

Fluorine Chemistry

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The intrinsic properties of the fluorine atom endow it with a pivotal role in chemistry. Fluorinated organic molecules are central in medicinal chemistry and agrochemical science and polymer science, while inorganic fluorinated species play an equally important role, particularly in materials science and energy-related fields. The profound impact of fluorine on molecular structure and reactivity necessitates specialized synthetic strategies and expertise, fostering the emergence of fluorine chemistry as a distinct discipline. It is therefore not surprising that fluorine chemistry has attracted sustained and widespread interest from a large segment of the scientific community for several decades.

We are delighted to introduce this special issue dedicated to "Fluorine Chemistry", which brings together recent advances, spanning polymer synthesis, new methods for the synthesis of fluorinated molecules, asymmetric catalysis, organometallic chemistry and polyhalogenated molecules. Collectively, the contributions offer a representative overview of current trends and emerging directions in fluorine chemistry.

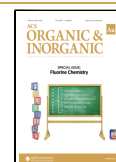
Fluoropolymers are of prime importance, in this context Ameduri and Copaert reported the synthesis of new fluorinated materials, bearing a boronic or boronate residue (DOI: [10.1021/acsorginorgau.5c00030](https://doi.org/10.1021/acsorginorgau.5c00030)). These materials exhibited improved thermal stability and open avenues for applications, including electronics and coatings. Riedel et al. disclosed in their article the preparation of nonclassical interhalogen compounds, with a central m_6 fluoride anion, i.e. $[\text{NEt}_4][\text{F}(\text{Br})_3]$ and $[\text{NEt}_4][\text{F}(\text{Cl})_3]$ (DOI: [10.1021/acsorginorgau.5c00064](https://doi.org/10.1021/acsorginorgau.5c00064)). The authors fully characterized the structures of these new intriguing compounds. In another article, Fredin, Vicić et al. showcased how organometallic chemistry is crucial in the fluorine chemistry field (DOI: [10.1021/acsorginorgau.5c00071](https://doi.org/10.1021/acsorginorgau.5c00071)). In this article, the authors showcased how Ir-pincer complexes can activate otherwise poorly reactive hydrofluorocarbon refrigerants. This work provides a basis for the repurposing of critical HFC with high global warming potential.

Several contributions in this issue focus on new methods for the construction of fluorinated molecules. El-Sepelgy and co-workers disclosed an interesting method for the decarboxylative fluorination of carboxylic acid (DOI: [10.1021/acsorginorgau.5c00024](https://doi.org/10.1021/acsorginorgau.5c00024)). This report combined a modern approach, namely ligand-to-metal charge transfer (LMCT), using cerium trichloride to synthesize fluorinated molecules. Besset, Mancheno and a co-worker reported the electrophilic trifluoromethylation of silyl enol ether catalyzed by NaBAR^f (DOI: [10.1021/acsorginorgau.5c00034](https://doi.org/10.1021/acsorginorgau.5c00034)). This trifluoromethy-

lation method highlights the role of $\text{Bar}^f_{24}^-$ anion to form a highly reactive species with the Umemoto's reagent, enabling the trifluoromethylation of silyl enol ethers. Grygorenko and co-workers describe a deoxyfluorination approach to access monofluorinated aryl- and alkenylboronates, providing a practical entry to fluorinated organoboron building blocks of interest for medicinal chemistry (DOI: [10.1021/acsorginorgau.5c00112](https://doi.org/10.1021/acsorginorgau.5c00112)). Dembinski reported the synthesis of original fluorinated benzodiazepines of interest, through the reaction of 2-fluoro-alk-3-ynones with ortho phenylenediamines. The reaction mechanism was studied by DFT calculations, and conformational analysis of the products was carried out (DOI: [10.1021/acsorginorgau.5c00116](https://doi.org/10.1021/acsorginorgau.5c00116)). In another contribution, Hoffman-Röder reported the synthesis of 6 fluorinated analogs of the known *Streptococcus pneumoniae* Type 14 glycotope. The authors' strategy relies on the synthesis of various fluorinated monosaccharide building blocks, followed by their assembly to tetrasaccharide; this report illustrates the rich chemistry of fluorinated glycosides (DOI: [10.1021/acsorginorgau.5c00108](https://doi.org/10.1021/acsorginorgau.5c00108)).

Given the importance of chirality in fluorinated molecules, asymmetric catalysis is also featured in this Special Issue. Akiyama and co-workers reported the catalytic enantioselective synthesis of b-trifluoromethyl nitro alkanes using a chiral calcium phosphate catalyst (DOI: [10.1021/acsorginorgau.5c00039](https://doi.org/10.1021/acsorginorgau.5c00039)). This reaction, using Hantzsch esters as a hydride source, allowed access to a large panel of structurally diverse enantioenriched b-trifluoromethyl nitro alkanes with excellent enantioselectivities. In the same vein, Paquin and co-workers reported the catalytic enantioselective reduction of b-trifluoromethyl and b-pentafluorosulfanyl ketones, to access chiral alcohols (DOI: [10.1021/acsorginorgau.5c00038](https://doi.org/10.1021/acsorginorgau.5c00038)). This transfer hydrogenation strategy focused not only on the usual trifluoromethyl group but also on the emergent pentafluorosulfanyl one, a non PFAS alternative to the latter. In another article, Crousse and co-workers reported the access to N-fluorinated azapeptoids (DOI: [10.1021/acsorginorgau.5c00073](https://doi.org/10.1021/acsorginorgau.5c00073)). In addition, beyond the synthesis of these

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novel azapeptoids, the authors synthesized polypeptides and studied their conformations.

The contributions collected in this issue highlight the recent advances and emerging trends in Fluorine Chemistry, encompassing the development of synthetic methods, organo-metallic chemistry, polymer science and inorganic chemistry. Collectively, these contributions reflect the breadth and vitality of this active research area. We warmly thank each of the researchers who contributed to this exciting issue, as well as all the reviewers for their thoughtful and constructive feedback. We trust that readers will find this issue both informative and stimulating.

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<https://pubs.acs.org/10.1021/acsorginorgau.6c00022>

Notes

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