

# Formation of Hetero-Guest Capsular Complexation and Direct Iodination of Anisole via Supramolecular Catalyst

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## Introduction

The Gibb group has performed expansive research on the properties of deep-cavity cavitand Octa-acid (OA) (Figure 2).<sup>1</sup> We are building on this work to examine the ability of OA to sequester hydrophobic guests. We will detail the sequestration of the constitutional isomers of hexane. NMR analysis will be used to investigate the formation of hetero-guest capsular complexes (Figure 1). We anticipate that the studies will provide information concerning reactions inside of water-soluble molecular capsule.

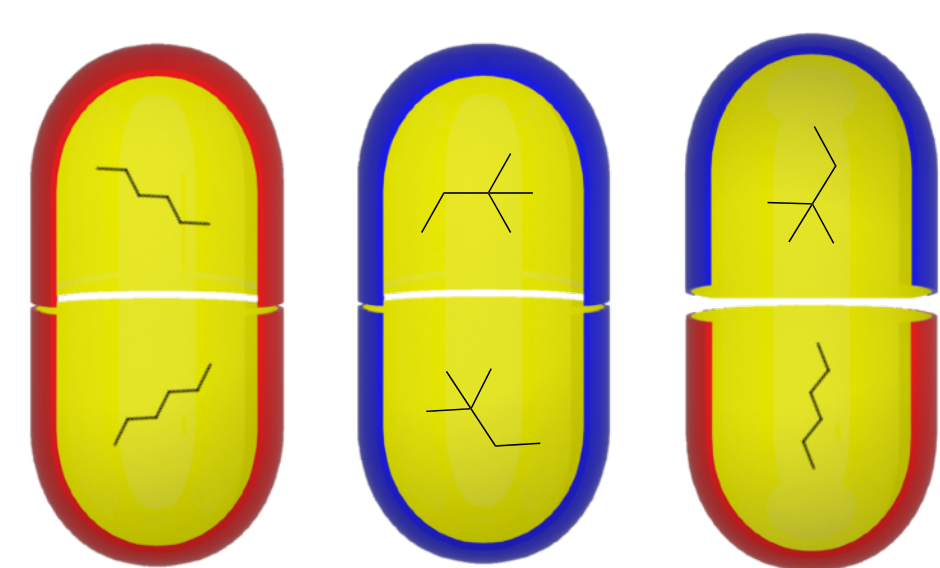


Figure 1: Graphical depiction of encapsulated guest with dimerized OA

## Water-Soluble, Deep-Cavity Cavitands

The synthesis of the Octa-Acid (OA) cavitand (Figure 2) is accomplished in six steps.<sup>2</sup> The final product consist of 8 water-solubilizing carboxylic acid groups and a hydrophobic pocket ideal for guest binding, and it has the capability to dimerize into a water-soluble molecular capsule capable of hosting hydrophobic guest.<sup>3</sup>

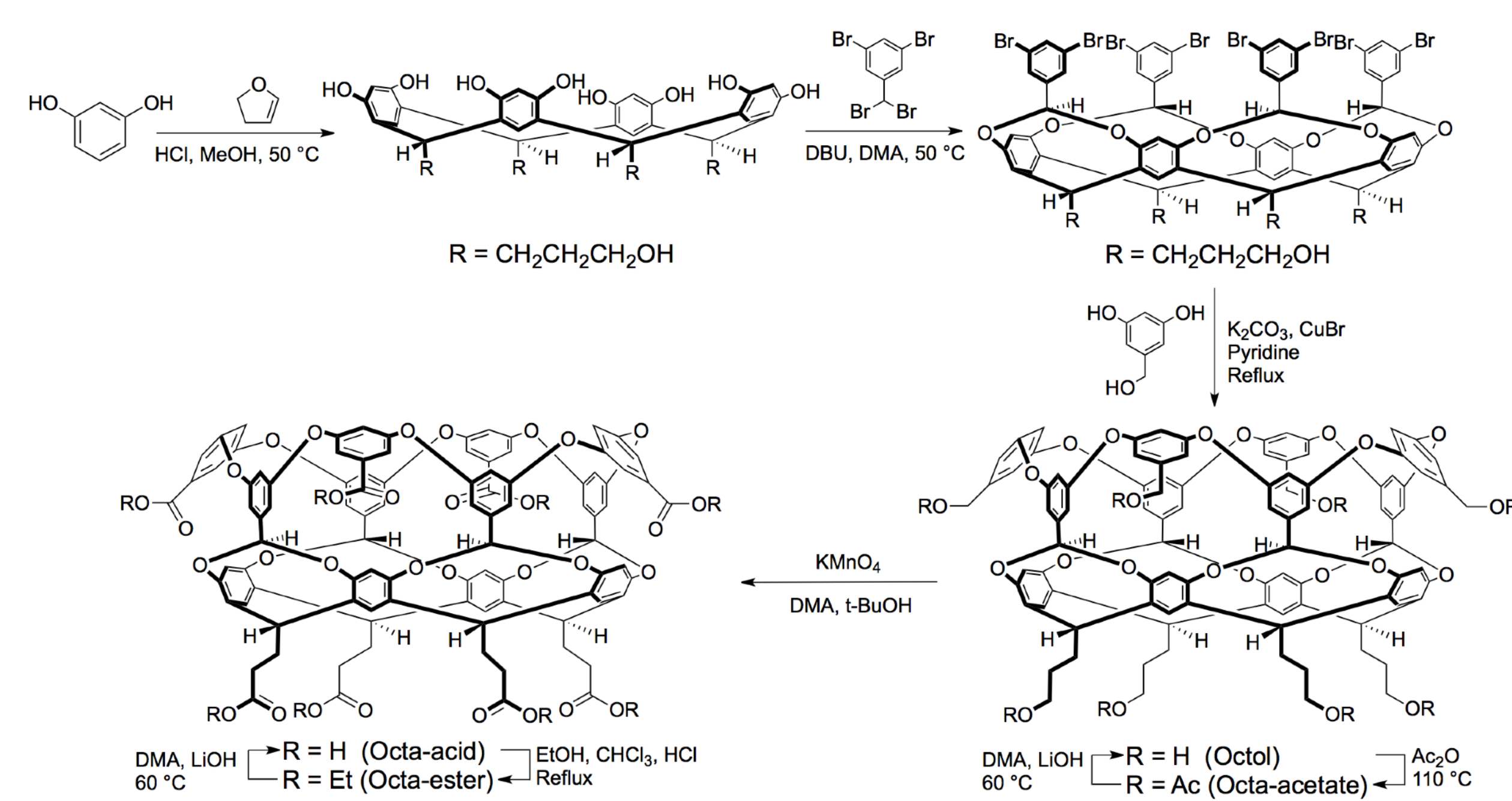


Figure 2: Non-linear synthesis of Octa-acid cavitand.

## Evidence of Hetero-guest Complexation

Evidence of hetero-guest complexation can be seen in Figure 3. With two guests present, a small, new doublet appears slightly up field from the doublet that is seen in the original spectrum. With no free guest in solution and concentrations in equal amount, there is no competition for binding inside the cavitand. This second doublet is evidence of a hetero-guest complexation, and was observed in all hexane isomer complexes (Table 1).

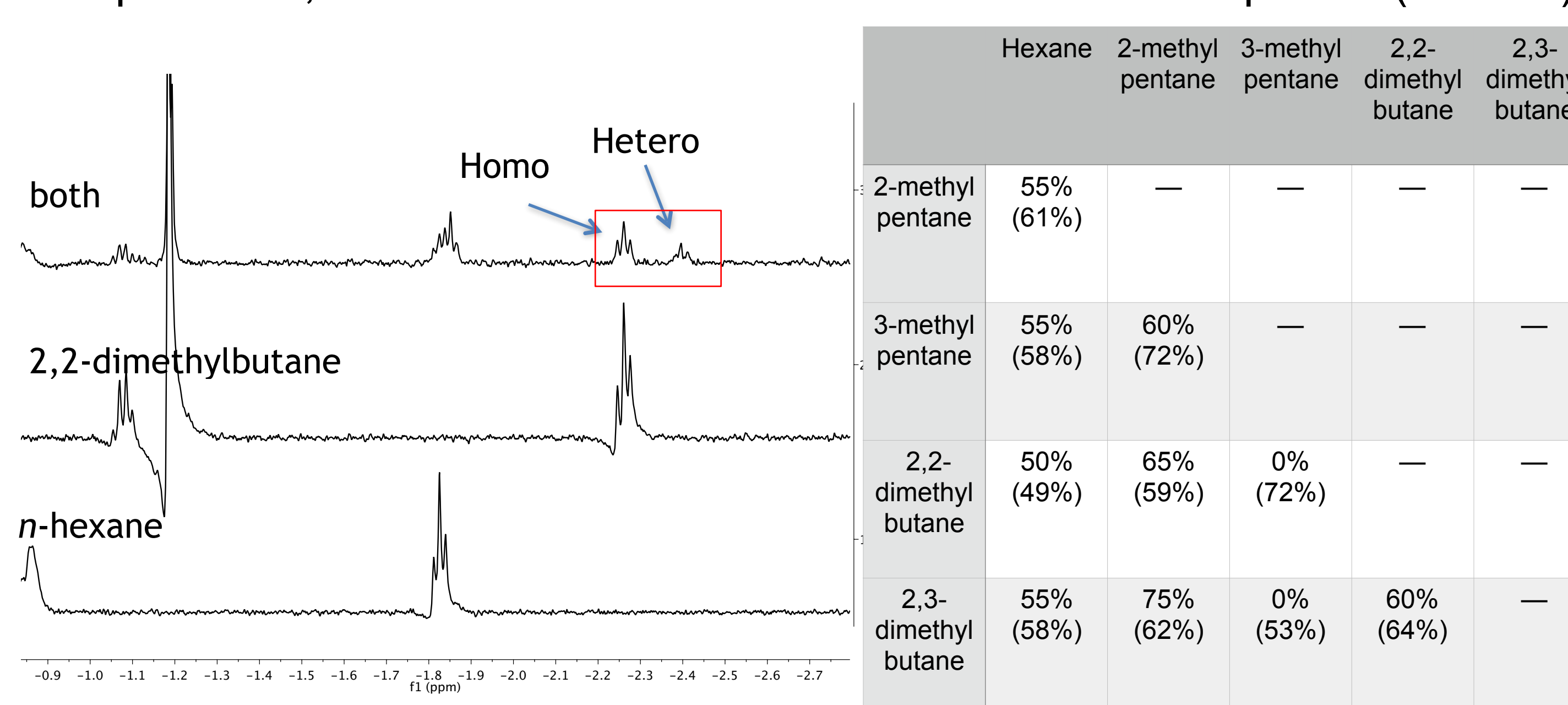


Figure 3: 1H NMR of *n*-hexane and 2,2-dimethylbutane

Table 1: Hexane isomers which displayed hetero-guest complexation

## Conclusion

Preferential binding has been demonstrated in competition studies between constitutional hexane isomers. The formation of hetero-guest complexes has been successfully established for all combinations of isomers. Further studies are ongoing, which will compare straight chain and cycloalkane homologs with one another for both separation and hetero-guest experiments.

## Introduction

Host-guest systems with catalytic behavior represent a promising area of supramolecular chemistry.<sup>4</sup> These systems operate by binding substrates or products and stabilizing transition states and/or increasing the effective concentration of reactive species within confined space. We will detail the catalyzed iodination of anisole via the cavitand TTMACI.

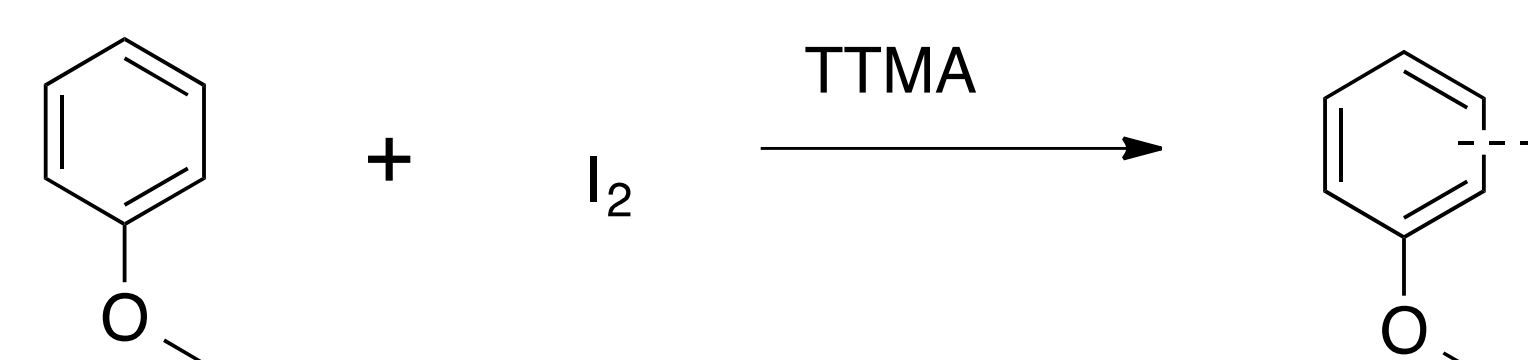


Figure 4: Reaction mechanism of 4-iodoanisole

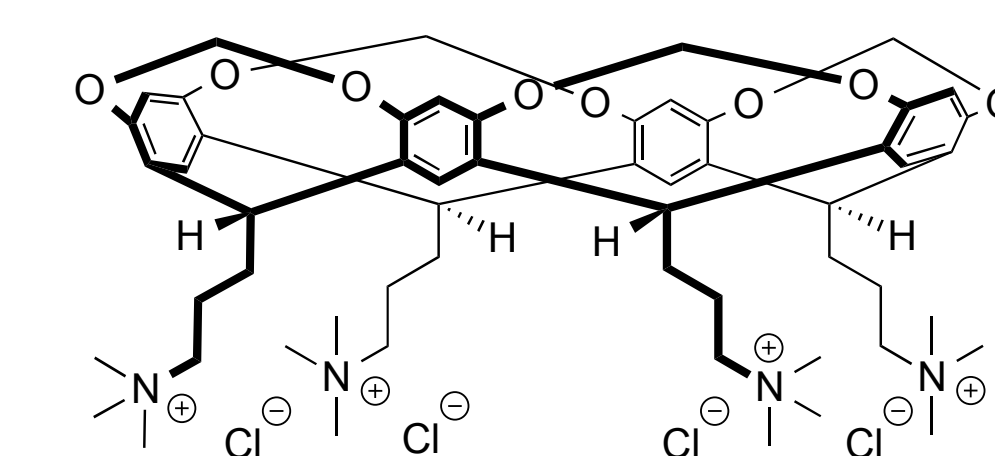


Figure 5: Tetrakis(trimethylammonium) chloride (TTMACI)

## Evidence of Direct Iodination of Anisole

Evidence of catalytic iodination can be seen in Figure 6. This can be shown by the formation of a new doublet peak at 6.7 ppm in the reaction with the TTMACI and not in the reaction that lacks it. According to Table 2, when TTMACI was present in the reaction after 20 hours the product was formed at a yield of 20% with high selectivity.

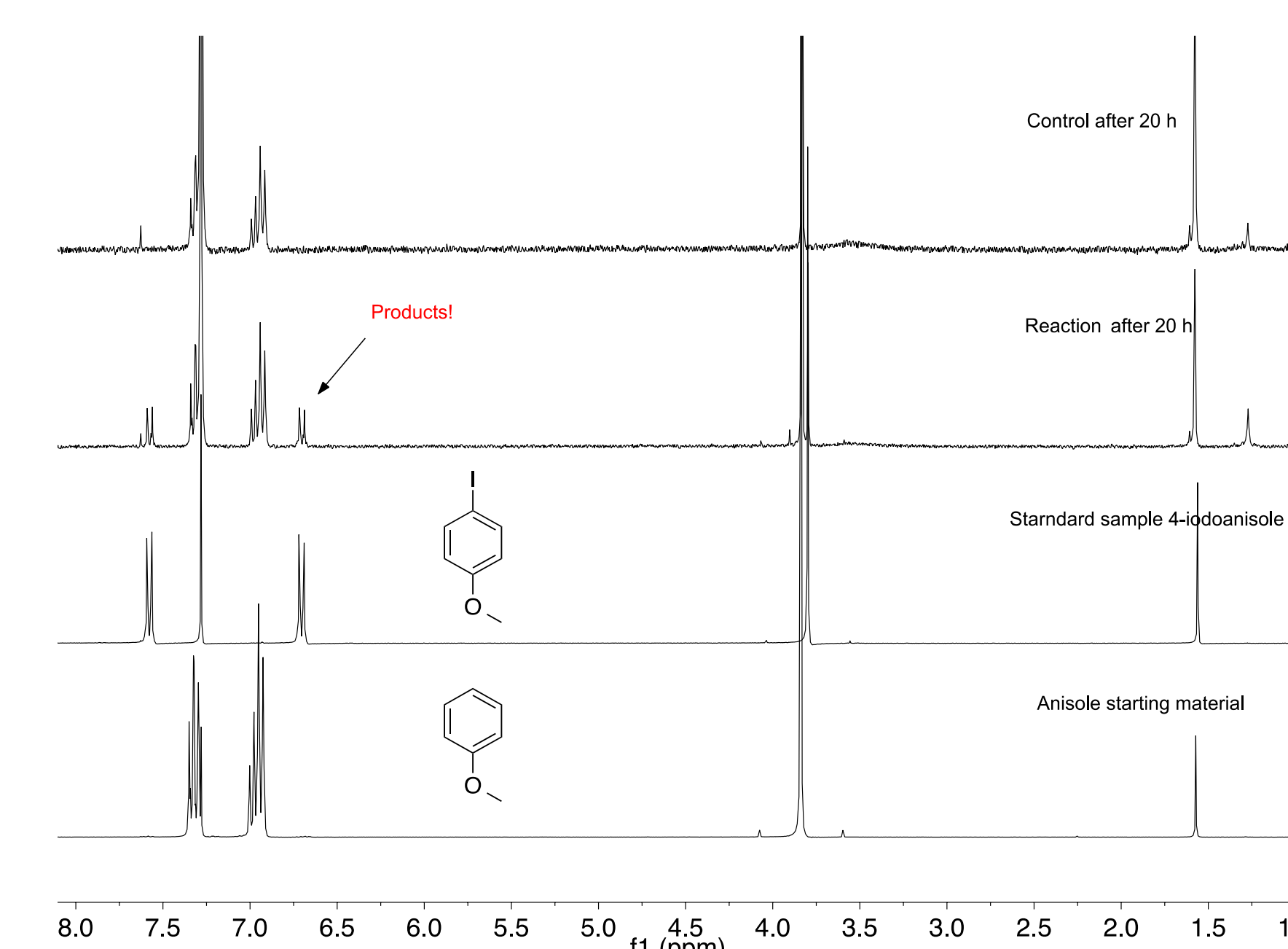


Figure 6: <sup>1</sup>H NMR spectra of anisole, 4-iodoanisole, reaction solution and control (extracted by CDCl<sub>3</sub>)

	Anisole (mM)	Iodine (mM)	TTMACI (mM)	Time(h)	Yield(%)	Selectivity
1	10	100	0.5	20	20	92:8
2	10	100	NA	20	0	NA

Table 2: Iodination reaction conditions

## Conclusion

In summary, we studied the reaction of iodine with anisole. We proved that they can't react in water or CDCl<sub>3</sub> at room temperature, and we found after adding the cavitand (TTMACI) as the catalyst, the reaction happened and with a high selectivity. The catalytic mechanism seems to be that iodine can bind strongly with the feet of cavitand in the water phase which facilitates the iodination of the anisole.

## References

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