

# A Trifunctional ATRP Initiator Bearing Adaptable Bonds

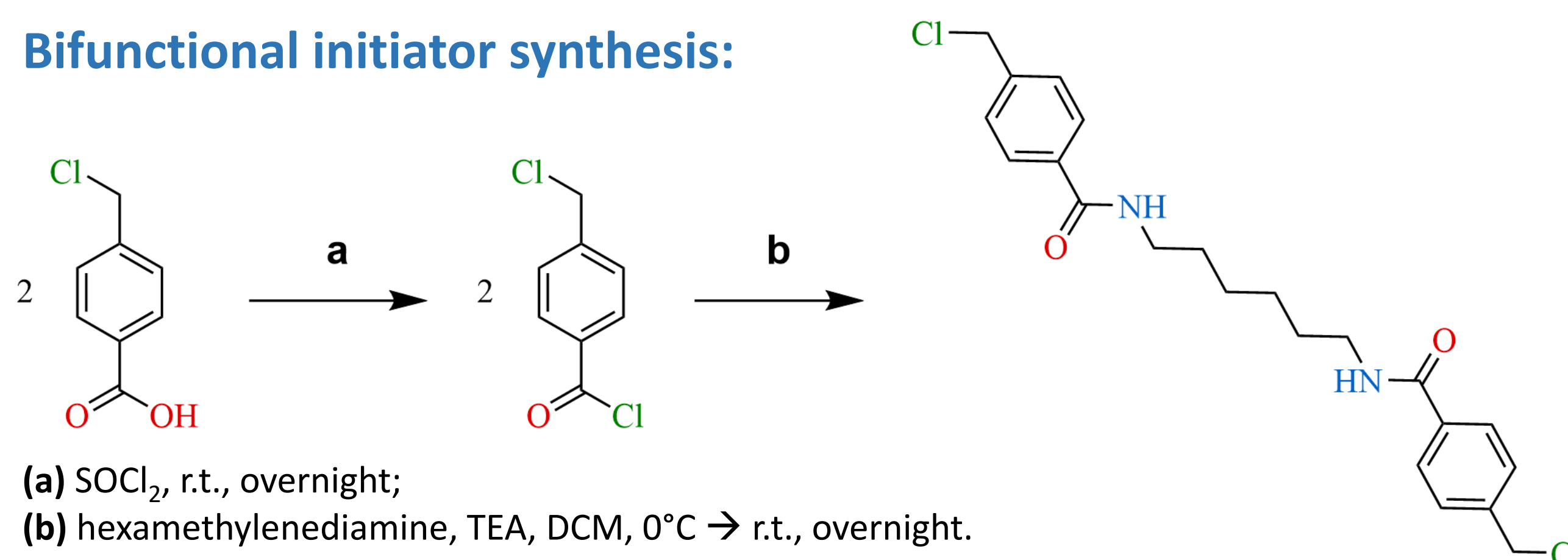
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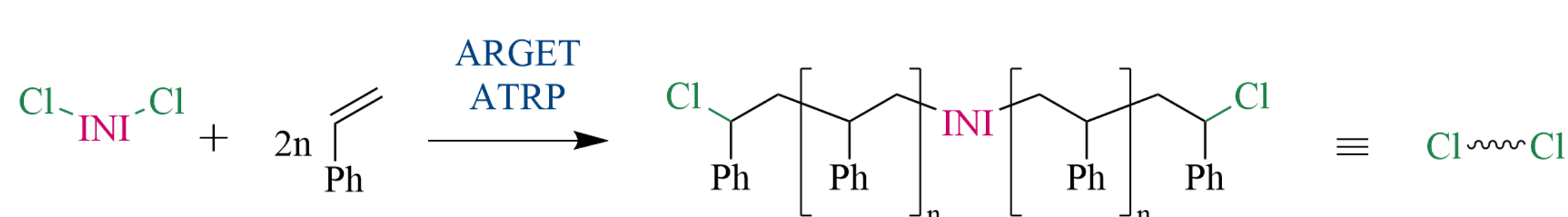
## Introduction

Polymers with well-defined molecular weight, topology, composition and functionality can be exploited to develop advanced materials with a wide range of applications. One of the most diffused techniques for obtaining these polymers is ATRP [1]. Functional groups can be introduced into the polymer by post-functionalization on the chain-end halogenated moieties, by direct introduction of punctually functionalized (co)monomers [2,3], or by using an ATRP initiator carrying the desired functionality. Unfortunately, the introduction of initiators containing labile functionalities, such as the aliphatic halide esters, could result in poor thermal stability of the polymer, as already observed by Altintas et al. [4]. Recently, we have synthesized a novel bifunctional benzamide-containing initiator which is successfully employed in ARGET ATRP of styrene [5], demonstrating enhanced thermal stability.

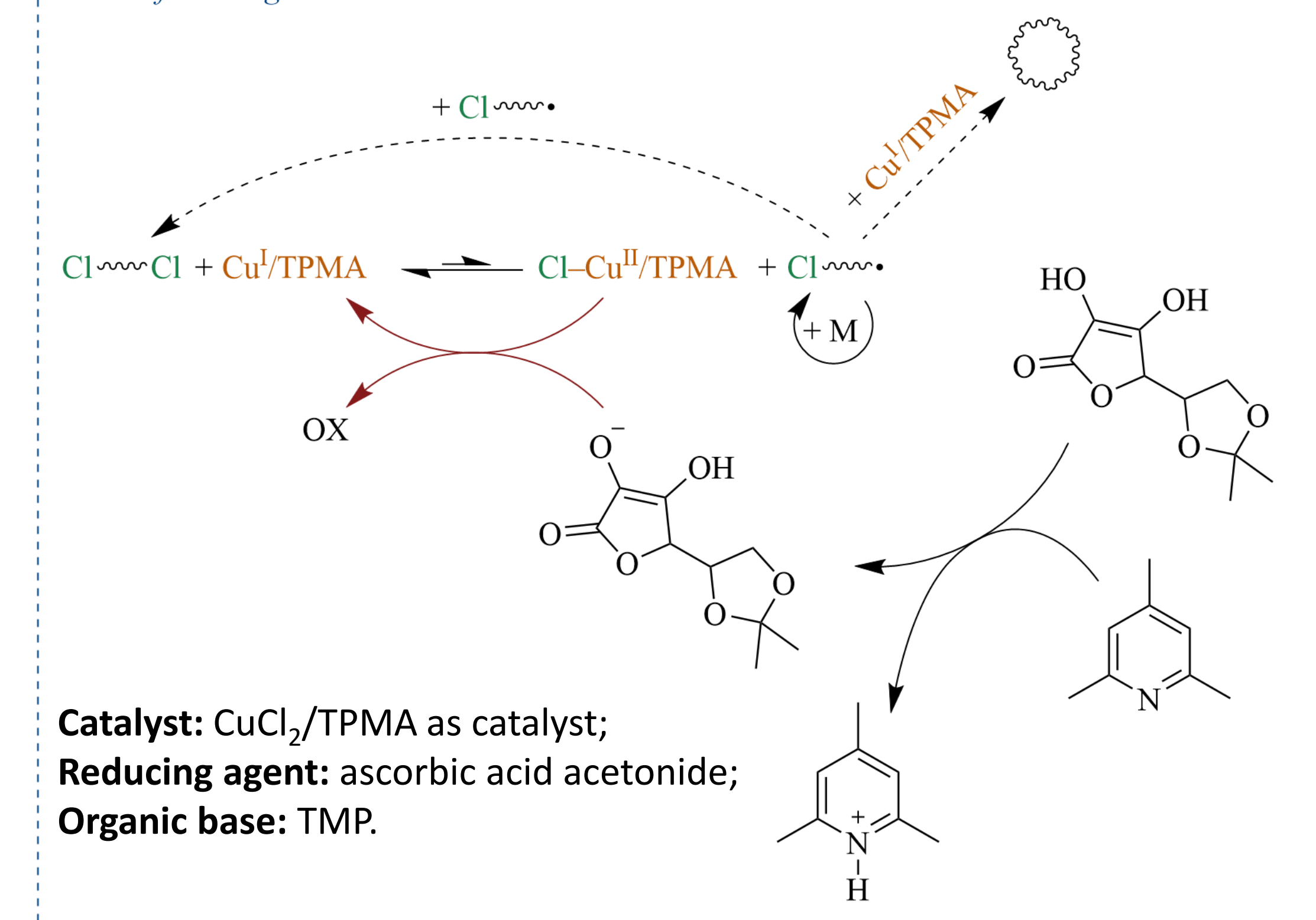
## Bifunctional initiator synthesis:



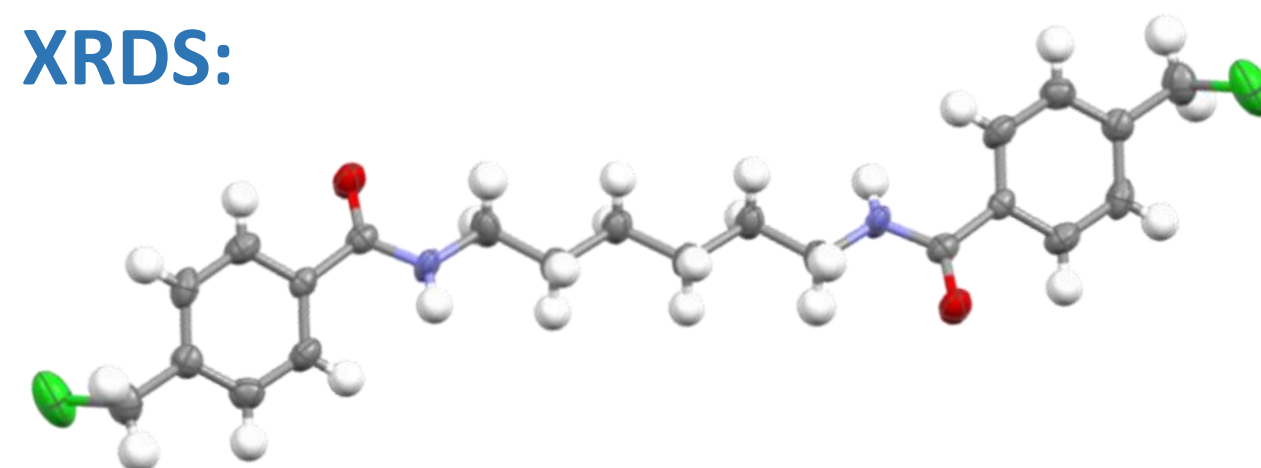
## ARGET ATRP mechanism:



via the following mechanism



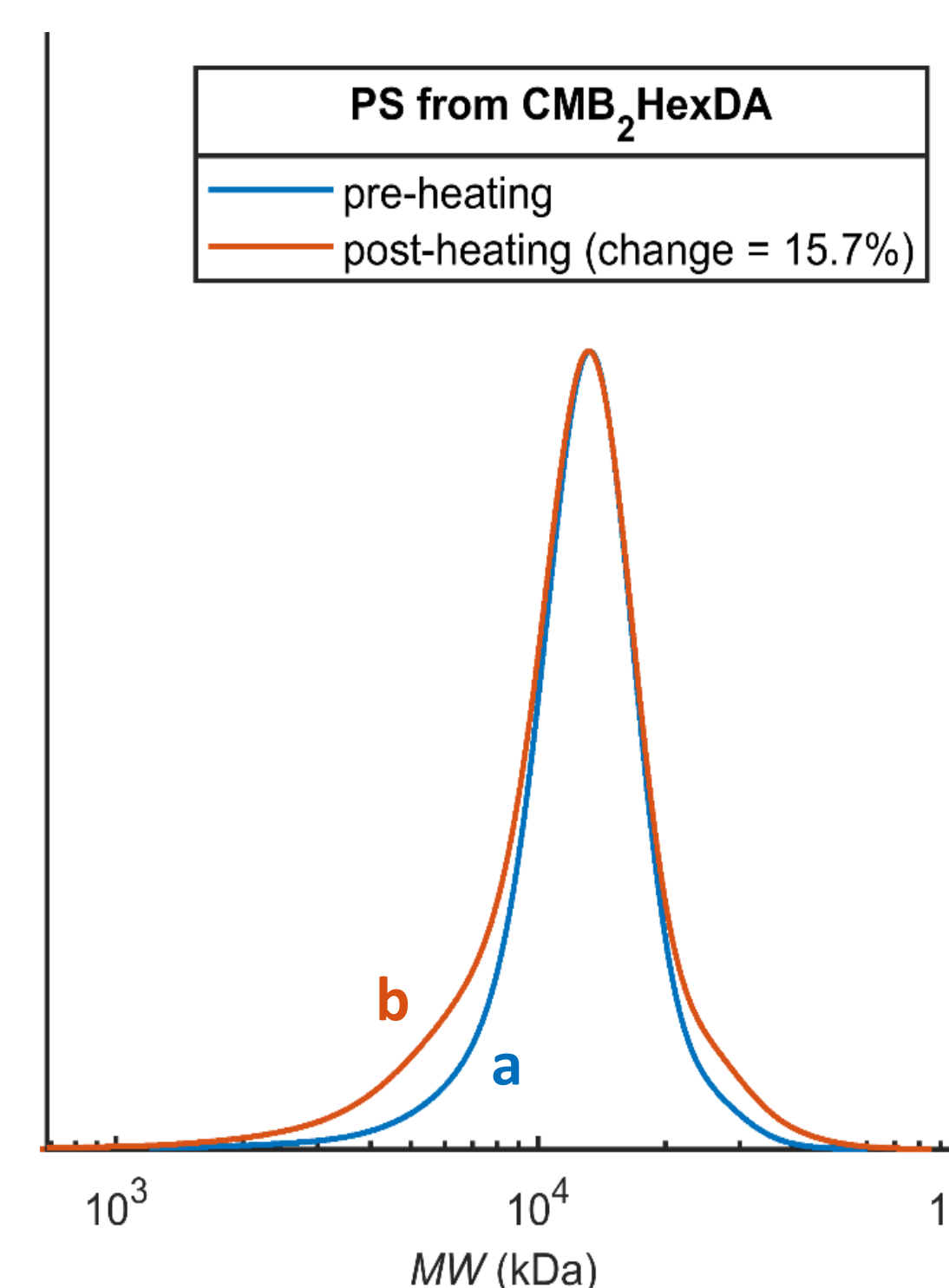
## XRDS:



## <sup>1</sup>H NMR:

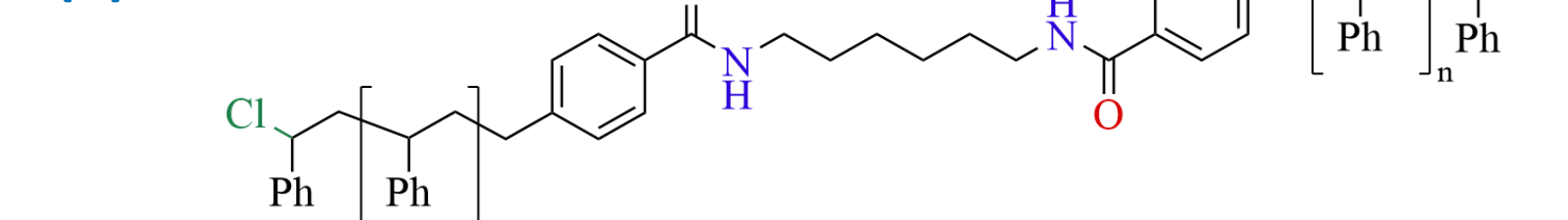
(600 MHz, DMSO):  $\delta$  8.46 (t,  $J = 5.5$  Hz, 2H, NH), 7.83 (m, 4H), 7.51 (m, 4H), 4.81 (s, 4H,  $\text{CH}_2\text{-Cl}$ ), 3.25 (q,  $J = 6.7$  Hz,  $J = 12.9$  Hz, 4H), 1.53 (m, 4H), 1.35 (m, 4H).

## GPC of $\alpha,\omega$ -dichloropolystyrene:

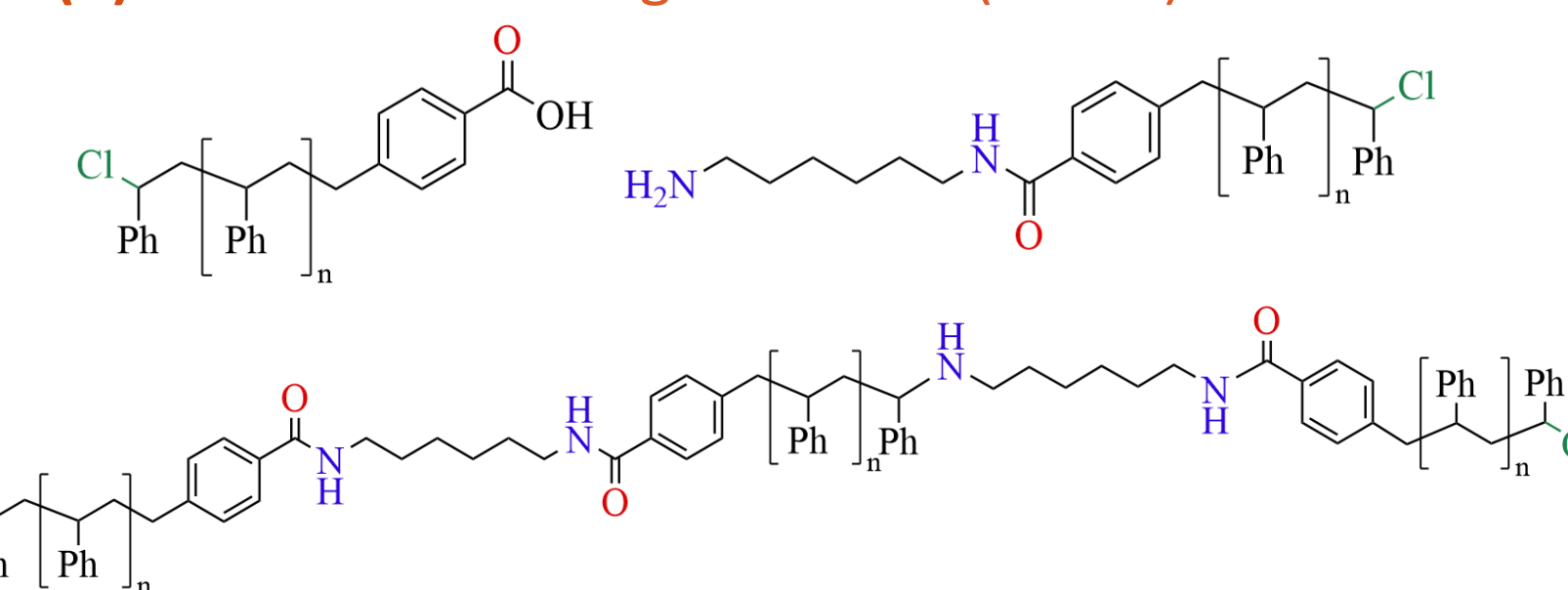


## Thermal treatment:

(a) Before

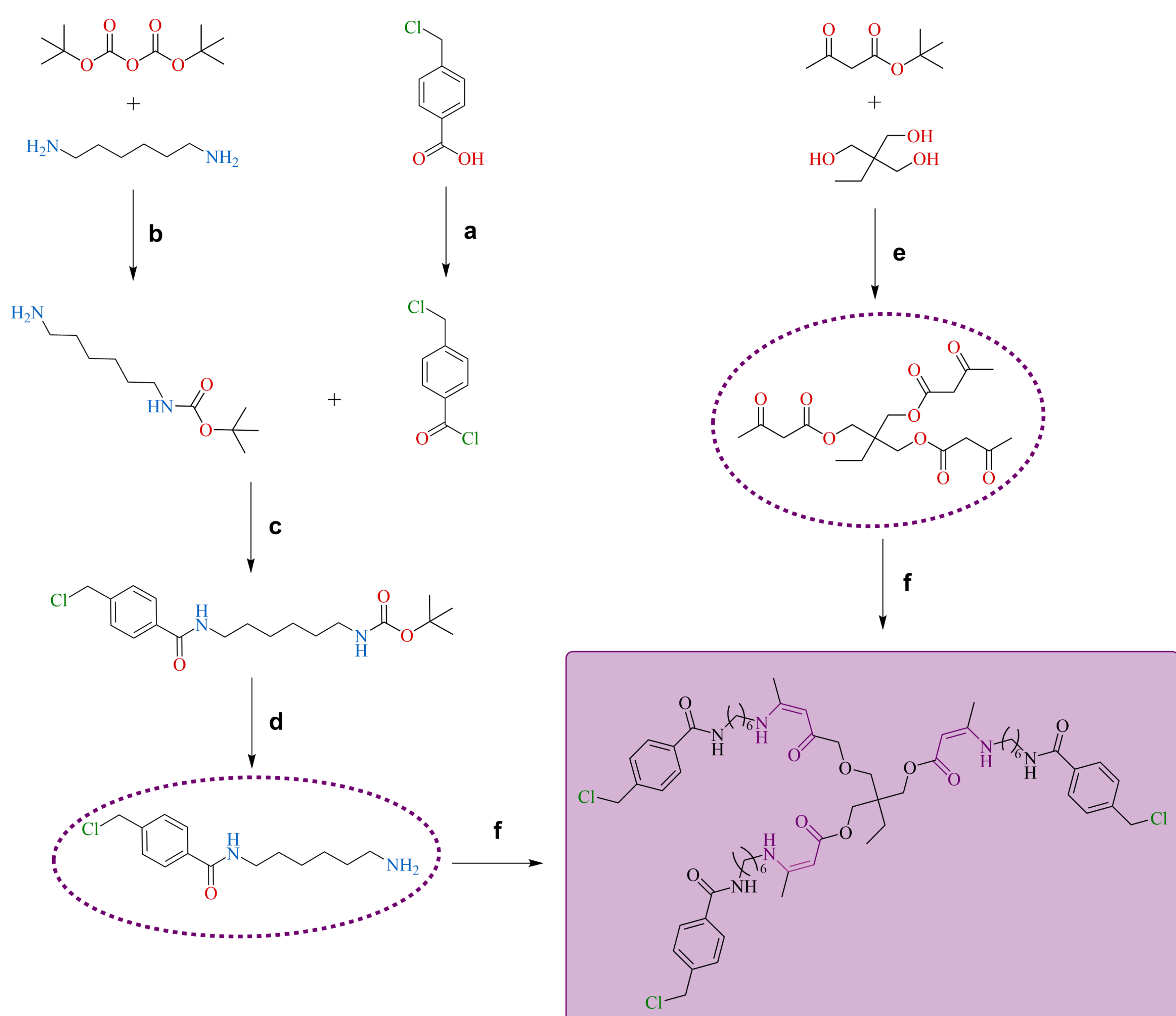


(b) After  $\rightarrow$  minor fragmentation (15.7%)



Covalent Adaptable Networks have attracted increasing interest as a promising solution to the poor recyclability of thermoset materials. CANs can combine the properties of conventional thermosets with the ability of topology reorganization, making reprocessing and self-healing possible. This could be achieved by introducing thermally or stimuli-triggered dynamic bonds into the polymer networks [6]. Our goal is to modify the structure of a benzamide-containing initiator into a trifunctional initiator bearing the vinylogous urethane dynamic bond.

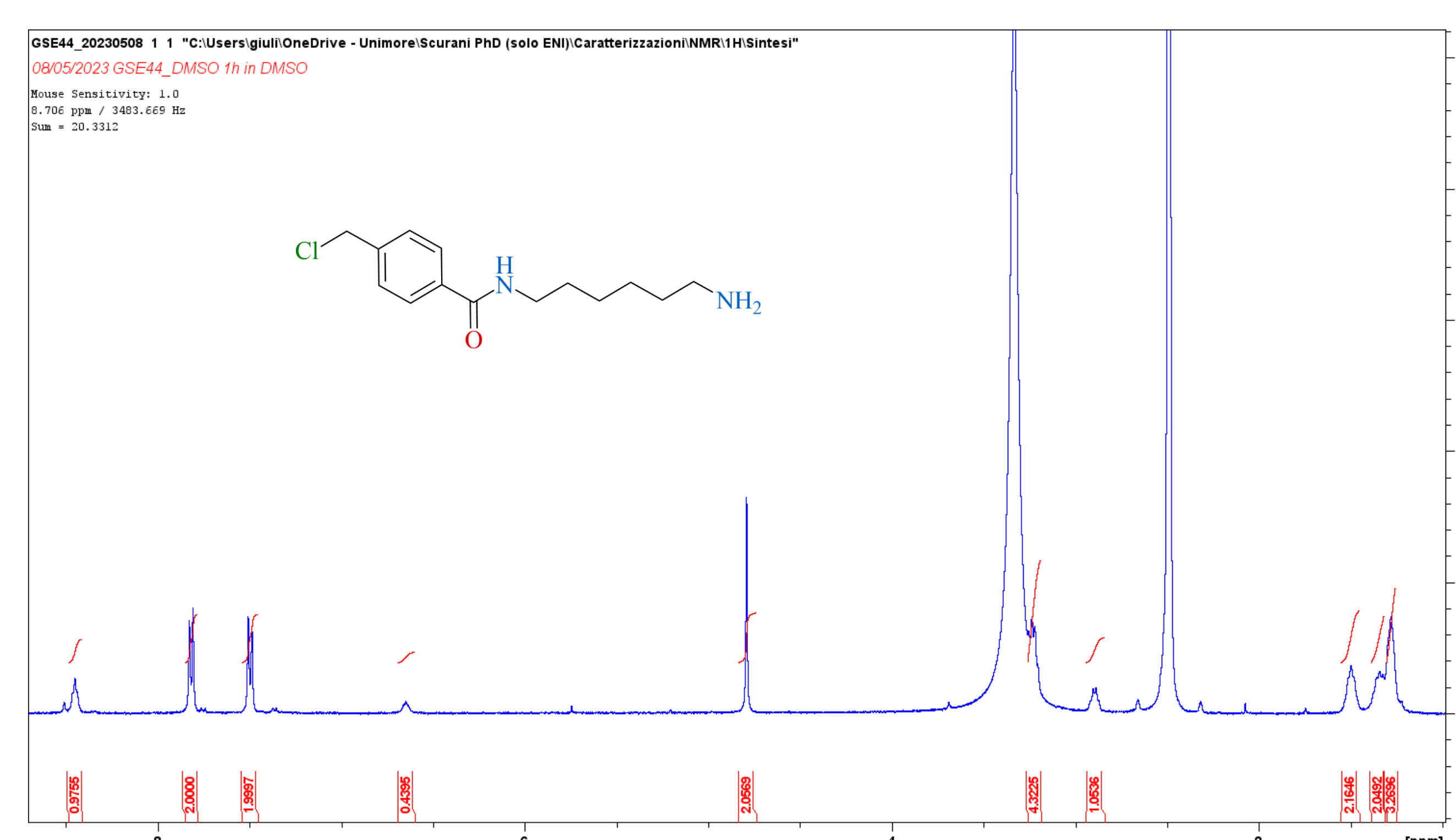
## Trifunctional initiator synthesis:



- (a)  $\text{SOCl}_2$ , r.t., overnight;  
 (b)  $\text{Boc}_2\text{O}$ , THF,  $0^\circ\text{C} \rightarrow \text{r.t.}$ , 22h;  
 (c) TEA, DCM,  $0^\circ\text{C} \rightarrow \text{r.t.}$ , 3h;  
 (d) TFA, DCM,  $0^\circ\text{C}$ , 1h;  
 (e)  $130^\circ\text{C}$ , 500 mbar, 4h;  
 (f) DMSO,  $\text{MgSO}_4$ , r.t., overnight.

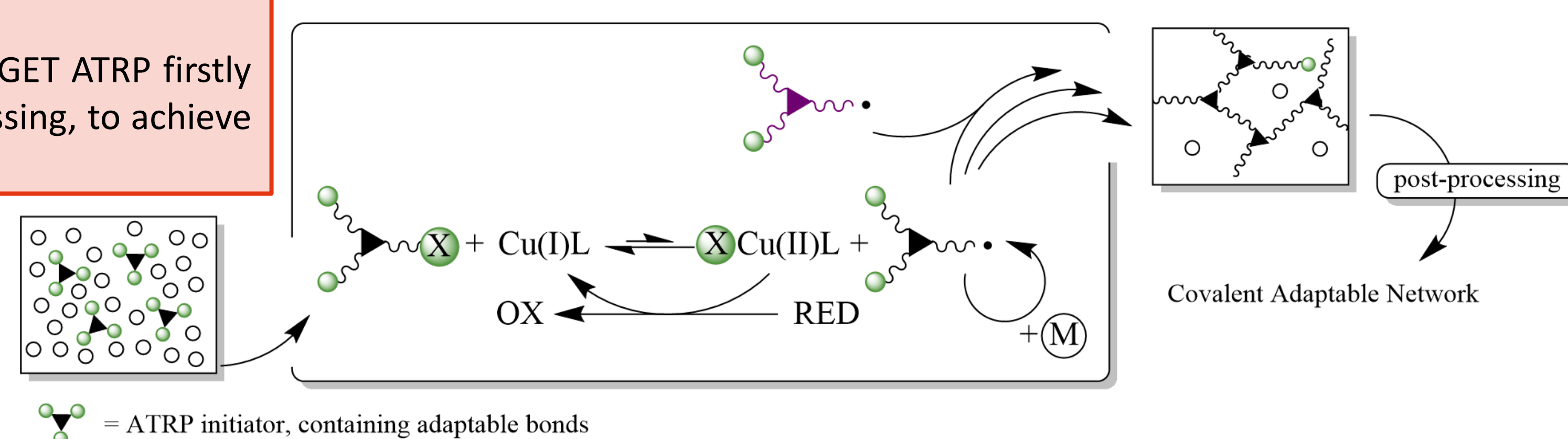
Optimized until step (e)  
 Further optimization of step (f)

## <sup>1</sup>H NMR:



## Future perspectives

The synthesized trifunctional initiator will be employed in the ARGET ATRP firstly to obtain a branched polymer and then, after optimal post-processing, to achieve a CAN, making the ATRP product recyclable.



## References:

- [1] K. Matyjaszewski, *Isr. J. Chem.* **2012**, 52, 206 – 220;
- [2] Y. Yagci et al.; *Prog. Polym. Sci.*, **2011**, 36, 4, 455-567;
- [3] K. Matyjaszewski, N. V. Tsarevsky; *J. Am. Chem. Soc.*, **2014**, 136, 18, 6513-6533;
- [4] Altintas, O. et al.; *Polymer Chemistry*, **2015**, 6, 2854;
- [5] Ghelfi, Ferrando, Longo, Buffagni WO 2019/215626 A1;
- [6] C. N. Bowman, C. J. Kloxin, *Angew. Chem. Int. Ed.* **2012**, 51, 4272 – 4274.