

# Sulfonic Acids as Linkers for Thermally Robust Metal Organic Frameworks

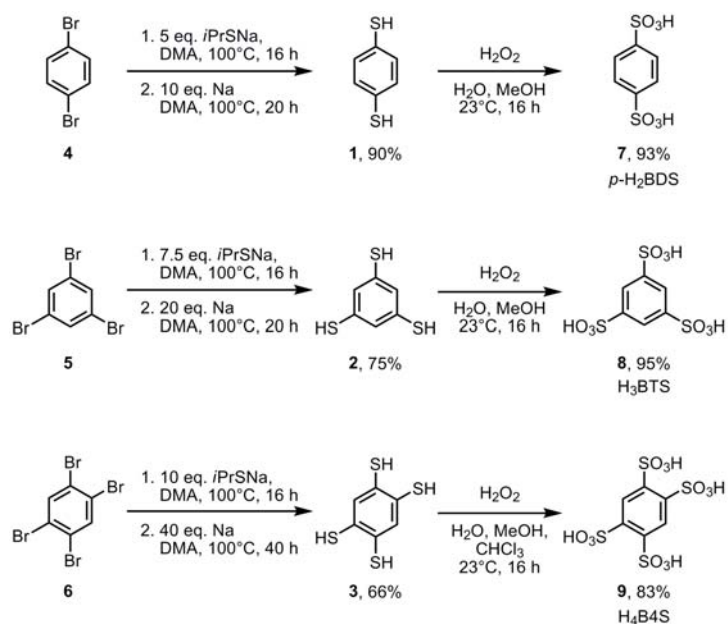
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In order to synthesize sulfonic acids mimicking common carboxylic acid linkers for the preparation of metal organic frameworks, we developed a convenient route for their preparation *via* the corresponding thiols. The thiols were prepared by a sequential one-pot procedure starting from readily available aromatic bromo compounds. An alternative route for the preparation of sulfonic acids is presented on the example of 2,3,5,6-tetrafluorobenzene disulfonic acid. Copper salts of all synthesized sulfonic acids were obtained and investigated by X-ray and DTA/TG studies.

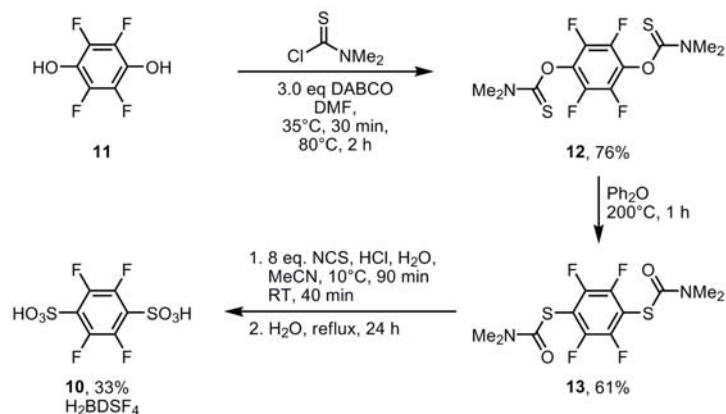
## Preparation of Aromatic Sulfonic Acids

In order to overcome the limits of direct sulfonation of aromatic compounds the thiols **1**, **2** and **3** were prepared by nucleophilic attack of *i*PrSNa on bromobenzenes **4**, **5** and **6**. Adding sodium for the reductive cleavage of the intermediate thioethers furnished the thiols **1**, **2** and **3** in good yields. Tedious workup was avoided during the preparation of the sulfonic acids **7**, **8** and **9**, as all components used for oxidation can be removed under reduced pressure.<sup>[1,2]</sup>



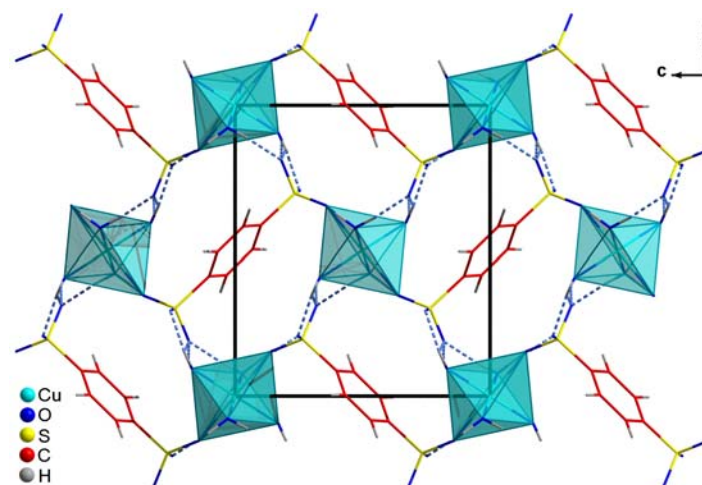
## Alternative Route towards Halogenated Sulfonic Acids

In order to achieve teflonization effects in the final framework 1,2,5,6-tetrafluorobenzene disulfonic acid (**10**) was prepared *via* Newman-Kwart rearrangement from tetrafluoro hydroquinone (**11**) in four steps.

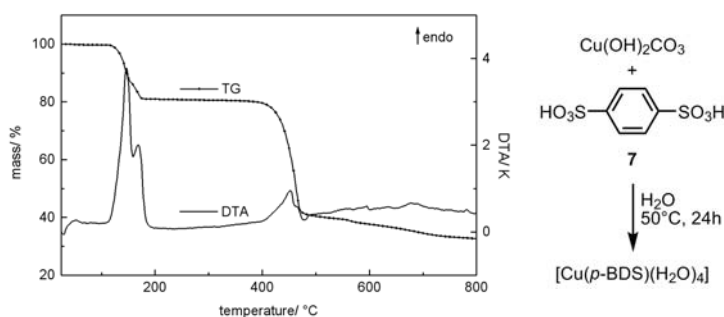


## Thermally Robust Frameworks

The reaction of Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> with the sulfonic acids reported herein is possible due to their stronger Brønsted acidity. Single crystals suitable for X-ray investigation could be obtained from each acid. [Cu(*p*-BDS)(H<sub>2</sub>O)<sub>4</sub>] forms chains, which are connected by hydrogen bonds to form a 3D network.



The thermal stability of all prepared Copper salts was investigated by DTA/TG-studies. All salts were remarkably stable. [Cu(*p*-BDS)(H<sub>2</sub>O)<sub>4</sub>], for example, decomposes at temperatures above 450°C.



## Conclusions

- Several formerly inaccessible aromatic sulfonic acids can be prepared by a simple one pot procedure from their corresponding bromobenzenes.
- Access to halogenated sulfonic acids can be provided by Newman-Kwart reaction of the phenols and oxidation of the resulting thiocarbamates.
- The copper salts of the described sulfonic acids proved to be remarkably stable at higher temperatures.

[1] A. Mietrach, T. W. T. Muesmann, J. Christoffers, M. S. Wickleder, *Eur. J. Inorg. Chem.* **2009**, 5328–5334.

[2] T. W. T. Muesmann, A. Mietrach, J. Christoffers, M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2010**, 636, 1307–1312.