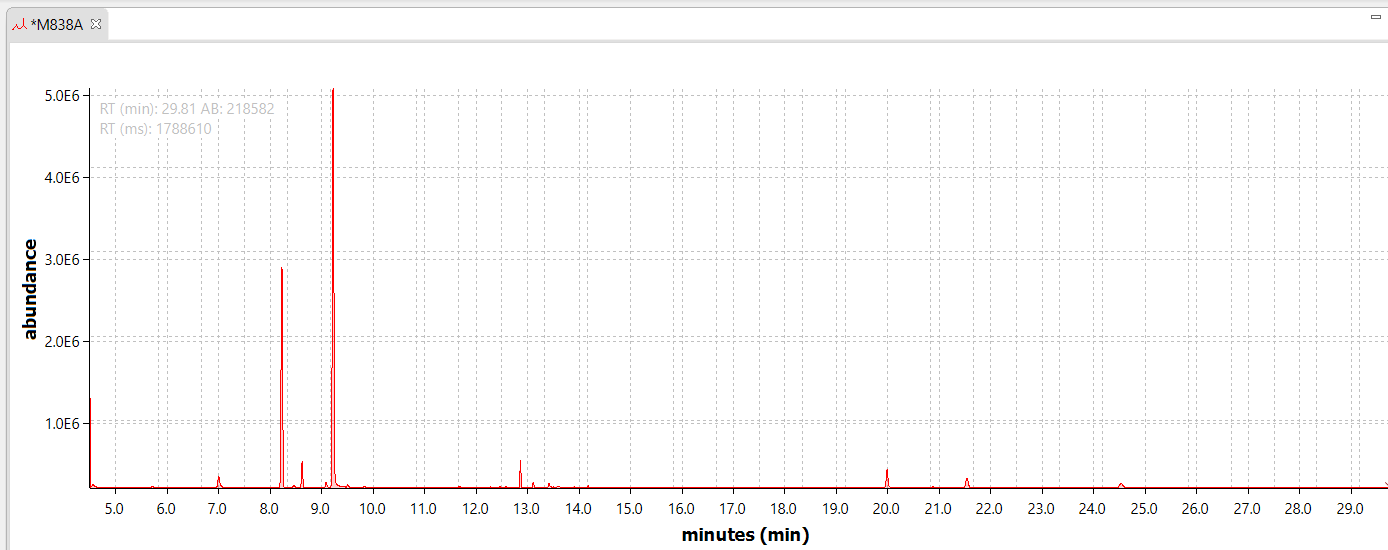
## Radical clock experiments

Radical clock experiments were performed on 1-(allyloxy)-2-chlorobenzene and *o*-butenylchlorobenzene.

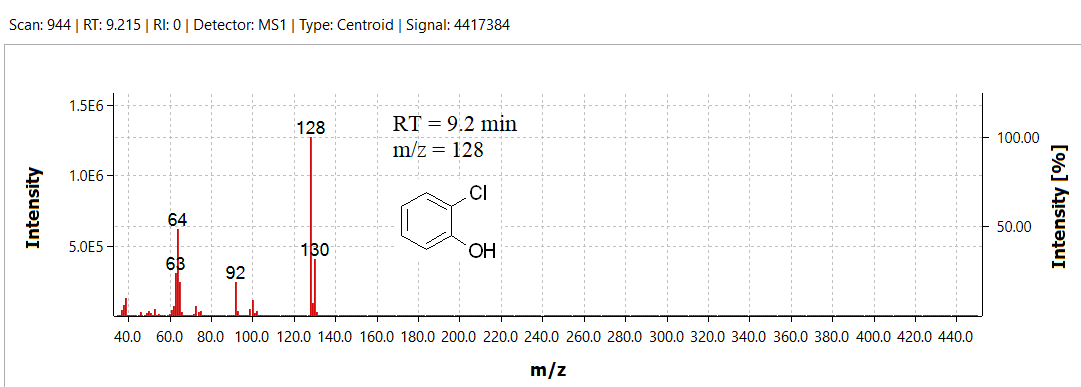
**Reaction with 1-(allyloxy)-2-chlorobenzene**

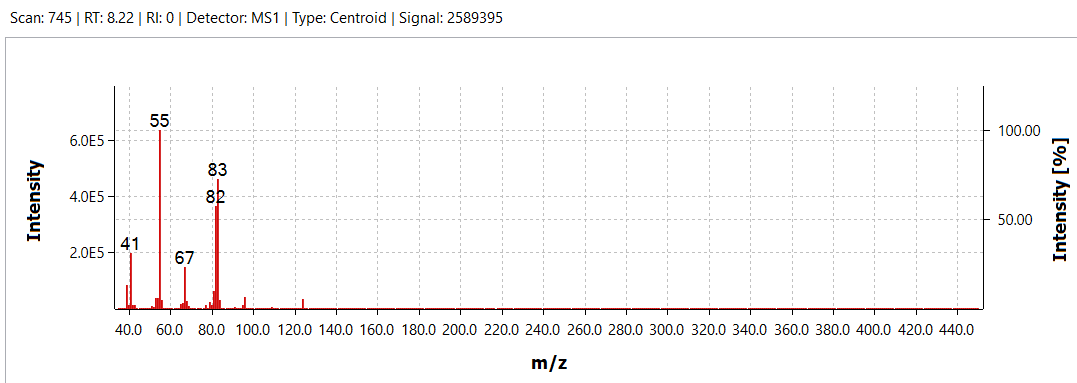


1-(Allyloxy)-2-chlorobenzene was subjected to the standard reaction conditions. After 15 minutes irradiation, the reaction crude was analyzed via GC-MS (see below, file attached “M838A.qgd”). Two main peaks were observed, identified as *o*-hydroxychlorobenzene (from C-O cleavage) and propenylcyclohexane. These might result from the nucleophilic attack of the cyclohexyl to the alkene, with consequent release of the hydroxychlorobenzene.



Chromatogram: M838A.qgd





Similar results were obtained for this reaction under dark (no irradiation, see file attached “M838B-Fe-nohv.qgd”)

**Reaction with *o*-butenylchlorobenzene**

The reaction between *o*-butenylchlorobenzene and cyclohexylmagnesium chloride mainly resulted in the formation of the expected coupling product, but a broad array of side products was observed, including some possibly deriving from a radical pathways. GC-MS data for the identified compounds are shown below (attached file “Mredo831-2eq-grig.qgd”).



Apart from dehalogenation of the aryl chloride, isomerization (loss of -CH3 fragments in some of the peaks, only possible from isomerized alkenyl chains) and hydrogenation of the alkenyl chain (both in the aryl chloride and the dehalogenated derivative) was observed. Reductive dehalogenation and hydrogenation might come from a Fe hydride intermediate formed upon -hydrogen elimination of the Fe-alkyl species [2]. The formation of bi(cyclohexane) from homocoupling of the Grignard reagent was also observed here, as in other examples in the scope.

Besides the formation of the expected coupling product (RT 10.81min), other products are observed with the same m/z values (RT 10.93, 11.20), but considerably different fragmentation patterns. The expected coupling product is recognizable by the loss of a –CH2CH=CH2 fragment (m/z 173, M-41, similar fragmentation in the starting aryl chloride), and a cyclohexyl (m/z 131). These peaks are not observed in the other products, which instead show the peak at m/z 117 (M-43, -CH2CH2CH3). This suggests that the butenyl chain in no longer present in the product and the fragmentation might be due to the (fused) alkylic residue (radical clock products). As these are minor compounds, we do not believe a free radical mechanism to be predominant under the reaction conditions.

Chromatogram: Mredo831-2eq-grig.qgd

