Synthesis and Characterization of three diketones: 1,4-di-2'-pyridinyl-1,4-butanedione, 1,4-di-3'-pyridinyl-1,4-butanedione and 1,4-di-4'-pyridinyl-1,4-butanedione

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Introduction

Pyridine is an important heterocycle in medicinal chemistry and materials science. The ring nitrogen alters its electronic properties, introduces hydrogen-bonding ability and improves metal coordination. These features make pyridine-containing compounds valuable in molecular design and synthesis.

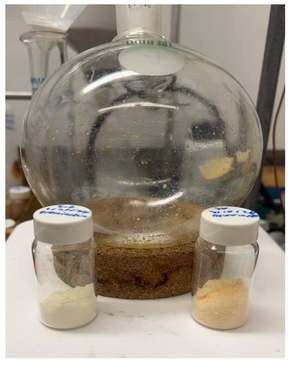
In this project, one of three structurally related bispyridyl diketones was synthesized, purified and characterized: 1,4-di-2'-pyridinyl-1,4-butanedione. The syntheses of its *meta* and *para* isomers, 1,4-di-3'-pyridinyl-1,4-butanedione and 1,4-di-4'-pyridinyl-1,4-butanedione, respectively, is planned.

Methodology & Synthesis

The target compounds are starting materials for the synthesis of pyridine-containing organic semiconductors, so they need to be created in high purity for subsequent synthetic steps. Focusing on Scheme #3, the α-halogenation reaction to create compound **5** was run in glacial acetic acid in the presence of molecular bromine, Br_2. A simple work-up consisting of vacuum filtration followed by washing with diethyl ether afforded **5**. The condensation reaction to create compound **6** involved an interesting reagent called 'Rongalite', sodium hydroxymethanesulfinate, which initiates free radical chain reactions to form C-C bonds under thermal conditions. Rongalite is a mild, inexpensive and green alternative to traditional transition metal-mediated radical coupling reactions. Purification of **6** entailed multiple extractions using ethyl acetate and water. The organic layer was dried, filtered and then the solvent removed using rotary evaporation. Compounds **5** and **6** were both prepared in relatively high purity.

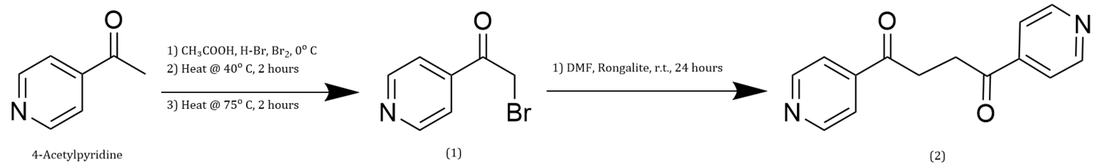
Showcase

Purified compounds **5** and **6** from Scheme 3

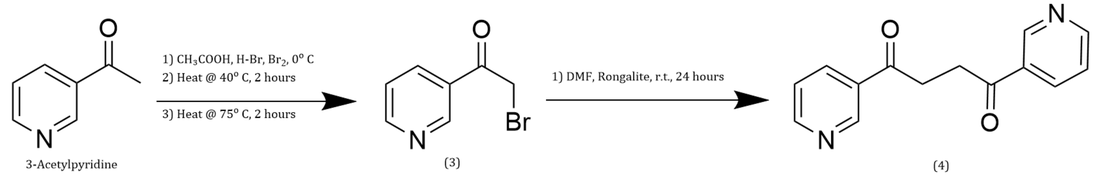


Syntheses of Target Compounds

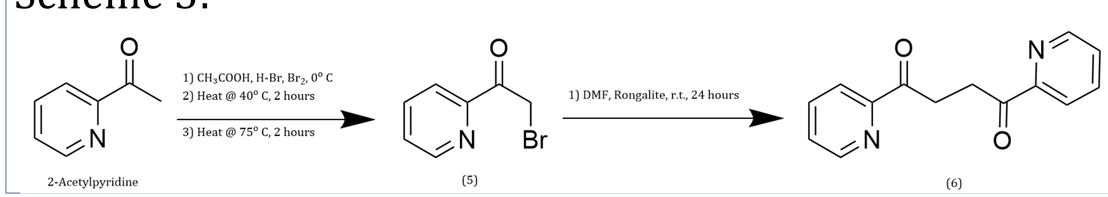
Scheme 1:



Scheme 2:

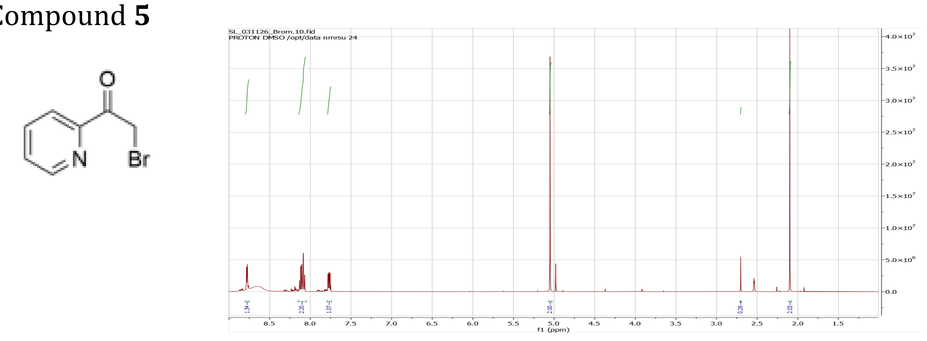


Scheme 3:

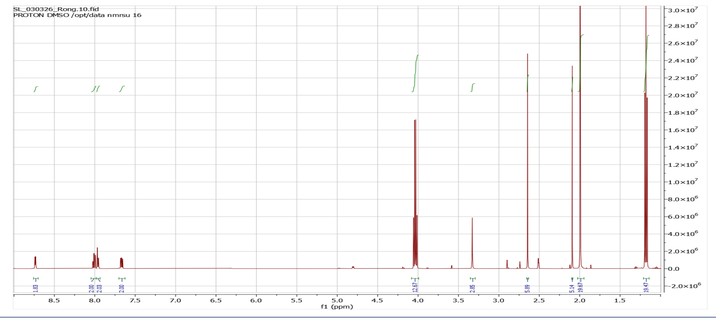


NMR Spectra

Compound **5**



Compound **6**



Results & Conclusions

Both compounds **5** and **6** from Scheme 3 were successfully synthesized, as confirmed ^{1}H NMR spectroscopy. The successful synthesis of **6** demonstrated here can be scaled to multigram quantities, and the same method should prove useful for the synthesis of isomers **4** and **2**, too. Compound **4** has the pyridyl nitrogen atoms in *meta* positions while compound **2** has the nitrogen atoms in *para* positions. These subtle changes in molecular structure will impact the electronic characteristics of the organic semiconductors prepared from them.

Compound **6** is commercially available for $200/gram. The *meta* isomer, compound **4** is also available commercially but it costs $5450/gram. The *para* isomer, compound **2** is not commercially available.

Future Work

In the future, both Scheme 1 and Scheme 2 will be followed to synthesize compounds **2** and **4**, respectively.

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References

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- Le, Nathan N.; et al *Synthesis of 1,4-Diketones via Titanium-Mediated Reductive Homocoupling of α-Haloketones*, *Synlett* , **2018**, *29*(16), 2195-2198