

# The Challenges Presented in the Synthesis of New Fluorinated Organic Linkers

Samuel Dickson, Dr. Douglas Genna

Abstract

Fluorinated Metal Organic frameworks have gained increase attention due to reported increase  $H_2$  and  $CO_2$  storage that may be caused by the exposed fluorine atoms. However, the synthesis of fluorinated organic molecules have proven to be a significant challenge do to unique electronegative and inductive effects that are not present in the nonfluorinated analogues. The present study has set to synthesize three new fluorinated organic linkers to be used for F-MOF synthesis and the challenges presented in each case.

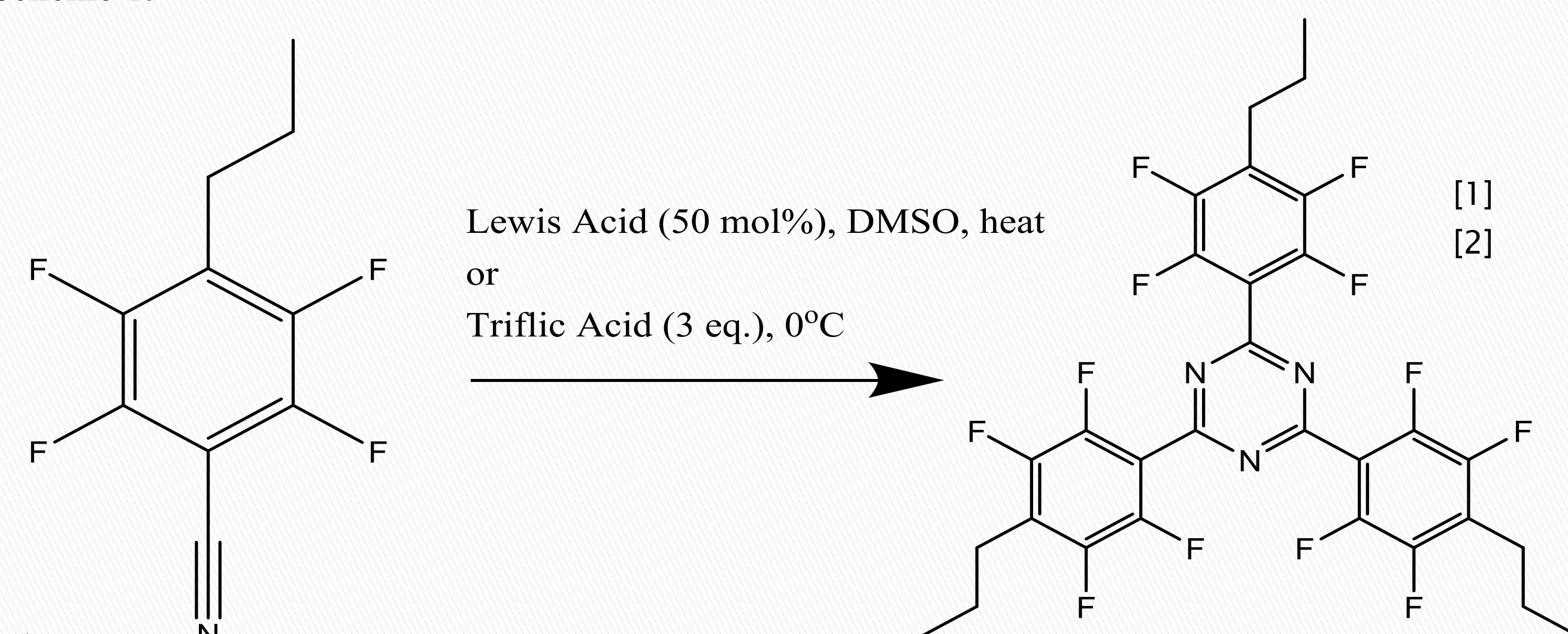
## Introduction

Fluorinated Metal Organic Frameworks (F-MOFs) have been gaining increase attention of the past several years due to reports that the exposed fluorine atoms have interesting  $H_2$  and  $CO_2$  storage properties<sup>[3]</sup>. However, reports of synthesis of F-MOFs are limited both due to the synthesis of the MOFs and the linkers. Perfluorinated carboxylic acids are generally more acidic than their nonfluorinated analogues and are less stable at higher temperatures that are necessary for MOF growth. The synthesis of the linkers also proves to be a challenge due to the complex electronegative and inductive effects<sup>[3]</sup> that the fluorine atoms have on the overall molecule that cause standard organic reactions to be unreliable. This study attempts to undergo the challenge of making fluorinated linkers using known organic reactions and subsequently using the products to create F-MOFs.

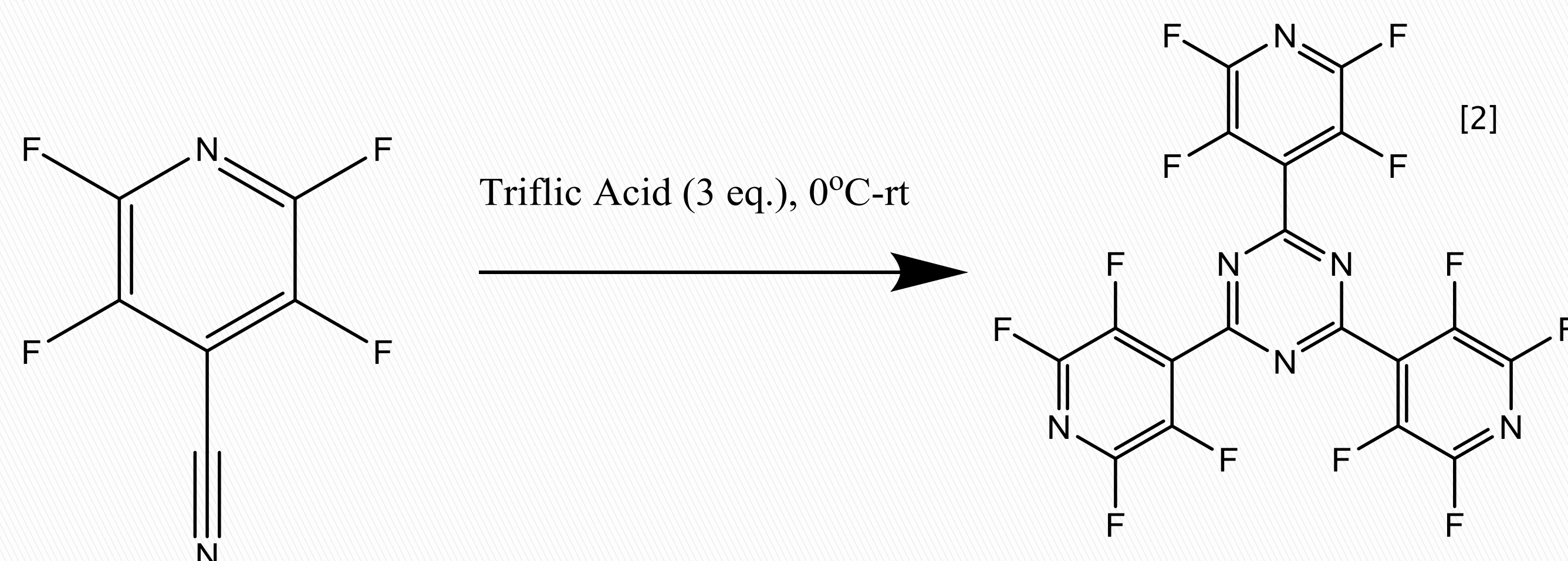
## Experimental

Scheme 1 and 2: involve the cyclization of three equivalents of starting material to yield a tri-substituted triazine.

Scheme 1:

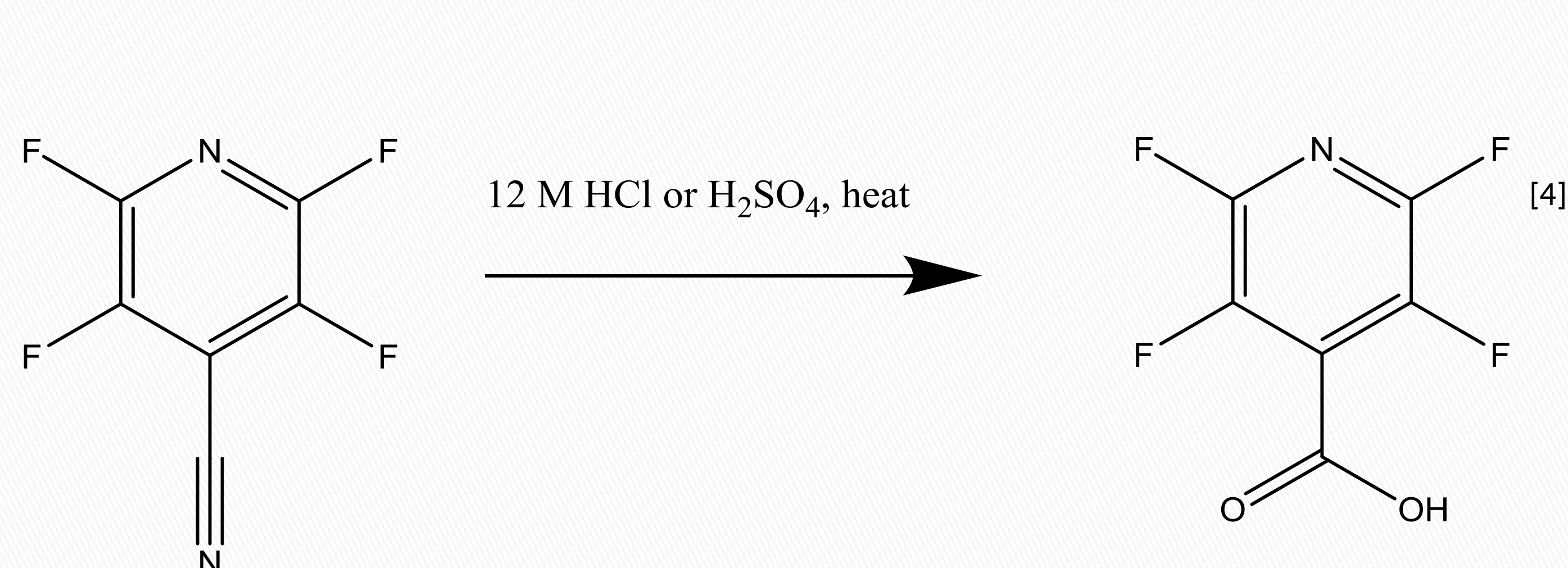


Scheme 2:



Scheme 3: Involves the hydrolysis of the nitrile to the carboxylic acid. Currently pursuing.

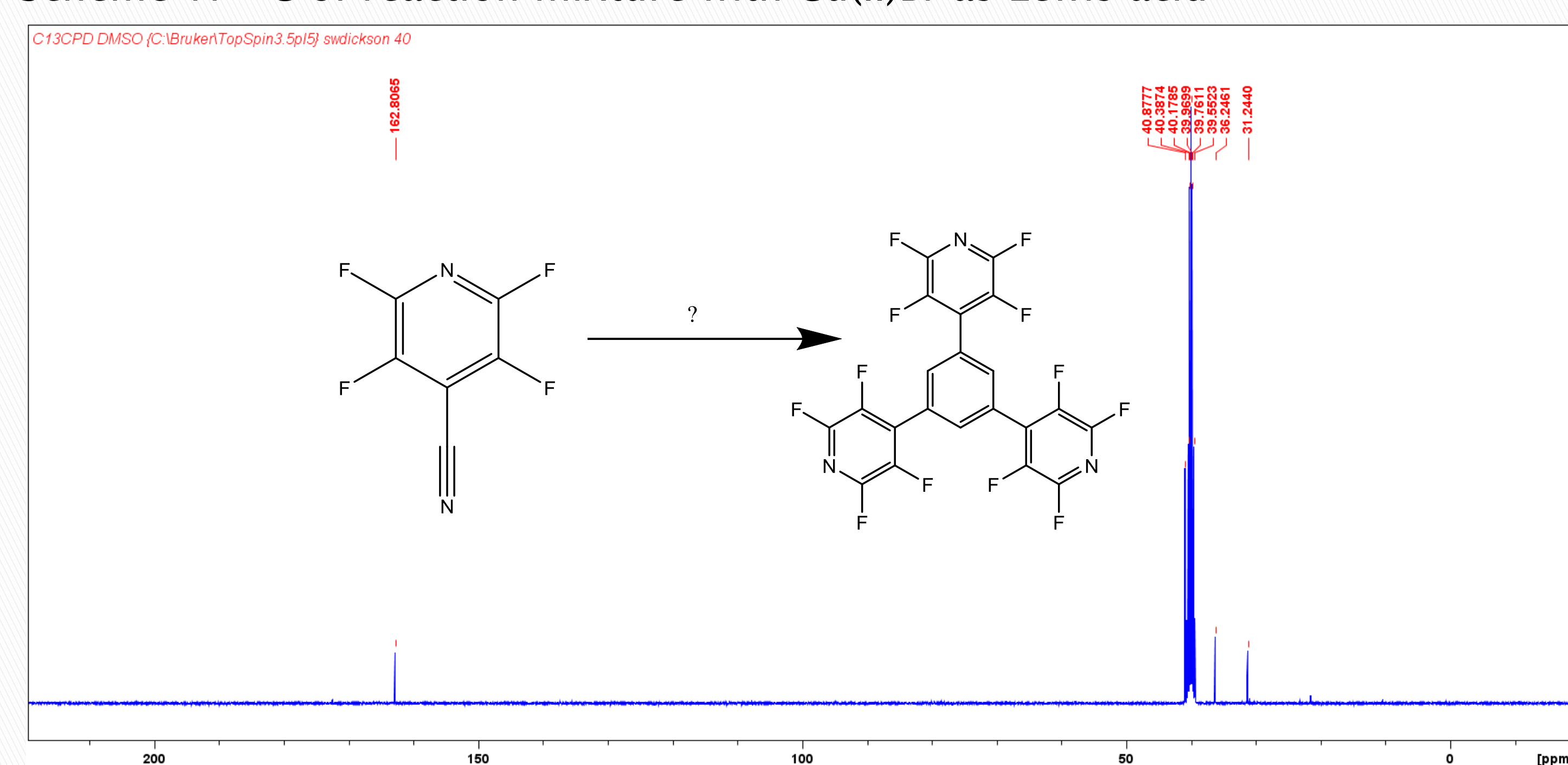
Scheme 3:



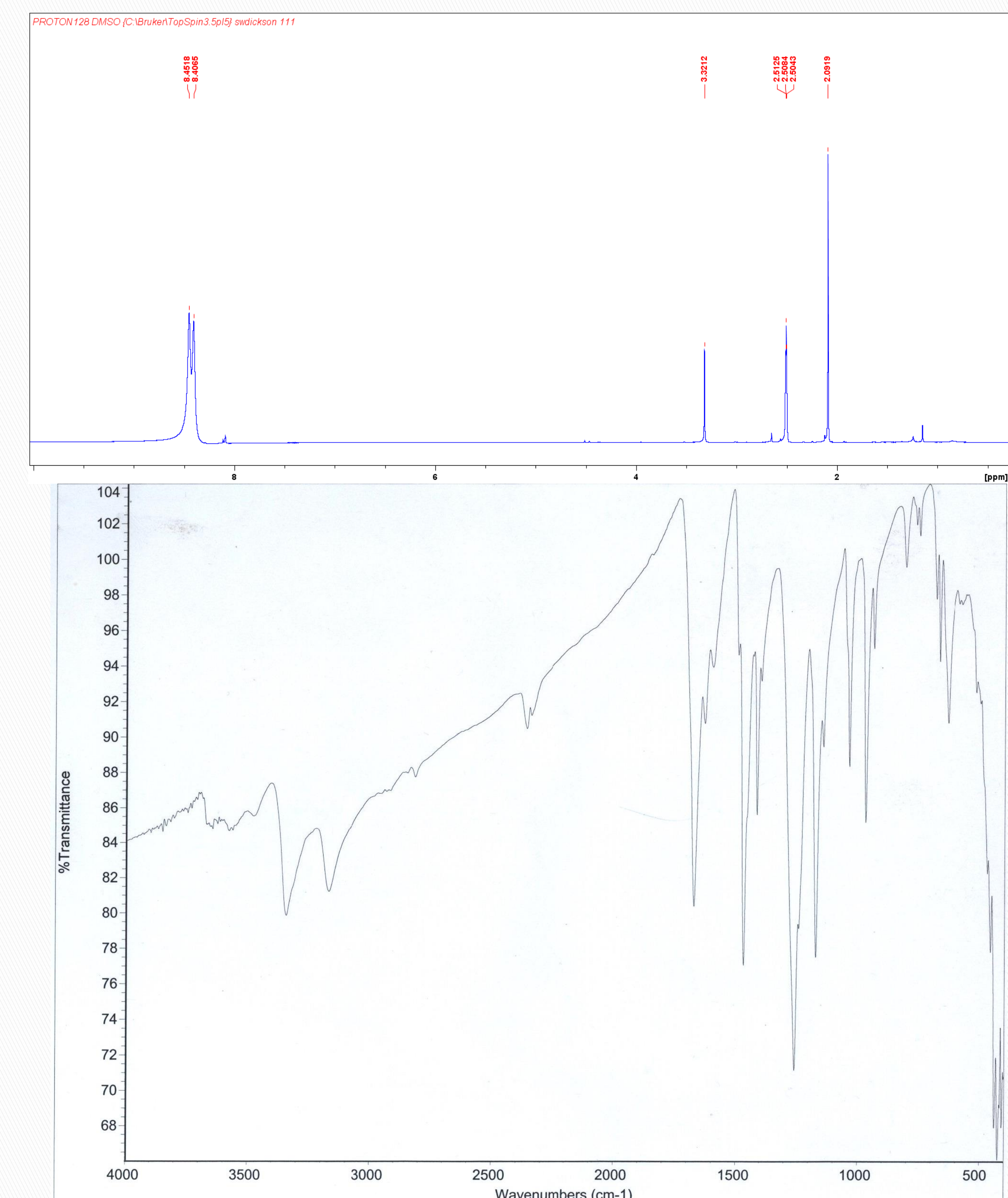
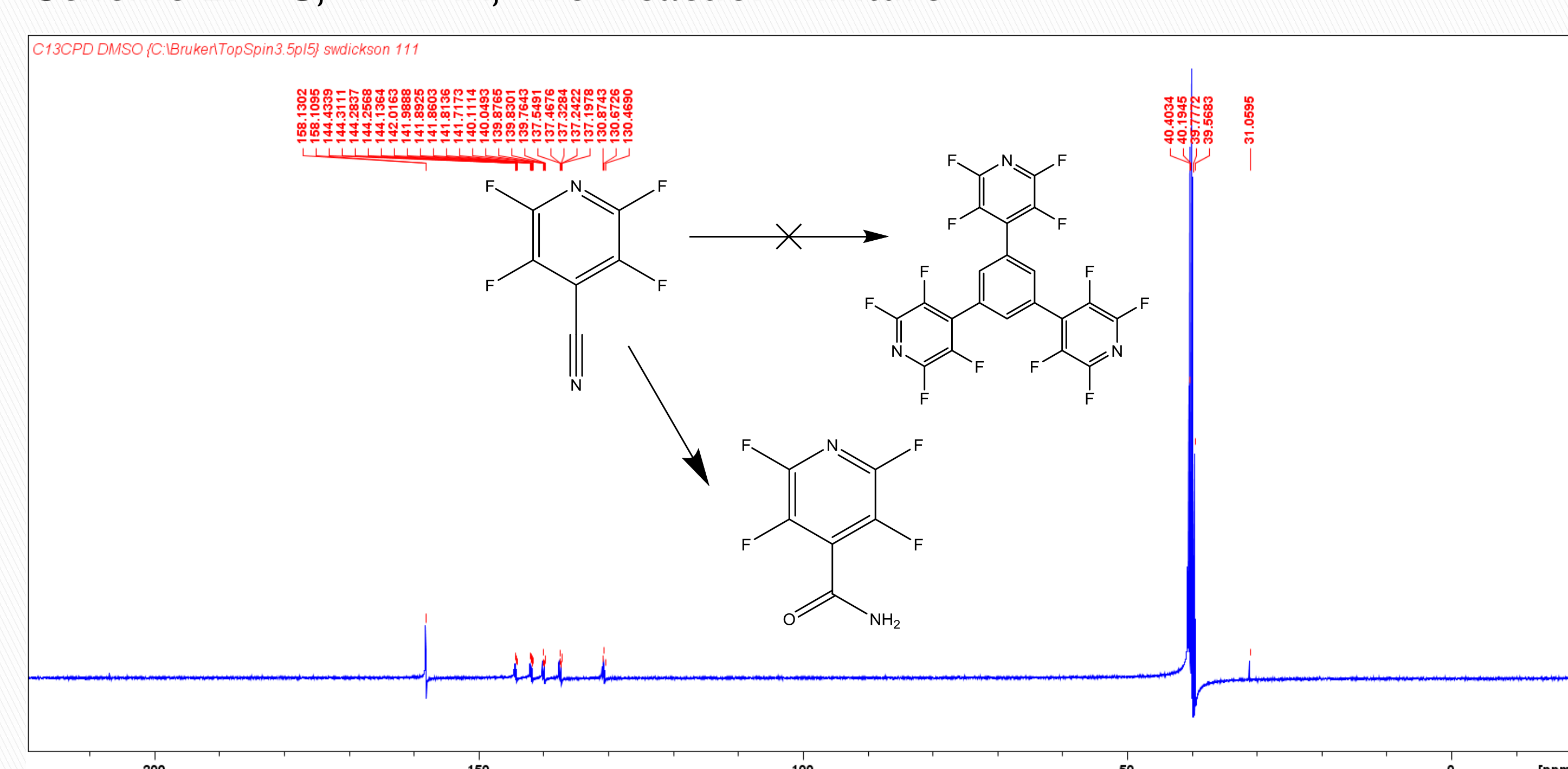
Scheme 1 and 2:

Trial	Lewis acid (50 mol%)	Solvent	Possible reaction?
1	No catalyst	DMSO	No
2	Copper (II) Chloride	DMSO	No
3	Copper (I) Chloride	DMSO	No
4	Copper (II) Bromide	DMSO	Yes
5	Rhodium (III) Chloride	DMSO	No
6	Indium (III) Chloride	DMSO	No
7	Scandium (III) Triflate	DMSO	No
8	Iron (II) Perchlorate	DMSO	No
9	Cesium Fluoride	DMSO	No
10	Triflic acid*	-	Yes

Scheme 1:  $^{13}C$  of reaction mixture with Cu(II)Br as Lewis acid



Scheme 2:  $^{13}C$ ,  $^1H$  NMR, IR of reaction mixture



## Conclusion

It was found in the conditions used for the synthesis of the fluorinate triazines that cyclization does not readily occur, rather the system more readily hydrolyzes the nitrile to an amide.

More work is being done to synthesis fluorinate organic molecules to be used as linkers in F-MOF chemistry.

## References

1. Debnath, P.; Majumdar, K.C. *Tetrahedron Letters*. 2014, 55, 6976-6978.
2. Herrera, A; et al. *J. Org. Chem.* 2014, 79, 7012-7024
3. Pachfule, P.; Raja, D.; Poddar, P.; Banerjee, R. *Cryst. Growth Des.* 2011, 11, 1215-1222.
4. Yali, G.; et al. *Zhonggou Yiyao Gongye Zazhi*. 2007, 38, 14-21.



YOUNGSTOWN  
STATE  
UNIVERSITY

Choose **Ohio** First

\*triflic acid used in both scheme 1 and 2 (3 eq).