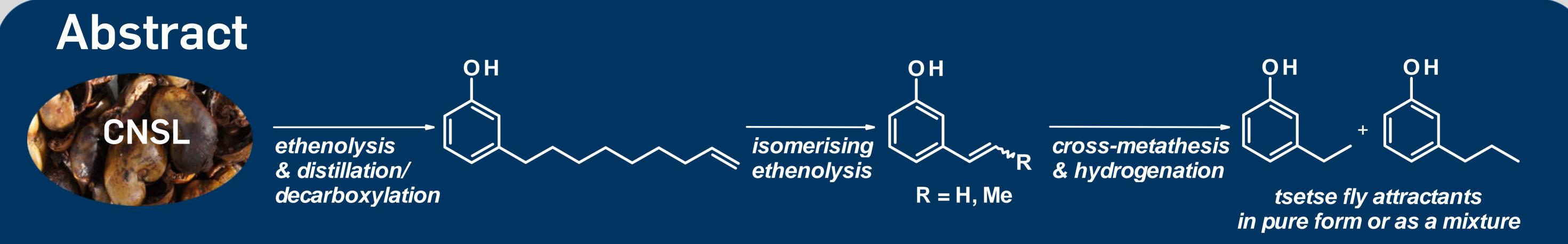
Chemical Valorisation of Cashew Nut Shell Liquid by Olefin-Metathesis



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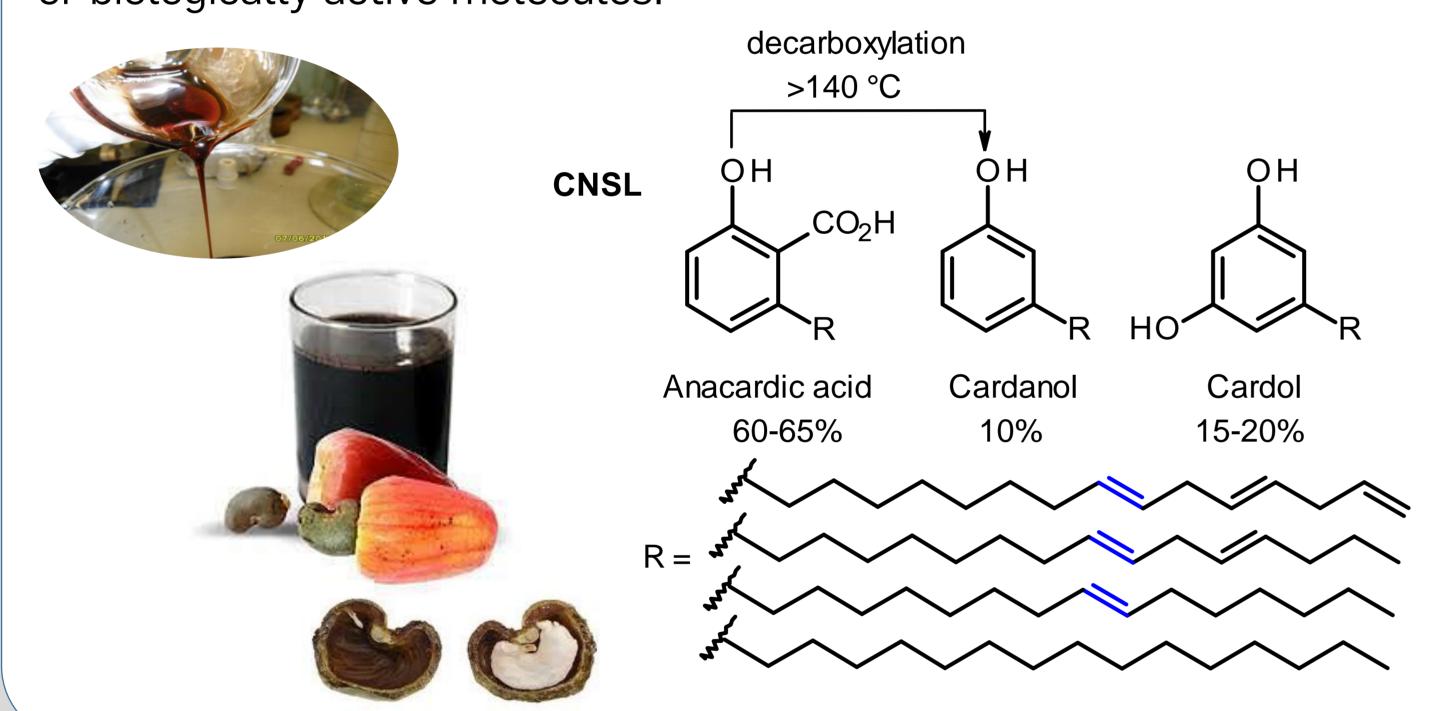




Starting from cashew nut shell liquid (CNSL), a widely unused waste by-product of the cashew nut industry, valuable chemicals have been obtained. Tsetse fly attractants were selectively synthesised by first converting CNSL into 3-(non-8-enyl)phenol and then shortening the olefinic side-chain via isomerising ethenolysis and a one-pot hydrogenation step. A tyrosinase inhibitor was also synthesised following a similar reaction pathway starting from CNSL.

Cashew Nut Shell Liquid

Cashew nut shell liquid is an unused, inedible natural resource for which no competition occurs between land use for food or raw material production. It consists of a mixture of phenolic compounds with a 15-carbon olefinic side-chain in the *meta* position.^[1,2] CNSL is obtained by extraction of cashew nut shells and represents a renewable starting material for a variety of valuable compounds used in material sciences or biologically active molecules.



Synthesis of Tsetse Fly Attractants^[3]

Starting from 3-(non-8-enyl)phenol, a mixture of styrene derivatives was obtained using **Pd-cat.**^[4] and a 2nd generation Hoveyda-Grubbs catalyst. Depending on the ethylene equivalents, the side-chain length distribution of the product mixture is adjustable.

$$C_{2}H_{4} (6 \text{ bar})$$

$$1.5 \text{ mol}\% \text{ Pd-cat.}$$

$$2.0 \text{ mol}\% \text{ M51}$$

$$THF, 16 \text{ h}, 50 \text{ °C}$$

$$C_{1}H_{2}H_{3}H_{4} (6 \text{ bar})$$

$$1) \text{ ethylene or butene}$$

$$2) H_{2} (5 \text{ bar}), \text{ MeOH}$$

$$50 \text{ °C}, 3 \text{ h}$$

$$6 \text{ Pd-cat.}$$

$$78\%, R = \text{Me}$$

$$84\%, R = \text{H}$$

Since both the kairomones 3-ethyl- and 3-propylphenol target different tsetse flies, an application of their mixture should also be advantageous for the use in traps.

Selective Ethenolysis of Anacardic Acid

The mixture of differently unsaturated anacardic acids, obtained by precipitation of CNSL, was selectively converted to a single compound, 3-(non-8-enyl)phenol, by ethenolysis followed by distillation with concomitant decarboxylation.

CNSL
$$C_2H_4$$
 (10 bar) C_2H_4 (10 bar) $C_2H_$

Using 1st generation Hoveyda-Grubbs catalyst **HG1**, the target molecule was isolated in 89% yield. The non-quantitative yield is due to the unreactive saturated derivative which remains in the distillation residue.

Synthesis of a Tyrosinase Inhibitor

The 6-(non-8-enyl)salicylic acid can be selectively obtained by ethenolysis of the crude CNSL and precipitation from the mixture, therefore shortening its synthesis by 2 steps. After cross-metathesis with 1-hexene as coupling partner and subsequent one-pot hydrogenation, the tyrosinase inhibitor 6-n-tridecylsalicylic acid was obtained.^[5]

The demonstrated reaction pathways emphasise the high synthetic potential of olefin-metathesis as a key technology in the valorisation of renewable resources and their incorporation in the chemical value chain.^[6]

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