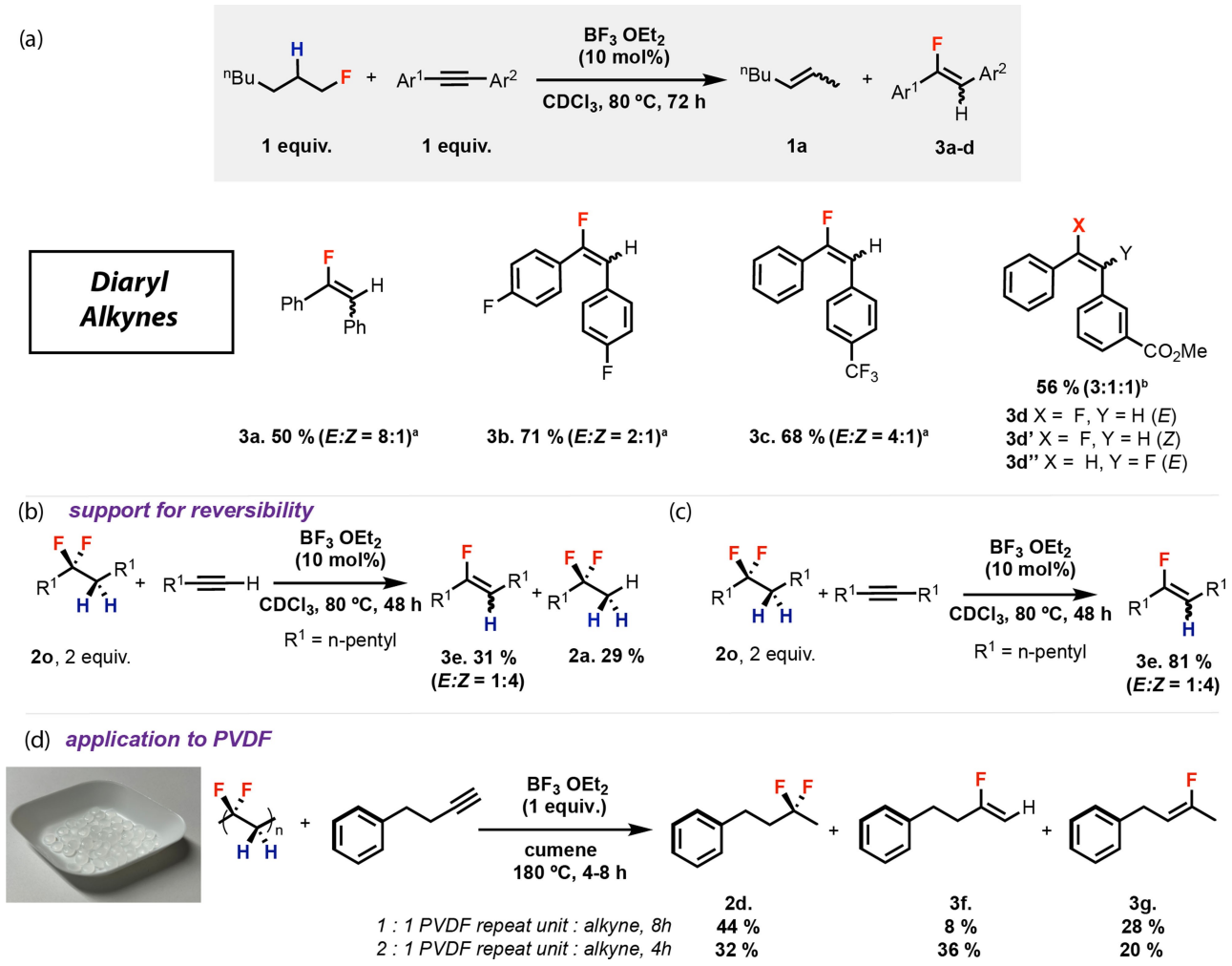


Figure 3. (a) HF shuttle catalysis to yield E:Z mixtures of fluoroalkenes. Fluoroalkane yield monitored by quantitative ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. [a]due to challenging purification **3 a–c** were isolated with 15–30% contamination from alkyne starting material. [b]the difluoroalkane product **3 d'''** was also observed in approximately 2% yield. Alkene yields were monitored by ^{1}H NMR spectroscopy using fluorobenzene as an internal standard. (b) Preparation of a fluoroalkene by HF shuttle catalysis using a difluoroalkane donor. (c) A comproportionation type reaction. (d) Proof-of-concept application in which poly(vinylidene difluoride) is used as the HF donor.

across the alkyne. An alternative transition state, **TS-2'** that leads to the anti-isomer in the hydrofluorination step could also be located but is higher in energy (33.3 kcal mol^{-1} from BF_3+OEt_2), most likely due to the greater degree of charge separation that occurs in this transition state. Modelling of the explicit solvation with Et_2O appears to be essential in these calculations. Alternative versions of **TS-2** that omit Et_2O could not be located.[34] Overall, the formation of 2-fluoroprop-1-ene from the first HF shuttling event is exergonic with $\Delta G°(353\ K) = -13.4$ kcal mol^{-1}.

In presence of a further equivalent of fluoroethane, the two stages of defluorination and fluorination can repeat, leading to a second HF transfer event ultimately forming 2,2-difluoropropane. The reaction of $HBF_4\cdot OEt_2$ with 2-fluoroprop-1-ene is calculated to occur by **TS-3** (27.6 kcal mol^{-1} from BF_3+OEt_2). Again, IRC calculations link **TS-3**, which is also highly asynchronous, directly to the product of fluorination, **Int-4.** Separation of the protonation and fluorination processes within **TS-3** is even more pronounced than within **TS-2**. $BF_3\cdot OEt_2$ is subsequently regenerated from **Int-4** with simultaneous formation of 2,2-difluoropropane. The overall reaction of two equiv. of fluoroethane with 1-propyne, is exergonic with $\Delta G°(353\ K) = -20.1$ kcal mol^{-1}.

Comparison of the local energy barriers for the key steps via **TS-1'**, **TS-2** and **TS-3** suggests that each catalytic stage occurs with a similar activation barrier, $\Delta G^{\ddagger}$ (298 K) ≈27–28 kcal mol^{-1}. The computational model is consistent with an 80 °C reaction.

Experimentally, $HBF_4\cdot OEt_2$ was observed to form in catalytic runs ($\delta_{1H} = 10.5$ ppm; $\delta_{19F} = -152$ ppm). $HBF_4\cdot OEt_2$ was also shown to be catalytically competent, as the reaction of 1-fluoroheptane, 1-dodecyne, and 10 mol % $HBF_4\cdot OEt_2$ formed **2b** in 61 % yield alongside a mixture of internal heptene isomers in 71 % yield. A mechanistic probe experiment in which pent-4-yn-1-ylbenzene was subjected to the catalytic conditions using 1-fluoroheptane as an HF donor led to intramolecular Friedel–Crafts alkylation. No products

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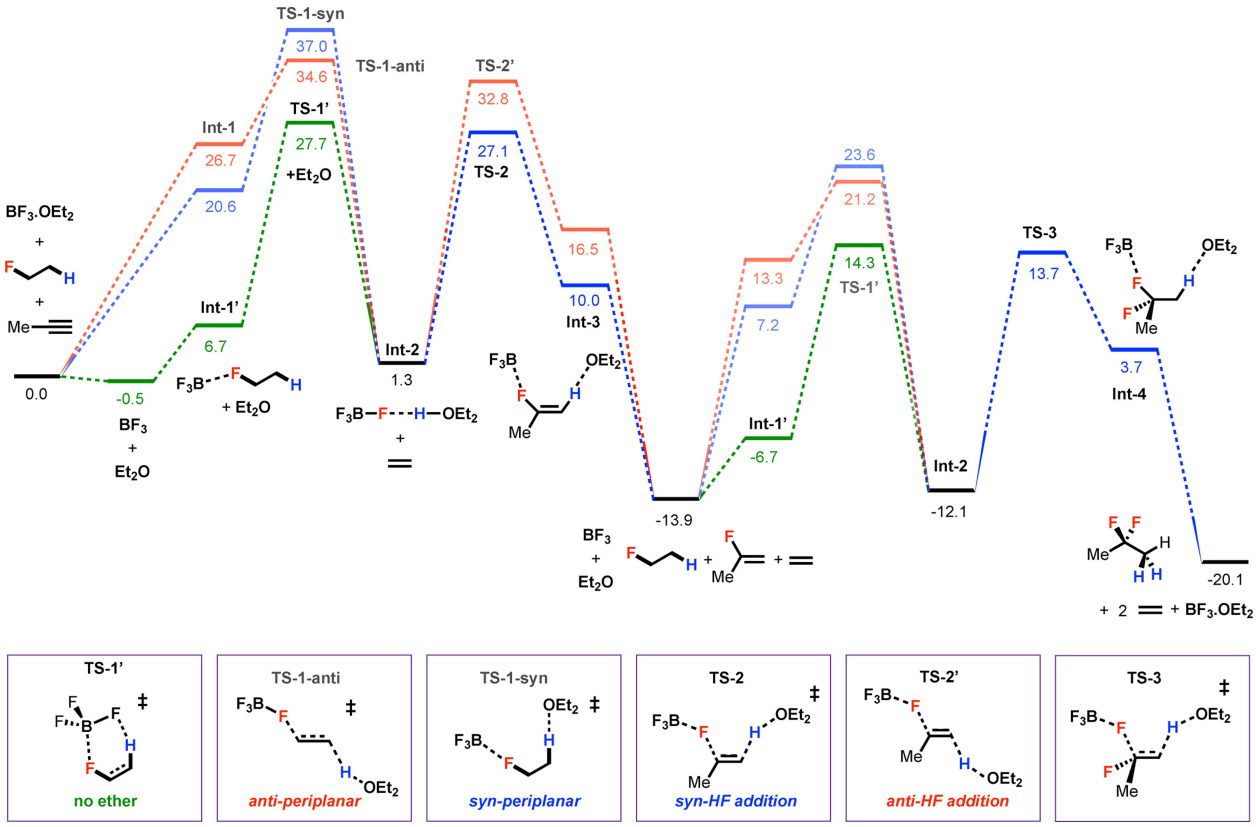


Figure 4. DFT calculated pathway for boron trifluoride etherate catalysed reaction of fluoroethane and 1-propyne. Calculated using the B3LYP hybrid functional. The 6–311 + + g** basis set was used for optimisation with a PCM solvation model, and single-point corrections were done using def2-QZVPPD with a SMD solvation model. Dispersion was included (GD3BJ). Energy values reported in kcal mol^{-1}.

of HF shuttling were observed. Repeating this reaction in the absence of the fluoroalkane lead to no consumption of the substrate. These findings are consistent with generation of $HBF_4 \cdot OEt_2$ in situ and its role in protonation of the alkyne substrate to generate species with carbocation character (see Supporting Information for details).

In summary, we report a new method to shuttle HF between fluoroalkanes and alkynes. The reaction operates with a simple commercial catalyst ($BF_3 \cdot OEt_2$) and can be performed without the need for handling toxic and corrosive HF based reagents. Our method can be applied to use of PVDF as an HF donor, and holds promise as a means for the chemical recycling of fluorocarbons. We are continuing to investigate applications in both synthesis and materials science.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Catalysis · Defluorination · Fluorination · HF Shuttling

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