Synthesis and Characterization of Tridentate Quinoline-based NCO Ligands

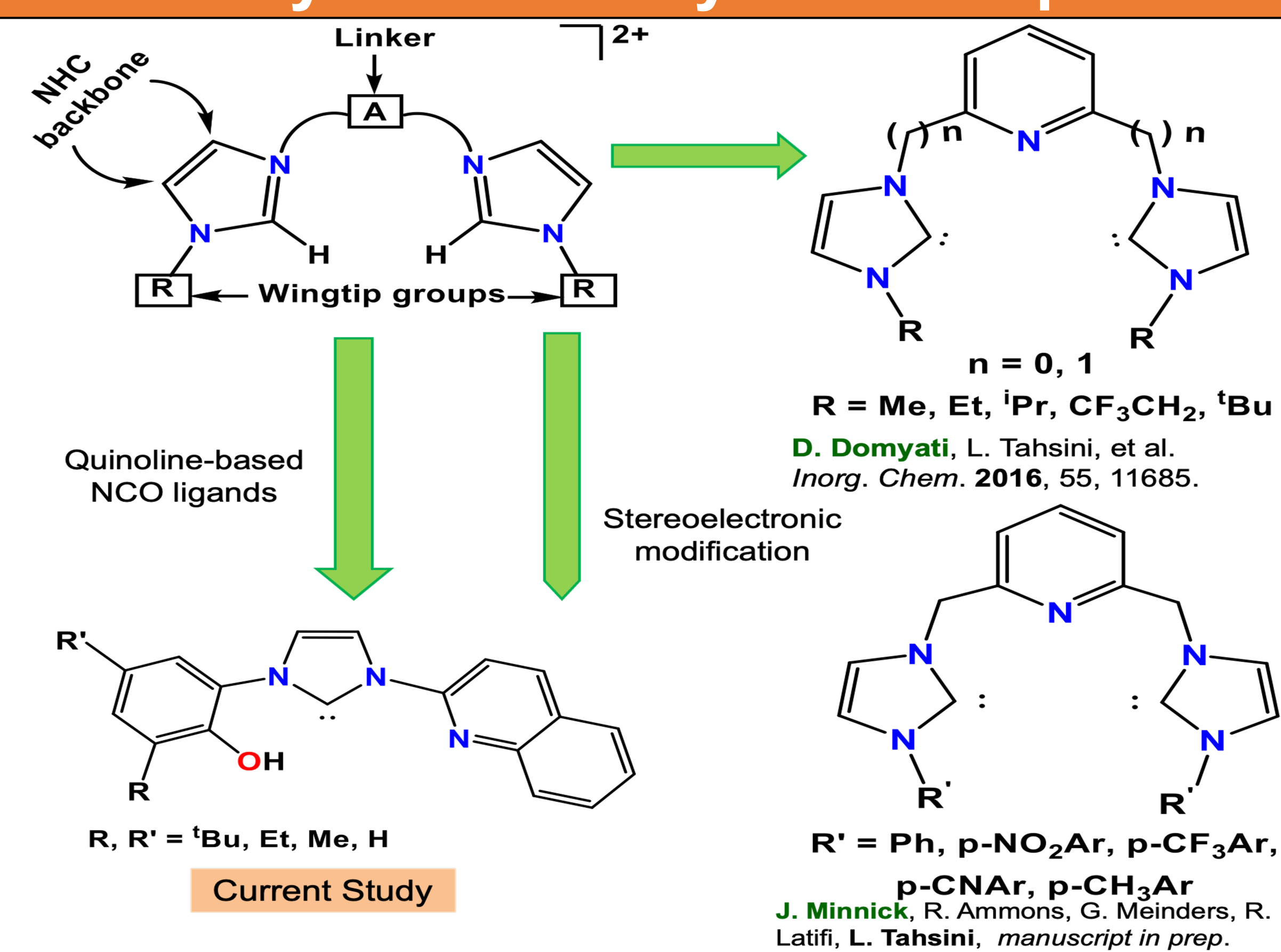## Department of Chemistry, Oklahoma State University
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Abstract

Over the last few decades, there has been growing interest in the coordination chemistry of N-heterocyclic carbenes (NHCs) and their use in catalysis, with pincer-type systems being particularly significant due to their ability to form chelates and undergo easy electronic and steric modifications. Our research group has developed Cu(I) complexes of pyridine-based NHC ligands, which we have explored for their potential in catalyzing C–C and C–X (X = O, N) cross-coupling reactions. Although high-valent {Cu-O2} species were identified as likely intermediates, we were unable to isolate a Cu(II) complex in the pincer CNC environment. In this study, we present the synthesis and characterization of novel tridentate NHC ligands containing phenol and quinoline wingtips, which are anticipated to stabilize higher oxidation states of transition metals such as Cu(II). Our current research endeavors center on developing various NCO ligands and examining their coordination chemistry.

## Previous CNC ligands and Cu complexes Synthesized by our Group

n = 0, 1
R = Me, Et, ^{i}Pr, CF$_3$CH$_2$, ^{t}Bu
D. Domyati, L. Tahsini, et al. *Inorg. Chem.* **2016**, 55, 11685.

Quinoline-based NCO ligands

Stereoelectronic modification

R, R' = ^{t}Bu, Et, Me, H

Current Study

R' = Ph, p-NO$_2$Ar, p-CF$_3$Ar, p-CNAr, p-CH$_3$Ar
J. Minnick, R. Ammons, G. Meinders, R. Latifi, **L. Tahsini**, *manuscript in prep.*

Conclusion & Future Direction

- Characterize each ligand and complex with ^{1}HNMR, ^{13}CNMR, X-ray crystallography, and elemental analysis.
- Using different techniques such as flash column
- The NCO ligands that were prepared can be used to form complexes with various metals, providing a versatile and tunable platform for further exploration.

Acknowledgements

Quinoline-based NCO Ligands Synthesis

1) Iodination


R = H, Me, ^{t}Bu
R' = Me, ^{t}Bu

Average yield = 91 %
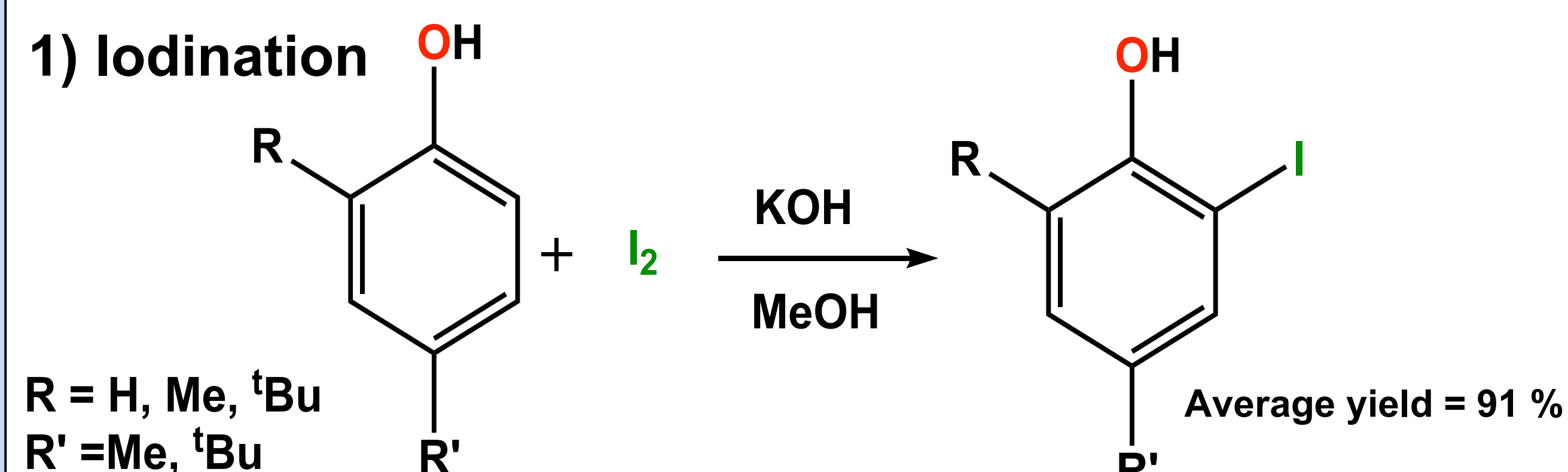
The process described involves several steps for the reaction of the reactants. The reactants are first mixed in a Schlenk flask. The mixture is then refluxed at 60°C for 2,4-Dimethyl phenol, R.T. for Di-tertbutyl phenol and 0°C for tertbutyl derivative all for 24 hours. After this, the mixture is quenched with Na$_2$SO$_3$ and acidified to a pH of 5 using 37% HCl. The resulting mixture is then extracted three times with 40 mL of DCM, followed by washing the organic layer with 50 mL water. The organic layer is then dehydrated with Na$_2$SO$_4$ and filtered using filter paper. The filtered mixture is then subjected to rotary evaporator (rota-vap) to remove the solvent, and the resulting product is analyzed using NMR.

2) C-N Coupling

R = H, Me, ^{t}Bu
R' = Me, ^{t}Bu

Average yield = 52 %
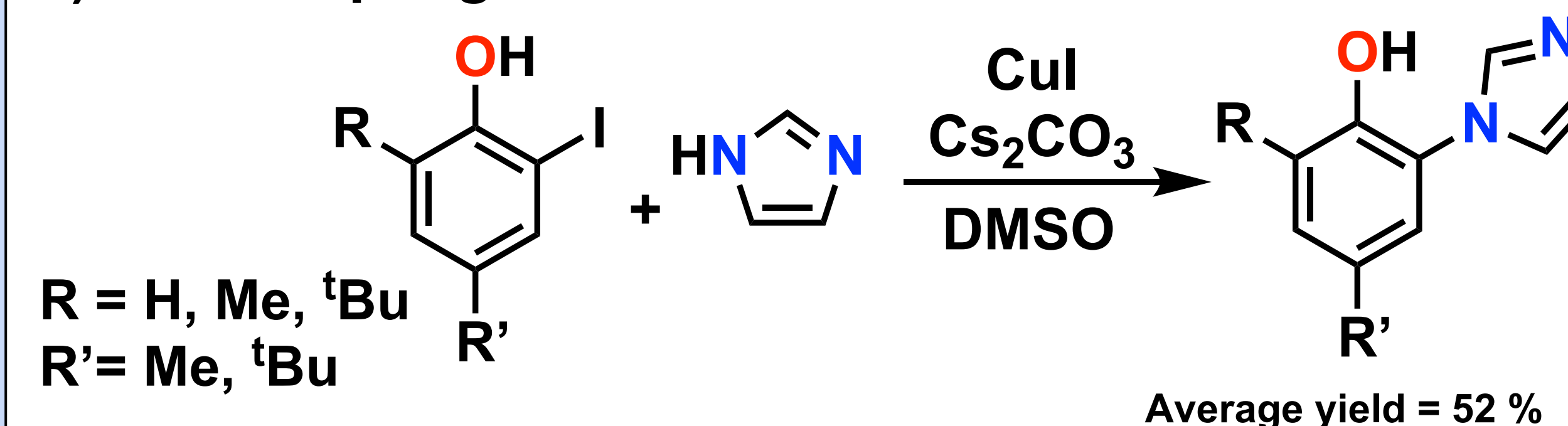
The iodinated product is mixed with the reactants in a 20 mL vial. It was then added to a preheated oil bath and refluxed at 125°C for 48 hours. After the reaction completed, it is transferred to a separation funnel with 15 mL water. The mixture is extracted with 3x40 mL of ethyl acetate. The organic layer was subsequently washed with 50 mL of water and dehydrated with Na$_2$SO$_4$. It is filtered using filter paper and subjected to rota-vap. The resulting material is run through a column and then again to rota-vap. Finally, the sample is characterized using NMR.

3) Quaternization

R = Me, ^{t}Bu
R' = Me, ^{t}Bu

Average yield = 94 %
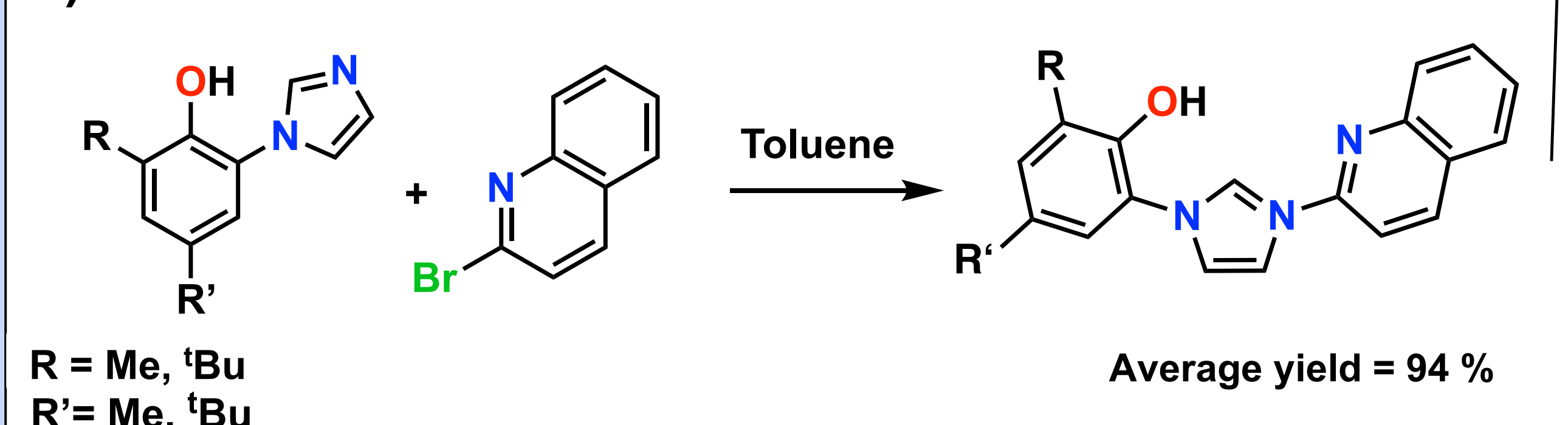
The C-N coupling product was mixed with the 2-bromoquinoline in a pressure flask and then transferred to a preheated oil bath. It is refluxed at 160°C for 48 hours and then allowed to cool down to room temperature. The mixture is subsequently filtered using a fritted funnel and dried under vacuum. Two distinct layers is obtained, with a white powder on top and a brown oil at the bottom in filtrate. The top layer was subjected to NMR analysis. Next, 3 mL of 1,4-Dioxane was added to the top layer and subjected to trituration for 1 hour for further purification. The mixture was then filtered using a fritted funnel and dried under vacuum, resulting in two layers again, with a white powder on top and a brown oil at the bottom. The proton NMR of the top portion on fritted funnel confirmed the structure of the ligand with no impurities.
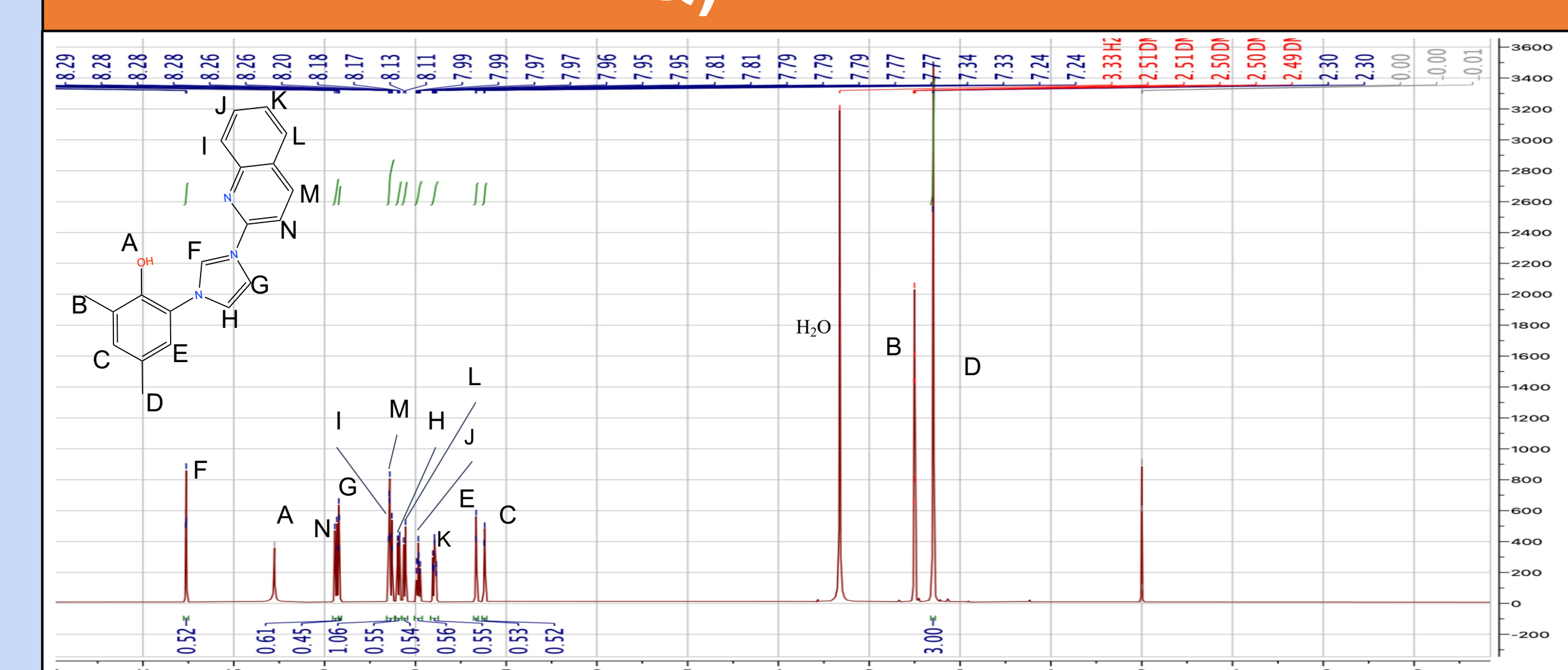
^{1}HNMR Characteristic of 2,4-Dimethyl-6-Iodophenol
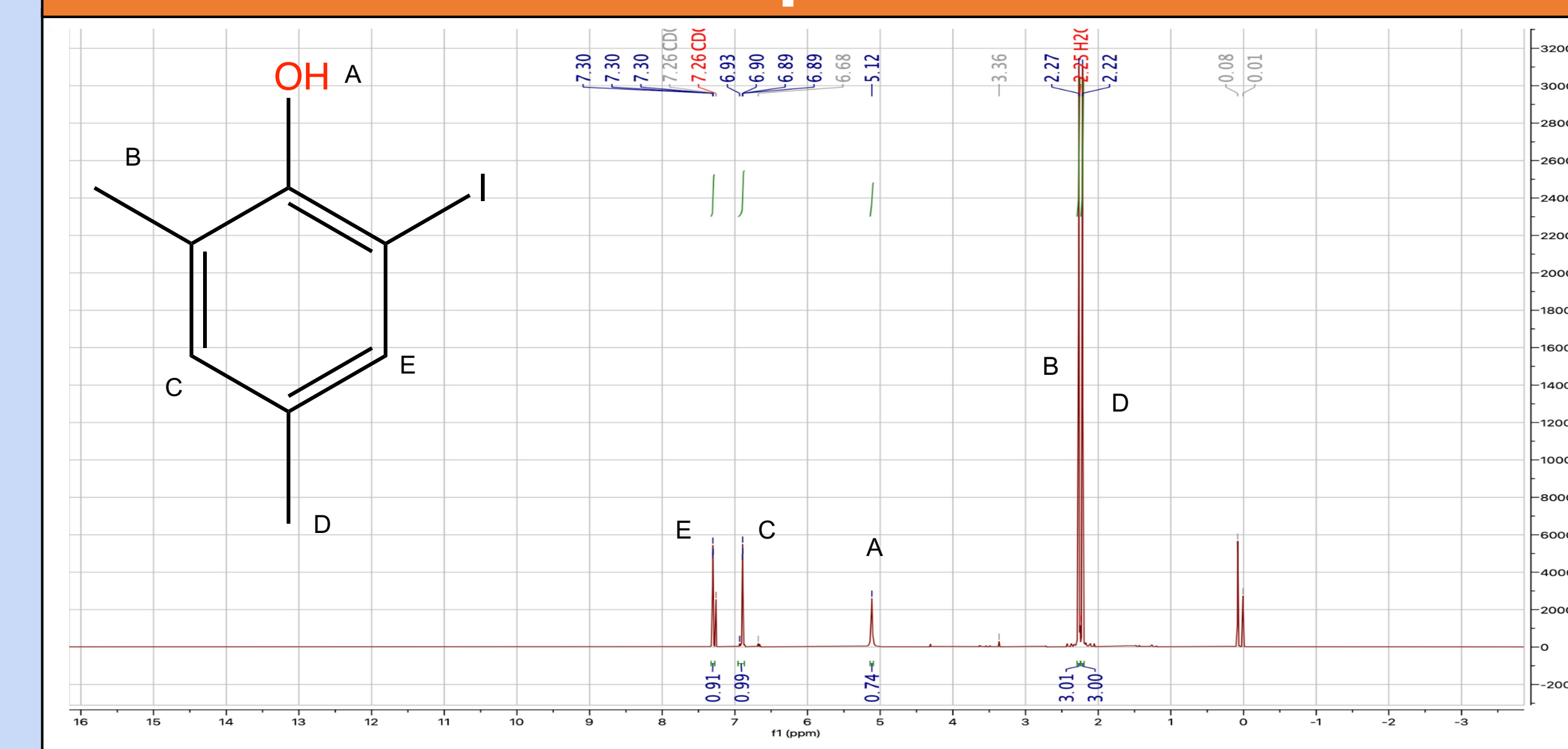
^{1}HNMR Characteristic of 2,4-Dimethyl-6-(1H-imidazole-1yl)-phenol
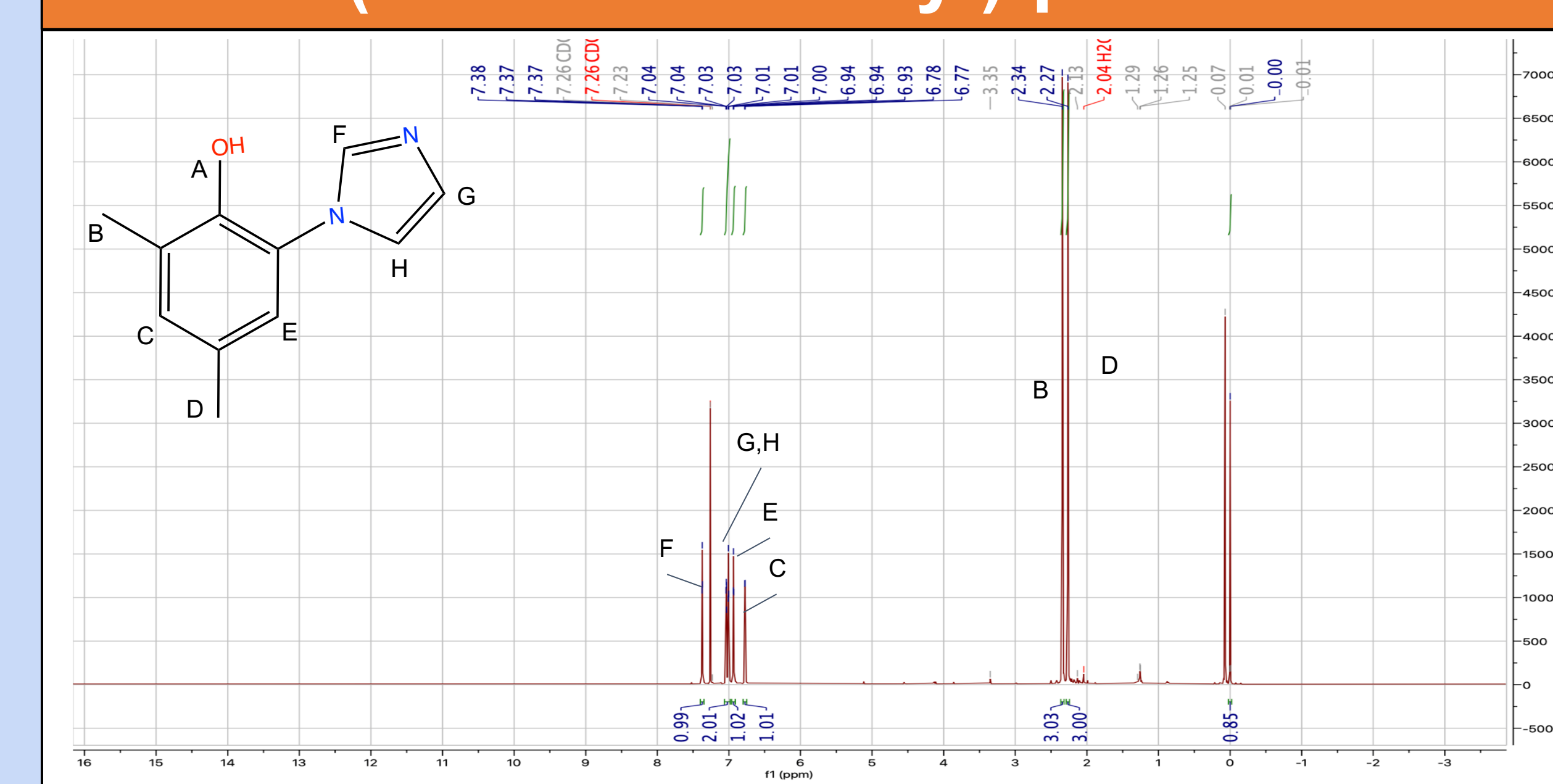
^{1}HNMR Characteristic of I(Dmep,2-Q)^{CNO}*HBr

References

1. Domyati, D., Hope, S. L., Latifi, R., Hearns, M. D., Tahsini, L. Inorg. Chem. 2016, 55, 22, 11685– 11693.
2. Minnick, J. L., Domyati, D., Ammons, R., Tahsini, L. Front. Chem. (2019) 7, 12.
3. Domyati, D., Latifi, R., Tahsini, L. J. Organomet. Chem. (2018) 860, 98-105.