

# Literature Report



## Visible-Light Mediated Metal-Free Synthesis of Trifluoromethylselenolated Arenes

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Reporter: Chang-Bin Yu

Checker: Xin-Wei Wang

June 24, 2019

Dalian Institute of Chemical Physics

Ghiazza, C.; Debrauwer, V.; Tlili, A.\* *et al. Angew. Chem. Int. Ed.* **2018**, *57*, 11781.

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# CV of Dr. Anis Tlili

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**Dr. Anis Tlili**

|                  |   |
|------------------|---|
| <b>2007-2008</b> | <b>M.S., University of Burgundy</b>                   |
| <b>2008-2011</b> | <b>Ph.D., ENSC Montpellier</b>                        |
| <b>2012-2013</b> | <b>Postdoc., LIKAT</b>                                |
| <b>2013-2014</b> | <b>Postdoc., CEA Saclay &amp; ICSN Gif-sur-Yvette</b> |
| <b>2014-now</b>  | <b>CNRS Research Fellow</b>                           |

## **Research Fields:**

- **Fluorine Chemistry**
- **Organometallic Chemistry**

# 内容

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- ◆ 引言
- ◆ 亲核三氟甲硒基试剂及应用
- ◆ 自由基三氟甲硒基试剂及应用
- ◆ 总结

# 引言

## Periodic table

|   | VA       | VIA      | VIIA     |  |
|---|----------|----------|----------|--|
| 3 | 15<br>P  | 16<br>S  | 17<br>Cl |  |
| 4 | 33<br>As | 34<br>Se | 35<br>Br |  |
| 5 | 51<br>Sb | 52<br>Te | 53<br>I  |  |
|   |          |          |          |  |

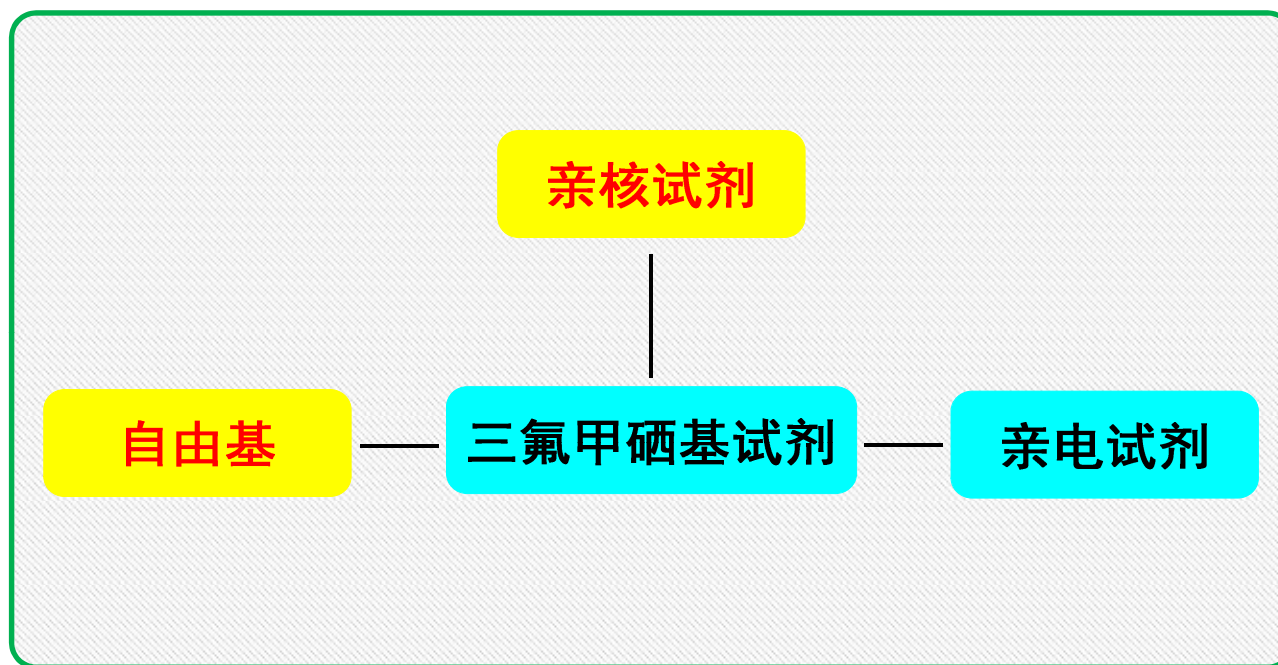
### 用途:

- ◆ 催化剂：电解锰等
- ◆ 营养元素：平衡氧化还原
- ◆ 光敏材料：干印术的光复制
- ◆ 配体等

- 1817年，永斯·雅各布·贝采利乌斯，(Selene)
- 1847年，Siemens首次合成二乙基硒
- 近几年，三氟甲硒基化合物的合成及应用被报道

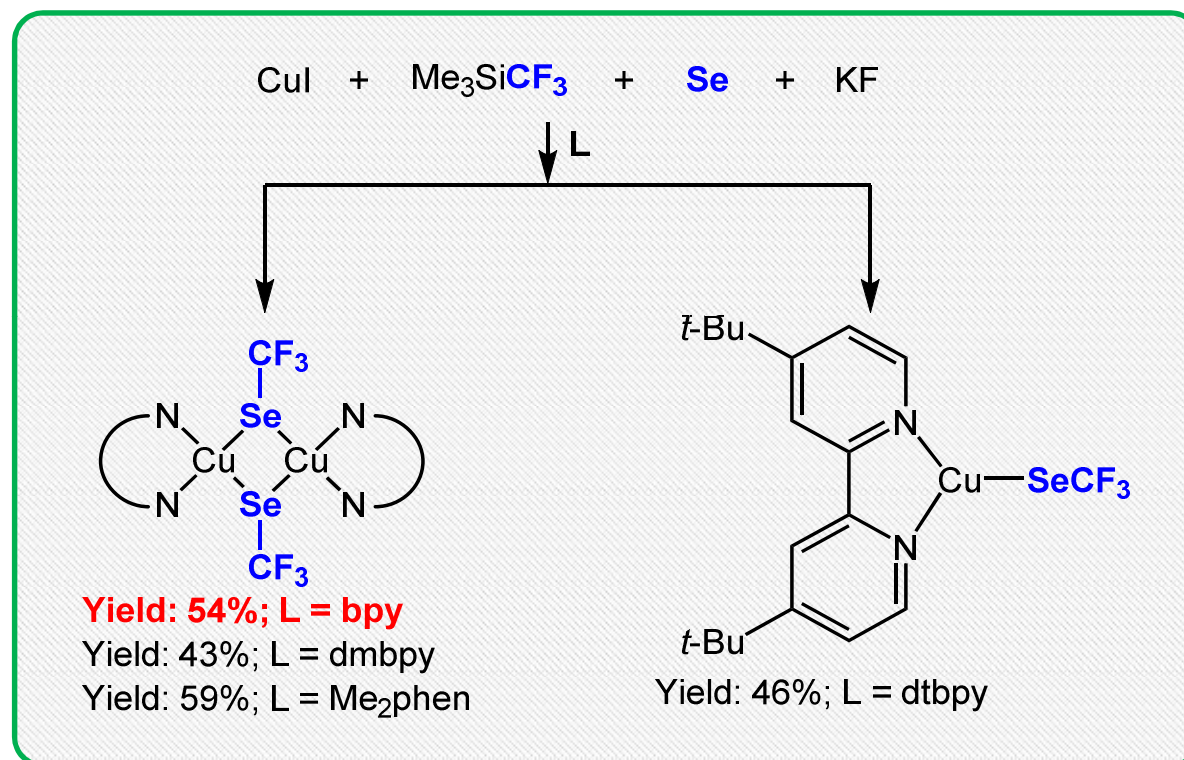
# 三氟甲硒基试剂

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# 亲核三氟甲硒基试剂-合成

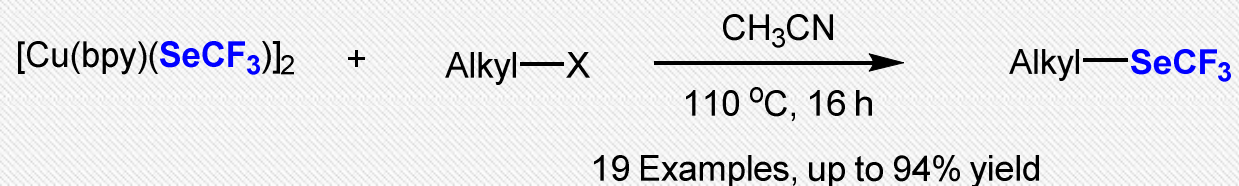
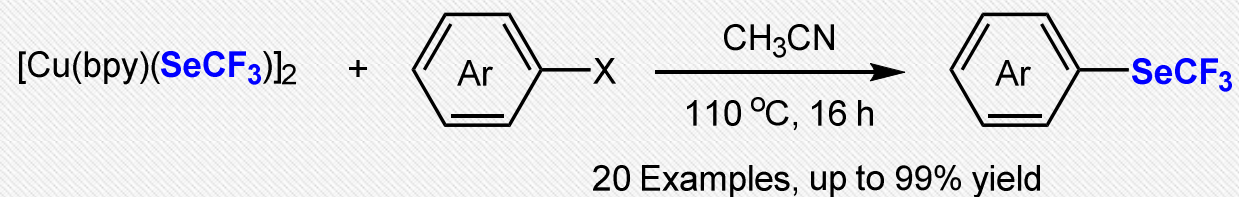
## Synthesis of $\text{Cu}(\text{SeCF}_3)$ Complex



Weng, Z. *et al. Chem. Eur. J.* **2014**, *20*, 657.

# 亲核三氟甲硒基试剂-应用

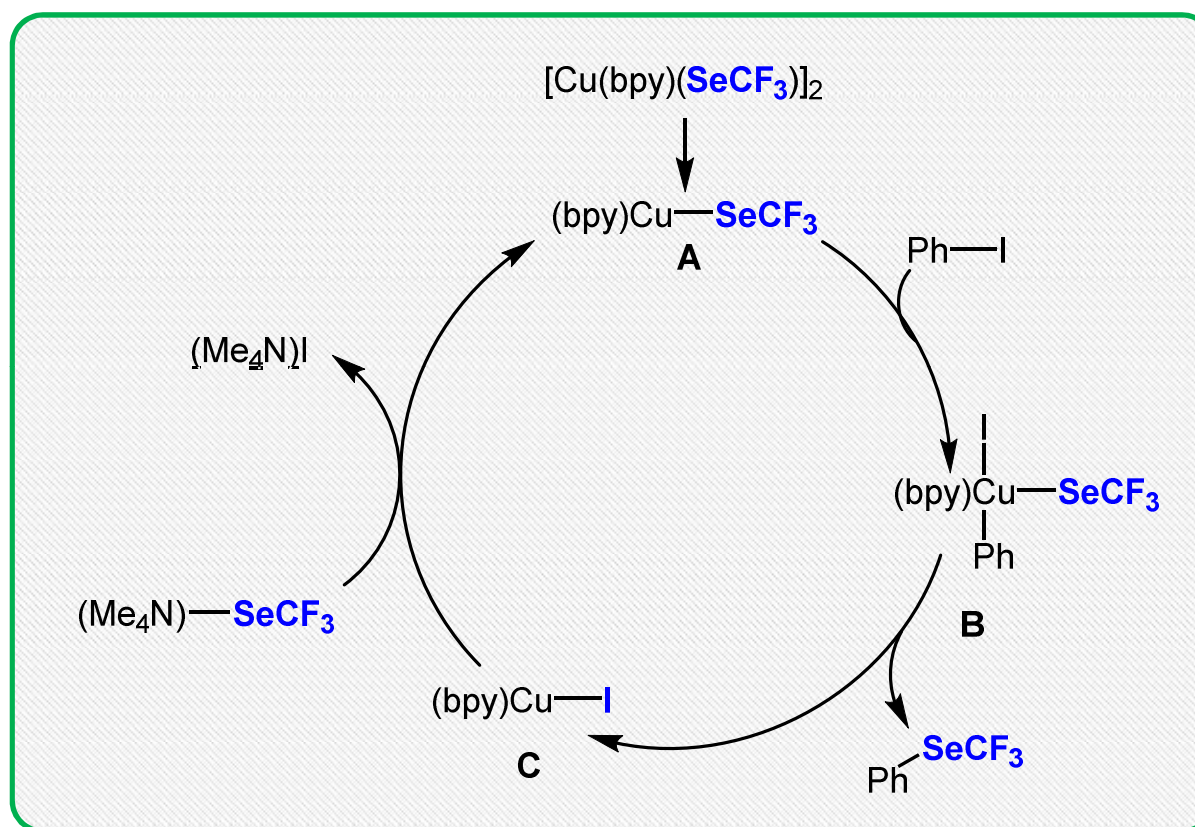
## Application of Cu(SeCF<sub>3</sub>) Complex



Weng, Z. *et al. Chem. Eur. J.* **2014**, *20*, 657.

# 亲核三氟甲硒基试剂-应用

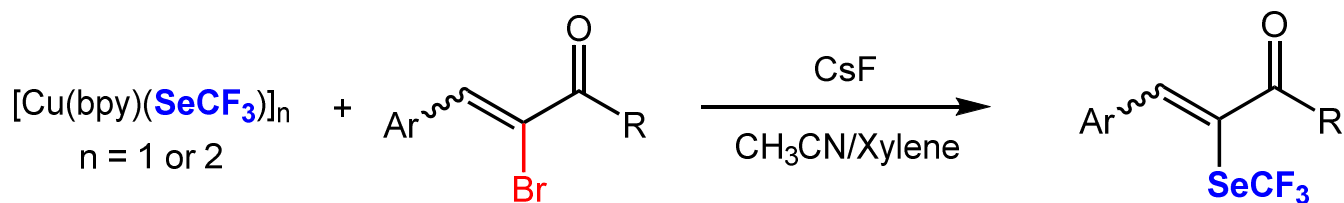
## Proposed Mechanism



Rueping, M. *et al. Chem. Eur. J.* **2013**, *19*, 14043.

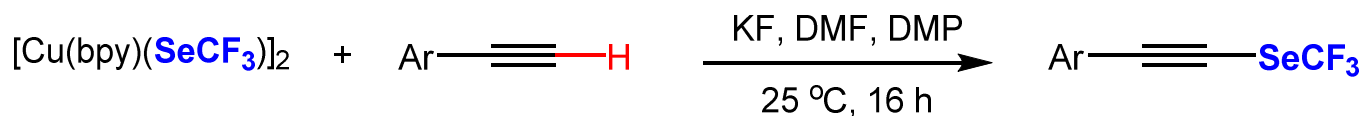


# 亲核三氟甲硒基试剂-应用



14 Examples, up to 88% yield

Weng, Z. *et al. Tetrahedron* **2014**, *70*, 672.

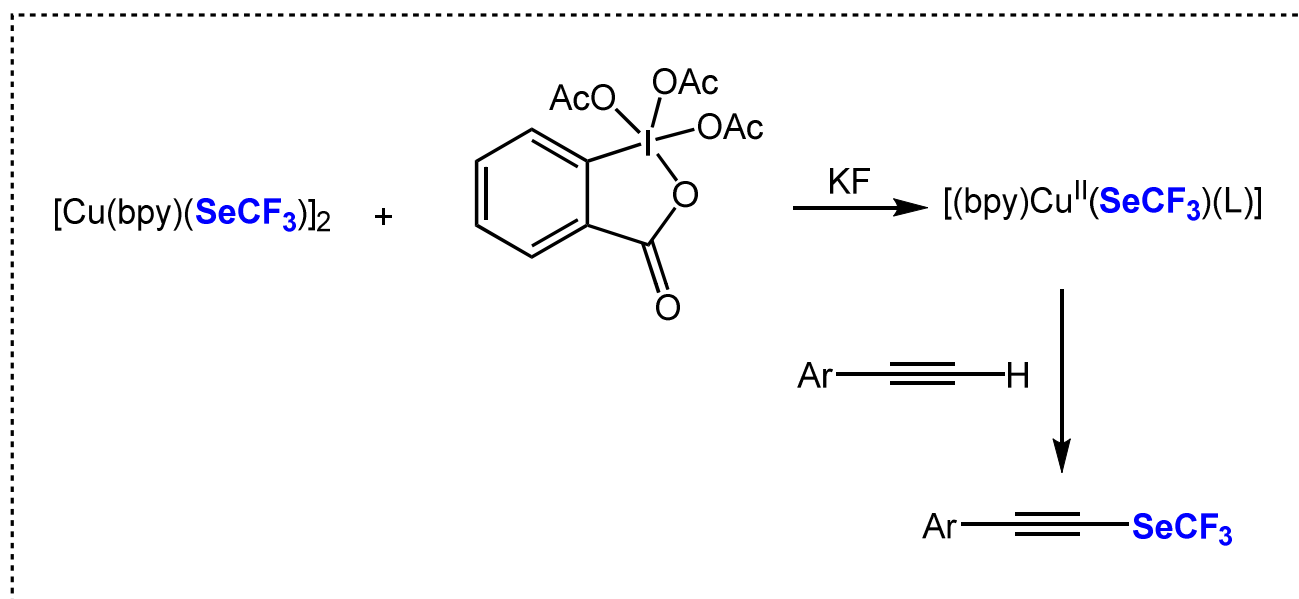


22 Examples, up to 87% yield

Weng, Z. *et al. Org. Chem. Front.* **2015**, *2*, 574.

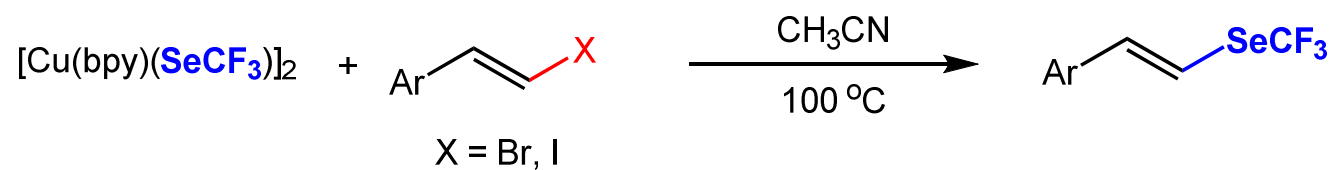
# 亲核三氟甲硒基试剂-应用

## Proposed Mechanism



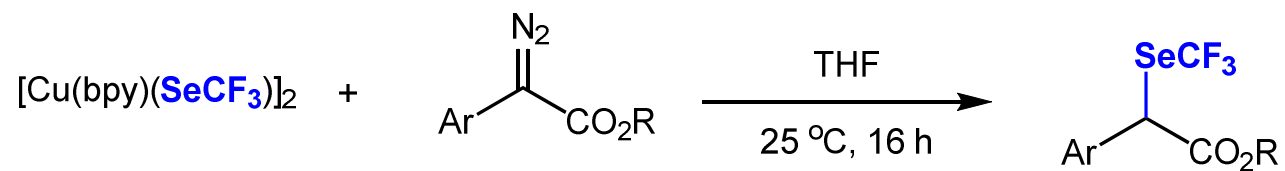
Weng, Z. *et al. Org. Chem. Front.* **2015**, *2*, 574.

# 亲核三氟甲硒基试剂-应用



19 Examples, up to 94% yield

Weng, Z. *et al. Tetrahedron* **2015**, *56*, 3838.



24 Examples, up to 99% yield

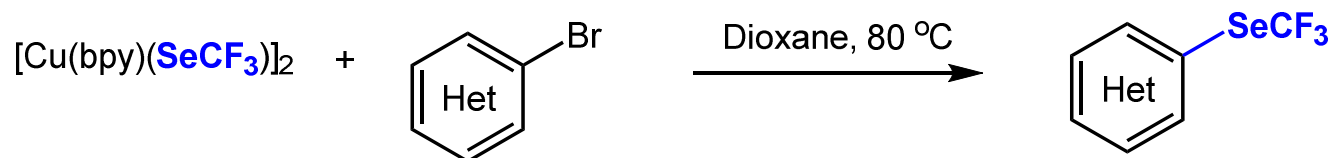
Weng, Z. *et al. J. Fluorine Chem.* **2018**, *216*, 43.

# 亲核三氟甲硒基试剂-应用



45 Examples, up to 99% yield

Weng, Z. *et al. J. Fluorine Chem.* **2017**, 204, 1.

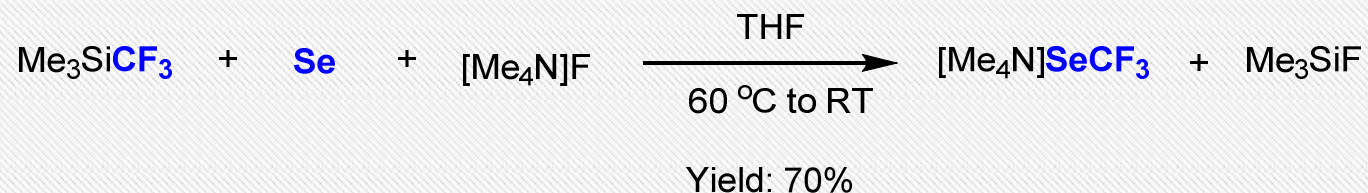


22 Examples, up to 94% yield

Weng, Z. *et al. Chin. J. Chem.* **2016**, 34, 505.

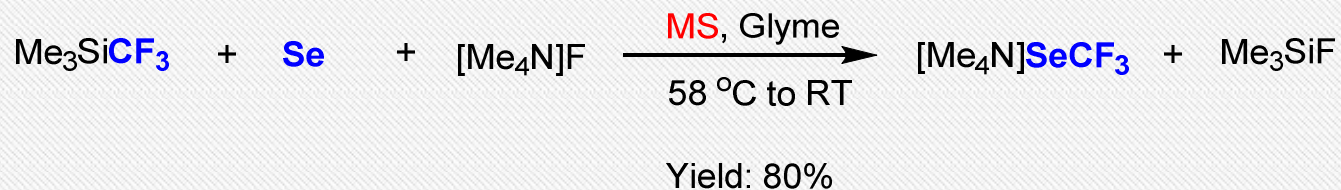
# 亲核三氟甲硒基试剂-合成

## Synthesis of [Me<sub>4</sub>N](SeCF<sub>3</sub>)



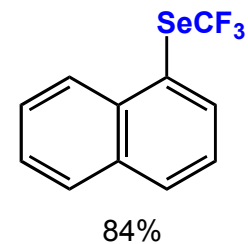
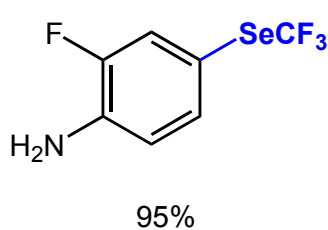
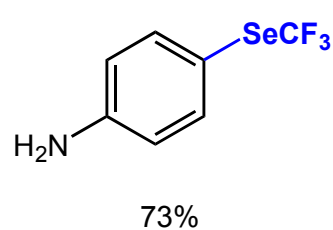
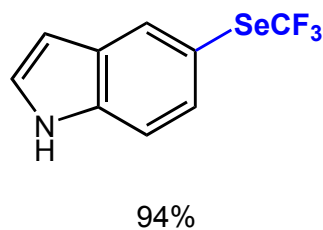
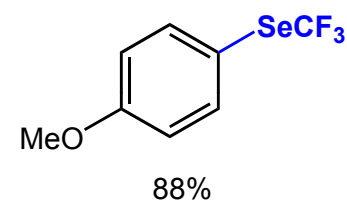
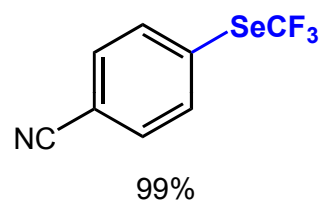
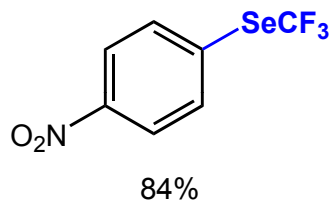
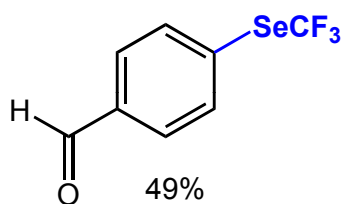
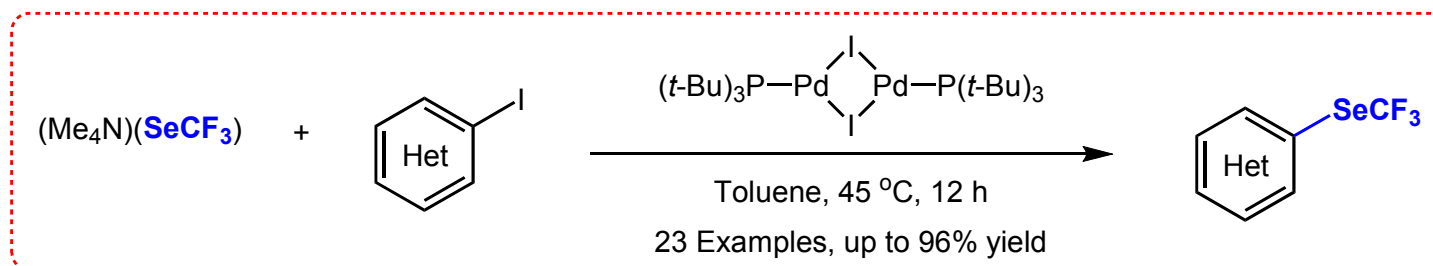
Tyrra, W. *et al. J. Fluorine Chem.* **2003**, 123, 183.

## Improved method



Schoenebeck, F. *et al. Angew. Chem. Int. Ed.* **2015**, 54, 10322.

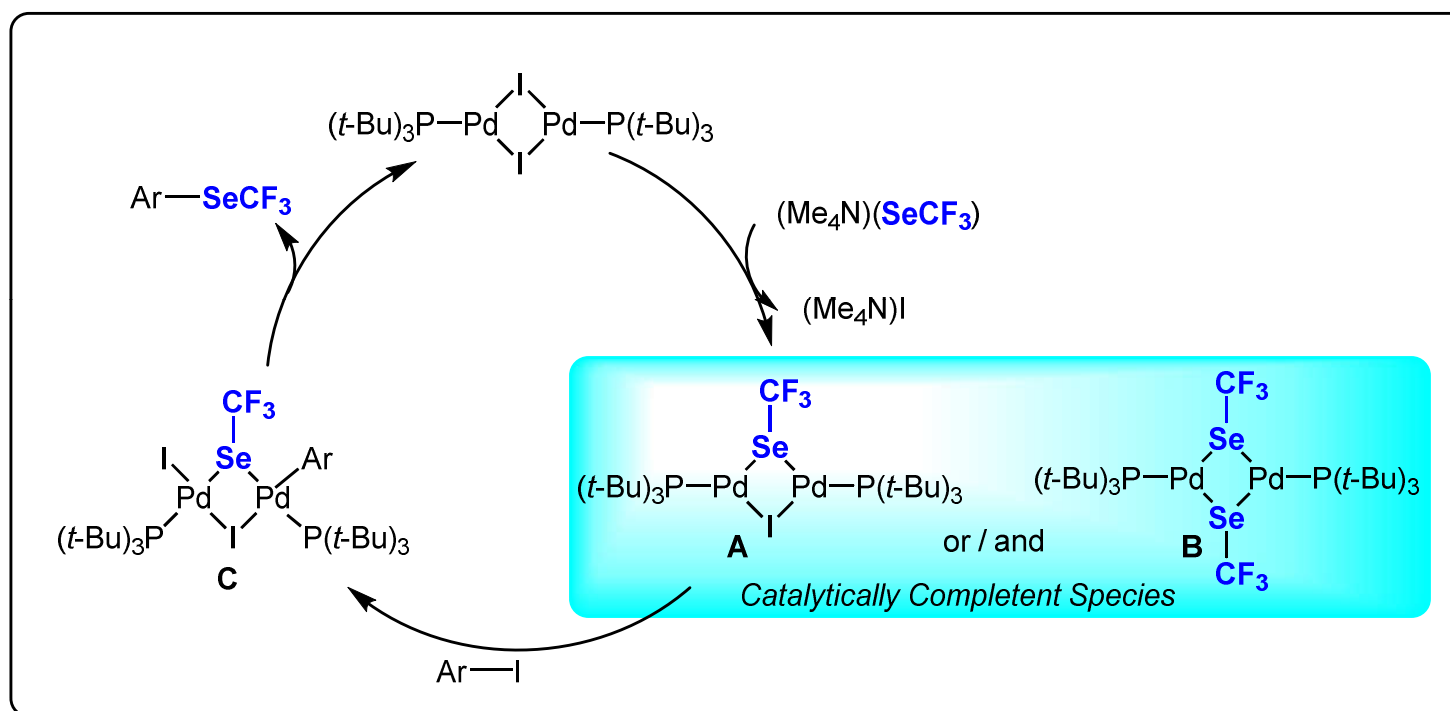
# 亲核三氟甲硒基试剂-应用



Schoenebeck, F. *et al. Angew. Chem. Int. Ed.* **2015**, *54*, 10322.

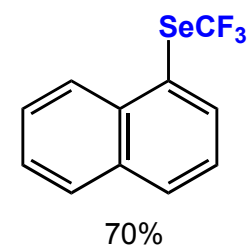
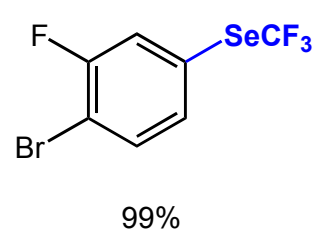
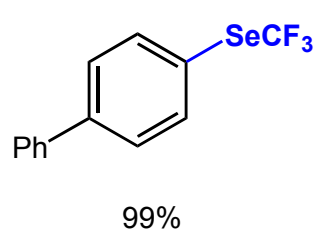
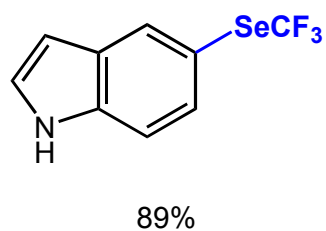
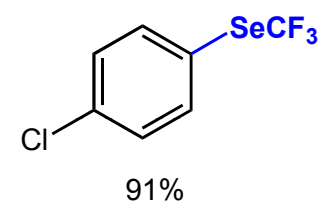
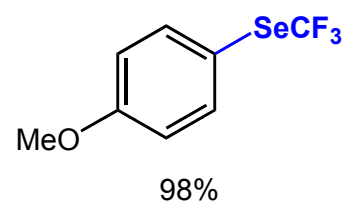
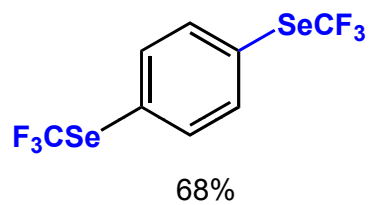
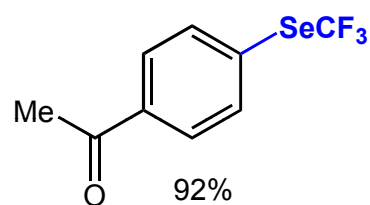
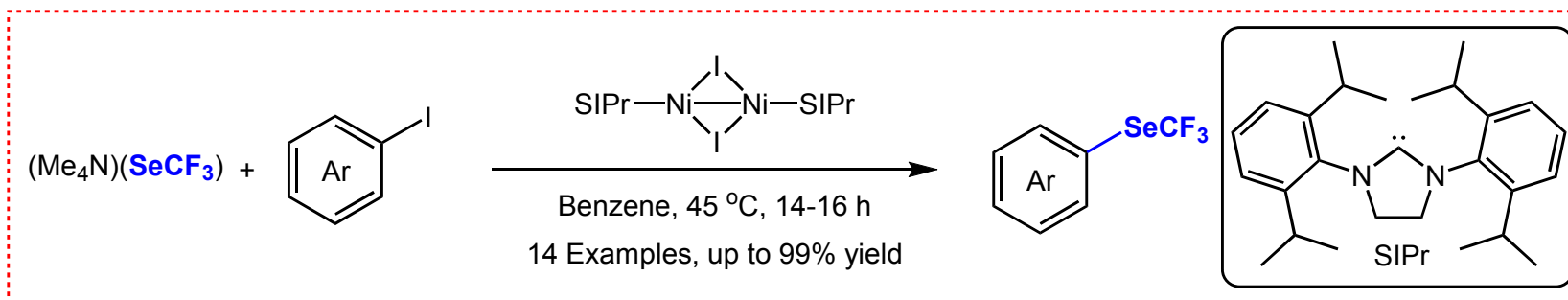
# 亲核三氟甲硒基试剂-应用

## Anticipated Pd-dimer Catalyzed C-SeCF<sub>3</sub> Coupling



Schoenebeck, F. *et al. Angew. Chem. Int. Ed.* **2015**, *54*, 10322.

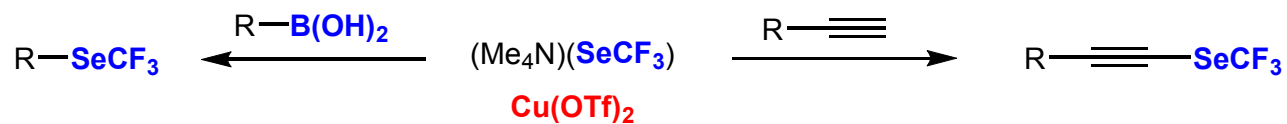
# 亲核三氟甲硒基试剂-应用



Schoenebeck, F. *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 13431.



# 亲核三氟甲硒基试剂-应用



20 Examples, up to 99% yield

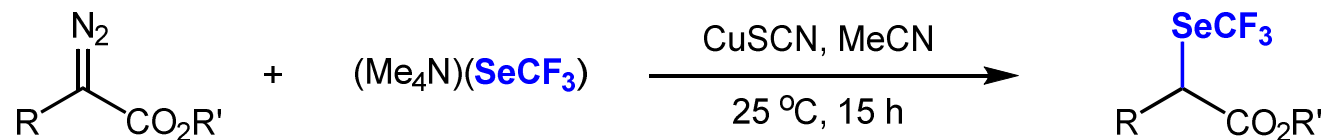
Rueping, M. *et al. Chem. Commun.* **2015**, 51, 4394.



34 Examples, up to 98% yield

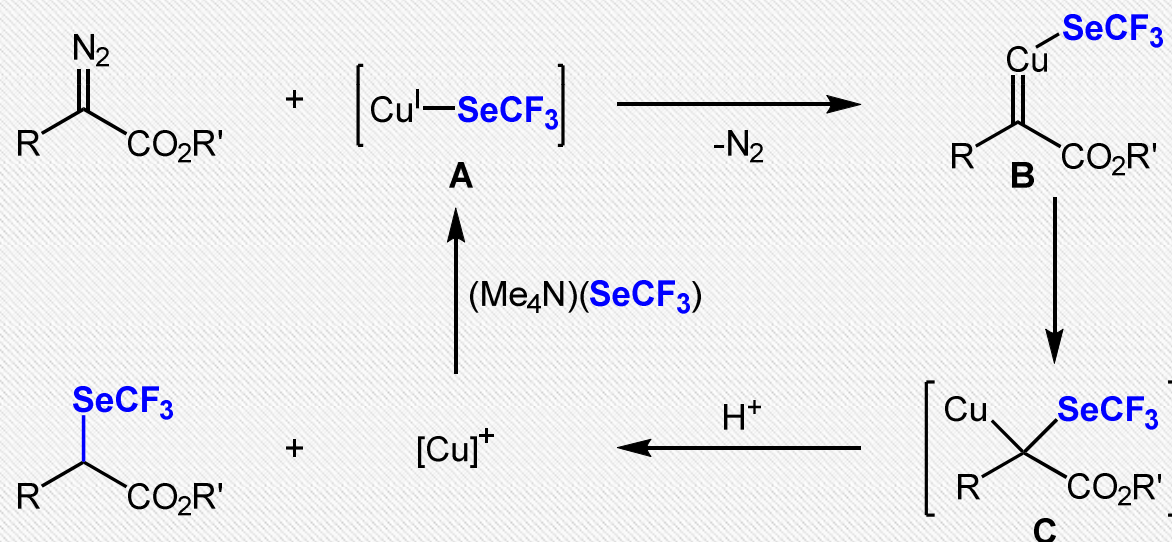
Goossen, L. J. *et al. Chem. Eur. J.* **2016**, 22, 79.

# 亲核三氟甲硒基试剂-应用



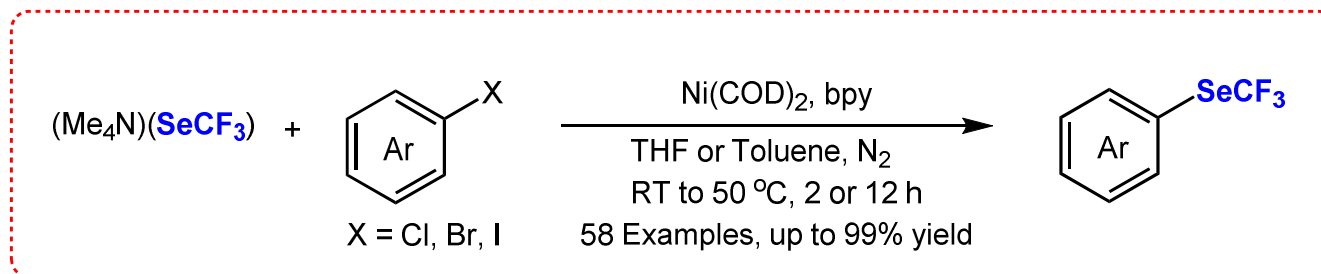
33 Examples, up to 98% yield

## Proposed Mechanism

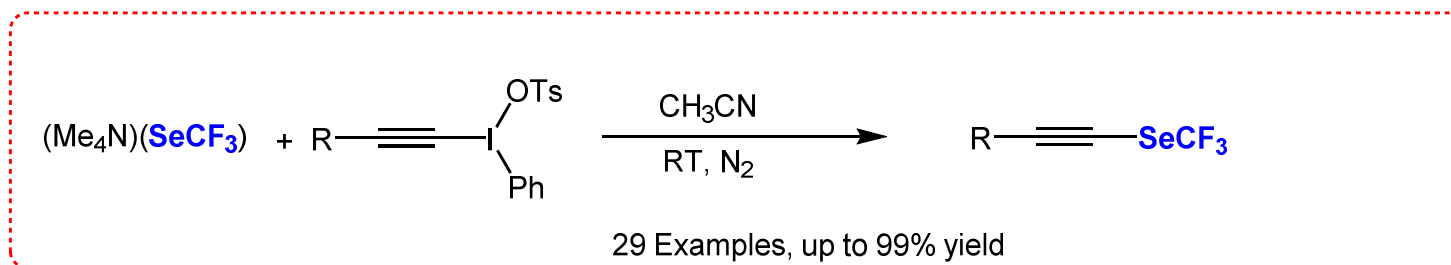


Goossen, L. J. *et al. Chem. Eur. J.* **2016**, *22*, 12270.

# 亲核三氟甲硒基试剂-应用

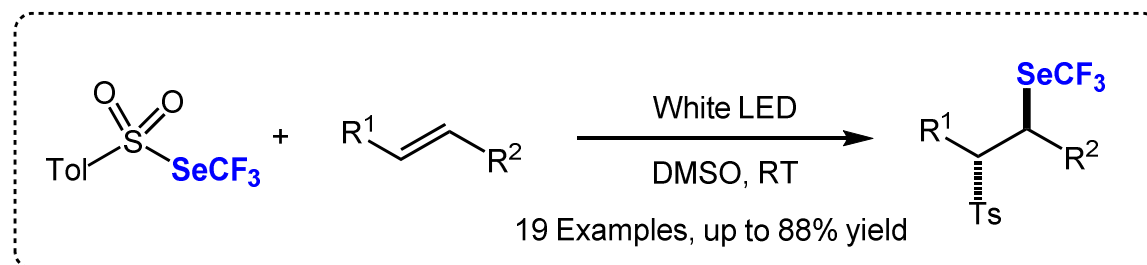


Zhang, C. P. *et al. Org. Lett.* **2017**, *19*, 3919.

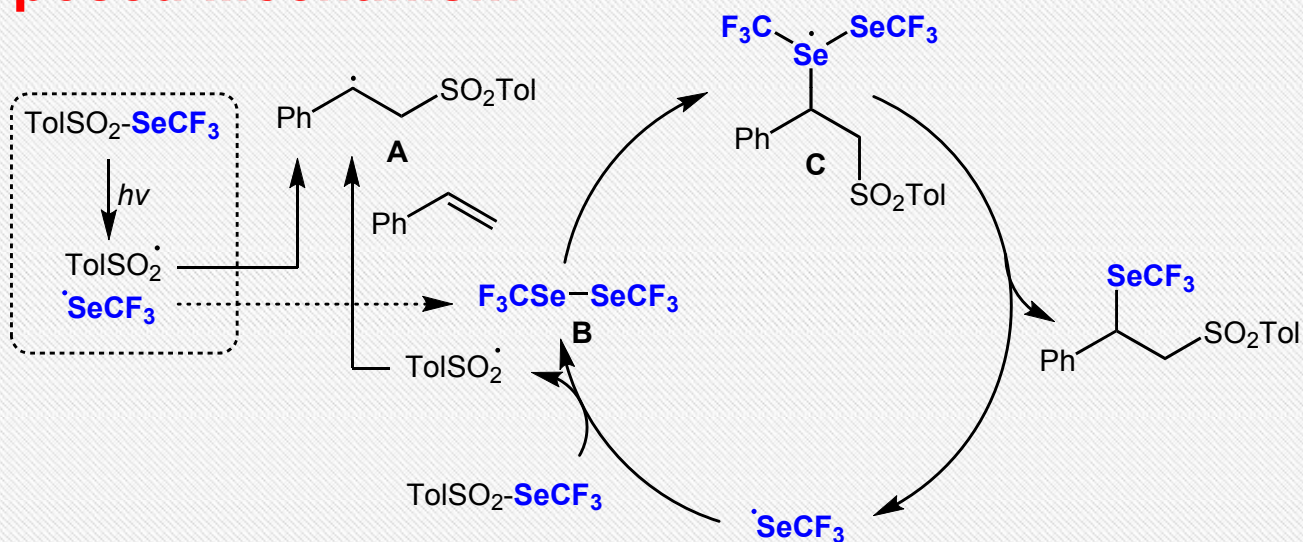


Zhang, C. P. *et al. Org. Biomol. Chem.* **2016**, *14*, 11502.

# 自由基三氟甲硒基化反应

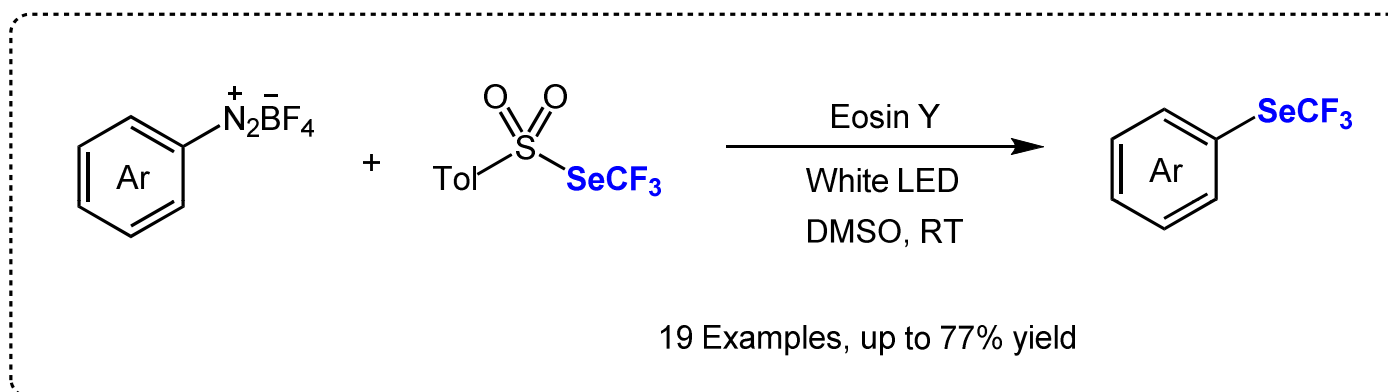


## Proposed Mechanism



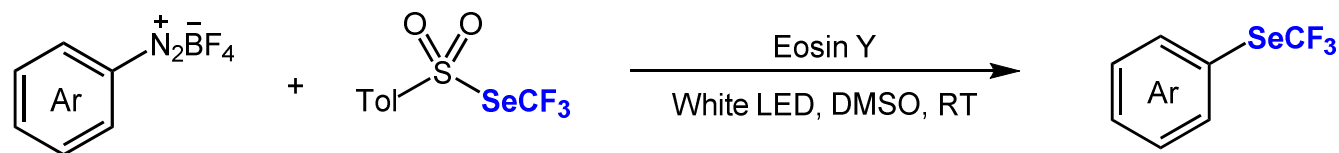
Tlili, A. *et al. Chem. Commun.* **2018**, 54, 9909.

# 自由基三氟甲硒基化反应



Tlili, A. *et al. Angew. Chem. Int. Ed.* **2018**, *57*, 11781.

# 自由基三氟甲硒基化反应

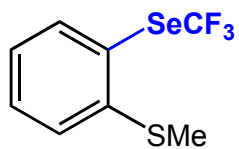


| Entry <sup>a</sup> | Deviation from standard conditions | Yield (%) |
|--------------------|------------------------------------|-----------|
| <b>1</b>           | <b>no change</b>                   | <b>77</b> |
| 2                  | DMF instead of DMSO                | 42        |
| 3                  | THF instead of DMSO                | < 1       |
| 4                  | ACN instead of DMSO                | < 1       |
| 5                  | No eosin Y                         | 0         |
| 6                  | No light                           | 0         |
| 7                  | No light and no eosin Y            | 0         |

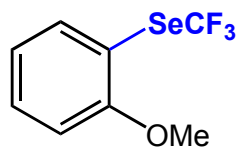
<sup>a</sup>Reactions were performed with TsSeCF<sub>3</sub> (0.3 mmol, 3 equiv), arene diazonium (0.1 mmol, 1 equiv), eosin Y (5 mol%), and solvent (1 mL).

Tlili, A. *et al. Angew. Chem. Int. Ed.* **2018**, *57*, 11781.

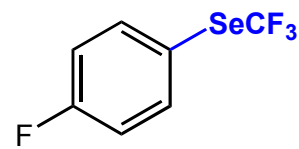
# 自由基三氟甲硒基化反应



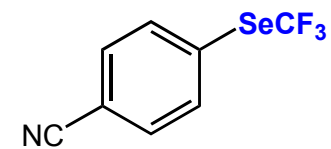
43%



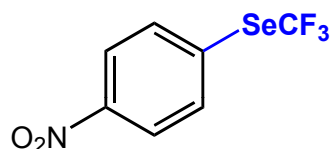
44%



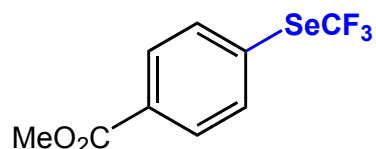
52%



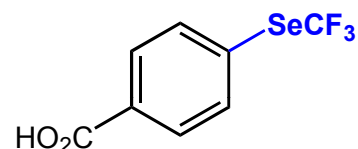
70%



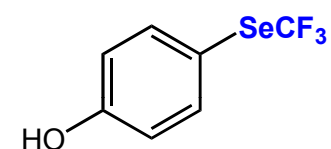
77%



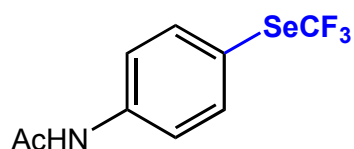
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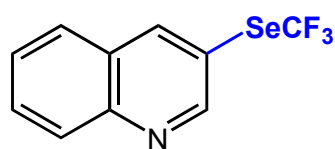
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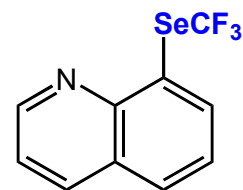
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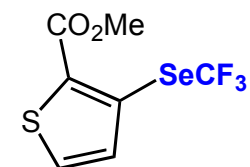
59%



48%



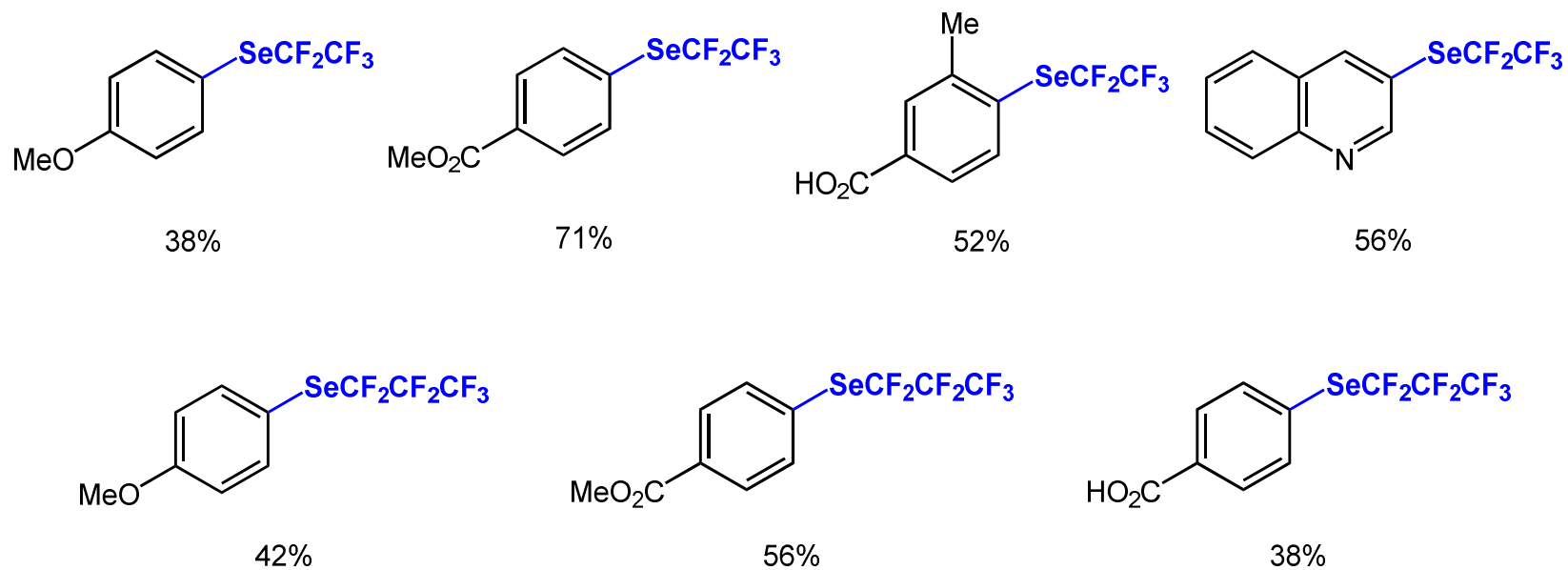
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Tlili, A. *et al. Angew. Chem. Int. Ed.* **2018**, *57*, 11781.

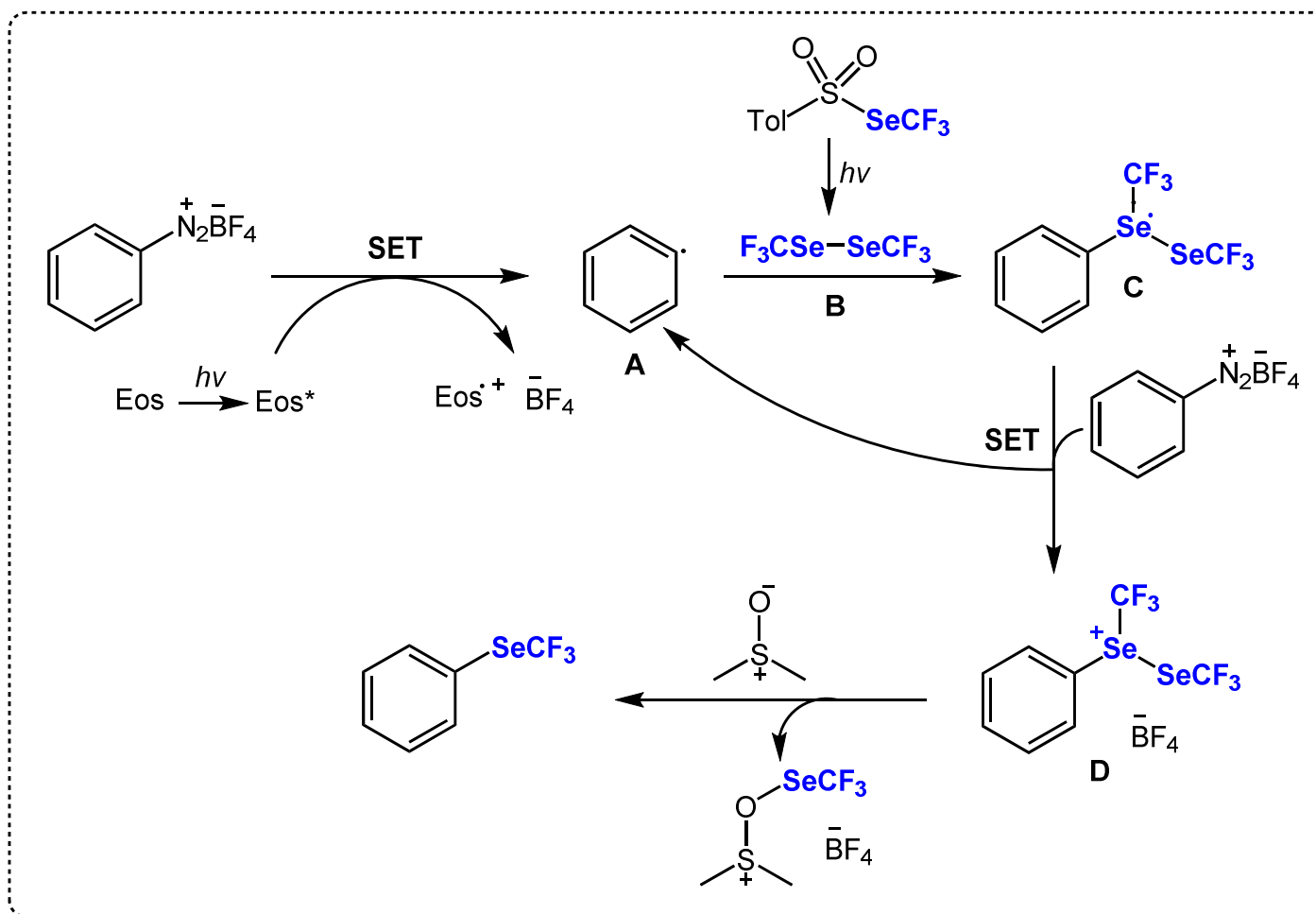
# 自由基三氟甲硒基化反应



Tlili, A. *et al. Angew. Chem. Int. Ed.* **2018**, *57*, 11781.

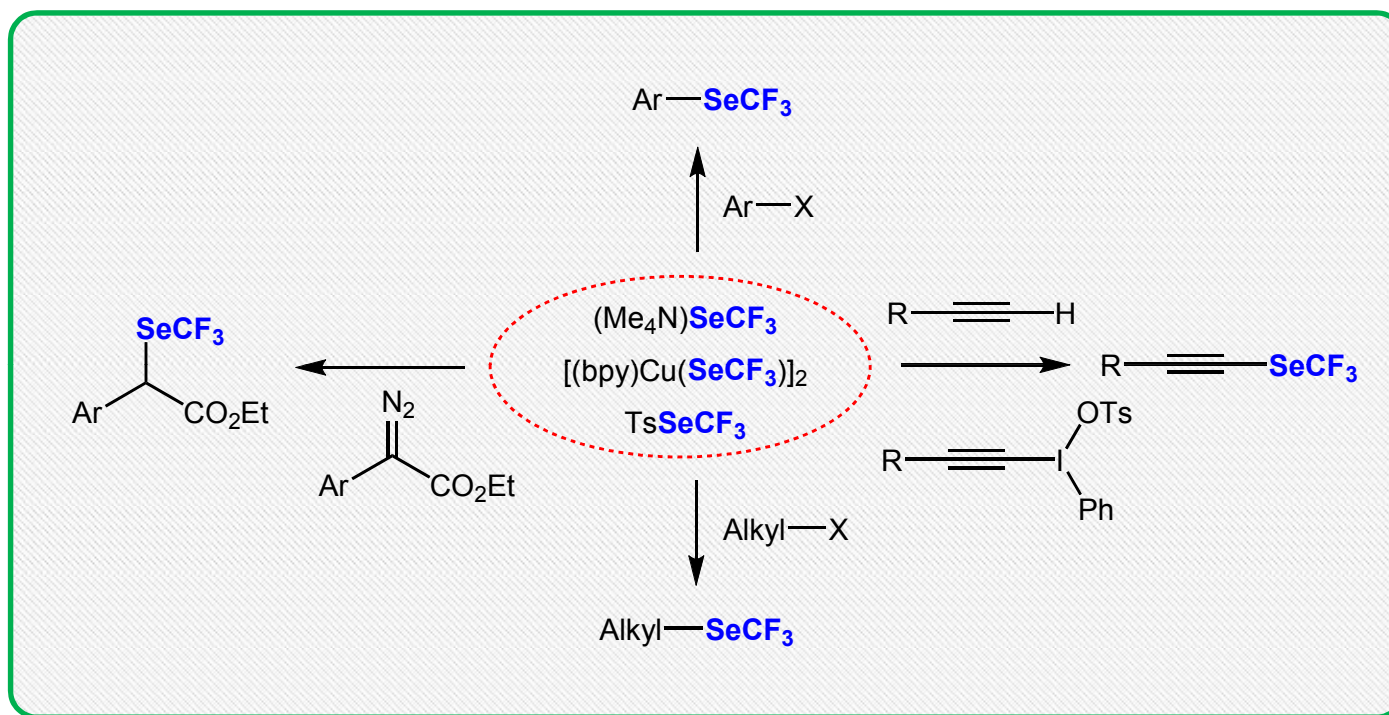


# Proposed Mechanism



Tlili, A. *et al. Angew. Chem. Int. Ed.* **2018**, *57*, 11781.

# Summary



# The First Paragraph

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The combination of the trifluoromethyl group with chalcogens has gained widespread interest in modern organofluorine chemistry. The unique properties resulting from this conjunction are the key factor for the growing interest in these compounds from life sciences and materials, as they affect the physicochemical properties.

# The Last Paragraph

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In conclusion, we have demonstrated that the synthesis of trifluoromethylselenolated arenes can be mediated by visible light under metal-free conditions. The reactions were performed with arene diazonium salts and trifluoromethyl tolueneselenosulfonate at room temperature. The reaction demonstrates a broad scope. Moreover, mechanistic investigations were performed including EPR spectroscopy, luminescence investigations, and cyclic voltammetry. EPR spectroscopy allowed us to identify two key intermediates, namely, the formation of trifluoromethylselenyl radical as well as a trivalent selenium radical species.

# The Last Paragraph

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Overall, based on the different experiments, a plausible mechanism has been proposed. New methods exploiting the formation of trifluoromethylselenyl radical are under investigation in our laboratory.

# Acknowledgement

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***Thanks***  
***for your kind attention !***