

Electrocatalytic generation of organic halide oligomers

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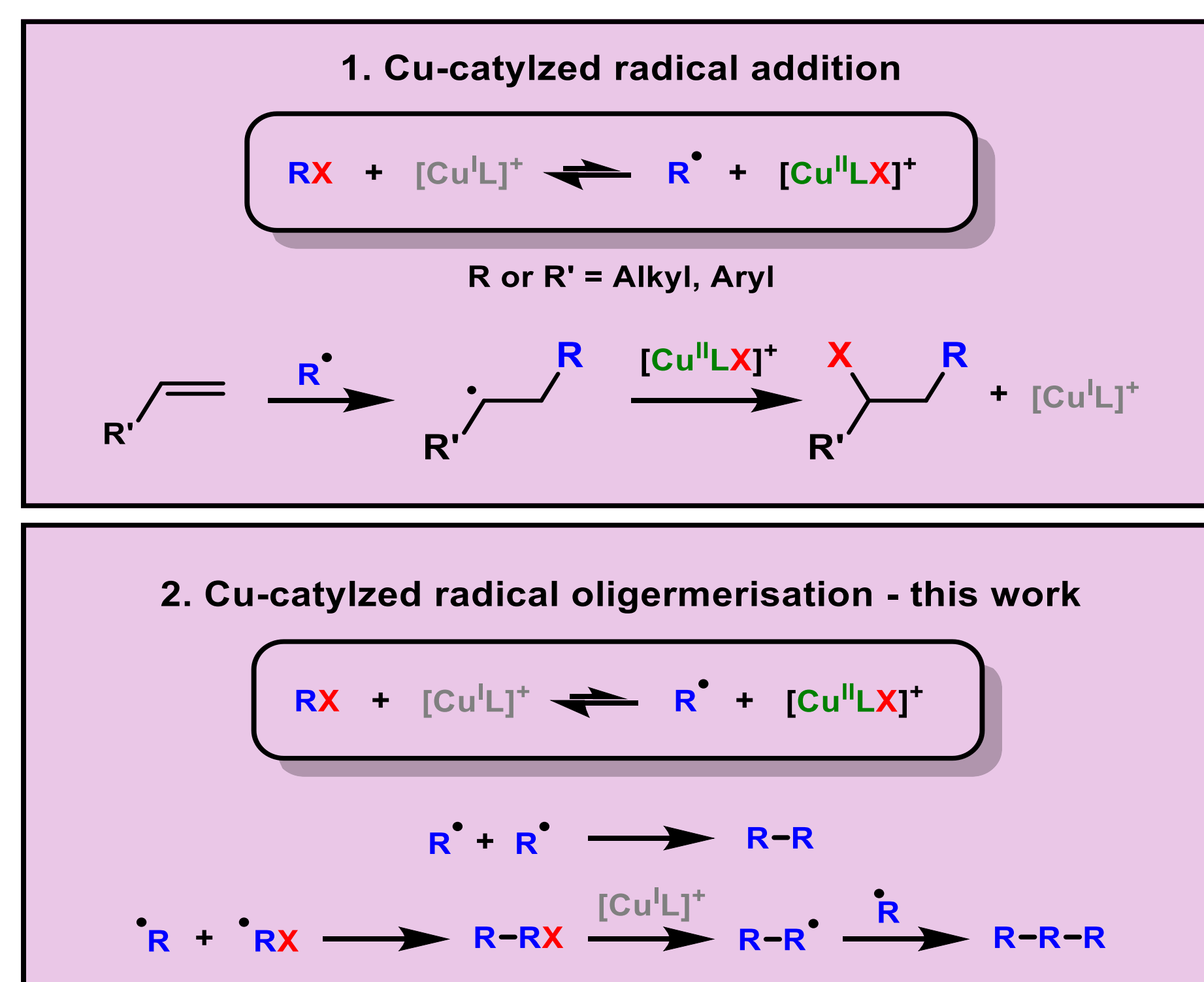
1. Introduction

One of the most promising advancements in atom transfer radical addition (ATRA) reactions is the discovery of electrochemically driven formation of the necessary active Cu(I) catalyst,¹ removing the need for stoichiometric chemical reductants and furthering the development of new synthetic methods for carbon-carbon bond formation.

Current research has focused on the mechanism of the catalytic cycle,² characterizing the reactive intermediates formed in solution³ and optimizing the scope of potential products,⁴ with comparatively little attention directed toward the reactivity of the polyhalogenated radical initiators.

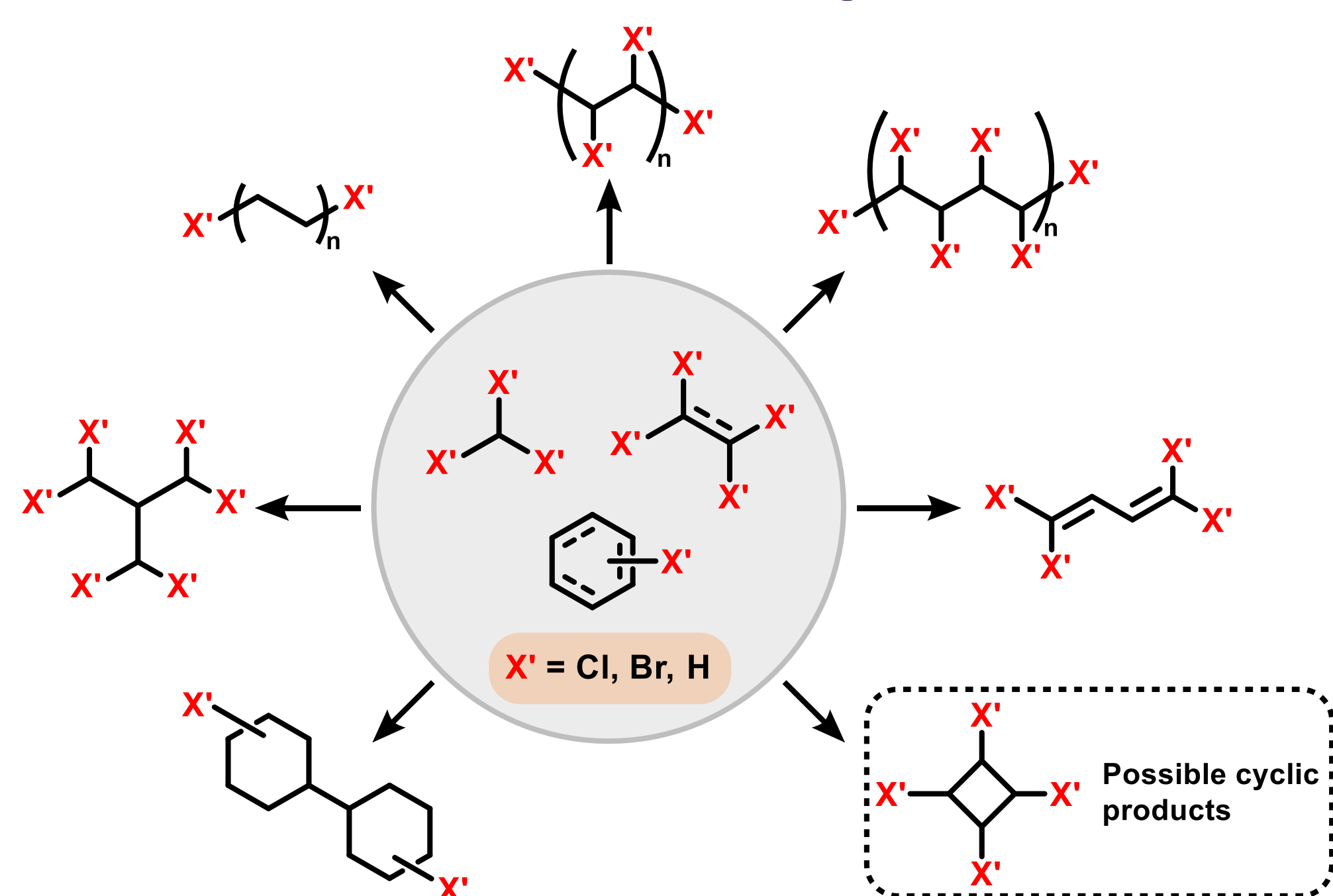
By investigating electrochemical synthesis reactions of these organic halides without the presence of a substrate, this project aims to increase understanding of the possible competing side reactions in the standard synthetic procedure and open possible avenues for the synthesis of exotic long chain alkanes from simple, readily available starting material.

Beyond a purely synthetic goal this project can hopefully show some environmental utility as a method for dealing with polyhalogenated waste products present in many industrial procedures.⁵



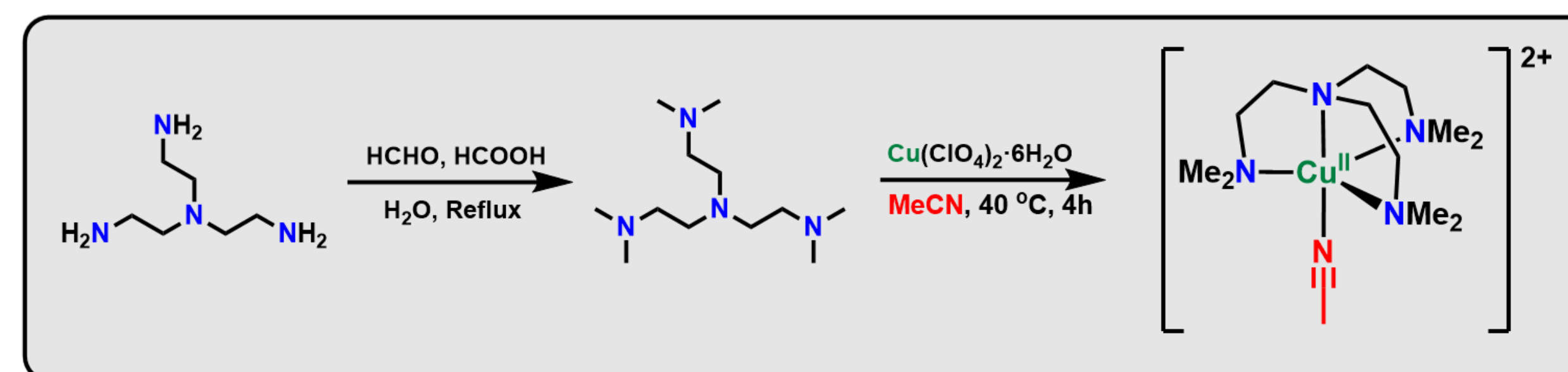
Scheme 1. (1) The Cu-catalysed eATRA work by Bernhardt and colleagues.⁴ (2) The modified eATRA without a substrate in this work.

2. Aims/Scope



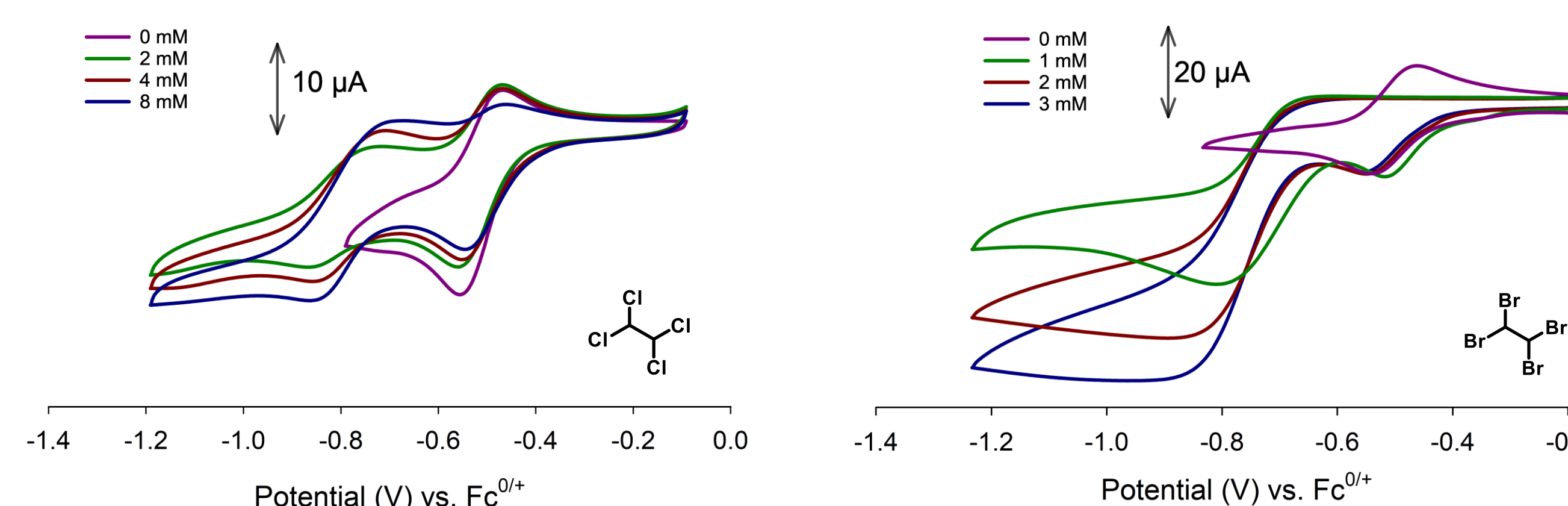
Scheme 2. The organic halides to be investigated in this work along with theorised possible products, consisting of straight chain oligomers and some branched variants, and perhaps less likely cyclic products.

3. Catalyst synthesis



Scheme 3. Synthesis of the Cu(II) catalyst complex – [Cu(II)Me₆Tren(NCMe)](ClO₄)₂

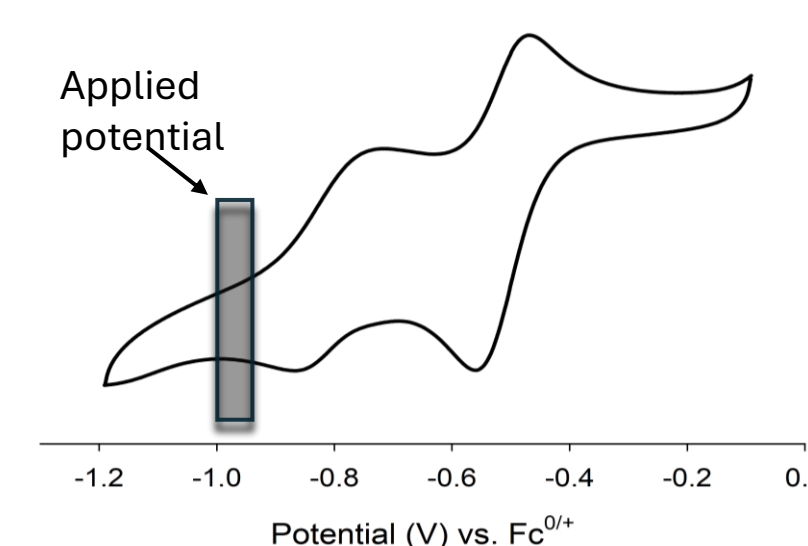
4. Cyclic voltammetry



Tetrachloroethane (left) and tetrabromoethane (right) show current amplification with increasing concentration in the presence of the Cu(II) complex indicative of catalytic behaviour, only quasi-reversible or non-reversible peaks indicating immediate chemical transformation. This makes them ideal for use in eATRA

➤ Peaks correspond to metal centre redox couples Cu(II) → Cu(I), accompanied by coordinate bond heterolysis. Cu(I) homolytically cleaves organic halide bonds forming the Cu(II) halido complex. Analogously the halido complex is reduced and organometallic Cu(II) forms readily.

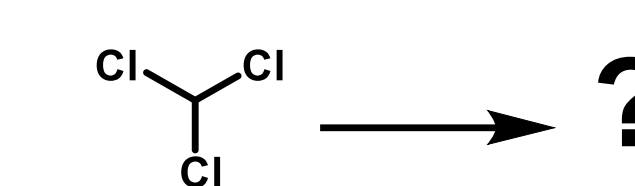
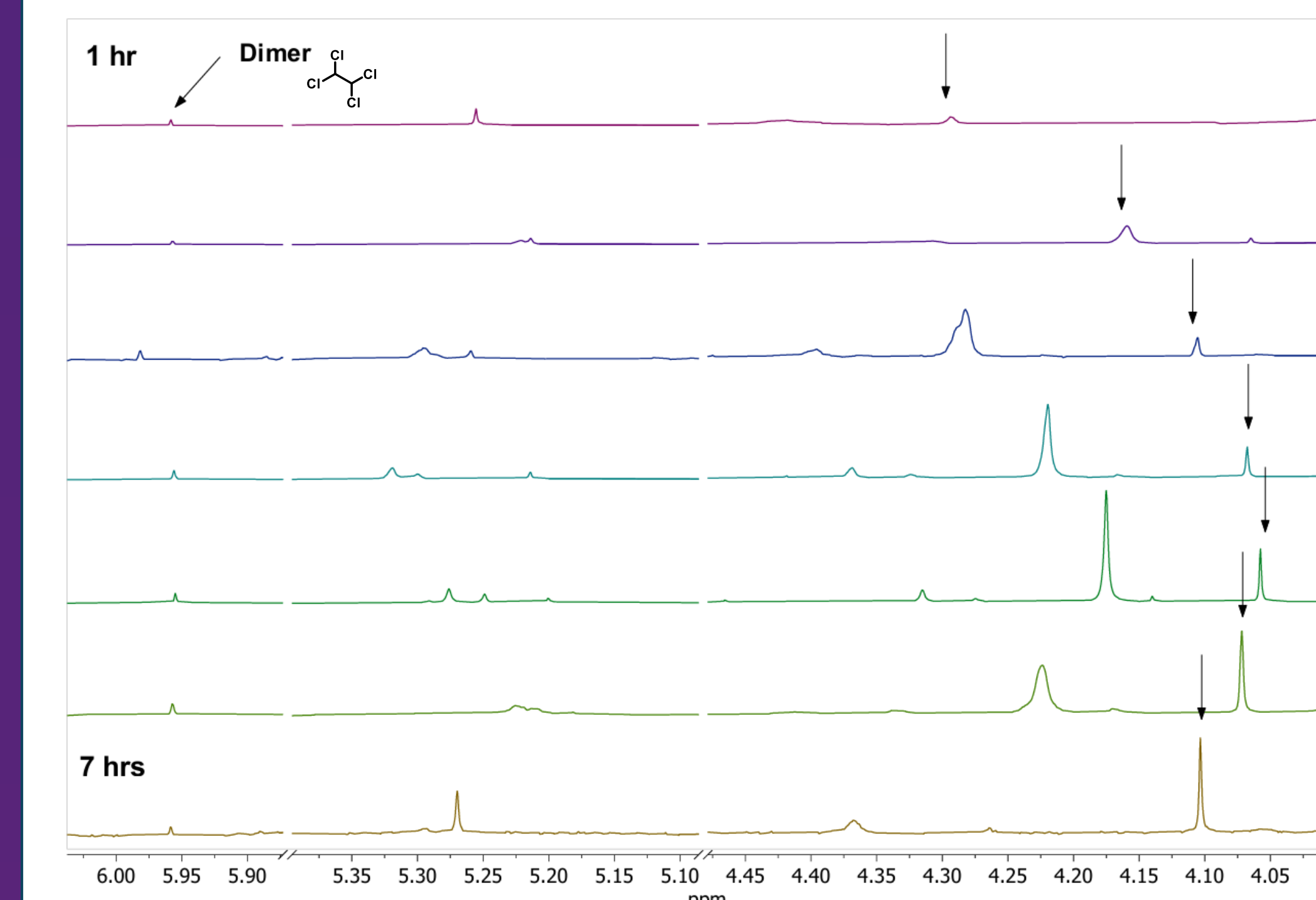
5. Bulk electrosynthesis procedure



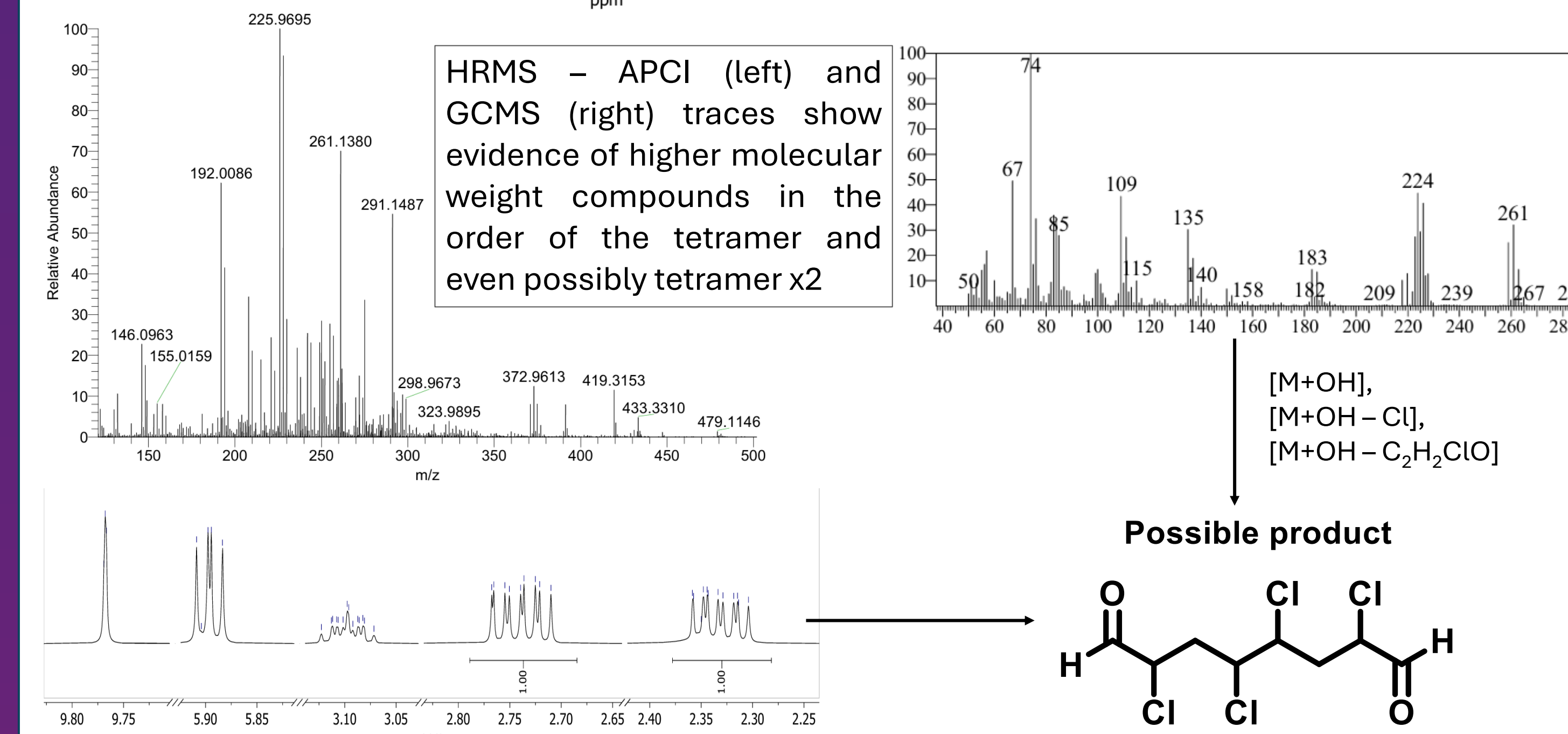
➤ By applying constant potential after the halido reduction as shown, Cu(I) and the alkyl halide radical form *in situ* and combine to form an organometallic complex which is a steady source of radicals for combination

Reaction conditions: Divided cell, constant potential, platinum working and counter electrode, and Ag^{+/0} reference electrode. Generally, 200 mg of alkyl halide, 10 mol% [Cu^{II}L(NCMe)]²⁺ in anhydrous MeCN (supporting 0.1 M Et₄N(ClO₄) electrolyte) was electrolysed at room temperature or at elevated temperature of 50 °C for 8 hours

6. Outcomes

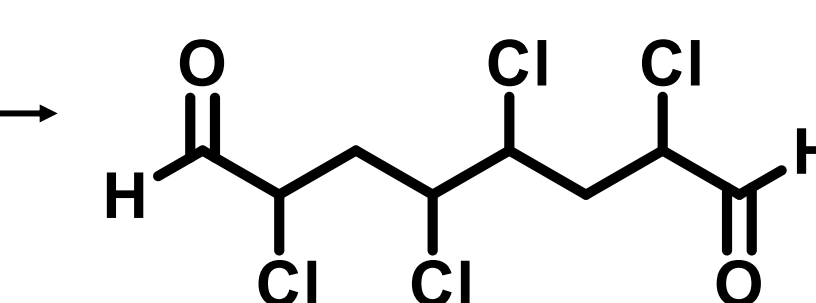


Time-course monitoring of the reaction to give insight to the mechanism. Dimerization appears almost immediately but does not seem to accumulate. There appears to be an intermediate that disappears as well as the compound indicated at 4.11 which increases throughout.

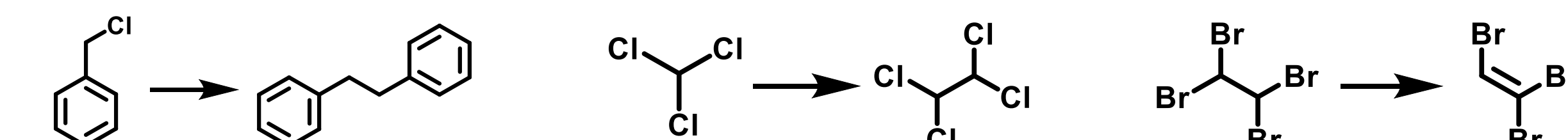


[M+OH],
[M+OH - Cl],
[M+OH - C₂H₂ClO]

Possible product



Other confirmed products



7. References

- [1] González, M. A.; Su, C.; Williams, C. M.; Bernhardt P. V. *Chem. Sci.*, **2022**, 13, 10506-10511.
- [2] González, M. A.; Williams, C. M.; Martínez, M.; Bernhardt, P. V. *Inorg. Chem.* **2023**, 62(11), 4662-4671.
- [3] Zerk, T. J.; Bernhardt P. V. *Inorg. Chem.*, **2017**, 56(10), 5784-5792.
- [4] Naher, M.; Su, C.; González, M. A.; Williams, C. M.; & Bernhardt, P. V. *Organometallics*, **2024**, 43(21), 2821-2830.
- [5] Wilsey, M. K.; Taseska, T.; Meng, Z.; Yu, W.; Müller, A. M. *Chem. Commun.* **2023**, 59 (80), 11895-11922.