

Synthesis of Non-Estrogenic Polymer Precursors by Isomerizing Metathesis

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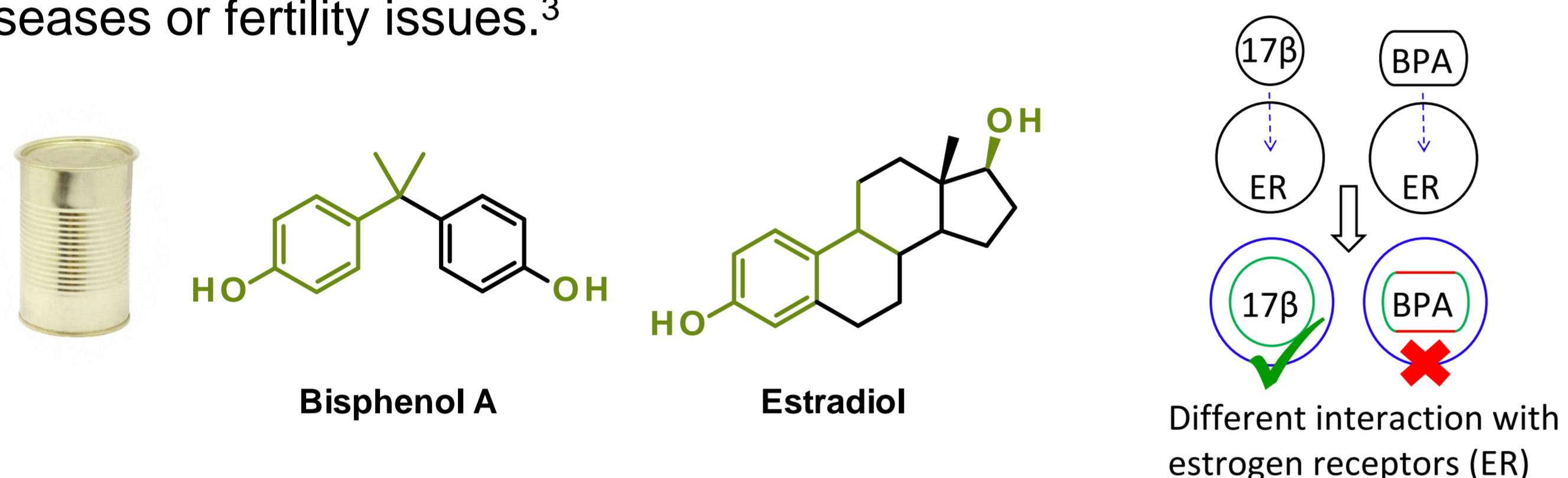
Abstract



The increasing concern about the side-effects of Bisphenol A (BPA), one of the most common polymer precursors, is raising the interest in finding sustainable non-toxic alternatives. Isomerizing metathesis was applied to renewable resources such as eugenol or cashew nutshell liquid (CNSL) in order to obtain dihydroxystilbene derivatives as potential replacements. We measured the estrogenic activity of these monomers and studied their reactivity in polymer synthesis in comparison to BPA. The estrogenic activity of monomers derived from cardanol was found to be in the same range as that of BPA, whereas eugenol-derived materials were found to be non-estrogenic and therefore a suitable BPA replacement.

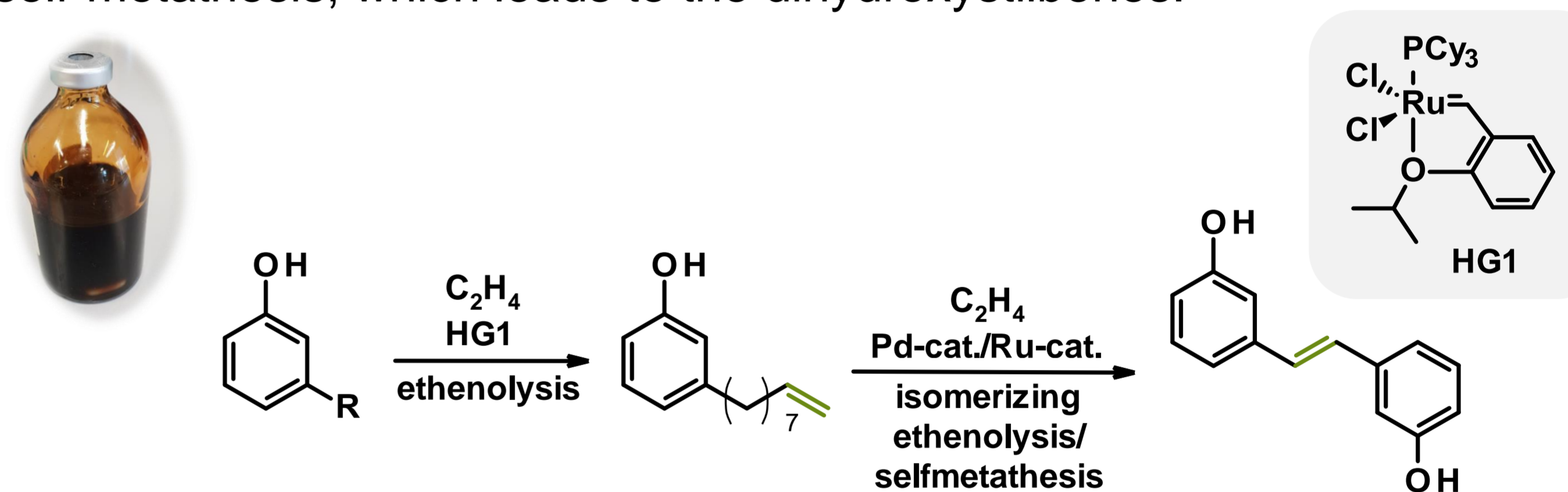
Introduction

Bisphenol A is the main precursor of polycarbonates and epoxy resins¹ used in the fabrication of many materials and commodity chemicals. However, BPA mimics the activity of estradiol (17 β)² and upon leaching from food packages, it can cause side-effects such as cardiovascular diseases or fertility issues.³

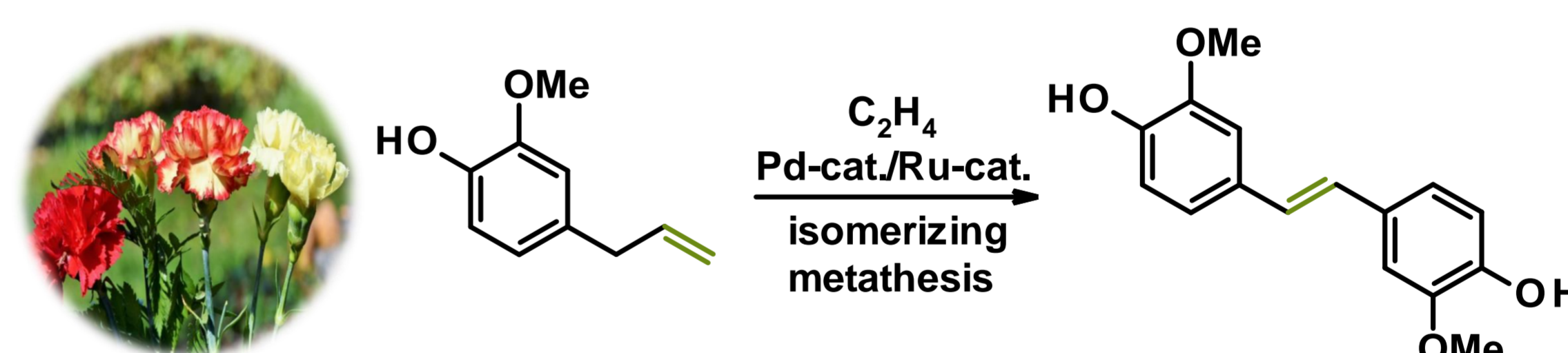


Synthesis of Polymer Precursors

The cardanol mixture was converted into 3-(non-8-enyl)phenol after ethenolysis and distillation. This reaction was followed by a one-pot derivatization consisting of an isomerizing ethenolysis and a subsequent self-metathesis, which leads to the dihydroxystilbenes.⁸



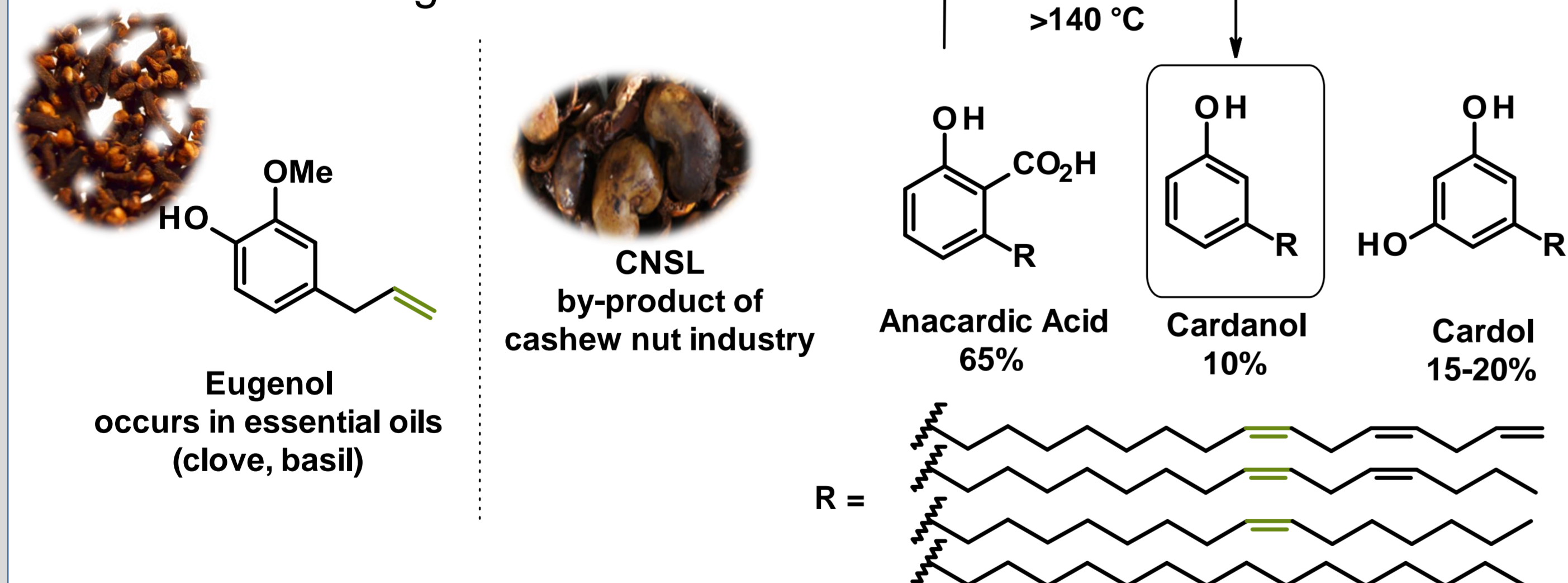
Starting from eugenol, a tandem process of an isomerization and a self-metathesis afforded the corresponding stilbene.



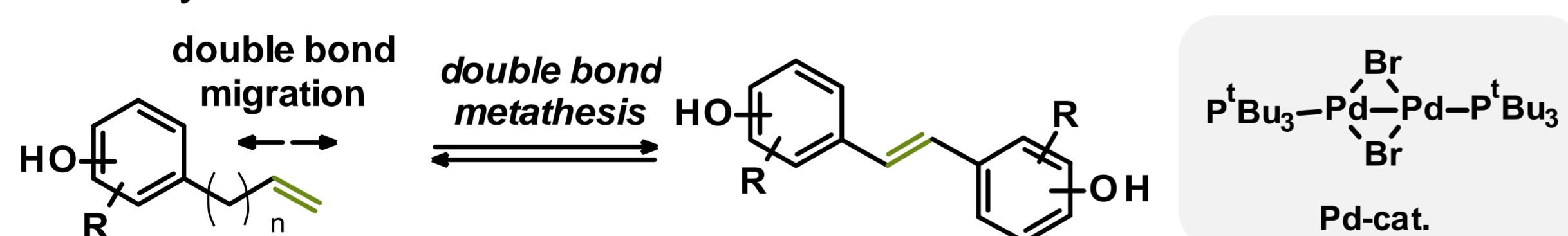
For diversification of the building blocks, di(hydroxyphenyl)ethane analogues of both stilbenes could be synthesized after a subsequent one-pot hydrogenation step.

Stilbene derivatives as alternatives to BPA

For a sustainable synthesis of monomers, widely available renewable resources, such as eugenol and cashew nutshell liquid (CNSL) were chosen as starting materials.^{4,5}

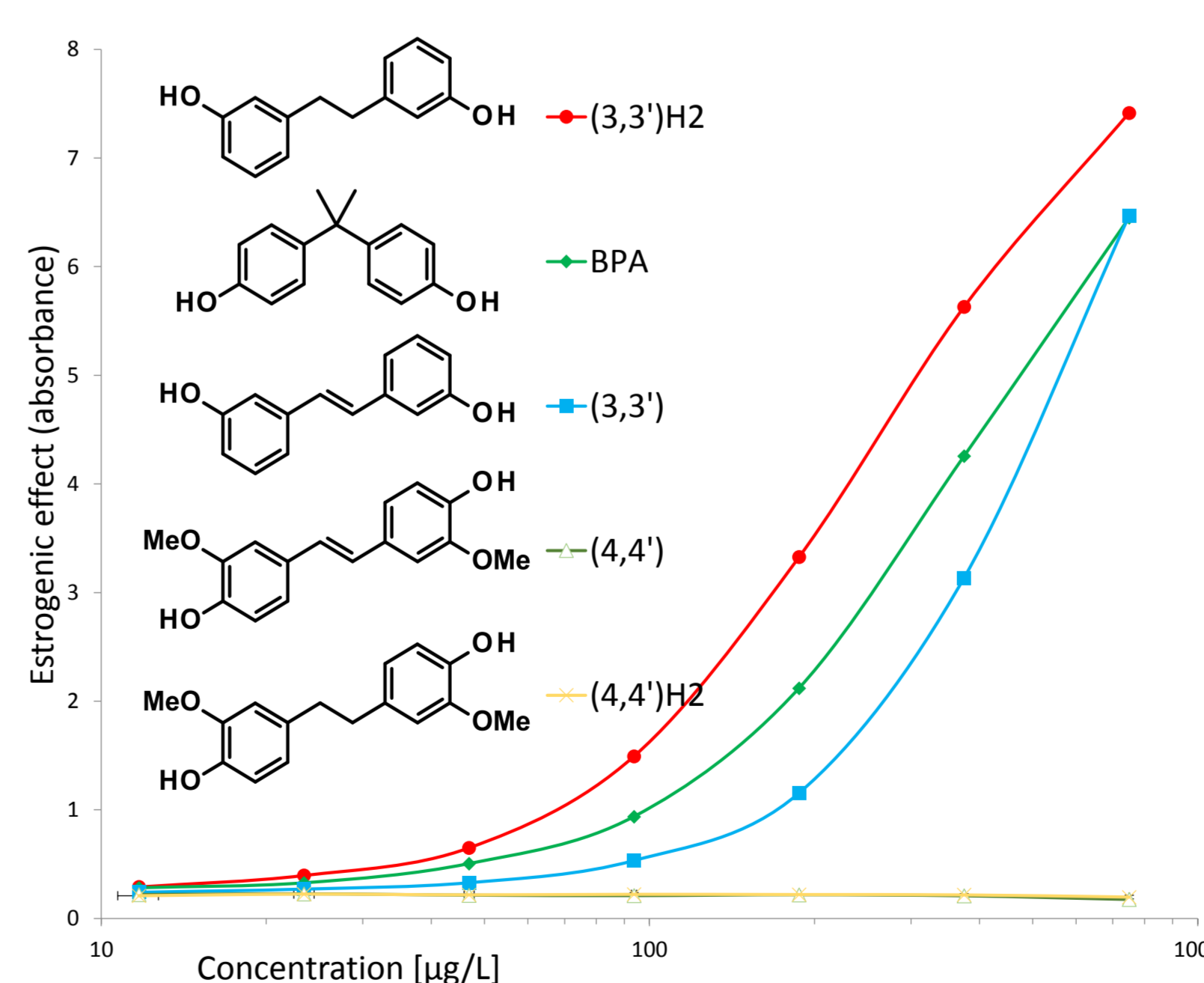


The aliphatic side chain is shortened using isomerizing metathesis as key step.⁶ This process is mediated by the uniquely active isomerization catalyst [Pd(μ -Br)(^tBu₃P)]₂ (Pd-cat.)⁷ and state-of-the-art a ruthenium metathesis catalysts.



The isomerization catalyst continuously moves the double bond along the aliphatic carbon chain, while the metathesis catalyst simultaneously shuffles the substituents at the double bond to form the stilbene.

Estrogenicity assay – Yeast Estrogen Screen (YES)⁹



Polycarbonate synthesis and the sustainable thiol-ene polymerization were chosen as applications to test the reactivity of these substrates towards polymer synthesis.

The polymers present similar properties to the ones derived from BPA, showing the potential of these monomers as alternative structures.

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