Summer 2017 Research Presentation

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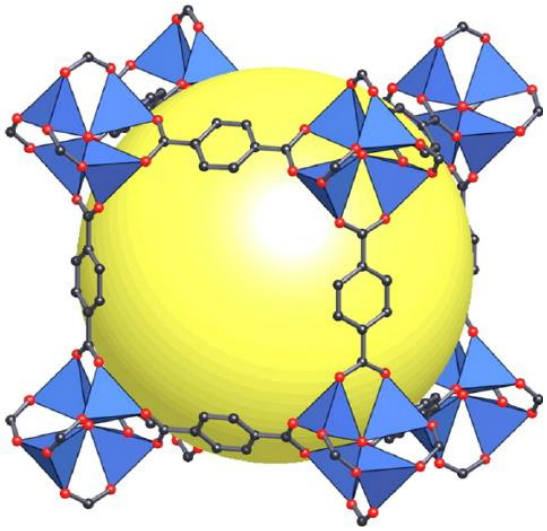
What are Metal Organic Frameworks?

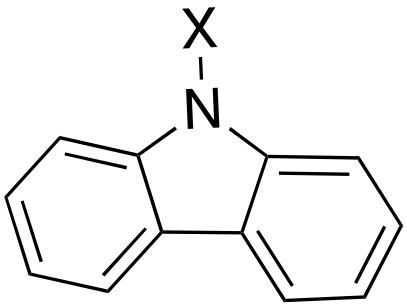
- Networks or clusters made up of organic ligands coordinated to metals.
- These coordinated networks form porous, crystalline structures.
  - The pores allows them to soak up and store high volumes of natural gas.
- The pore size of the metal organic framework determines its ability to store natural gas.
  - Useful for gas storage, catalysis, drug delivery etc.



MOF-5
($Zn_4O(BDC)_3$)

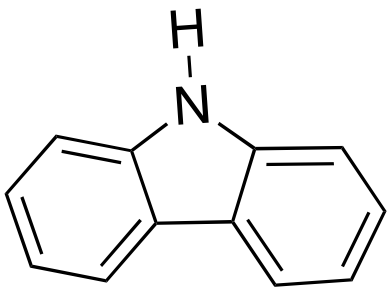
My Research

- My research specifically has been focused on synthesizing derivatives of the 9H carbazole ligand and attempting to metalate them to $Cu(NO_3)_2$ and other various metals.
- In particular, I've focused on adding primary, secondary and tertiary backbones to the 9-H carbazole ligand.
  - Primary Backbones→ X = H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_2CH_2CH3$, docecyl, octadecyl
  - Secondary Backbones→ 2-iodo-butane, 1-iodo-2-methyl propane, 2-iodo-propane
    - I was only successfully able to add the 2-iodopropane backbone to the carbazole ligand.
      - Various temperatures and equivalents were used in an attempt to yield the other two secondary backbones, but these attempts were unsuccessful.
  - Tertiary Backbones → 1-iodo-2-methyl-butane
    - Various temperatures and equivalents were used in an attempt to yield the tertiary backbone, but these attempts were unsuccessful.



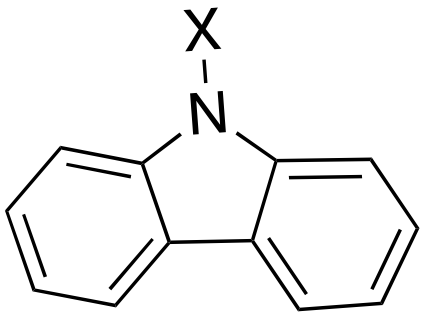
9-X Carbazole Ligand

My Research



+ 1.5 EQVT
Alkyl Iodide

6.25 EQVT
KOH/DMF
*12 hours

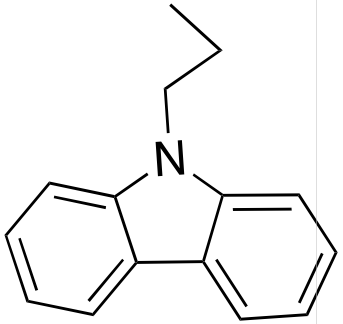


* The reaction is generally performed at room temperature (25°C) for primary backbones, while adding heat (~80°C) is necessary for secondary backbones.

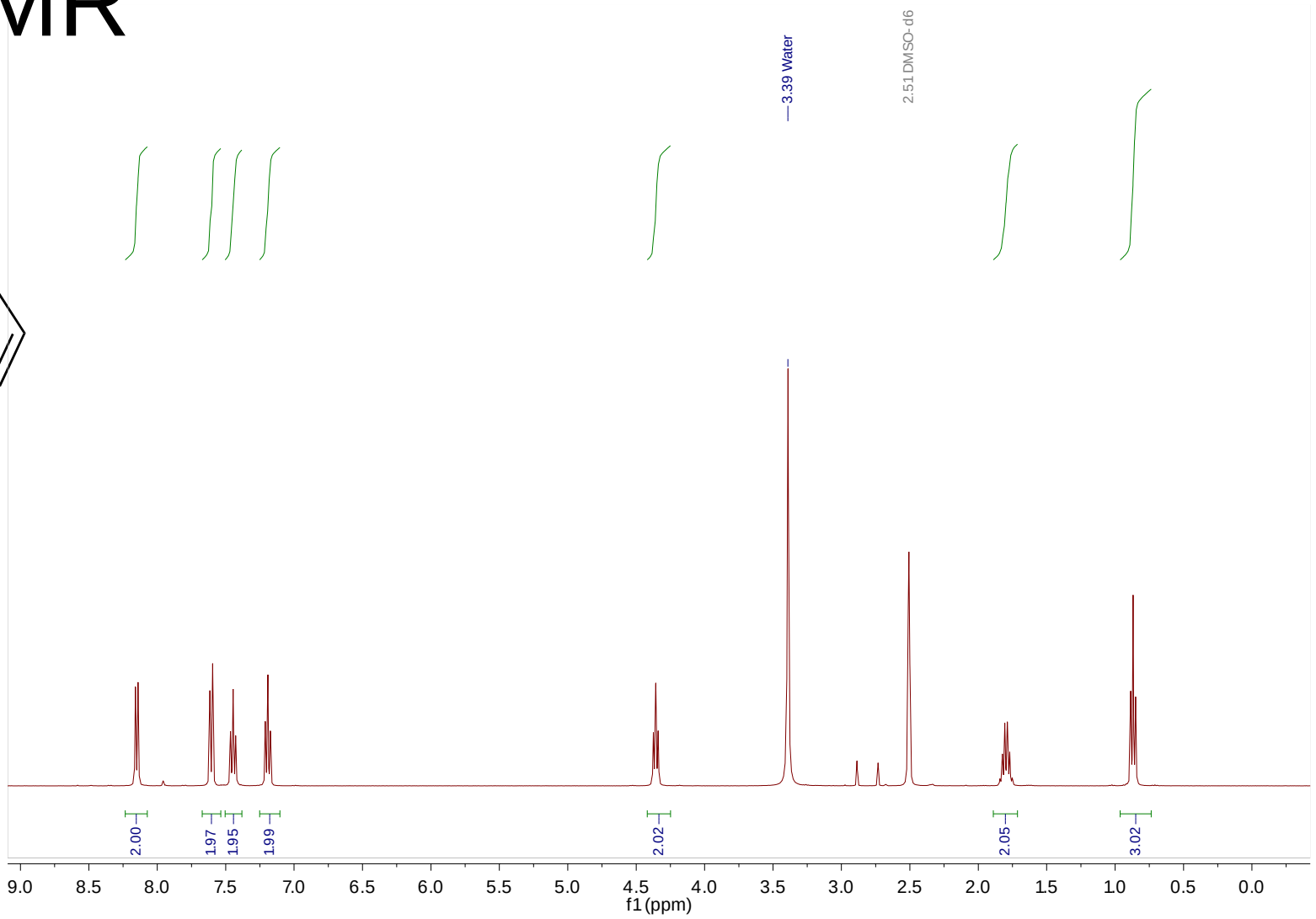
X = Methyl, ethyl, propyl, butyl, pentyl, hexyl, dodecyl, octadecyl, isopropyl

Brunner, K.; Dijken, A. V.; Börner, H.; Bastiaansen, J. J. A. M.; Kiggen, N. M. M.; Langeveld, B. M. W. Carbazole Compounds as Host Materials for Triplet Emitters in Organic Light-Emitting Diodes: Tuning the HOMO Level without Influencing the Triplet Energy in Small Molecules. *Journal of the American Chemical Society* **2004**, *126* (19), 6035–6042.

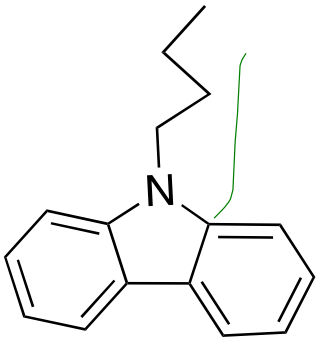
^{1}H NMR



Propyl Backbone

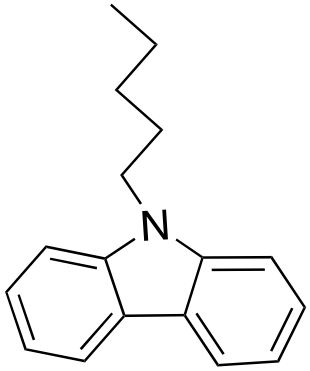


^{1}H NMR

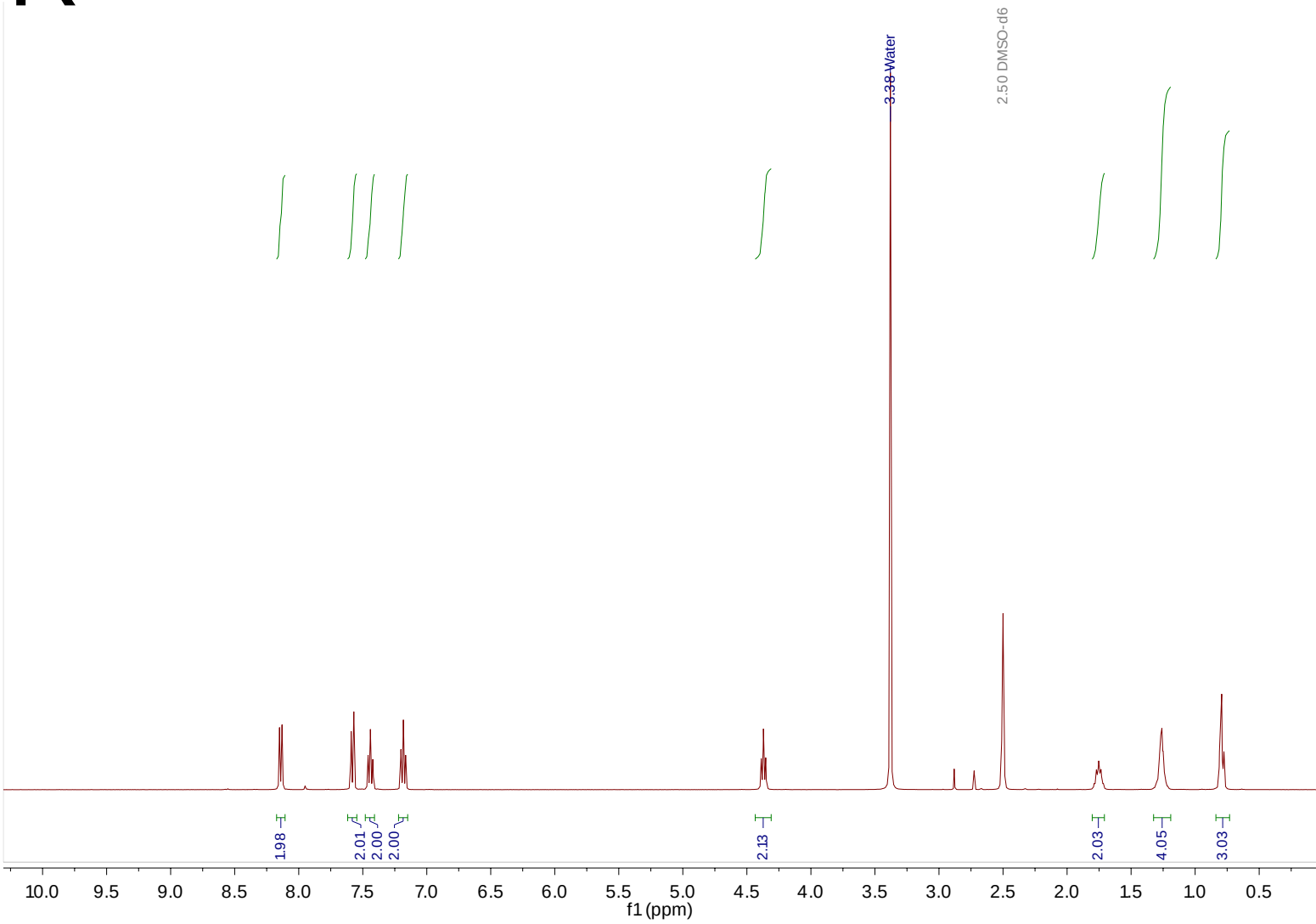


Butyl
Backbone

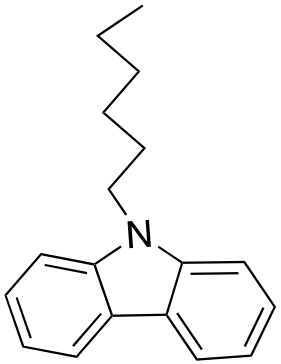
^{1}H NMR



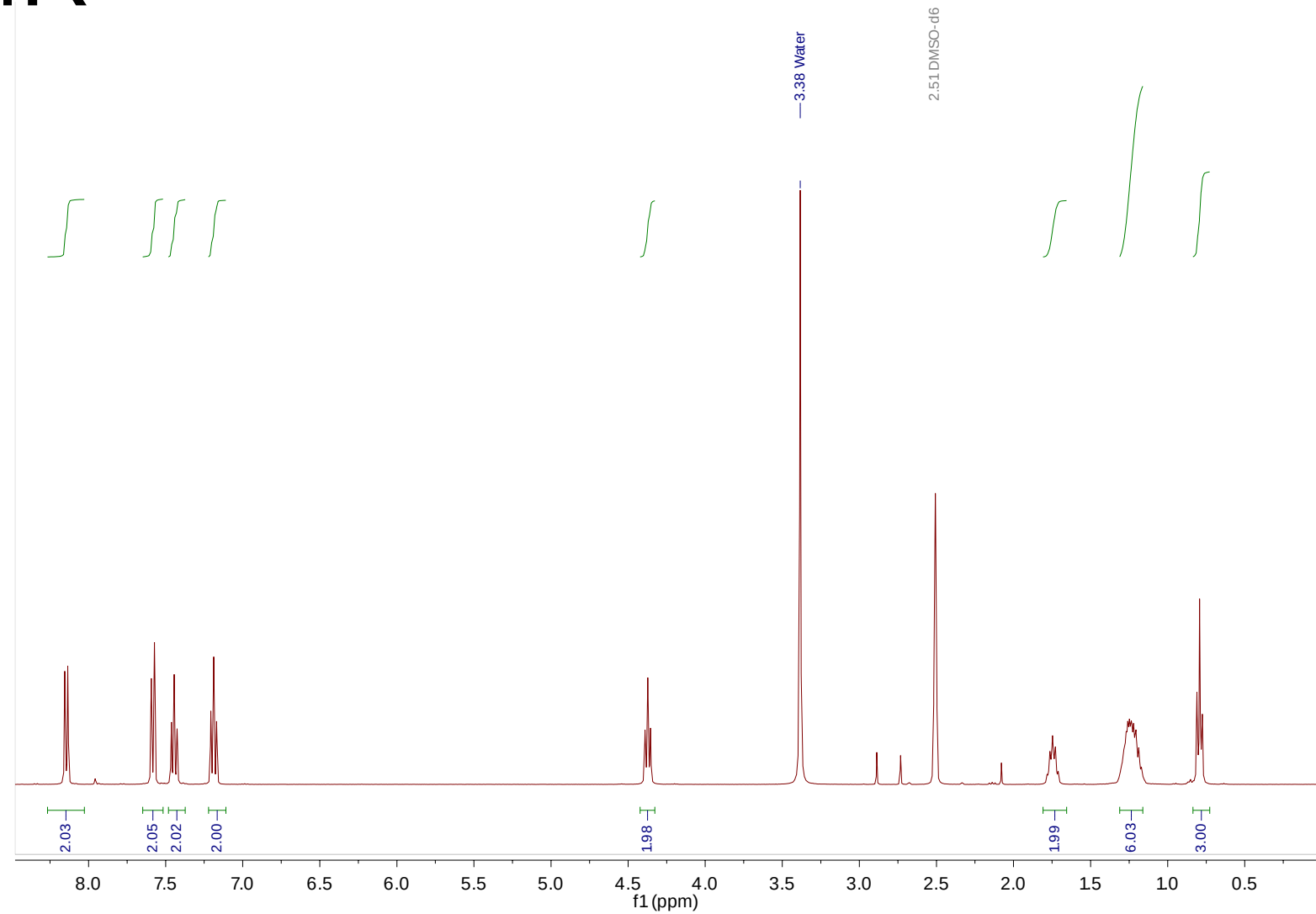
Pentyl Backbone



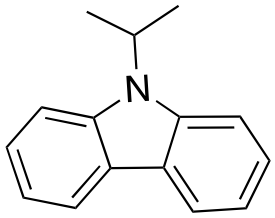
^{1}H NMR



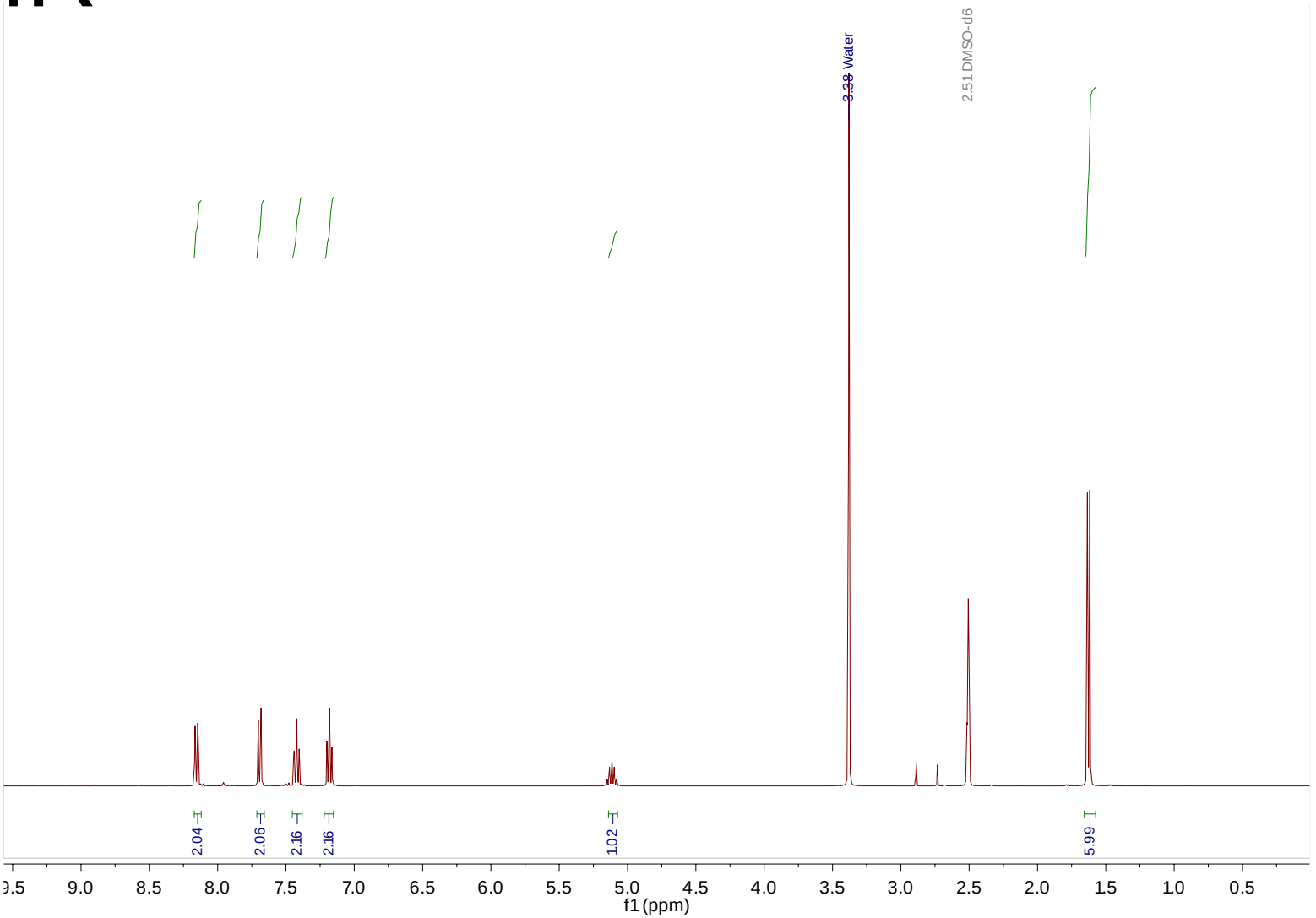
Hexyl Backbone



^{1}H NMR



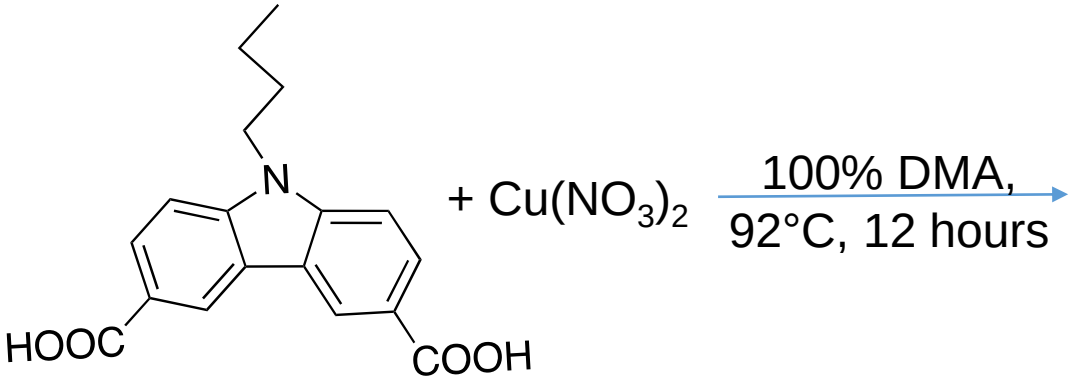
Isopropyl Backbone



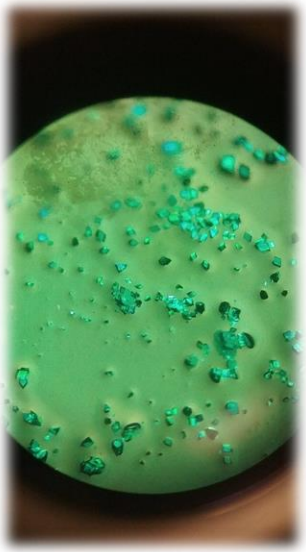
9-X CDCA Metalations

- 9-Methyl CDCA, 9-Ethyl CDCA metalations have been unsuccessful so far due to the insolubility of the ligand.
- 9-Propyl and 9-Butyl CDCA ligand metalations have yielded crystals/sheets/crystalline powder.
- 9-Pentyl and 9-Hexyl CDCA ligands have not been metalated yet.

9-Butyl CDCA Metalations

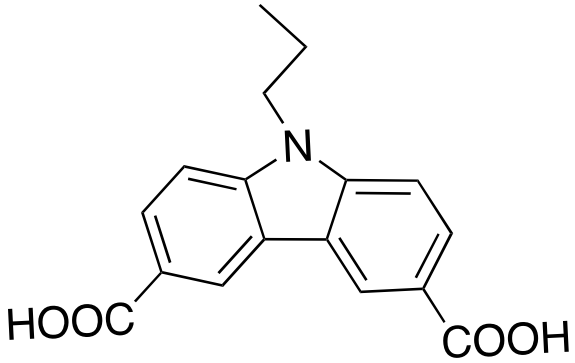


- Biggest crystals were yielded with 100% DMF or 100% DMA at 92°C
- Crystals are insoluble in most solvents except DMPU, DMSO and THF



These crystals appear to be sheets upon doing further investigating.

9-Propyl CDCA Metalations

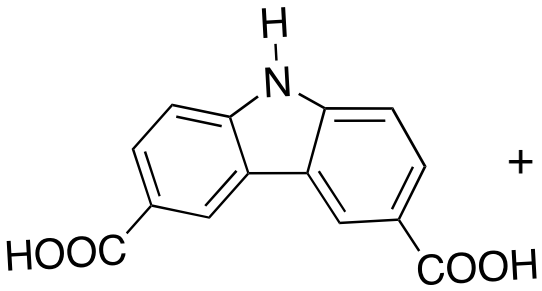


+ $Cu(NO_3)_2$

100% DMA,
2 EQVT
Benzoic Acid
92°C
Overnight

Crystals

9-H CDCA Polyhedra



+ $Cu(NO_3)_2$

DMF/EtOH
(1:1)
95°C
Overnight

Polyhedra

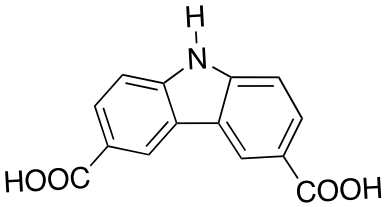
López-Olvera, A.; Sánchez-González, E.; Campos-Reales-Pineda, A.; Aguilar-Granda, A.; Ibarra, I. A.; Rodríguez-Molina, B. CO2 capture in a carbazole-Based supramolecular polyhedron structure: the significance of Cu(Ii) open metal sites. *Inorg. Chem. Front.* **2017**, *4* (1), 56–64.

9-H CDCA Metalations

Purple Crystals?

$Co(OAc)_2$

100% DMF



$Ni(OAc)_2$

100% DMF

Powdered Out

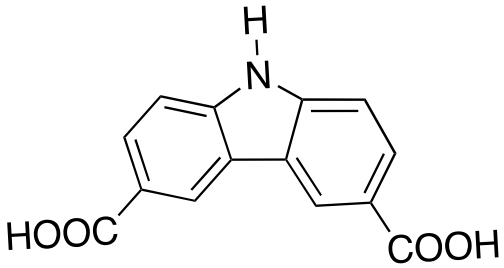
$Zn(OAc)_2$
DMF, DMA, DMPU

Powdered Out

$Mn(NO_3)_2$
DMF, DMA, DMPU

Tiny Clear Crystals/Powder from DMF (110°C) and DMPU (110°C)

9-H CDCA Metalations



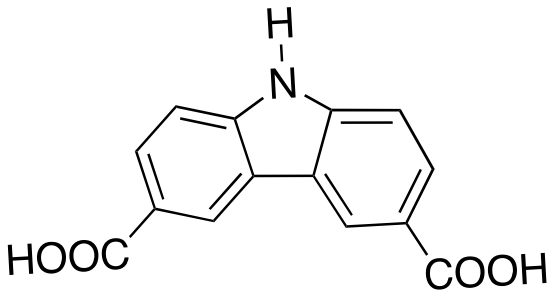
+ $Co(CO_2CH_3)_2$

100% DMF
110°C~ 3 days

Purple Hexagonal Sheets/Crystals?

- Set up experiment with various ratios of DMF/MeOH and DMF/EtOH, still on 110°C hot plate
- Cobalt polyhedra are generally dark green/black, so it is likely that these purple crystals are not polyhedra.

9-H CDCA Metalations



+ $Mn(NO_3)_2$

100% DMPU, 1 EQVT Pyridine
110°C

Small, white crystals

Future Work

- Optimize conditions for 9-Propyl CDCA and 9-Butyl CDCA crystals
  - Attempt to recrystallize the ones already made to remove impurities and make the crystals larger
- Begin to metalate 9-Hexyl, 9-Pentyl CDCA Ligands
- Figure out conditions that will allow for the addition of the tertiary backbone (1-iodo-2-methyl-butane) to carbazole ligand
- Figure out conditions that will allow the two remaining secondary backbones to be added to carbazole ligand (2-iodo-butane, 1-iodo-2-methyl propane)