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cis-Specific cyanofluorination of vinyl azides enabled by electron-donor-acceptor complexes: synthesis of α-azido-β-fluoronitriles

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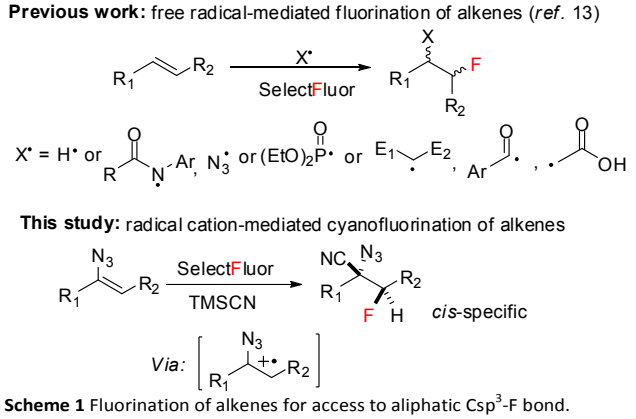
Shu-Wei Wu,[a] Jia-Li Liu[a] and Feng Liu*[a,b]

Here we report a novel electron-donor-acceptor (EDA) complex-enabled three-component cyanofluorination of vinyl azides under metal-free conditions in a *cis*-specific manner. This reaction protocol is operationally simple without exclusion of either moisture or oxygen, allowing to access a wide range of highly-functionalized α-azido-β-fluoronitriles that bearing quaternary carbons are difficult to be obtained by existing methods.

The electron-donor-acceptor (EDA) complex-enabled organic synthesis is a mild and sustainable approach, emerging as a valuable platform for access to a range of products from relatively simple feedstocks under transition-metal-free conditions.[1] Although the physicochemical properties of EDA complexes have been extensively studied since the 1950s,[2] their use in synthetic chemistry remains underexplored.[1] Recently, synthetic achievements involving EDA complexes[3] include, for instance, radical perfluoroalkylation,[3a-d] asymmetric alkylation,[3e-g] intramolecular cyclization,[3h] and biaryl coupling.[3i-j] For the continued advancement of this field, the design and development of novel and efficient strategies to prepare useful organic molecules, such as fluorinated compounds, is highly desirable.

We have an intense interest in the transformation of alkenes into fluorine-containing compounds[4] due to the great utility of organofluorine compounds as pharmaceuticals, agrochemicals, and materials.[5] In the past ten years, the development of efficient and direct fluorination protocols has been of considerable significance.[6] In spite of the great progress made in the transition-metal catalysed construction of Csp^2-F bond via C-H activation[7] and cross-coupling reactions,[8] the techniques for direct access to aliphatic Csp^3-F bond is relatively underdeveloped owing to the challenges in the achievement of satisfactory regioselectivity.[9] In addition to the benzylic[10] and allylic fluorination,[11] the fluorination via olefin functionalization provides a practical approach for the precise installation of a fluorine atom on alkanes.[12] Recently, radical fluorination of alkenes via iron or silver catalysis has received significant attention (Scheme 1).[13] However, the lack of stereo-control was often encountered in the fluorination of alkenes.



Scheme 1 Fluorination of alkenes for access to aliphatic Csp^3-F bond.

Within the realm of open-shell chemistry, alkene radical cations display a combination of free radical and cation chemistry that confers a fascinating manner of reactivity and selectivity on them.[14] Inspired by this concept, we questioned whether the fluorination of olefins via alkene radical cation intermediates might be rerouted to deliver fluorinated products in good regio- and stereo-selectivity. Thus, we describe herein a metal-free and mild protocol for regio- and stereo-selective cyanofluorination of vinyl azides with Selectfluor as a fluorine source and TMSCN as a cyanating reagent, affording α-azido-β-fluoronitriles that bearing quaternary α-carbons are difficult to access by existing methods (Scheme 1). To the best of our knowledge, this reaction represents the first example of synthesis of α-azido-β-fluoronitriles via cyanofluorination of vinyl azides.

[a] *Jiangsu Key Laboratory of Translational Research and Therapy for Neuro-Psycho-Diseases and Department of Medicinal Chemistry, College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China. E-mail: fliu2@suda.edu.cn*
[b] *Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China.*
† These authors contributed equally to this work.
Electronic Supplementary Information (ESI) available: Experimental details, characterization data, and copies of ^1H and ^{13}C NMR spectra for all compounds. See DOI: 10.1039/x0xx00000x

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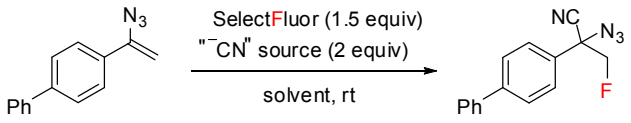
Table 1 Optimization of reaction conditions [a]



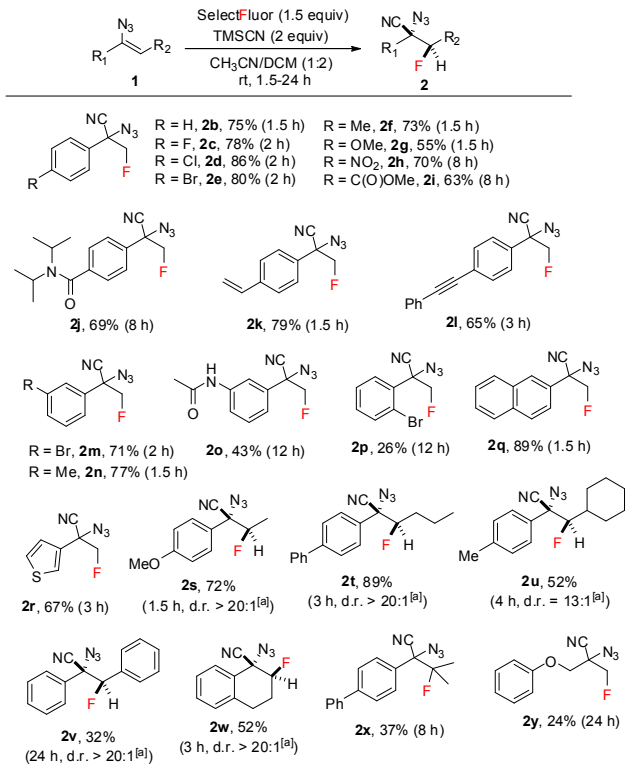
1a **2a**

entry	solvent	"-CN" source	*t* (h)	yield (%)[b]
1	DCM	TMSCN	24	< 5
2	DMF	TMSCN	24	< 5
3	MeCN	TMSCN	0.5	37
4[c]	MeCN	TMSCN	0.5	< 5
5	MeCN/DCM (1:1)	TMSCN	1	65
6	**MeCN/DCM (1:2)**	**TMSCN**	**1.5**	**78**
7	MeCN/DCM (1:3)	TMSCN	3	77
8	MeCN/DCM (1:4)	TMSCN	8	77
9	MeCN/DCM (1:2)	TBSCN	24	< 5
10	MeCN/DCM (1:2)	nBu$_4$NCN	24	< 5
11	MeCN/DCM (1:2)	CuCN	24	< 5
12[d]	MeCN/DCM (1:2)	TMSCN	1.5	75

[a]**1a** (0.2 mmol), Selectfluor (0.3 mmol) and "$^-$CN" source (0.4 mmol) in organic solvent or co-solvent (2 mL). [b]Isolated yield. [c]CsF (0.4 mmol). [d]In the dark.

Initially, examination and optimization of the reaction parameters were carried out under natural light using vinyl azide **1a** as the model substrate, Selectfluor as the source of atomic fluorine and TMSCN as the source of nucleophilic cyanation reagent (Table 1). A brief screening of organic solvents revealed that a co-solvent system was critical to furnishing the desired product in good yields (entries 5–8) since each solvent alone turned out to be inferior (entries 1–3). We were delighted to identify the solvent mixture CH_3CN/DCM (1:2) as the best one in terms of chemical yield (entry 6). It should be noted that a prolonged reaction time was needed to consume **1a** when increasing the ratio of DCM (entries 5–8). Employing CsF as the "TMS^+" scavenger, to our surprise, the reaction was inhibited (entry 4). An evaluation of other nucleophilic cyanogen sources showed that TMSCN was the most effective one compared to TBSCN, tetrabutylammonium cyanide, and copper(I) cyanide (entry 6 *vs.* entries 9–11). The reaction also proceeded smoothly in the dark (entry 12), which reveals that light is not essential for this transformation. Additionally, the reaction was surprisingly insensitive to air, so all the reactions were run under an aerobic atmosphere.

Typically, EDA complex exhibits a new absorption band, the charge-transfer (CT) band, which is shifted to longer wavelength compared to the UV-vis absorption spectra of its individual components.[2] In many cases, this band lies within the visible region, thus showing a distinctive coloration. In early stage of our investigations, we did observe that a noticeable yellow colour appeared immediately when adding white solid Selectfluor into an acetonitrile solution of **1a** (Figure 1a, see ESI†). Moreover, the optical absorption spectrum showed a bathochromic shift to the visible spectral region, above 450 nm, where neither the substrate nor Selectfluor absorbs (Figure 1b, see ESI†). It is no doubt that an EDA complex formed between vinyl azide **1a** and Selectfluor in acetonitrile.



Scheme 2 Scope for cyanofluorination of vinyl azides. [a] The d.r. value was determined by ^{19}F NMR spectroscopy of the product.

With the optimized reaction conditions established (Table 1, entry 6), we next investigated the scope of this protocol (Scheme 2). A number of vinyl azides bearing a variety of substituents were examined, showing that a wide range of substrates and functional groups are tolerated (**2a–y**). In most cases, a high conversion of vinyl azide occurred within 8 h. Substrates bearing electron-donating and electron-withdrawing groups at the *para* or *meta* positions on the phenyl rings provided the corresponding α-azido-β-fluoropropanenitriles in good yields (**2b–o**), although the highly electron-rich substrates with a methoxyl group or an acetamido group gave relatively low yields (**2g** and **2o**). This cyanofluorination appears to be sensitive to steric effects and prolonged reaction time was required, producing the desired *o*-bromide only in 26% yield (**2p**). Notably, the cyanofluorination of vinyl azides with alkenyl (**2k**) and alkynyl (**2l**) groups on phenyl rings was readily proceeded without compromising the chemical yields. Besides phenyl rings, the naphthyl (**2q**) and thienyl (**2r**) moieties were also well compatible with the reaction conditions. This protocol was subsequently applied to non-terminal (*Z*)-vinyl azides (**2s–w**) and tetrasubstituted alkene (**2x**), furnishing the desired products in

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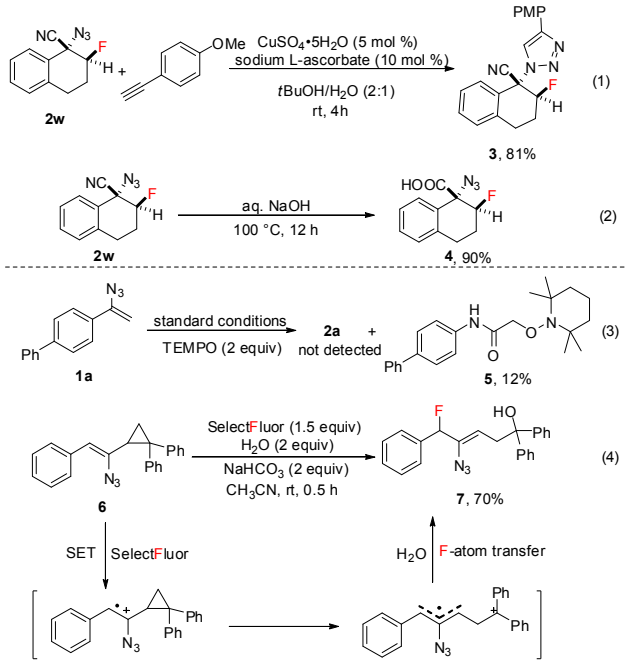
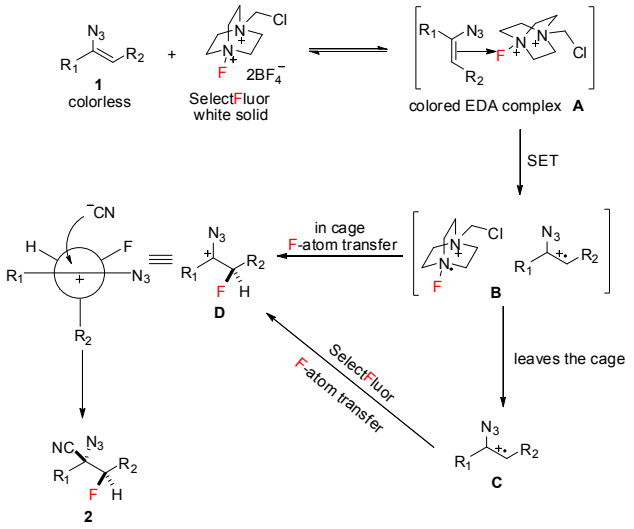
acceptable yields with excellent stereoselectivities, albeit with some stereochemical erosion in the example of **2u**. The stereochemical outcome of these reactions could be determined by the reactive conformation of the carbocation intermediate **D** (Scheme 4). Despite the good reactivity of aryl vinyl azides, we found that alkyl vinyl azide (**2y**) performed poorly. It was reasoned that the conjugated π-system with aryl moiety might be crucial to the formation of EDA complex and following electron transfer.



Scheme 3 Further transformations and control experiments.

Overall, access to highly-functionalized fluorine-containing products by cyanofluorination of vinyl azides provides an opportunity to rapidly generate useful synthons for further transformations. To illustrate this point, we conducted copper-catalysed click reaction and hydrolysis reaction, converting **2w** into the desired fluorinated 1,2,3-triazole (**3**) (Scheme 3, eq 1) and carboxylic acid (**4**) (eq 2) in 81% and 90% yields respectively. Meanwhile, the *cis*-cyanofluorination can be unambiguously confirmed by the crystal structures of **3** and **8** (see ESI†).[15] Furthermore, control experiments were performed to gain more insights into the reaction pathway. In the presence of radical scavenger TEMPO, no fluorine-incorporated products were found, but the TEMPO adduct **5** was obtained (eq 3). As might be expected, the reaction of cyclopropyl vinyl azide **6**, a radical probe, with Selectfluor and water gave the ring-opening product **7** in 70% yield (eq 4).[4b,16] It is of note that ring opening of the reporter group in the radical cation intermediate could be ultrafast ($k > 1 \times 10^{11}$ s^{-1}).[16] These results strongly support the involvement of a radical process in the EDA complex-enabled cyanofluorination.

On the basis of above observations and our previous publication,[4b] a plausible mechanism was depicted in Scheme 4. At first, the formation of an EDA aggregate **A** would take place. In contrast to recent synthetic achievements involving the intermediacy of a photoactive EDA complex,[1] the subsequent single electron transfer (SET) is activated thermally, leading to the generation of an alkene radical cation (**C**) within **B**, followed by a fast fluorine atom transfer in cage to yield the carbocation intermediate **D**. The final step is a nucleophilic cyanation, furnishing the desired cyanofluorination product in a stereo-controlled fashion. On the other hand, out-of-cage diffusion and following atomic fluorine transfer, as an alternative pathway, cannot be excluded at the present stage.



Scheme 4 Proposed mechanism.

In summary, we have developed an operationally simple and unprecedented protocol for the synthesis of *α*-azido-*β*-fluoronitriles from vinyl azides under mild reaction conditions. The investigations indicated that an EDA complex-enabled generation of alkene radical cation and subsequent fluorine atom transfer could be involved in the reaction. Moreover, this transformation showed excellent regio- and stereo-selectivity, as well as tolerance of a broad range of functional groups. Other applications of EDA complex as an efficient strategy for the development of novel and useful synthetic methods are underway in our lab.

Acknowledgements

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