

## Regio- and stereoselective halogenation reactions of SF<sub>5</sub>-alkynes

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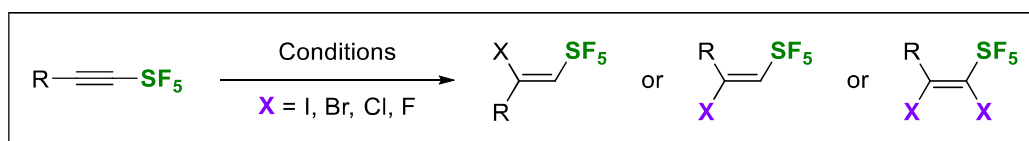
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SF<sub>5</sub>-Containing haloalkenes are usually obtained by the addition of SF<sub>5</sub>X gas (X = Cl, Br) onto the corresponding terminal alkynes but the *E*-stereoselectivity is usually observed under radical condition,<sup>1</sup> or a mixture of *E/Z* isomers under thermal conditions.<sup>2</sup> Surprisingly, the hydrohalogenation of SF<sub>5</sub>-alkynes is so far limited to a single example of hydrofluorination under gold-catalyzed conditions giving the *Z*-fluoroolefin in low yield.<sup>3</sup> Recently, our group proved that SF<sub>5</sub>-alkynes are highly reactive toward the addition of N-, O-, and S-nucleophiles yielding in all cases a single regio- and stereoisomer.<sup>4</sup> We then wondered if the SF<sub>5</sub>-alkynes could react both as electrophiles or nucleophiles depending on the reaction conditions, so we selected the hydrohalogenation as benchmark reactions. Herein is presented efficient strategies to perform hydrohalogenation with all the halogens (I, Br, Cl and F) and methods to access both the *E* and the *Z*-SF<sub>5</sub>-haloalkenes following two different mechanisms, with relative configuration of all the stereoisomers confirmed by X-ray diffractions. Dihalogenation reactions with I<sub>2</sub>, ICl and Br<sub>2</sub> are also discussed. Moreover, preliminary DFT calculations are presented to confirm the reaction mechanisms and to explain the high regio- and stereoselectivity.



### References

- <sup>1</sup> S. Ait-Mohand, W. R. Dolbier, *Org. Lett.* **2002**, *4*, 3013.
- <sup>2</sup> L. Popek, T.-M. Nguyen, N. Blanchard, D. Cahard, V. Bizet, *Tetrahedron* **2022**, *117-118*, 132814.
- <sup>3</sup> R. Gauthier, M. Mamone, J.-F. Paquin, *Org. Lett.* **2019**, *21*, 9024.
- <sup>4</sup> L. Popek, J. J. Cabrera-Trujillo, V. Debrauwer, N. Blanchard, K. Miqueu, V. Bizet, *Angew. Chem. Int. Ed.*, **2023**, *62*, e202300685.