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ARTICLE

Conversion of trifluoromethyl into ester along with polyethers upcycling by cation-transfer catalyzed C–O/C–F metathesis

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Ester and trifluoromethyl groups play crucial roles in chemistry and drug design. However, the implementation of interconvesion from trifluoromethyl into ester under wide condition is not an easy work because the C–F bond of trifluoromethyl group possesses high bond energy and extremely difficult to break. Herein, we for the first time present a silylium-ion-initiated method for intermolecular C–F/C–O metathesis, enabling selective activation of inert C(sp^3)–F and C(sp^3)–O bonds. This approach facilitates the defluoroalkoxylation of trifluoromethyl-substituted substrates and polyfluoroalkanes when combined with ethers or polyethers, thus builds a bridge to convert trifluoromethyl groups into ester/ketone groups along with polyethers upcycling. We provided crystallographic evidence to clearly confirm that this reaction involves the formation of silyloxonium ions and Meerwein-type salt intermediates, followed by cationic ligand transformations.

Introduction

The functionalization of inert bonds represents a fundamental challenge in organic chemistry. Central to this pursuit is the carbon–fluorine bond, which plays a crucial role in synthetic chemistry and drug design (Scheme 1A), while also contribute to persistent fluorinated waste.[1-5] Despite its exceptional strength (up to ~130 kcal/mol for C(sp^3)–F centers),[6] the trifluoromethyl group, which is readily available in commercially abundant compounds, has emerged as a versatile synthetic handle. Recent advances have enabled its use in diverse catalytic transformations, including hydrodefluorination, halogen exchange, and C–C/C–heteroatom bond formation.[7-24] Encouraged by these advances, the development of direct and efficient methods to convert trifluoromethyl groups into diverse functionalities through mechanistically novel pathways is scientifically interesting. Such methods would also significantly facilitate access to chemically useful functional groups.

Catalytic chemical bond metathesis reaction has garnered significant attention in recent years because it provides a low-energy and redox-neutral pathway for bond activation and formation, enabling the cleavage of strong and inert bonds that are difficult to break through other pathways.[25-32] Inspired by recent elegant examples on acidic main-group-catalyzed C–O single bond metathesis[33-35] as well as C–F bond cleavage,[36-40] we wonder if metathesis involving the C–F and C–O bond exchange can proceed smoothly under the mild conditions in the presence of acidic main-group catalysts. If this method works smoothly, it would enable the interconversion between trifluoromethyl group and ester group by consecutive C–F/C–O bond exchanges, and the high reaction temperature decreased its synthetic value in practical applications (Scheme 1B, right). Notably, Dai and coworkers recently achieved this conversion using a heterogeneous catalyst, however at high temperature of 300 °C, underscoring the need for a milder catalytic protocol (Scheme 1B, left).[41] Despite recent advancements in main group catalysis, main group-catalyzed C–F/C–O bond metathesis reaction has never been realized due to the high bond dissociation energies and selectivity challenges. Apparently, several challenges for such a strategy are anticipated: 1) the well-documented homo-metathesis of C–O bonds to generate cyclic ether, and 2) the competitive defluorinative hydrogenation of C–F bond (Scheme 1C).[42,43]

Silylium ions, strongly Lewis acidic silicon-based cations, have shown exceptional ability to activate various inert bonds.[44-52] More recently, Oestreich and co-workers discovered that the silylium ion can also efficiently activate C–O bond in methanol, furnishing the methylation of arenes.[53] Inspired by these catalytic patterns, we questioned whether the carbenium ion formed after fluoride abstraction could also activate ether C–O bonds, *via* Meerwein-type salt[54,55] reactive intermediate. If this transformation is achievable, such an approach would represent a rare metal-free example of intermolecular bond exchange between two robust single bonds (C–F and C–O), which incorporating silicon, the second most abundant element in Earth's crust, as a viable catalyst.

Here, we report the implementation of the C–F/C–O bond metathesis reaction by employment of silylium ions, strongly Lewis acidic silicon-based cations, which were generated *in situ* *via* hydride abstraction using excess Si–H, as the catalysts and

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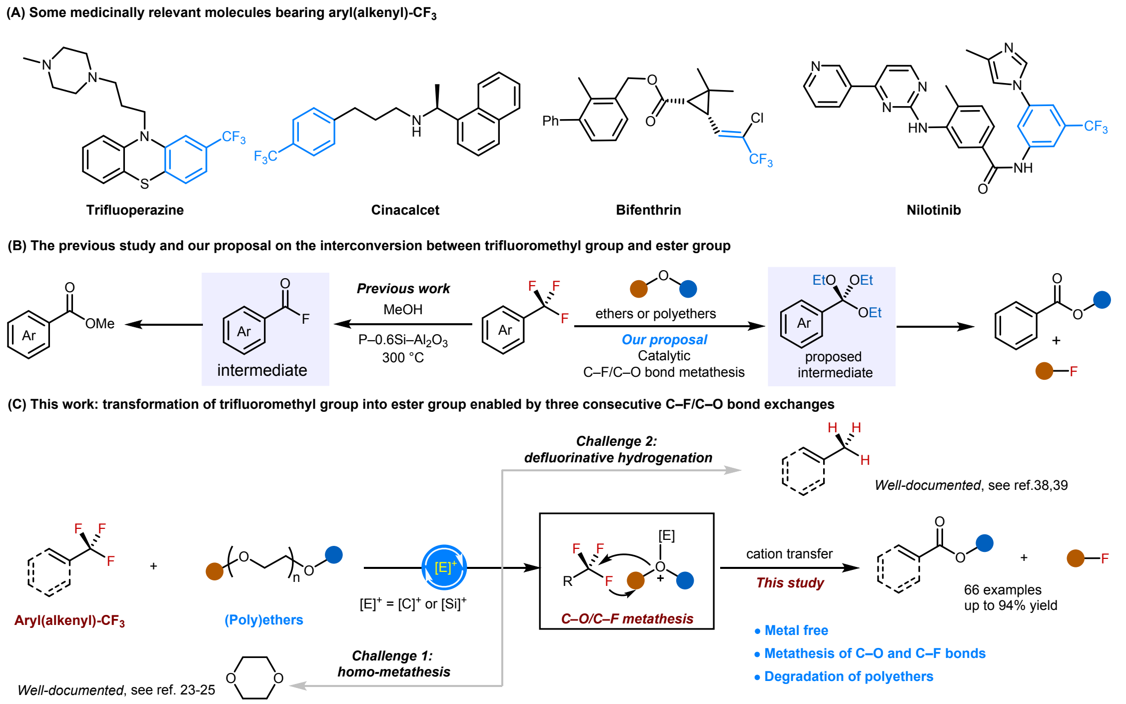
ethers or polyethers as the defluoroalkoxylation reagent (Scheme 1C). This C–F/C–O bond metathesis reaction is efficient and scalable, providing a catalytic means of transforming the aryl–CF_3 or alkenyl–CF_3 into aryl–COOR or alkenyl–COOR.

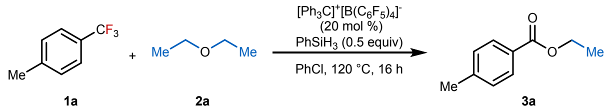


Scheme 1 The state of the art of this work: intermolecular C–O/C–F metathesis enabled by cation transfer.

Results and discussion

With these selectivity challenges of competing C–O homo-metathesis and hydrodefluorination in mind, we launched a reaction between (trifluoromethyl)toluene **1a** and diethyl ether **2a** in a weakly coordinating solvent, chlorobenzene (Table 1). We evaluated *in situ* generation of different silyliums ion by treating phenylsilane (0.5 equiv) with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (20 mol %) at room temperature for 15 minutes prior to substrate addition. Gratifyingly, the defluoroalkoxylation proceeded efficiently, affording ester product **3a** in 95% yield (GC-MS) after 16 hours at 120 °C, and no defluorohydrogenative product was observed (entry 1). This result supports our hypothesis that C–F/C–O bond exchange can occur. The decomposition of triethoxyalkyl intermediate was proposed to furnishe the ester product under strongly acidic condition. Reducing the $[Ph_3C]^+[B(C_6F_5)_4]^-$ initiator loading to 15 mol% led to a moderate yield (entry 2). Other Lewis acids, including directly use of $[Ph_3C]^+[B(C_6F_5)_4]^-$, as well as $AlCl_3$ and $B(C_6F_5)_3$, proved less effective, delivering lower yields between 16% and 83% (entries 3–5). In comparison, Et_3SiH and $MeSiHCl_2$ as the silicon source gave decreased yields of 33% and 19%, respectively (entries 6, 7). Alternative solvents, including toluene and dichlorobenzene, were also tested but did not outperform chlorobenzene (entries 8, 9). Finally, temperature optimization revealed that 120 °C is critical for high efficiency, as lowering temperature to 100 °C led to a decreased yield (entry 10).

Table 1 Reaction conditions optimization.[a]



1a + **2a** → **3a**

entry	deviation from standard conditions	Yield (%)[b]
1	**None**	**95 (89[c])**
2	$[Ph_3C]^+[B(C_6F_5)_4]^-$ 15 mol % instead of 20 mol %	70
3	$[Ph_3C]^+[B(C_6F_5)_4]^-$ 20 mol % without $PhSiH_3$	13
4	$AlCl_3$ (20 mol %)	7
5	$B(C_6F_5)_3$	83
6	Et_3SiH (0.5 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (20 mol%)	33
7	$MeSiHCl_2$ (0.5 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (20 mol%)	19
8	toluene instead of PhCl	62
9	1,2-dichlorobenzene instead of PhCl	81
10	100 °C instead of 120 °C	51

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mL), indicated initiator (15~20 mol %), PhCl, 120 °C, 16 h, Ar. [b] Yields were determined by GC-MS using naphthalene as internal standard. [c] Isolated yield.

Having established the feasibility of silylium-ion-initiated C–F/C–O metathesis, we next evaluated the substrate scope and limitations of this cation transfer protocol (Scheme 2). Substrates with methyl or alkoxy groups at different positions on the aromatic ring reacted well, delivering products in good to excellent yields (**1a**–**1f**), with minimal impact from steric hindrance. However, halogenated analogues showed reduced

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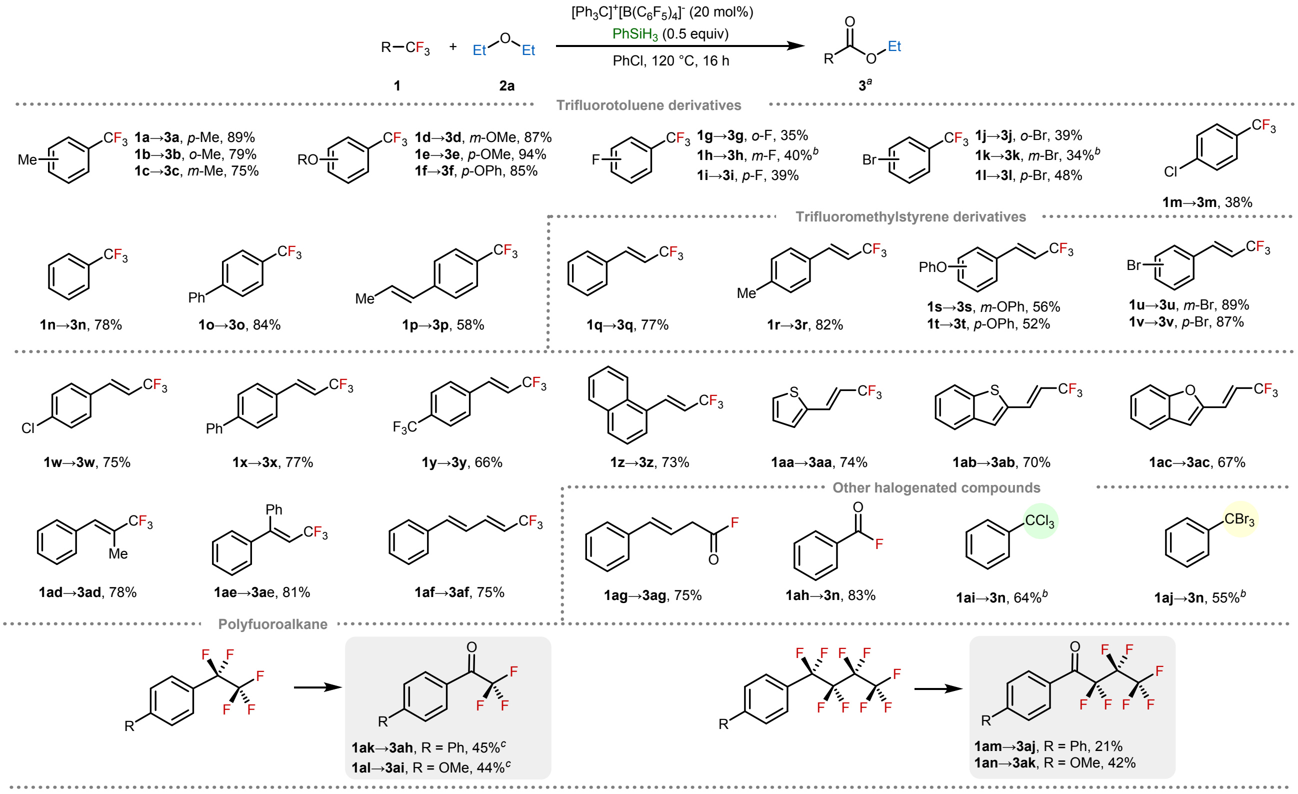
reactivity, affording only moderate yields. Meta-substituted halogenated substrates were particularly challenging and required an increased amount of silane (3.0 equiv) to achieve satisfactory conversion (**1g**-**1m**). Conjugated substituents, including phenyl and alkenyl groups, remained intact under the reaction conditions (**1o**, **1p**), highlighting the functional group tolerance of the protocol. Moreover, a range of trifluoromethylstyrenes derivatives bearing various substituents, including electron-donating groups (e.g., methyl), halogens (Cl, Br), phenyl, and naphthyl groups, were well tolerated, affording the corresponding ester products in good yields (**1q**–**1x, 1z**). Notably, when a *para*-trifluoromethyl group was introduced on the aromatic ring (**1y**), the reaction occurred selectively at the allylic position, leaving the benzylic C–F bonds untouched. Heteroaromatic substrates bearing electron-donating sulfur or oxygen atoms, such as thiophenyl, benzothiophenyl, and benzofuranyl derivatives, also underwent smooth transformation under these strongly Lewis acidic conditions (**1aa**–**1ac**). Importantly, no Friedel–Crafts alkylation or heteroarene degradation were observed. Additionally, alkene-substituted trifluoromethylstyrenes with 1- or 2-position substituents reacted efficiently to yield the desired esters (**1ad**–**1ae**), and a terminal CF_3-containing conjugated diene also delivered product in 75% yield (**1af**). The method also proved effective for acyl fluorides: both alkyl and aryl variants underwent smooth C–F/C–O metathesis to provide ester products in good yields (**1ag**, **1ah**). We further explored the compatibility of other carbon–halogen bonds. Trichlorotoluene and tribromotoluene produced the corresponding esters in moderate yields under the optimized conditions, suggesting partial extension of the reactivity beyond fluorinated substrates (**1ai**, **1aj**).

Given the environmental importance of addressing polyfluoroalkyl substances (PFAS), we explored the protocol's applicability to polyfluoroalkanes. Benzylic C–F bonds could be selectively activated, producing phenyl polyfluorinated ketones in moderate yields (**1ak**–**1an**). However, attempts to functionalize less activated C–F bonds in aliphatic polyfluoroalkanes were unsuccessful, even under elevated temperatures (140 °C) and prolonged reaction times (48 h).



Scheme 2 Scope of trifluoromethyl derivatives for intermolecular C–O and C–F metathesis. ^{a} Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mL), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (20 mol %), $PhSiH_3$ (0.1 mmol), PhCl (0.2 mL), 120 °C, 16 h, Ar. ^{b} $PhSiH_3$ (0.6 mmol) instead of $PhSiH_3$ (0.1 mmol). ^{c} PhMeSiHCl (0.6 mmol) instead of $PhSiH_3$ (0.1 mmol). See the SI for experimental details.

With the feasibility of C–F/C–O metathesis established, we next explored the scope of ethers as alkoxylation partners using trifluoromethylstyrene **1q** as the model substrate (Scheme 3). Symmetrical ethers bearing bulkier or longer alkyl chains, such as isopropyl, *n*-butyl, and *n*-octyl groups, performed well, delivering the corresponding esters in good yields (**2a**–**2d**). Notably, a bromo-substituted ether also proved compatible,[56] affording product **2e** without evidence of debromination. When asymmetric ethers were used, product distribution became more complex, raising the question of regioselectivity, specifically, which alkyl fragment acts as the fluoride acceptor and which is transferred into the ester product. Methylbutyl and methylhexyl ethers gave the desired products in 68% and 86% yield, respectively (**2f**, **2g**), with product ratios favoring incorporation of the longer alkyl group (short:long = 22:78 and 35:65). This suggests that steric

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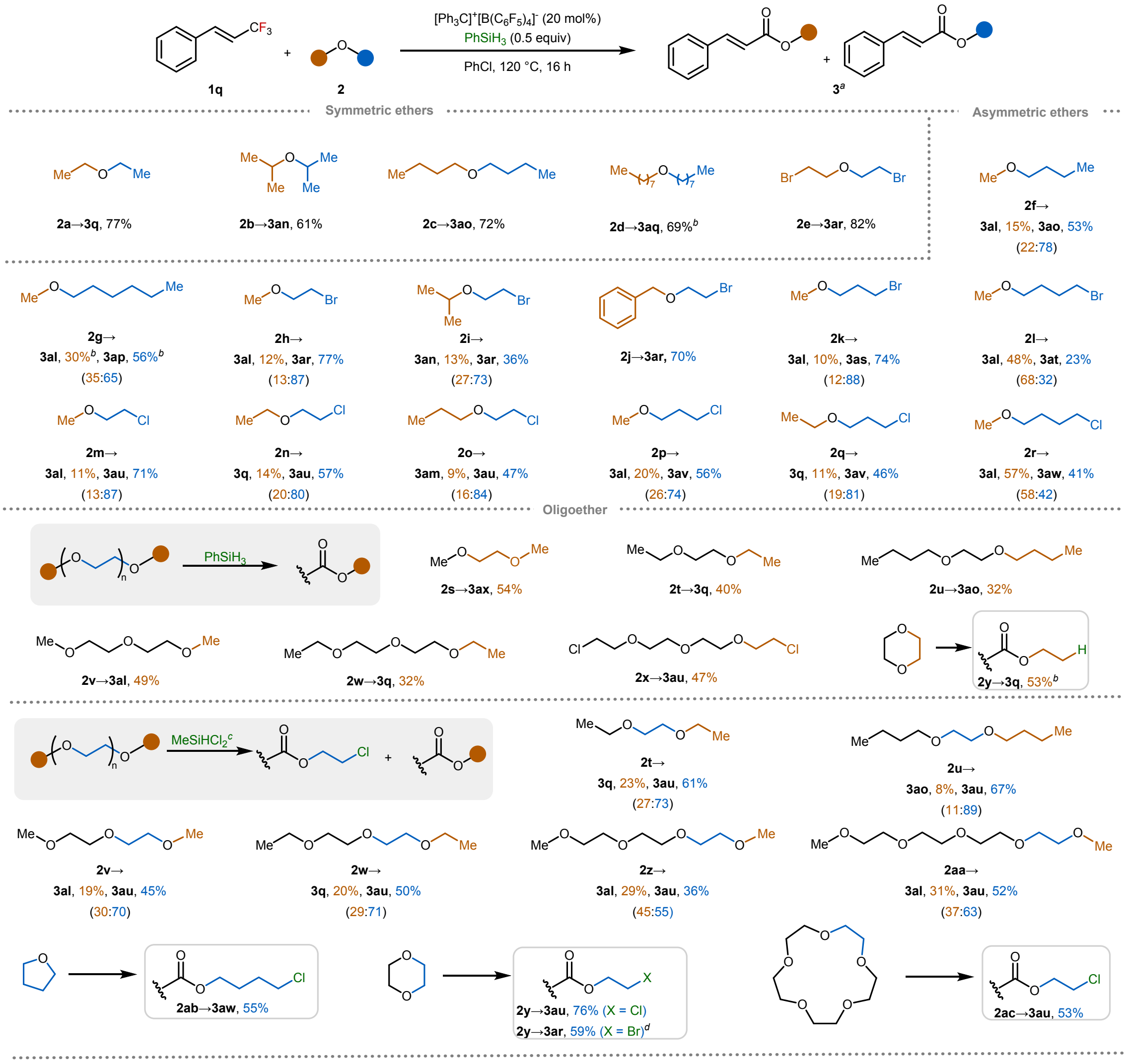
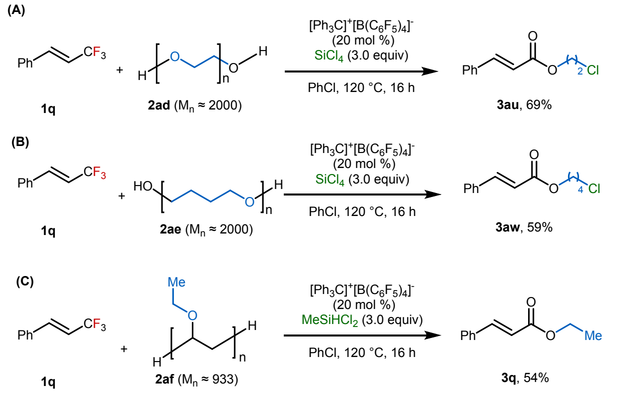
and/or electronic factors may bias the direction of alkyl transfer. To further investigate this trend, we examined bromoethyl ethers with various alkyl substituents. In these cases, smaller groups such as methyl, isopropyl, and benzyl were preferentially eliminated, while the bromoethoxy moiety was mainly retained in the product (**2h**–**2j**). A similar pattern was observed with methyl bromopropyl ether, where the bromopropyl group was selectively transferred to product (**2k**). These results support a mechanistic model in which the smaller, more volatile alkyl group is more readily abstracted as a fluoroalkane, while the bulkier fragment forms the ester. Interestingly, when the bromoalkyl chain was extended to four carbons, the regioselectivity reversed, with a higher proportion of the methyl-derived ester observed (Me:bromobutyl = 68:32, **2l**). This shift may result from increased steric hindrance of the longer alkyl chain during the defluoroalkoxylation step. Chloroalkyl ethers showed similar regioselectivity under the same conditions (**2m**–**2r**). In contrast, diaryl and arylalkyl ethers were unreactive under the optimized conditions.



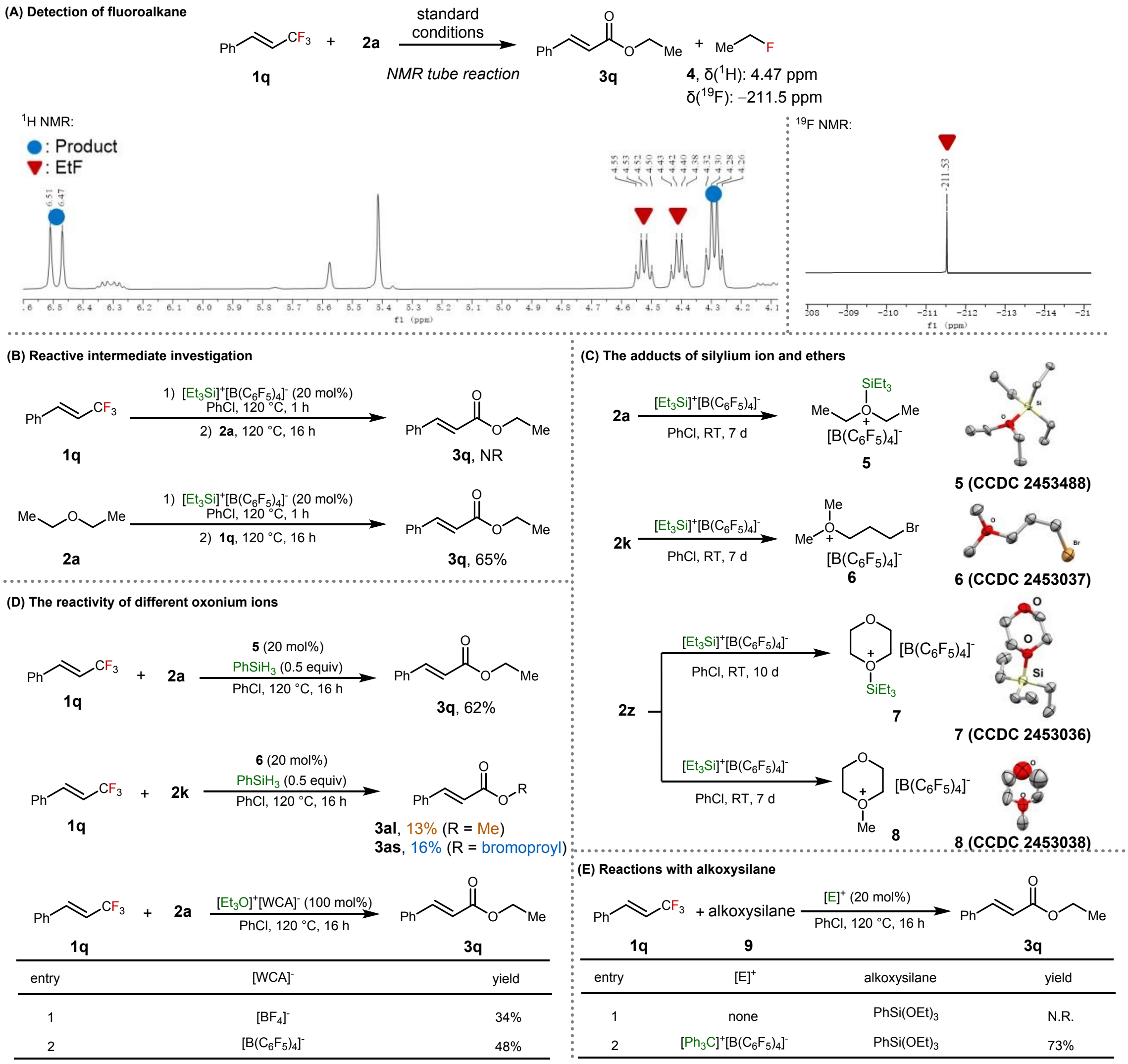
Scheme 3 Scope of ether derivatives for intermolecular C–O and C–F metathesis. ^{a} Reaction conditions: **1q** (0.2 mmol), ether **2** (0.4 mL), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (20 mol%), $PhSiH_3$ (0.1 mmol), PhCl (0.2 mL), 120 °C, 16 h, Ar. ^{b} $PhSiH_3$ (0.6 mmol) instead of $PhSiH_3$ (0.1 mmol). ^{c} $MeSiHCl_2$ (0.6 mmol) instead of $PhSiH_3$ (0.1 mmol). ^{d} Me_3SiBr (0.6 mmol) was used. See the SI for synthetic details.

We then turned to glycol, diglycol, and higher glycol ethers, which are common components in pharmaceuticals, cosmetics, and consumer products. Using phenylsilane as the silicon source, we observed a reversal of selectivity relative to dialkyl ethers: the terminal alkyl groups of the glycol ethers were selectively incorporated into the esters (**2s**–**2x**), albeit in moderate yields. When excess phenylsilane (3.0 equiv) was employed, it fulfilled two roles in the reaction system: generating the catalytically active silylium species and supplying protons to promote ring-opening of cyclic ether intermediates. Under these conditions, transfer of the ethylene linkage occurred efficiently, affording the ester product in 53% yield (**2y**). This result led us to hypothesize that product distribution might be influenced by the terminating anion. Indeed, when chlorosilanes were used instead of phenylsilane, mixed products derived from both chloroethyl and terminal alkyl fragments were observed. In these cases, the chloroethyl-derived products predominated (**2t**–**2aa**). A range of cyclic ethers, including tetrahydrofuran (THF), dioxane, and 15-crown-5, also proved reactive under chlorosilane-mediated conditions, yielding the corresponding chloroalkyl esters in good yields (**2ab**, **2y** and **2ac**). These findings highlight the broad substrate compatibility and functional group tolerance of the cation-transfer-enabled C–F/C–O metathesis.

Encouraged by the successful application of our protocol to oligoethers, we next investigated its utility in C–F/C–O metathesis involving polyethers. Specifically, we examined polyethylene glycol (PEG) and polytetrahydrofuran (polyTHF), each with a number-average molecular weight of ~2000 g/mol. Under reaction conditions using $[Ph_3C]^+[B(C_6F_5)_4]^-$ (20 mol%) and $SiCl_4$ (3.0 equiv), both polymers underwent decomposition, accompanied by activation of the C–F bond. This transformation afforded the corresponding chloroethyl ester products **3au** and **3aw** in reasonable yields (Scheme 4A and 4B). We further extended the protocol to poly(vinylethyl ether) (PEVE), a polymer featuring ethoxy side chains. When treated with $MeSiHCl_2$ (3.0 equiv) instead of $SiCl_4$, the reaction successfully transferred the ethoxy moiety to the ester product, yielding the desired compound in 54% yield (Scheme 4C). Given the ubiquitous use of polymers in modern materials and products, developing efficient strategies for their chemical recycling is of growing importance. These results demonstrate the potential of our cation-shuffle-enabled C–F/C–O metathesis to not only functionalize fluorinated compounds but also to contribute to polymer upcycling by transforming polyethers under mild conditions.



Scheme 4 Application of C–O/C–F metathesis in polyethers.



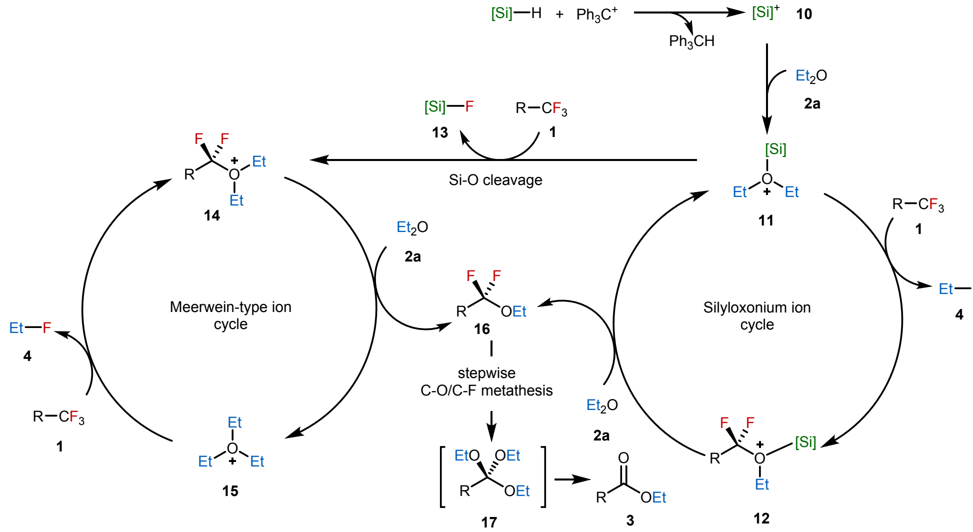
entry	[WCA]-	yield
1	$[BF_4]^-$	34%
2	$[B(C_6F_5)_4]^-$	48%

entry	[E]+	alkoxysilane	yield
1	none	$PhSi(OEt)_3$	N.R.
2	$[Ph_3C]^+[B(C_6F_5)_4]^-$	$PhSi(OEt)_3$	73%

Scheme 5 The mechanistic studies. (A) Detection of fluoroalkane by ^1H and ^{19}F NMR. (B) Reactive intermediate investigation. (C) The adduct of silicon cation and ethers. (D) The reactivity of different oxonium ions. (E) Reactions with alkoxysilane. For experimental details, please see SI.

To gain mechanistic insight into the cation-transfer-enabled C–F/C–O metathesis, we began by analyzing the reaction mixture of **1q** and **2a** using NMR spectroscopy. In the ^{1}H NMR spectrum, a diagnostic doublet of quartets at δ = 4.47 ppm with a $^{2}J(F,H)$ coupling constant of 47.1 Hz indicated the formation of CH_3CH_2F, which was further confirmed by a characteristic ^{19}F NMR signal at δ = –211.5 ppm (Scheme 5A).[57,58] Quantitative NMR analysis using an internal standard revealed that fluoroethane was formed in approximately 70% ration relative to the internal standard, indicating that fluoroalkane generation can be the dominant fate of fluoride (Figure S1). These results provided direct evidence of C–F bond cleavage and replacement by an alkoxy group. To clarify the sequence of bond activation, we conducted control experiments to determine whether the silylium ion preferentially engages with the C–F or C–O bond. When the reaction mixture was first treated with **1q** at 120 °C or room temperature, followed by addition of **2a** and heating, only a trace amount of ester product was observed, along with an allylic isomer detected by NMR (Scheme 5B, top and Figure S2). However, reversing the order, adding **1q** after pre-mixing the silylium ion with **2a**, resulted in a 65% yield of ester **3a** (Scheme 5B, bottom). This suggests that the silylium ion first coordinates with the ether oxygen rather than abstracting fluoride directly from the trifluoromethyl group, and the defluoroalkoxylation is likely to proceed *via* a concerted mechanism.

To support this hypothesis, we mixed stoichiometric amounts of $Et_3Si^+[B(C_6F_5)_4]^-$ and **2a** in chlorobenzene. The resulting silyloxonium ion **5** was successfully isolated and characterized (Scheme 5C). When the asymmetric ether **2k** was used instead, we obtained a crystal structure consistent with a Meerwein-type salt **6**, bearing two methyl groups and one bromopropyl moiety. To further explore silylium and ether coordination in the absence of C–F bonds, we treated triethylene glycol dimethyl ether (TEGDME) with the silylium reagent. This led to the formation of cyclic oxonium ions **7** and **8**, with a silyl and methyl substituent, respectively. These structures provide first crystallographic evidence for Lewis acid-catalyzed intramolecular C–O/C–O metathesis of aliphatic ethers, aligning with prior reports by Morandi and Greb. Single crystals of intermediates **5**–**8** were obtained *via* vapor diffusion from hexane at room temperature.[59] To verify the roles of oxonium ions as mechanistic intermediates, we directly applied silyloxonium ion **5** and Meerwein-type salt **6** in catalytic reactions between **1q** and their corresponding ethers (**2a** and **2k**). The reaction involving **5** gave the ester product in yields comparable to those under standard conditions, while **6** produced a mixture of ester products in diminished yield (Scheme 5D), Furthermore, when the reaction was conducted using stoichiometric Meerwein-type salts $Et_3O^+BF_4^-$ and $Et_3O^+[B(C_6F_5)_4]^-$ in the absence of silane, both the ester product and fluoroethane were detected, confirming that fluorine transfer from carbon to carbon is operative (Scheme 3D, bottom and Figure S3). To the best of our knowledge, this mode of reactivity is unprecedented and offers a new mechanistic paradigm for C–F functionalization. Moreover, these results suggest that both oxonium species are catalytically relevant, but the silyloxonium ion is likely the more reactive and effective intermediate for alkyl group transfer. the reaction of **1a** with an alkoxysilane (**9**) proceeded smoothly in the presence of a catalytic amount of trityl cation, further confirming the participation of silyloxonium species in the reaction mechanism (Scheme 5E). Finally, when (triethoxymethyl)benzene was subjected to the standard reaction conditions, the corresponding ester product was obtained in 89% yield, supporting its role as a intermediate in the catalytic cycle (for details, see the SI).[60]



Scheme 6 Proposed mechanism of cation-transfer-enabled C–F/C–O metathesis. Counter anion was omitted for clarity.

Based on our experimental findings, we propose that the formation of oxonium intermediates and subsequent ligand exchange processes are keys to the success of the cation-transfer-enabled C–F/C–O metathesis. The proposed catalytic cycle is depicted in Scheme 6. The reaction is initiated by hydride abstraction from a hydrosilane by a trityl salt, generating a highly electrophilic silylium ion **10**. This species coordinates with an ether to form a silyloxonium ion **11**, which serves as a central intermediate in the catalytic cycle. In the catalytic cycle at right side, the fluoride on **1** was abstracted by a cationic alkyl group on **11**, along with a formation of fluoroalkane **4**. Simultaneously, RCF_2^+ transferred to oxygen atom resulting in the formation of a new silyloxonium species **12**. The silicon cation then jumped to another ether molecule with the formation of alkoxylation intermediate **16**, completing the C–F/C–O metathesis and regenerating the catalytic intermediate, silyloxonium ion. Alternatively, the silyl group may act as the fluoride acceptor, forming a Meerwein-type intermediate **14** containing three alkyl substituents. This species can participate in alkyl cation transfer, producing a new Meerwein-type salt **15** attached with the substrate moiety and simultaneously facilitating alkoxylation of the C–F bond to continue the catalytic cycle. Notably, the key compound **16** arising from either of these mechanistic routes, could undergo a sequential C–O/C–F bond exchange, followed by elimination to furnish the final ester product **3**.

Conclusions

In this study, we have developed a silylium ion-initiated method for the C–F/C–O metathesis of trifluoromethyl group and ethers, providing a versatile and efficient approach to activate and transform otherwise inert C–F and C–O bonds. The ability to selectively exchange these bonds under mild conditions offers significant potential for resource utilization and environmental sustainability, particularly in the context of polyfluoroalkyl substances and biomass derived polyethers. Mechanistic investigations confirm the involvement of key intermediates, such as silyloxonium ions and Meerwein-type salts, which play crucial roles in the transformation. These findings open new avenues for further exploration of cation shuffle catalysis in organic synthesis, offering a promising strategy for the selective activation and transformation of stable chemical bonds in both synthetic and environmental contexts.

Author contributions

Z. L., D. Z. and X. S. performed the experiments. Q. W. conceived the concept, directed the project and wrote the paper.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available in the supplementary information (SI) of this article. Supplementary information: experimental procedures, single-crystal X-ray data, NMR and HRMS spectra. See DOI: 10.1039/x0xx00000x.

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59 CCDC deposition numbers 2453488, 2453037, 2453036 and 2453038 (for **5**, **6**, **7** and **8**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
60 Ketal intermediates were observed in the reaction of polyfluoroalkyl substances (**1ak**-**1an**) by the GC-MS detection, suggesting a sequential C–O/C–F metathesis in the reaction process.

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Conversion of trifluoromethyl into ester along with polyethers upcycling by cation-transfer catalyzed C–O/C–F metathesis

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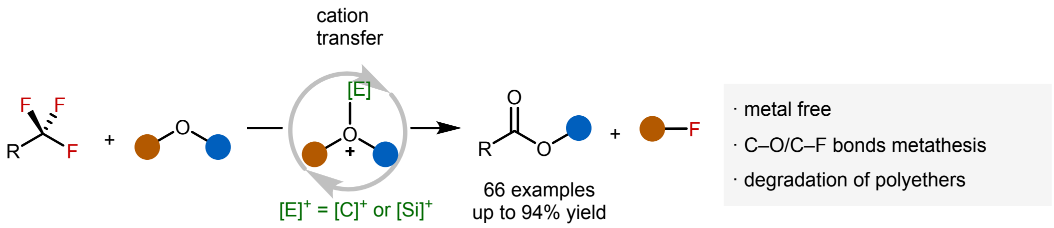

Herein report a silylium ion-catalyzed method for the metathesis of inert C–F and C–O bonds in trifluoromethyl groups and ethers. This versatile protocol shows broad functional group tolerance, with applications to polyethers and polyfluoroalkanes. Mechanistic studies identify silyloxonium ions and Meerwein-type salts as key intermediates in the transformation. These findings highlight the potential of cation shuffle catalysis for both organic synthesis and environmental applications.

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The data that support the findings of this study are available in the supplementary information (SI) of this article. Supplementary information: experimental procedures, single-crystal X-ray data, NMR and HRMS spectra. See DOI: 10.1039/x0xx00000x.