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Hydrofluoroether Synthesis through One-Pot Anodic Iodoalkoxylation of Alkenes

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Abstract: The incorporation of carbon-fluorine bonds can profoundly influence the chemical and physical properties of drugs, agrochemicals, and materials. Different methods allow the installation of CF_3, CF_2H units and C–F bonds including trifluoro- and difluoromethoxylations, reflecting the limited diversity of reactions available to synthetic chemists. We introduce the 2,2,2-trifluoroethoxy group through an electro-oxidative iodination of alkenes as a versatile substituent for fluorine chemists. An iodoarene serves as an unusual iodine source facilitating the 1,2-iodoalkoxylation of a broad range of industrially relevant aliphatic alkenes in high yields (31–98%) showing high Markovnikov regioselectivity.

Fluorinated organic compounds are well known to possess enhanced lipophilicity and metabolic stability compared to their non-fluorinated analogues.[1,2] Presently, about 20% of commercial drugs contain fluorine atoms, bearing mostly aryl fluorine bonds among other fluorinated structures.[3,4] About 16% of currently used agrochemicals exhibit fluorinated moieties. The high prevalence of fluorinated substructures such as arylfluorides or trifluoromethyl moieties reflects the limited availability of efficient synthetic routes to access other fluorinated substructures. It does not necessarily indicate that such substituents are more likely to produce more beneficial characteristics than other fluorinated functional groups.[3] Hydrofluoroethers are under-explored fluorinated fragments that have recently attracted much attention due to their weak solvation ability and high hydrophobicity. They are promising targets in the design of improved lithium metal batteries.[5,6] Thus, sustainable and easy routes to access such targets is highly desirable.

Iodinated organic molecules have been extensively used in areas of applied chemistry such as catalysis,[7,8,9] agrochemicals[10] and pharmaceuticals.[11,12] Additionally, iodine substituents can be exchanged through nucleophilic substitution or cross-coupling reactions,[13,14,15] making them valuable intermediates for further modification.[16,17] The synthesis of β-iodoethers from alkenes typically follows three strategies: (i) using a chemical oxidant or reductant with an iodine source such as $NaIO_4$ or I_2;[18,19,20,21,22] (ii) using a stoichiometric electrophilic iodine reagent such as *N*-iodosuccinimide,[23,24,25] *N*-iodosaccharin,[26] or triiodoisocyanuric acid;[27] and (iii) using an electrochemical redox reaction with an iodide source such as NH_4I or *n*-Bu_4NI.[16,17] These methods can form fluorinated β-iodoethers only from activated alkenes such as styrene derivatives or heteroaryl-alkenes, and they cannot be readily translated to unactivated alkenes.[25,28,29] Thus, a widely applicable methodology for the synthesis of β-iodoethers remains elusive, despite such motifs found in drug molecules and bioactive compounds such as lensoprazole, flecainide and silodosin[30] as the trifluoroethoxy group increases lipophilicity and metabolic stability[31] (Figure 1).

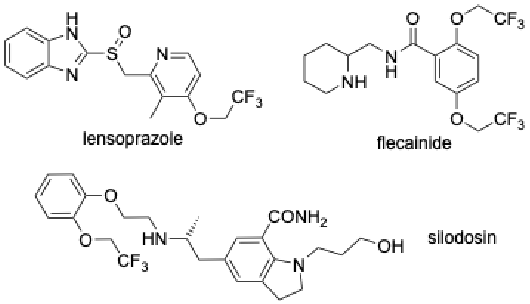


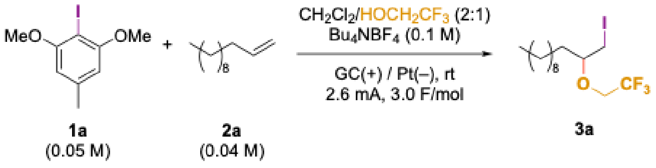
Figure 1. Examples of drugs with trifluoroethoxy moieties.

Herein, we report the electrochemical synthesis of β-iodo(2,2,2-trifluoroethoxy) ethers by oxidative addition of trifluoroethanol to alkenes. The reaction is regioselective, enabling the functionalization of feedstock alkenes that could be used as building blocks to produce complex fluorinated structures. The iodine is obtained from 2-iodo-1,3-dimethoxy-5-methylbenzene, representing an unusual source of iodine.

To evaluate the reaction, we subjected a mixture of 2-iodo-1,3-dimethoxy-5-methylbenzene **1a**, 1-dodecene **2a** and Bu_4NBF_4 as electrolyte in a solvent mixture of 2,2,2-trifluoroethanol (TFE) and dichloromethane (1:2 v/v) to a current of 2.6 mA (2.0 mA/cm^2)

using a glassy carbon (GC) anode and a platinum (Pt) cathode until a total charge of 3.0 F/mol has passed (Table 1). A modest yield of 62% was observed, along with a thin orange layer of passivation products over the anode (Table 1, entry 1). Replacing the anode material by stainless steel (SS) or Pt resulted in a diminished yield of 51% and 31%, respectively (Entries 2 and 3). A systematic study of the electrolyte shows increased yields with BF_4^- as the counteranion, Bu_4NBF_4 led to the best performance (Entries 4–7).

Table 1. Optimisation of the electrochemical 1,2-iodoalkoxylation of alkenes.[a]



Entry	Deviation from reaction conditions[a]	**3a** Yield [%][b]
1	-	62
2	SS anode	51
3	Pt anode	31
4	Bu_4NClO_4 instead of Bu_4NBF_4	54
5	Bu_4NPF_6 instead of Bu_4NBF_4	38
6	Et_4NBF_4 instead of Bu_4NBF_4	56
7	Me_4NBF_4 instead of Bu_4NBF_4	51
8	4.0 F/mol instead of 3.0 F/mol	62 (57)
9	6.8 mA, 4.0 F/mol[c]	63
10	6.8 mA, 4.0 F/mol, 2 min of sonication every 0.5 F/mol[c]	83
11	6.8 mA, 4.0 F/mol[c,d,e]	84
12	13.6 mA, 4.0 F/mol[c,d]	83
13	27.2 mA, 4.0 F/mol[c,d]	58
14	13.6 mA, 3.0 F/mol[c,d]	79
15	13.6 mA, 2.0 F/mol[c,d]	83
16	13.6 mA, 1.0 F/mol[c,d]	45
17	13.6 mA, 2.0 F/mol, 0.04 M of **1a**[c,d]	57
18	13.6 mA, 2.0 F/mol, 0.05 M of Bu_4NBF_4[c,d]	71
19	13.6 mA, 2.0 F/mol, 6 °C[c,d]	79
20	13.6 mA, 2.0 F/mol, 15 °C[c,d]	85
21	13.6 mA, 2.0 F/mol, 25 °C[c,d]	69
22	15 °C, no electricity[c,d,e]	<1
23	13.6 mA, 3.0 F/mol, 15 °C[c,d,e]	82 (71)

[a] 0.15 mmol of **1a** (1 equiv.), 0.12 mmol of **2a**, electrode surface = 1.3 cm^2. [b] ^{19}F NMR yields calculated vs. 4-fluorotoluene (internal standard), isolated yield in parentheses. [c] 5 ml of solvent mixture, electrode surface = 2.72 cm^2. [d] continuous sonication. [e] 0.5 mmol of **1a** and 0.4 mmol of **2a**.

Increasing the applied charge to 4.0 F/mol did not change the yield (Entry 8). Since the passivation on the anode was persistent, the alkene concentration was evaluated, but alkene polymerization leading to passivation could be excluded (see supporting information, Figure S1). The available surface of the electrode is a critical factor for the completion of the reaction. An increased electrode surface / decreased concentration of alkene facilitated increased yields and allowed a scale up of the process (Entry 9). The introduction of sonication provided a further rise in yield to 84% (Entries 10 and 11). Enhancing mass transfer through sonication on electrode surfaces has already been investigated by Kuhn *et al*.[32] Employing sonication and higher currents of 13.6 mA / 27.2 mA resulted in yields of 83% and 58%, respectively, together with a significant reduction in reaction time (Entries 12 and 13). Different applied charges were investigated, obtaining an 83% yield with 2.0 F/mol, thus increasing the efficiency and reducing the duration of the process (Entries 14–16). Sonication also granted uninterrupted 'cleaning' of the electrode surface, whereby any deposited material was dislodged from the surface. This is essential given the heterogenous aspect of electrochemical reactions and a key point for scale up prospects. Using 0.04 M of **1a** lowered the yield to 57% (Entry 17). Halving the electrolyte concentration slightly reduces the yield to 71% (Entry 18). Due to the inherent warming of the sonication bath, controlled temperature experiments were conducted where 15 °C was optimal with a yield of 85% (Entries 19–21). An experiment without electricity demonstrated its necessity in this method as less than 1% of the product was obtained (Entry 22). Since the optimization was performed at the 0.2 mmol of alkene scale (0.04 M), we evaluated the applied charge needed for the 0.4 mmol scale (0.08 M), indicating that 3.0 F/mol led to complete consumption of the starting material, attaining the optimized conditions (entry 23). The effect of different iodoarenes was evaluated using iodobenzene, 4-iodotoluene, 2-iodoanisole, and 2-iodo-1,3-dimethoxybenzene instead of **1a** affording product yields of <5%, 7%, 21%, and 58%, respectively. This indicates that **1a** is superior in the target transformation than less electron-rich and less activated iodoarenes. Additionally, it was confirmed that the product is stable under electrolysis conditions (see supporting information, Figure S4).

With the optimized conditions in hand (Table 1, entry 23), the methodology was applied to a wide range of aliphatic and aromatic alkenes (Figure 1A). Linear alkenes afforded good yields (up to 74%) and an excellent regioisomeric ratio between 12:1 and 25:1 (**3a**–**3d**). Cyclohexene-derived products **3e** and **3f** are formed in only 38% and 59% yield with the reduced yield due to their volatility. The procedure tolerates functional groups such as halogen, phthalimide, and hydroxyl protecting groups based on silicon, with yields up to 82% (**3g**–**3i**). Derivatives of 3-bromostyrene and 4-(trifluoromethyl)-styrene proved challenging to isolate due to their volatility, affording products **3j** and **3k** in isolated yields of only 31% and 42%, respectively.

Allylarenes provided products **3l** and **3m** with excellent yields up to 98% albeit with lower regioselectivities. Alkenes such as vinylcyclohexane susceptible to carbocation rearrangement afforded regioisomeric mixtures with a combined yield of 84%.

Norbornene products **3o** were isolated and characterized with a combined yield of 45%, providing further information on the

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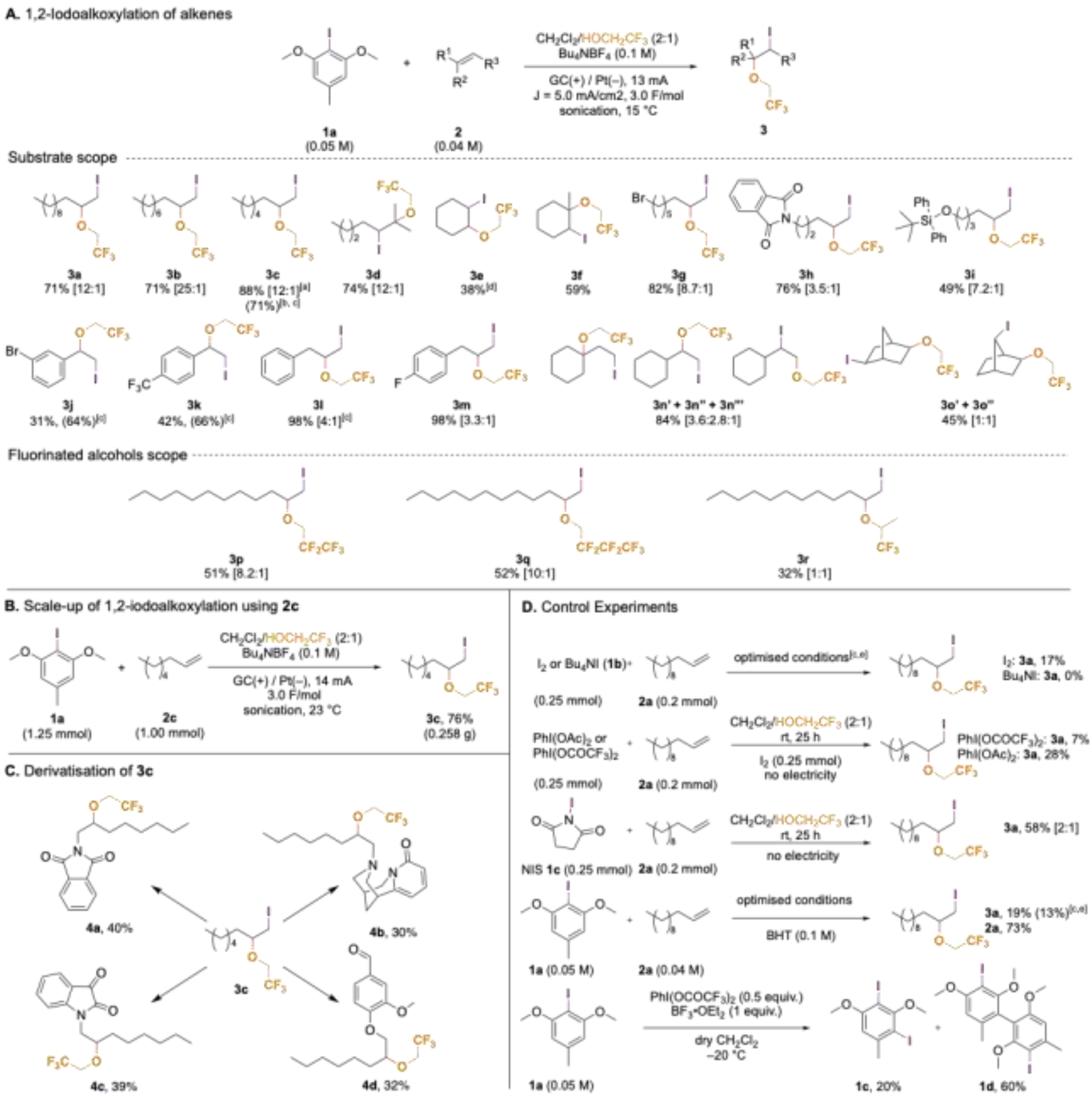

Figure 2. A) Scope of 1,2-iodoalkoxylation of alkenes. **B)** Scale-up of 1,2-iodoalkoxylation of **2c**. **C)** Derivatisation of **3c**. **D)** Control experiments. Isolated yields are shown. Calculated ^{19}F NMR and ^{1}H NMR yields are given in parentheses. Regioisomeric ratios are given in brackets. [a] Reaction performed with an electrode distance of 2 mm. [b] Reaction perform ed with an electrode distance of 5 mm. [c] Reaction was performed on a 0.2 mmol scale (alkene). [d] Reaction was performed on a 0.12 mmol scale (alkene). [e] Reaction was performed without sonication.

reaction mechanism. The methodology was, however, inapplicable to electron rich aromatic compounds due to their propensity to undergo anodic oxidation in preference to the iodine donor **1a**. Likewise, redox sensitive substituents, such as free hydroxyl groups, are not tolerated (see supporting information). The reaction with other fluorinated alcohols instead of TFE was also explored as a recent publication used 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as a nucleophile in an iodine(III) mediated reaction.[33] 2,2,3,3,3-Pentafluoro-1-propanol (PFP) and 2,2,3,3,4,4,4-heptafluoro-1-butanol (HFB) provided the corresponding products **3p** and **3q** with moderate yields of 51% and 52%, respectively, maintaining favorable regioselectivity for Markovnikov products. Reaction with 1,1,1-trifluoro-2-propanol delivered the diastereomers of the Markovnikov-type product **3r** in a lower yield of 32%. With 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as fluorinated alcohol It was impossible to isolate the corresponding hydrofluoroether.

A decrease of the distance between the electrodes from 5 mm to 2 mm increased the yield of compound **3c** from 71% to 88% (Figure 1A). To further illustrate the synthetic utility, a scale-up experiment using **1a** (1.25 mmol) and 1-octene (1.0 mmol) provided the 1,2-iodoalkoxylated product **3c** in 76% isolated yield (0.258 g) after 10 h (Figure 1B). To show the potential for further applications, **3c** was used as an alkylating agent (Figure 1C) to afford the products **4** in typically moderate yields without further

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optimisation. Meanwhile, the trifluoroethoxy group is robust and not prone to nucleophilic substitution.

Products **3f**, **3n', 3o'** and **3o''** (Figure 1A) suggest the presence of carbocationic intermediates, which could originate from an iodonium ion. Moreover, the regioselectivity for iodide and trifluoroethanol addition is consistent with Markonikov's rule for electrophilic addition to alkenes. Further control experiments were conducted to obtain insights into the mechanism of this reaction (Figure 1D). To investigate the formation of an iodonium intermediate, different iodine sources were tested. A reaction with iodine instead of **1a** delivered **3a** with a yield of 17%. Replacing **1a** with tetrabutyl-ammonium iodide **1b** did not lead to the formation of **3a**, negating a possible direct oxidation of iodide. Chemical oxidation of iodine was previously reported using [bis(trifluoroacetoxy)iodo]benzene or (diacetoxyiodo)benzene as oxidants.[34] Reactions without electricity afforded the product **3a** with diminished yields of 7% and 28%, respectively. *N*-Iodosuccinimide (NIS, **1c**) was also used as a source of I^+ instead of **1a,** providing compound **3a** in 58% yield together with a significant drop in regioselectivity (2:1). Addition of the radical trap BHT (2,6-di-*tert*-butyl-4-methylphenol) resulted in a considerable drop in yield of **3a** to 19% (73% recovered **2a**). The cyclic voltammogram of **1a** showed two successive oxidative waves, while no oxidation or reduction of **2a** was observed (see supporting information, Figure S2). An SET oxidation of iodoarenes was proposed by Kita[35] and later by Waldvogel[36] and Powers.[37,38] A reaction with **1a**, [bis(trifluoroacetoxy)iodo]benzene and $BF_3•OEt_2$ resulted in the formation of diiodinated compounds **1c** and **1d**[39] with isolated yields of 20% and 60%, respectively, suggesting the presence of radical inter-mediates due to the oxidation of **1a**. The release of iodine from iodobenzene under high current density electrolysis has also been observed previously.[40]

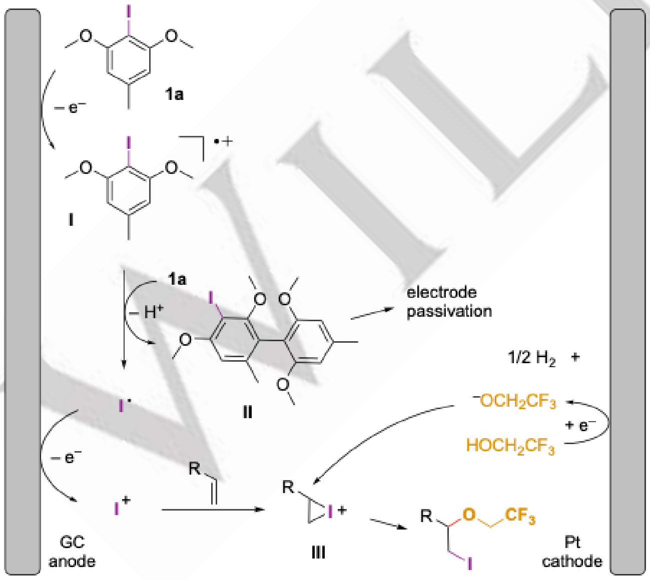

Figure 3. Proposed reaction mechanism. GC: glassy carbon

Based on the above results and previous studies,[35,37] a plausible mechanism is proposed for the 1,2-iodooxygenation (Figure 3). Initially, iodoarene **1a** is oxidised to the radical cationic species **I**, which couples with another molecule of **1a** in bulk, delivering a free iodine atom and another iodoarene-type compound **II**, which is susceptible to further oxidation as compound **1a**, and is presumed to be responsible for the passivation. The iodine radical is oxidised to I^+, forming the iodonium ion **III** with the alkene. Nucleophilic substitution of **III** with the alkoxide $CF_3CH_2O^-$ generated together with hydrogen at the cathode provides the target compound. The electrogenerated base has much higher nucleophilicity that trifluoroethanol accelerating the reaction compared to a non-electrochemical protocol. An intense green colour was seen at the beginning of the reaction, gradually changing to dark orange, which could account for the radical cationic intermediate **I** and its subsequent passivation, while hydrogen bubbling was observed during the entire process (see supporting information, Figure S4B).

In summary, using an unusual iodine source and a hydrogen evolution reaction, we have developed an electrochemical synthesis of ß-iodohydrofluoroethers from different alkenes in yields ranging from 31–98%. This strategy allows the access towards valuable fluorine-containing iodinated building blocks in one step. Furthermore, no chemical oxidants, harsh reaction conditions, inert atmosphere or metal catalysts had to be used. The products can be used as alkylating reagents, showing their potential as building blocks in synthesis.

Experimental Section

General procedure for the synthesis of 3

The electrolysis was performed in a 5 mL undivided cell using an IKA Electrasyn 2.0 equipped with glassy carbon (GC) anode and platinum (Pt) cathode (submerged surface area 2.72 cm^2). A solution of the corresponding alkene **2** (0.4 mmol, 0.8 equiv.), 2-iodo-1,3-dimethoxy-5-methylbenzene (**1a**, 139 mg, 0.5 mmol, 1.0 equiv.) and Bu_4NBF_4 (165 mg, 0.5 mmol, 0.1 M) in a mixture of CH_2Cl_2/TFE (2:1 v/v, 5mL) was electrolyzed at a constant current of 13.6 mA ($J = 5.0$ mA/cm^2) under continuous sonication until 3.0 F/mol was applied. The sonicator bath was kept at 15 °C by adding small portions of ice. After the electrolysis, the solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel using the indicated solvent mixture (see supporting information).

General procedure for the synthesis of 4

A solution of 1-iodo-2-(2,2,2-trifluoroethoxy)octane (**3c**, 57 mg, 0.169 mmol, 1.0 equiv.), the corresponding substrate (0.169 mmol, 1.0 equiv.), and K_2CO_3 (58 mg, 0.423 mmol, 2.5 equiv.) in dimethylformamide (1 mL) was stirred at room temperature. After the complete consumption of **3c**, 10 ml of distilled water was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$, filtrated, and dried in vacuo. The crude product was purified by column chromatography on silica gel using the indicated mixture of solvents (see supporting information).

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Keywords: electrochemistry • hydrofluoroethers • hypervalent iodine • iodination • 2,2,2-trifluoroethoxy

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