Investigation of Sulfilimines

and their physical properties

Spezialisierungsmodul

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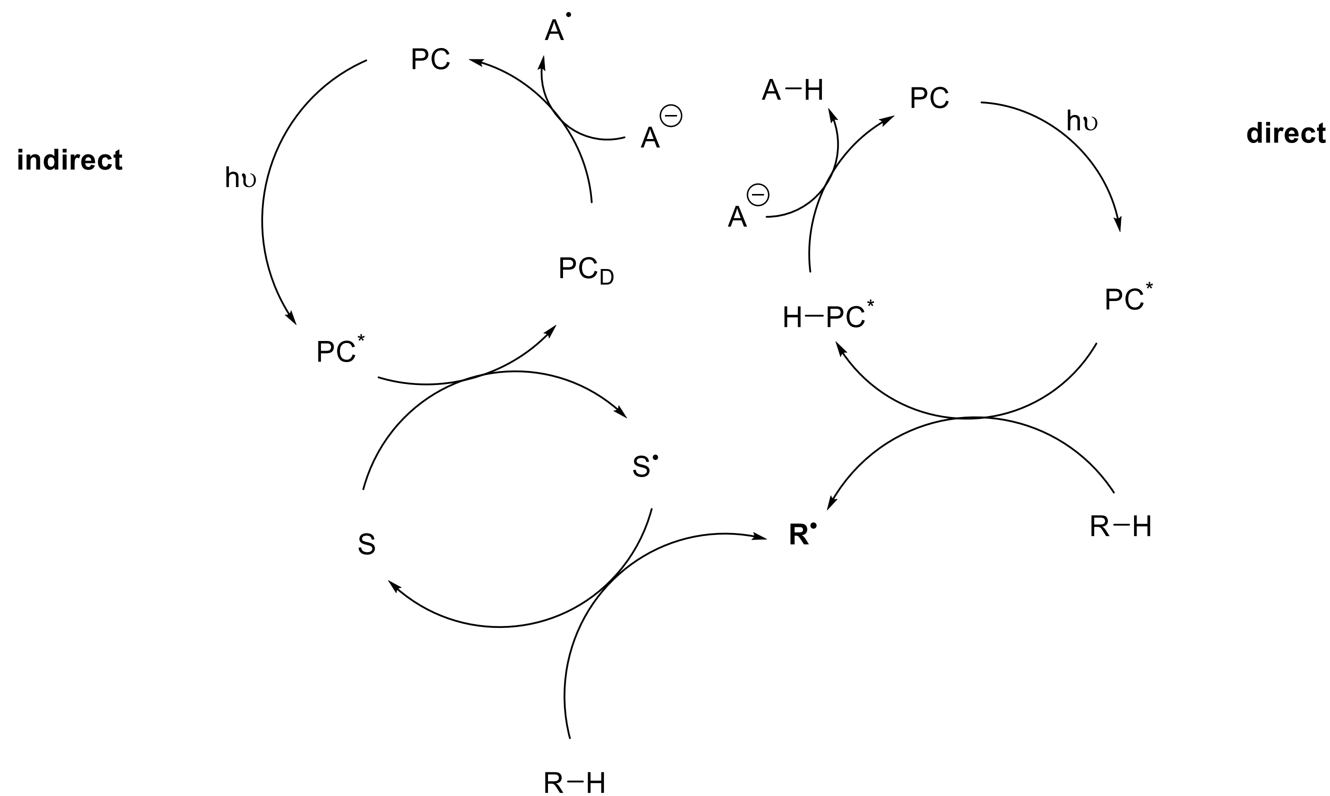
- By using C – H functionalizations, synthesis can be designed to be more atom-, redox- and step-economical

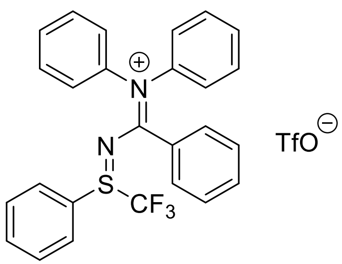
- HAT processes can be used to selectively activate C – H bonds



L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315-1345.; M. Salamone, M. Bletti, *Acc. Chem. Res.* **2015**, *48*, 2895-2903.

1 2

- Complete charge separation
- No change in geometry in the transition state



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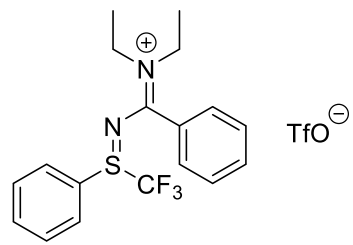

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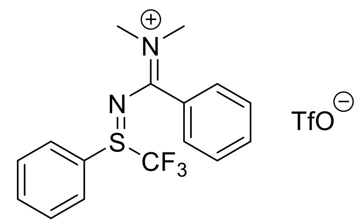

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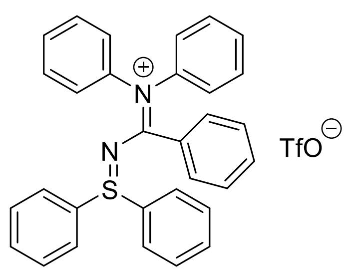

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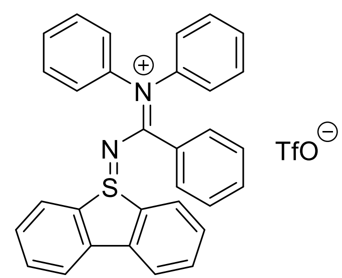
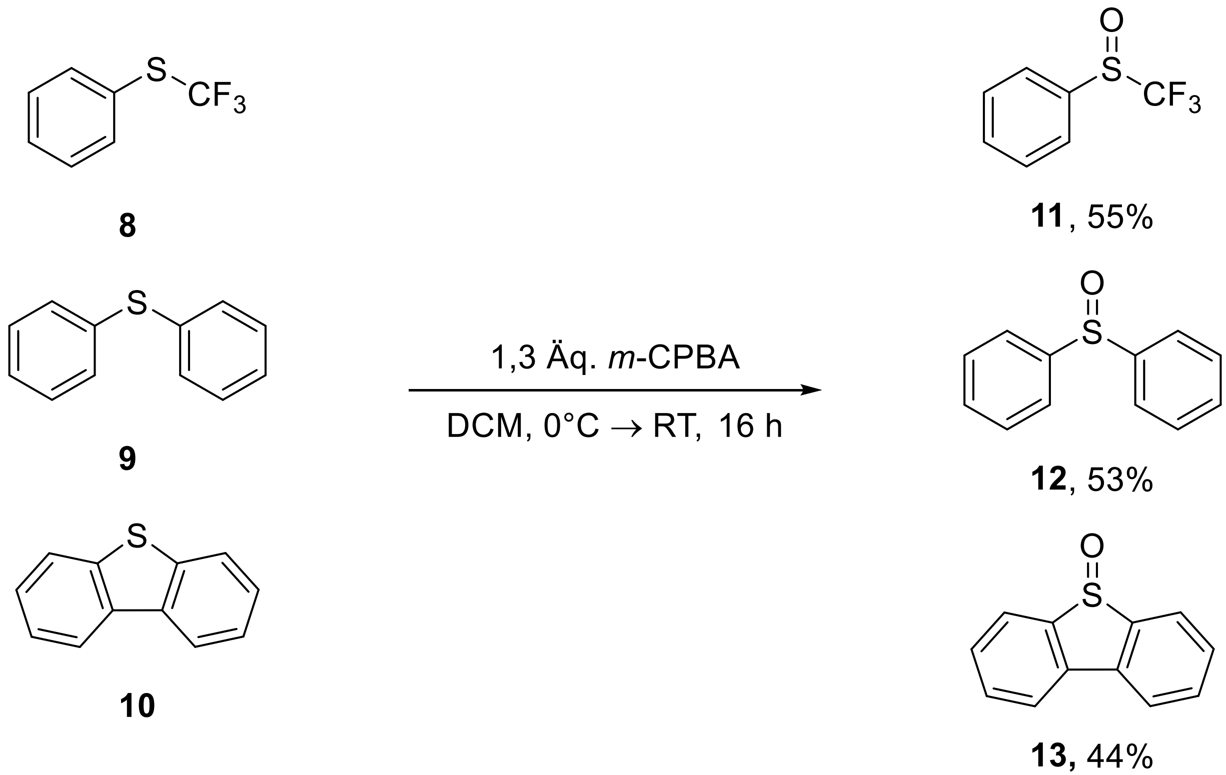


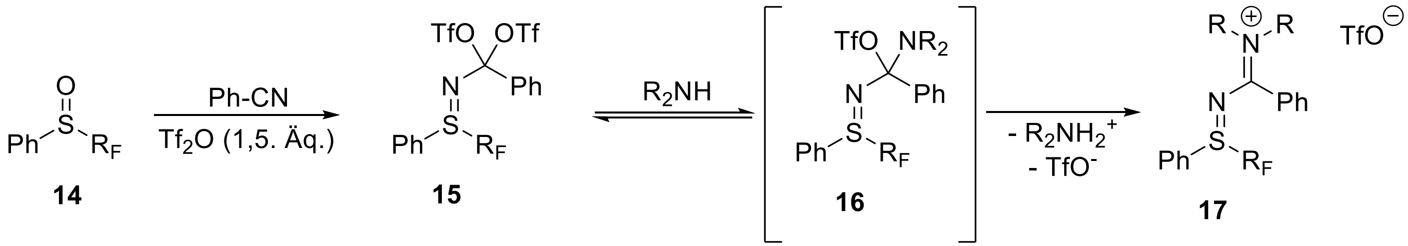
7

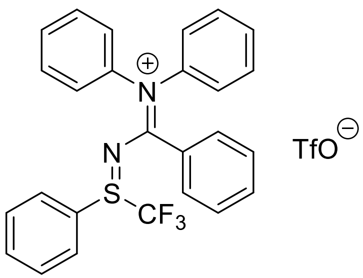
S. G. Clarke, J. Kenyon, H. Phillips, *J. Chem. Soc.* **1927**, 188.

Synthesis

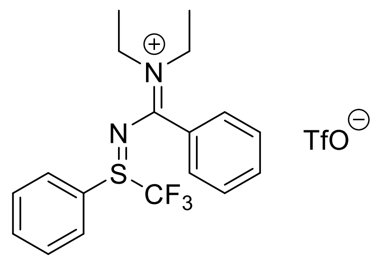


D. Kaiser, L. F. Veiros, M. Nuno, *Chem. Eur. J.* **2016**, *22*, 4727-4732.

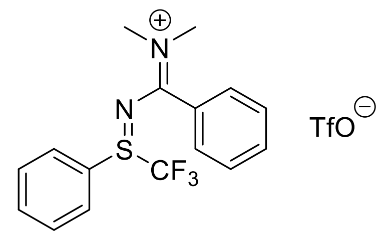




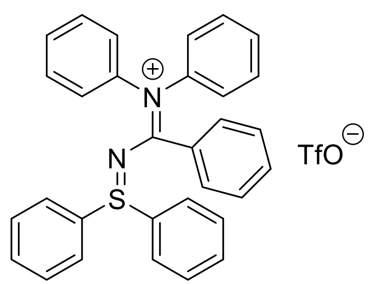
3, 72%



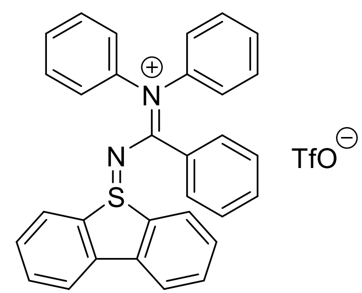
4, n.b.



5, 5%



6, 4%

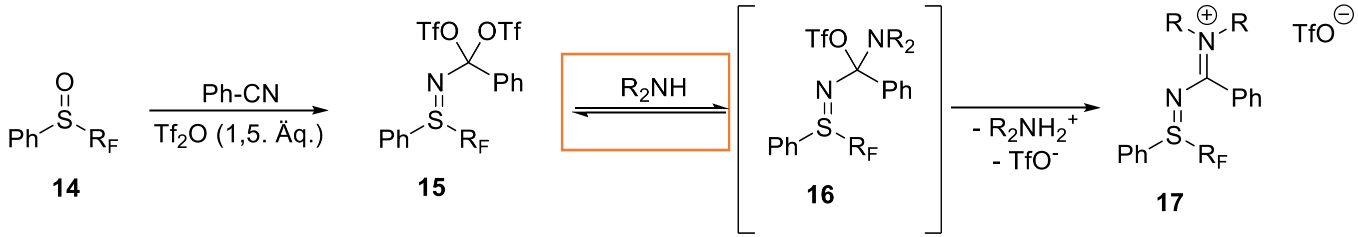


7, n.b.

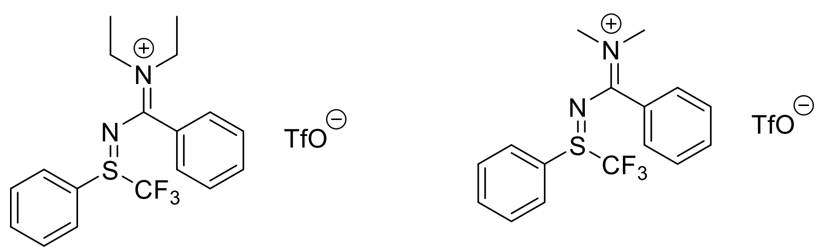
C. Urban, Y. Macé, F. Cadoret, J.-C. Blazejewski, E. Magnier, *Adv. Synth. Catal.* **2010**, *352*, 2805-2814.

What are the problems?

1. The synthesis:



- Amines are not nucleophilic enough



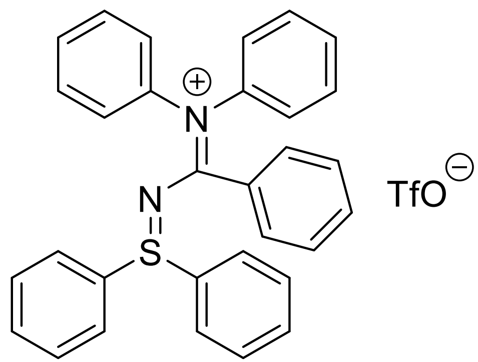
4, n.b.

5, 5%

C. Urban, Y. Macé, F. Cadoret, J.-C. Blazejewski, E. Magnier, *Adv. Synth. Catal.* **2010**, *352*, 2805-2814.

2. The purification:

- The imines can interact with the silica gel
- In addition the molecules are salts

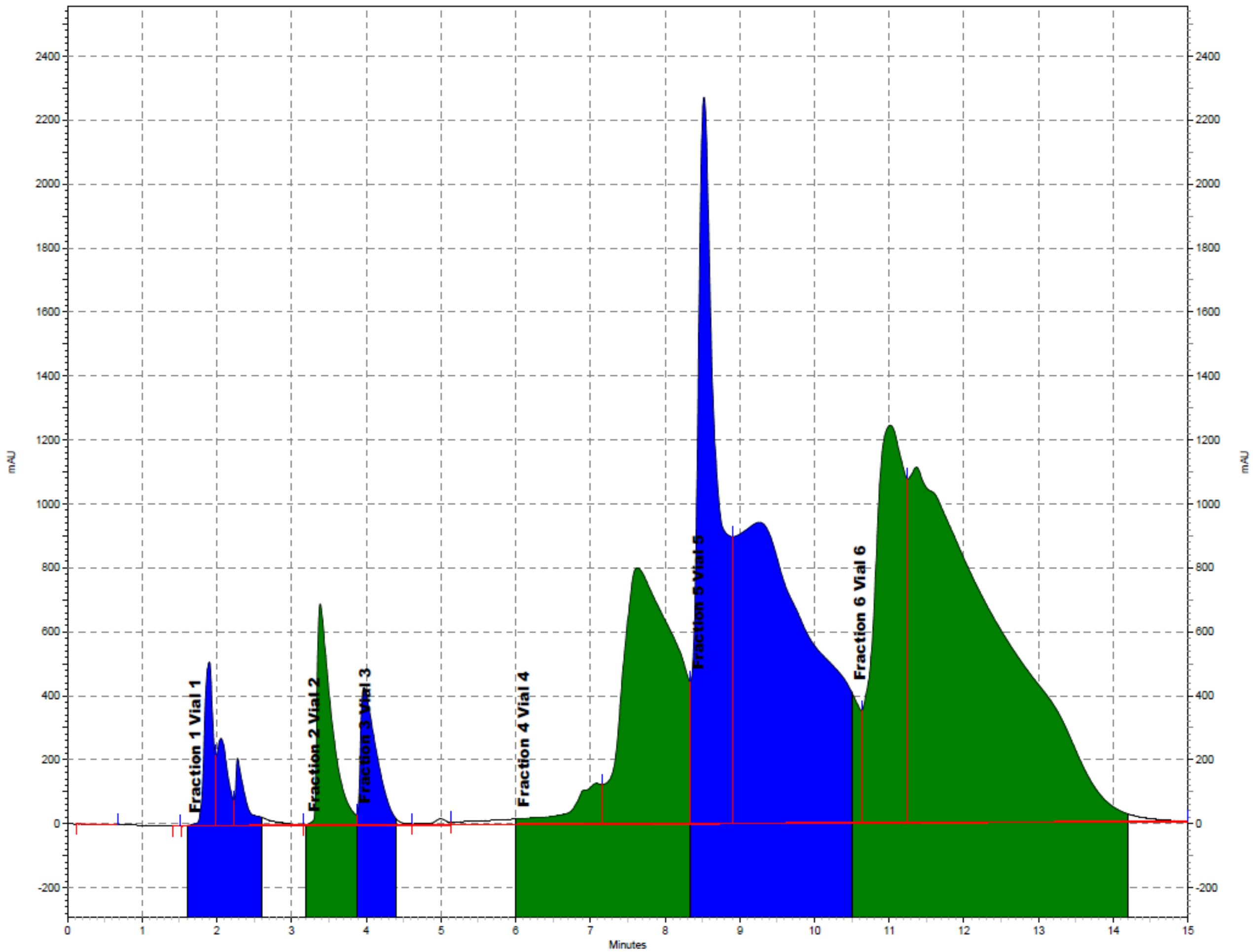


6, 4%

- Attempt by separation on *high performance liquid chromatography* (HPLC) in combination with reversed-phase silica gel

What are the problems?

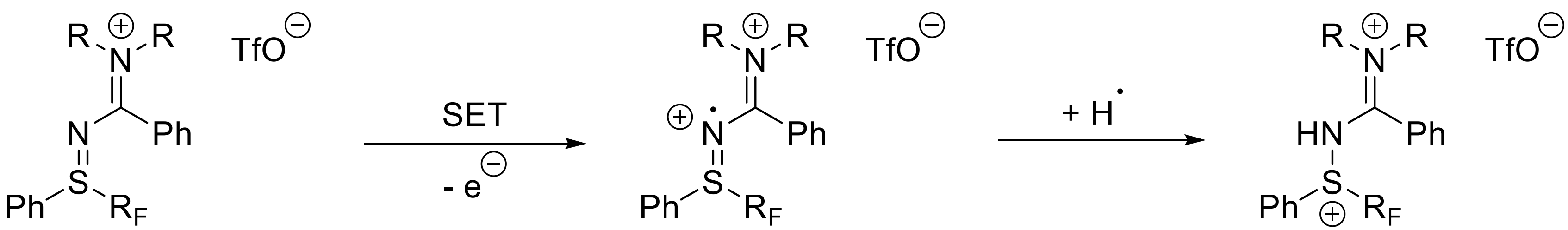
2. The purification:



270 nm, Eurospher II CN, 0,318CV/min., 80% EtOAc, 20% n-Hexan.

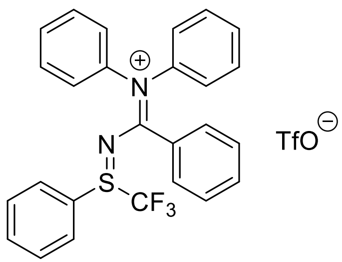
- Calculating the BDE(N-H) of **20**

- Measurement of the oxidation potential and the absorption maximum

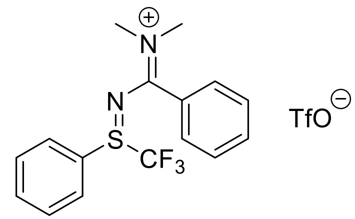


18 **19** **20**

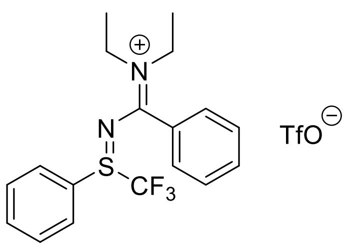
Measurement of the oxidation potential and the absorption maximum



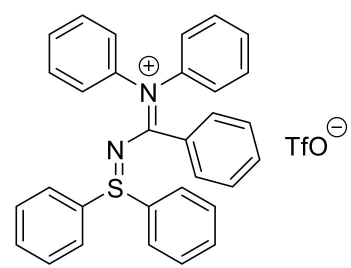
3
0.54 V
261.27 nm



4
0.71 V
349,81 nm



5
0.63 V
n.b.

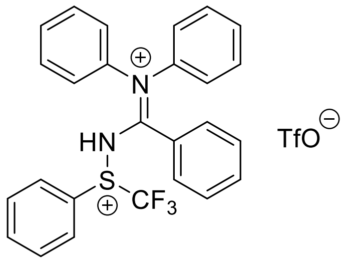


6
0.58, 0.76, 0.88 V
261.63 nm

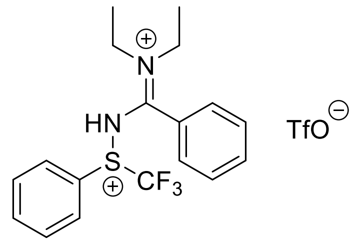
Determined by cyclic voltammetry in Acetonitril/DMSO vs. SCE

Results

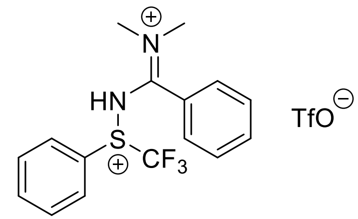
Calculating the BDE(N-H)



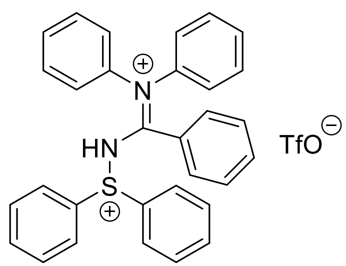
3
ΔH (N-H) = 80.91 kcal/mol
ΔG (N-H) = 73.28 kcal/mol



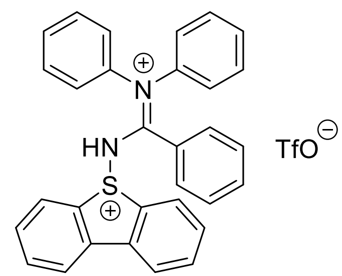
4
ΔH (N-H) = 102.37 kcal/mol
ΔG (N-H) = 105.52 kcal/mol



5
ΔH (N-H) = 105.52 kcal/mol
ΔG (N-H) = 96.46 kcal/mol

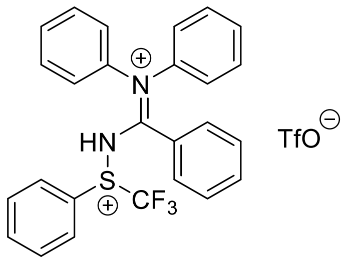


6
ΔH (N-H) = 85.24 kcal/mol
ΔG (N-H) = 78.68 kcal/mol



7
ΔH (N-H) = 92.97 kcal/mol
ΔG (N-H) = 79.55 kcal/mol

Calculations at M08hx/def2TZVP-level.



21
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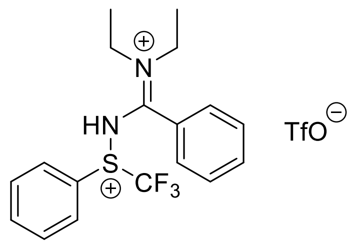

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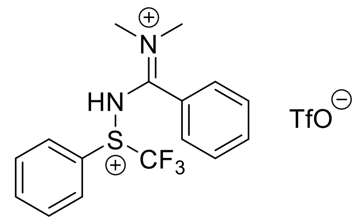

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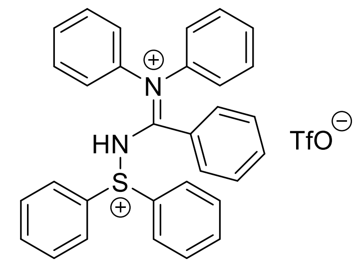
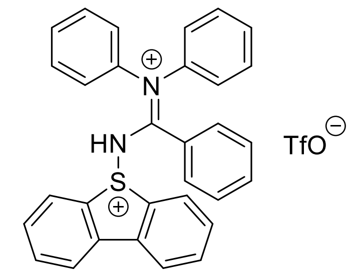
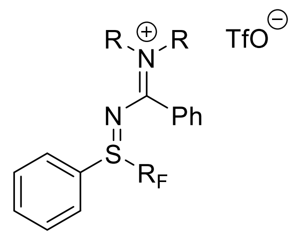


24
ΔH (N-H) = 85.24 kcal/mol
ΔG (N-H) = 78.68 kcal/mol



25
ΔH (N-H) = 92.97 kcal/mol
ΔG (N-H) = 79.55 kcal/mol



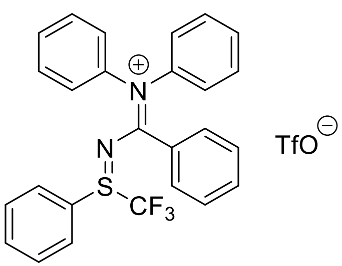
R= -Ph, -Et, -Me $\longrightarrow$ Decreasing + I effect

R_F= -CF_3, -Ph $\longrightarrow$ Increasing + I effect

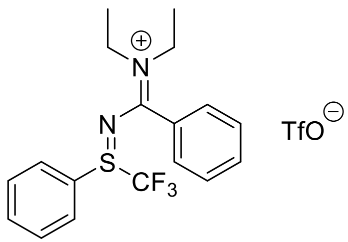
$\Longrightarrow$
BDE is increasing

Calculations at M08hx/def2TZVP-level.

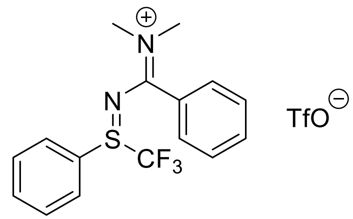
Summary and Outlook



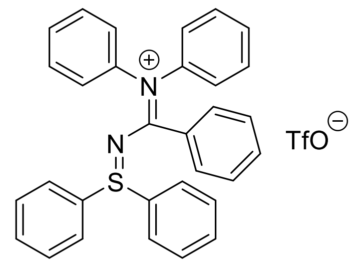
3, 72%



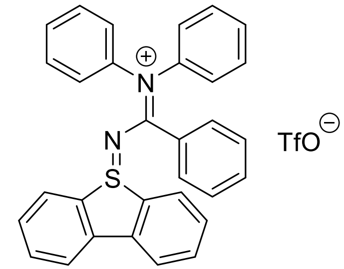
4, n.b.



5, 5%



6, 4%



7, n.b.

- There are two major problems:
    1. The synthesis
    2. The purification

- The separation with an HPLC did not succeed either

- Quantum mechanical calculations for the N-H bonds were made

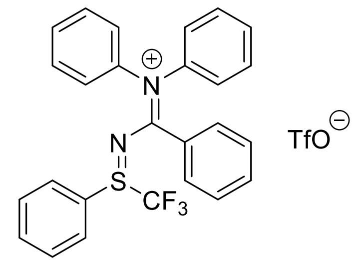
- Cyclic voltammograms and UV/Vis-Spectra were recorded

Summary and Outlook

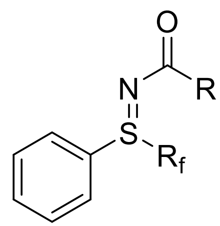
- In this work the sulfilimines were not used as HAT catalysts

- Only sulfilimine **3** was synthesized in sufficient quantity and purity
  - BDE (N – H) of 81 kcal/mol

- The differentiation of the sulfilimines is difficult



3



26

- Molecule **26** is not a salt and therefore should be easier to purifiy

Acknowledgment

Prof. Dr. Peter R. Schreiner

Frederik R. Erb

PRS Group