2nd International Symposium and Workshop of the Global Green Chemistry Centres (G2C2)

Two Oceans Aquarium, Cape Town, South Africa

25th August 2014

SYNTHESIS OF BENZOLACTONE, KAIROMONE AND OTHER CHEMICALS FROM ANARCADIC ACID

Egid B. Mubofu, University of Dar es Salaam, Tanzania


30°E
35°E
40°E
UGANDA
Lake
Victoria
Bukoba
Equator
KENYA
RWANDA
BURUNDI
Mwanza
Serengeti Plain
Mt.
Kilimanjaro
5895m
Arusha
Moshi
Ngorongoro
Crater
Masai
Steppe
Kigoma
Tabora
Tanga
Pemba
5°S
INDIAN
UNITED REPUBLIC
OF TANZANIA
Dodoma
Zanzibar
OCEAN
Great Rift Valley
Lake Tanganyika
Morogoro
Dar es Salaam
DEM.
REP.
OF
CONGO
Lake
Rukwa
Iringa
Mafia
Mbeya
10°S
ZAMBIA
Lake Nyasa
Lindi
10°S
Songea
Mtwara
MALAWI
MOZAMBIQUE
0
200 miles
0
200 kilometres
35°E
©Oxford Cartographers
40°E


UDSM-
CoNAS-
CHEMISTRY DEPT

CoNAS Research themes

- Environment and climate change
- Earth Sciences
- Food security
- Natural products
- Renewable Energy
- Material Science

The department has three research groups

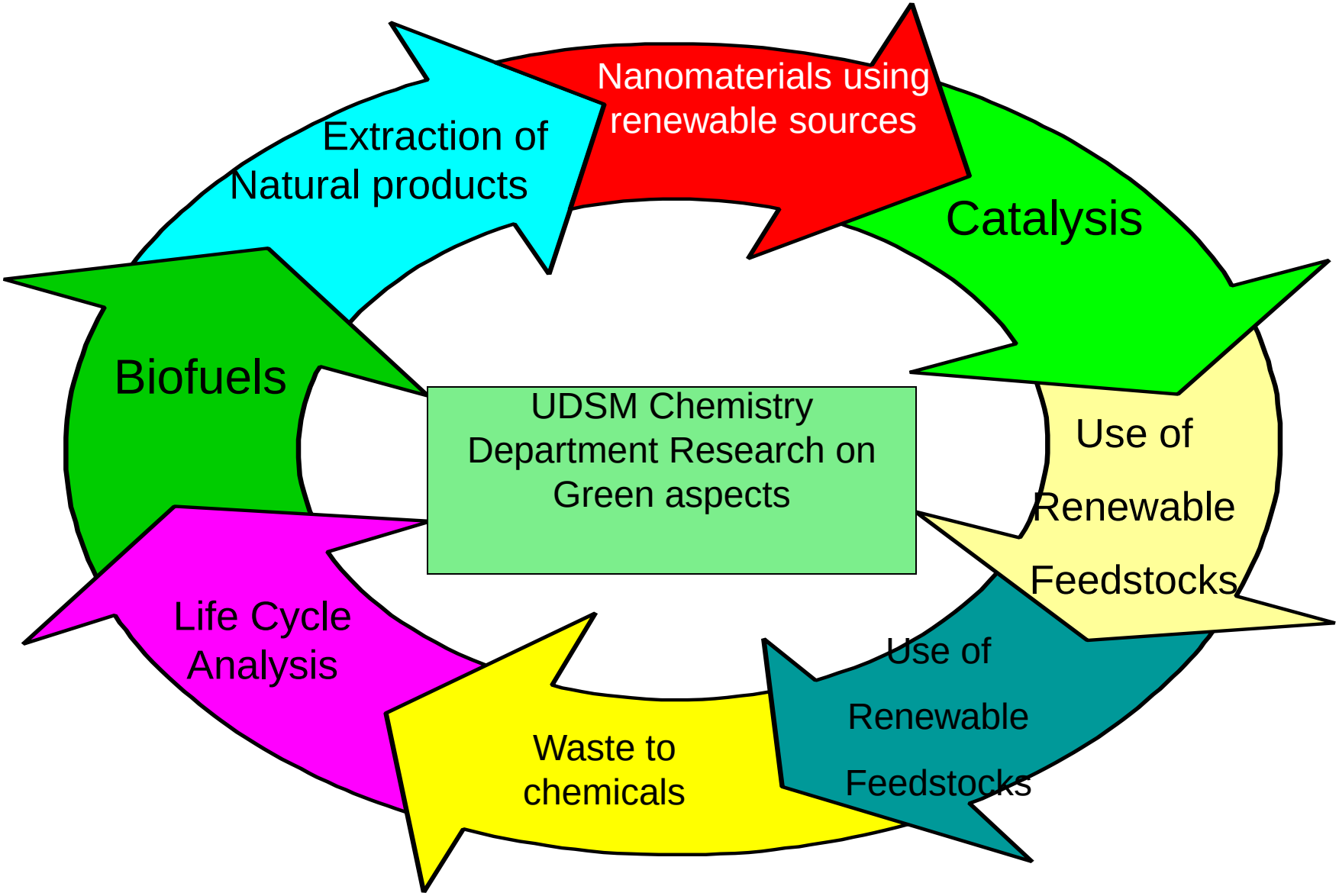
Research Groups (50 Staff)

Materials, Environmental and Green Chemistry
17 Staff

Analytical, Environmental and Chemometrics Chemistry
16 Staff

Natural Products and Organic Synthesis
16 Staff

Green Chemistry Research aspects at Chemistry dept Udsm



What can the cashew plant provide?

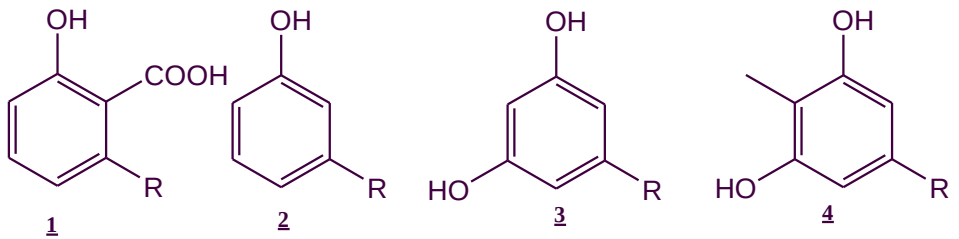
THE ROYAL SOCIETY

The Leverhulme Trust

CNSL

Isolation

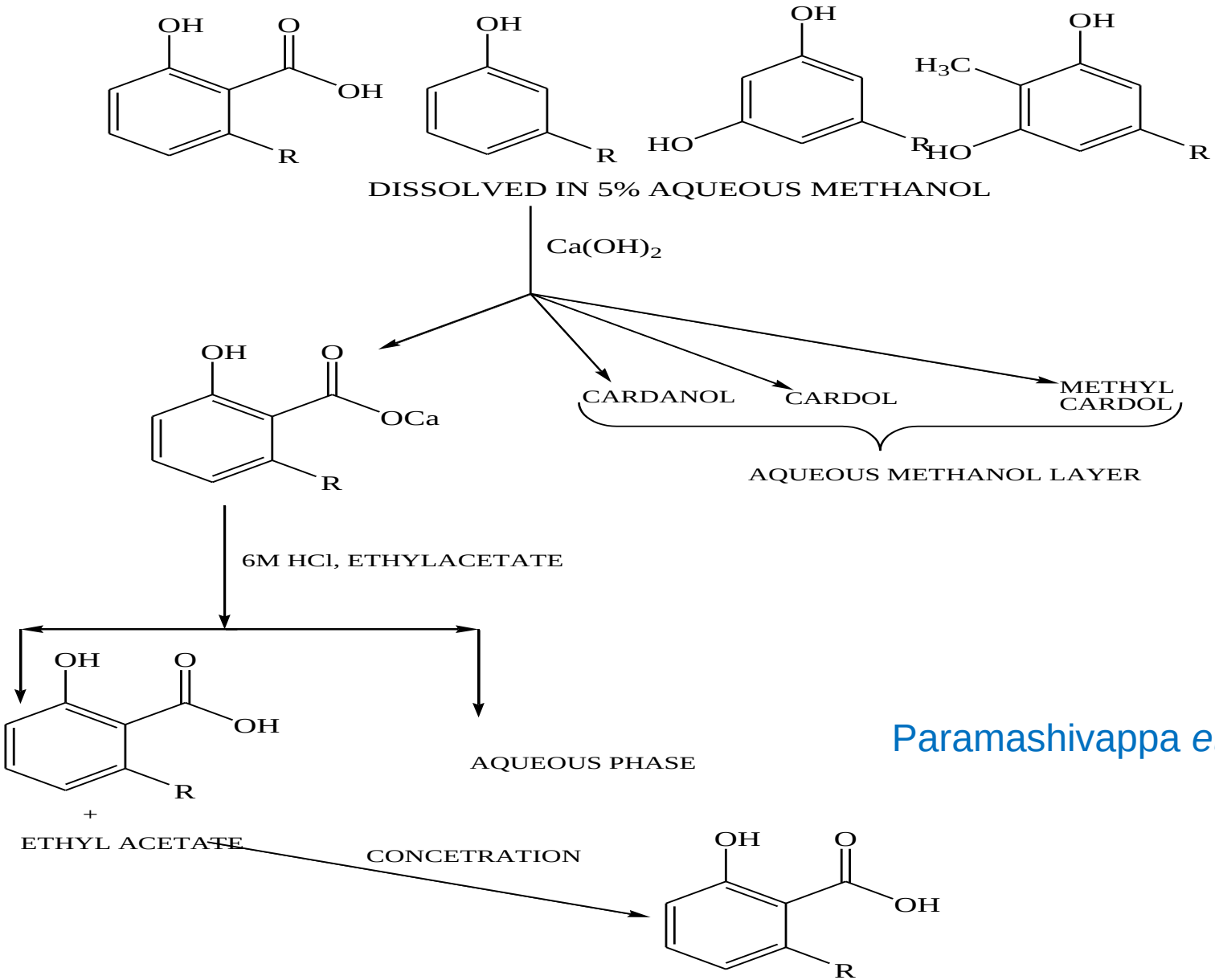
Extraction



Where R= $C_{15}H_{31-n}$ and n= 0,2,4,6 π electrons

Phenolic compounds of CNSL include: 65% anacardic acid (**1**), 10 % cardanols (**2**), 10% cardols (**3**) and 15 % methyl cardols (**4**)

ISOLATION OF ANACARDIC ACID VIA CALCIUM ANACARDATE PROCEDURE



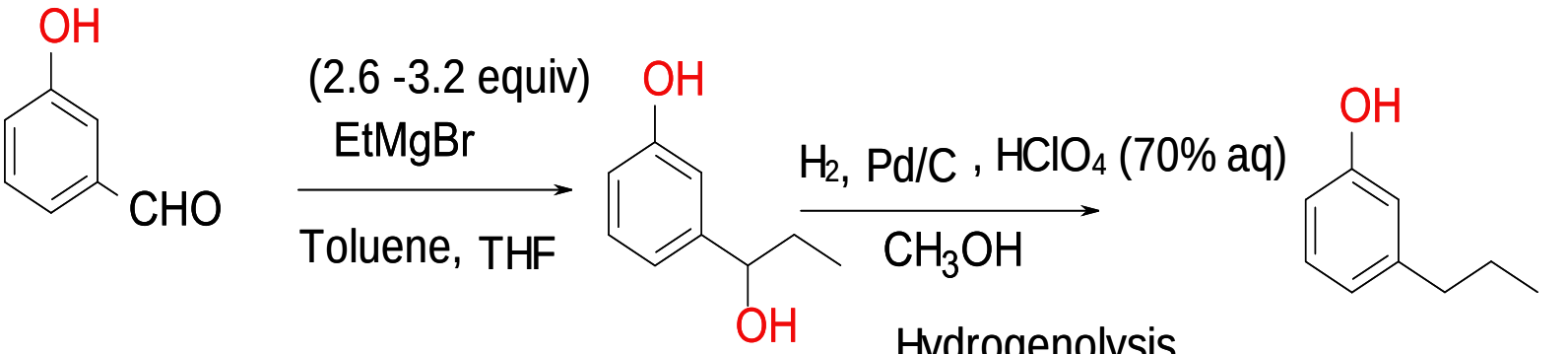
Paramashivappa *et al. 2001*.

Chemicals and Materials from CNSL e.g Kairomone 3-propylphenol and Detergents)

Monomers and other chemicals derived from CNS

Nanomaterials/Crystals

Kairomone (3-propylphenol) and detergents



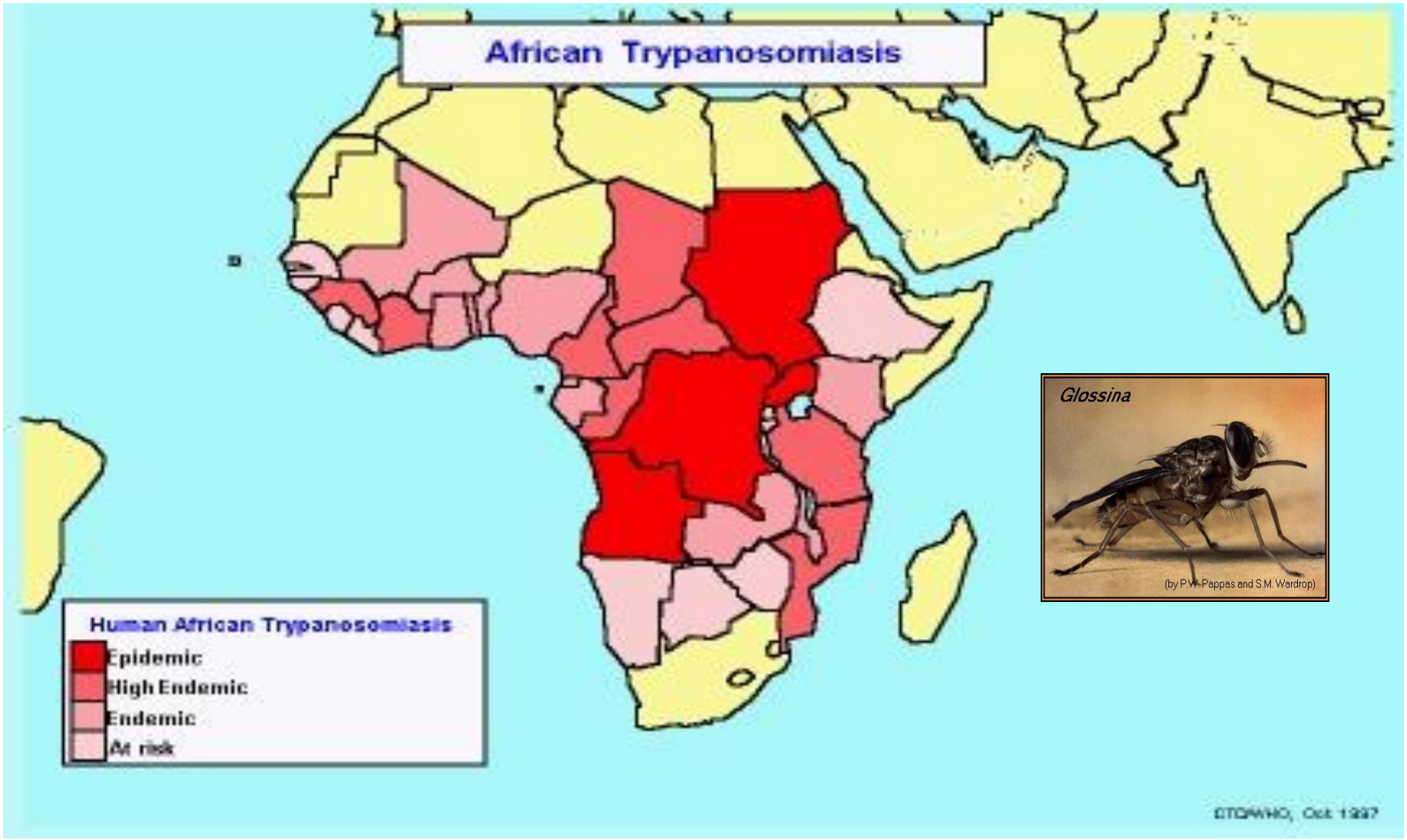
3-Hydroxybenzaldehyde

Benzayl alcohol

3-(1-Hydroxypropyl)phenol

3-n-propylphenol

Why 3-propylphenol?



Why 3-propylphenol?

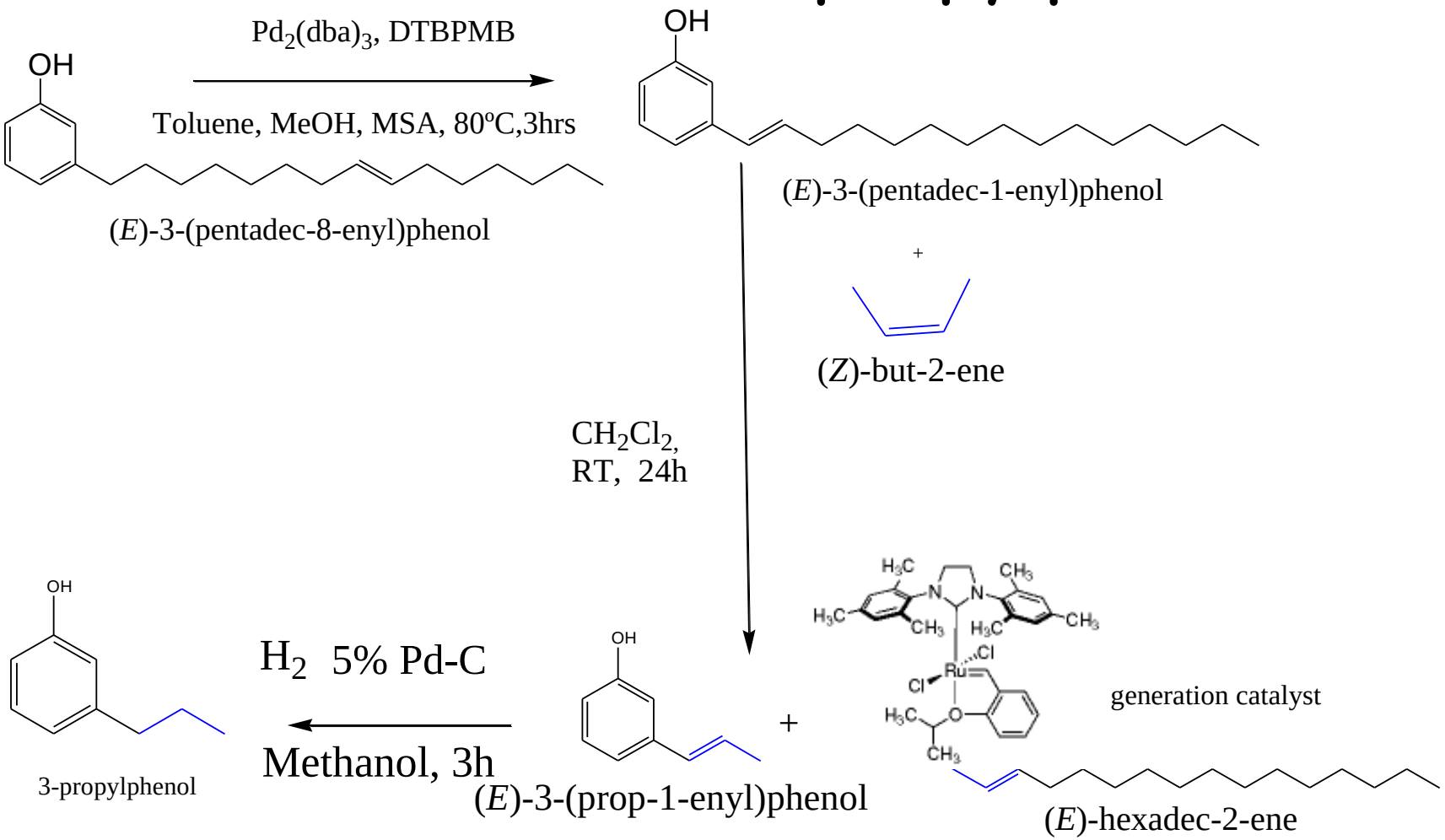
Smells like cow's urine

Serves as tsetse fly attractant to fake cows.

Fake cows are impregnated in advance with insecticide to kill the flies.

http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1121279 retrieved on 5th Oct 2009

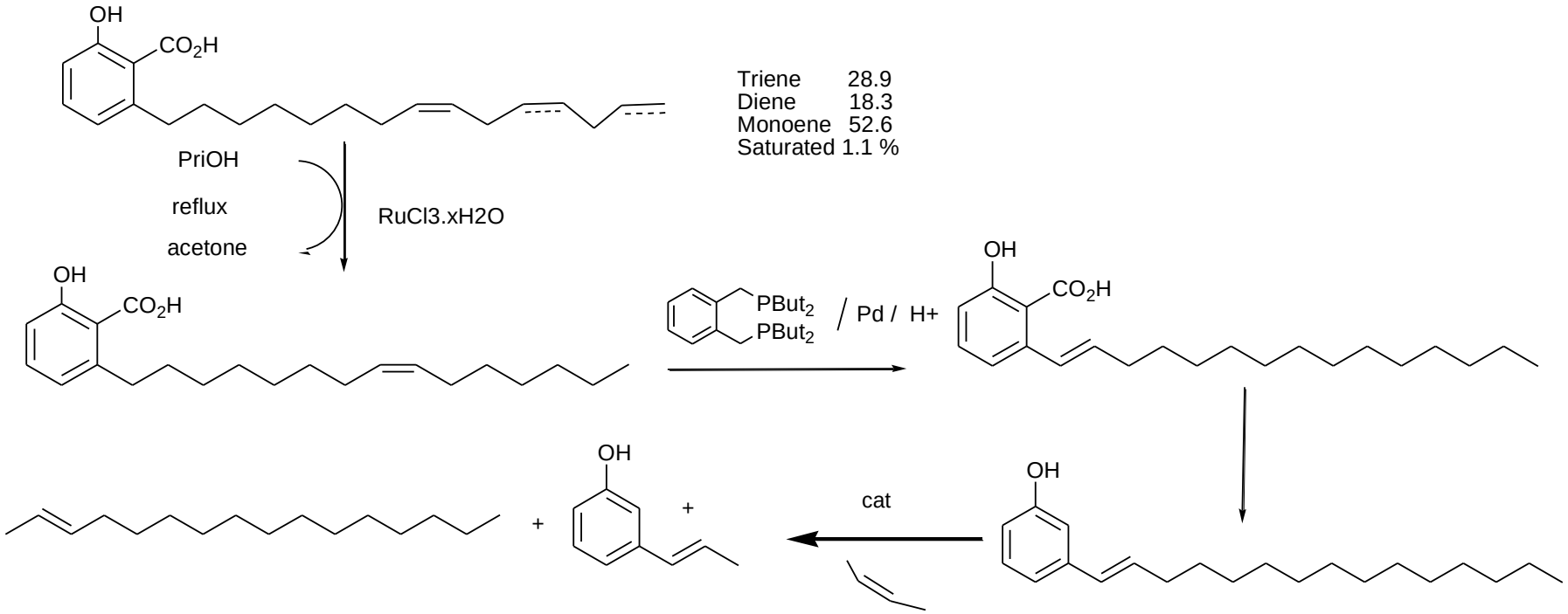
The route to 3-propylphenol



Mmongoyo et al. *Eur. J. Lip. Sci. Technol.*(2012)***114:****1183-1192.**

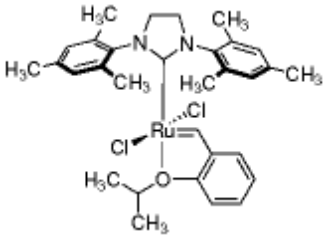
Propylphenol from isomerisation of monoene anacardic acid

Synthesis of propylphenol from cardanol has been achieved and reported albeit in low yield. We are investigating synthesis of propylphenol from anacardic acid to improve the yield.

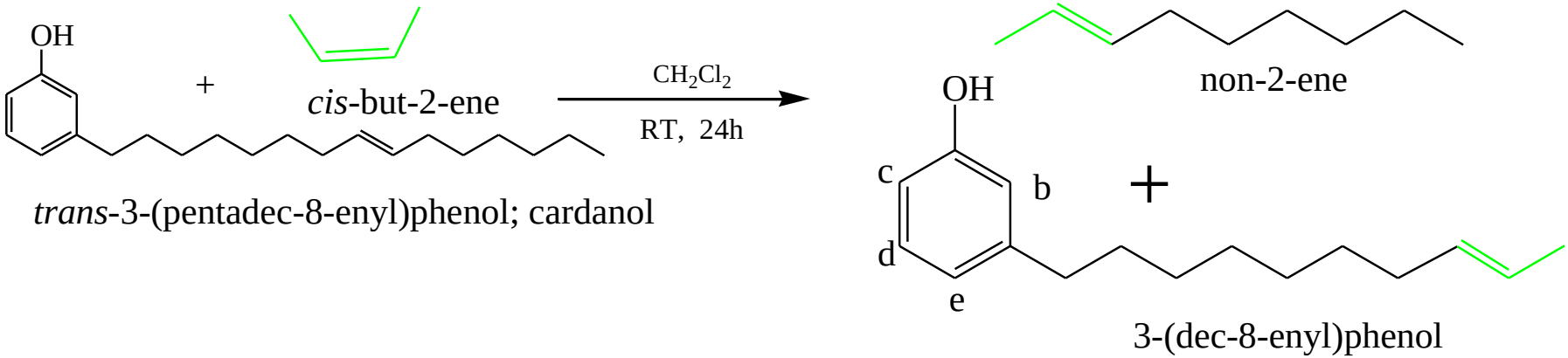


The carboxylic acid in the 2 position relative to the chain increases the conjugation length and hence the stabilisiation of the conjugated isomer.

Synthesis of a detergent



Hoveyda-Grubbs 2nd generation catalyst

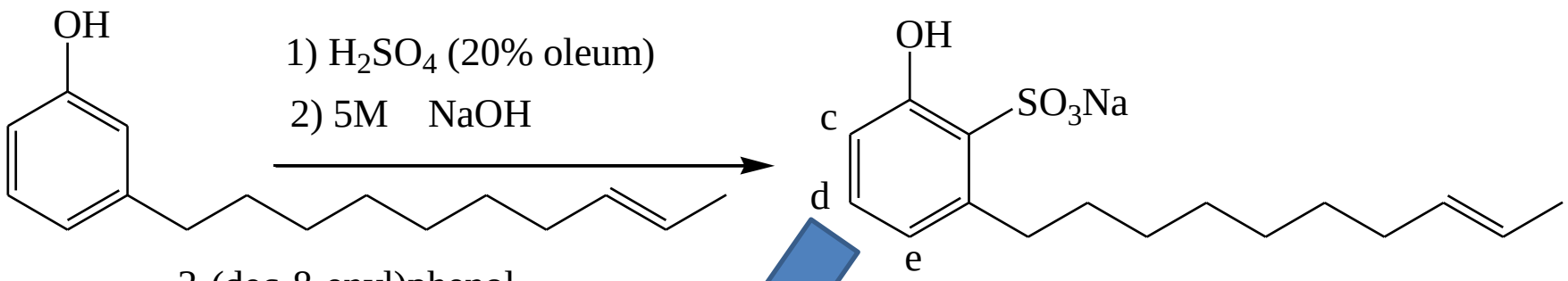


trans-3-(pentadec-8-enyl)phenol; cardanol

3-(dec-8-enyl)phenol

100% conversion

Sulfonation of 3-(dec-8 enyl)phenol



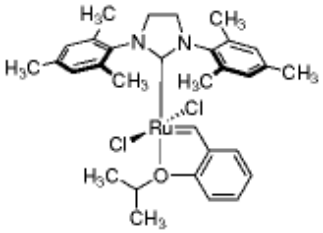
3-(dec-8-enyl)phenol

sodium 2-(dec-8-enyl)-6-hydroxybenzenesulfonate

96.13% yield (m.p = 366 - 368°C).

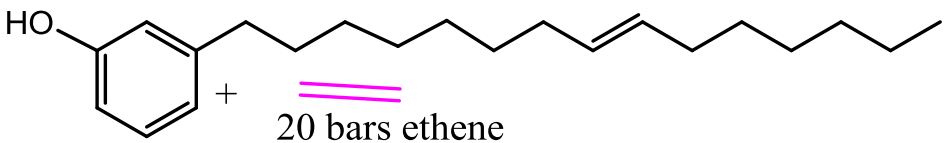
Synthesis of 1-octene and 3-(non-8-enyl)phenol from monoene cardanol

- 1-octene is an industrially important chemical for production of aldehydes through hydroformylation reactions
- Polyethylene comonomer, detergent and alcohols



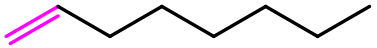
Hoveyda-Grubbs 2nd generation catalyst

DCM, RT, 24 HOURS



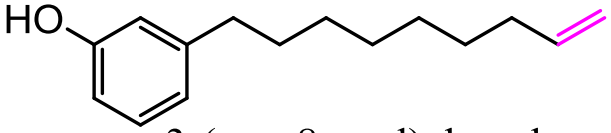
20 bars ethene

Monoene cardanol



1-octene

64.86 % yield

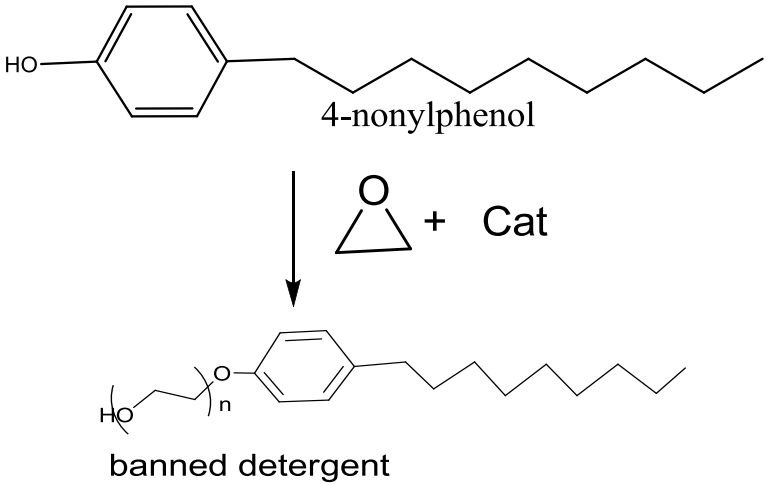


3-(non-8-enyl)phenol

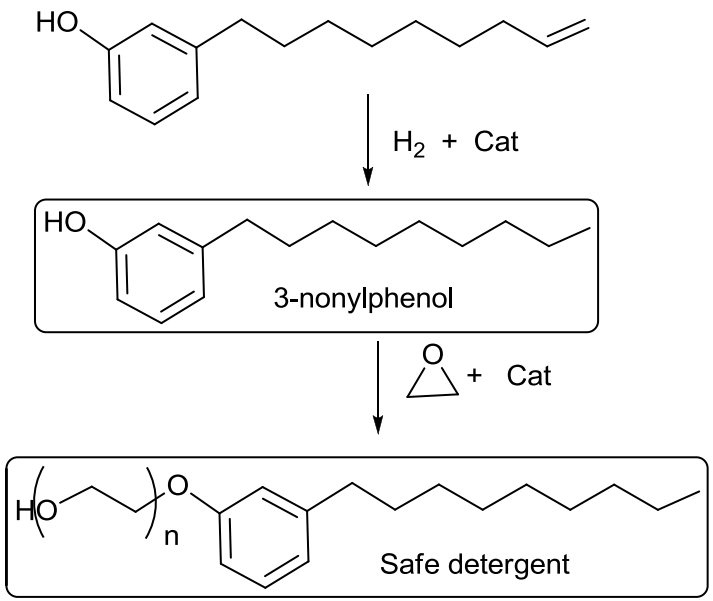
76. 39 % yield

Why 3-nonylphenol? Why NOT 4-nonylphenol?

On reaction with ethene oxide, 4-nonylphenol gives ethoxylates, which are powerful and important detergents (1000s of tones per year).
However, they have been found to be endocrine disruptors. Hence banned from EC.



Ethoxylates of 3-nonylphenol are expected to be non-endocrine disruptors.

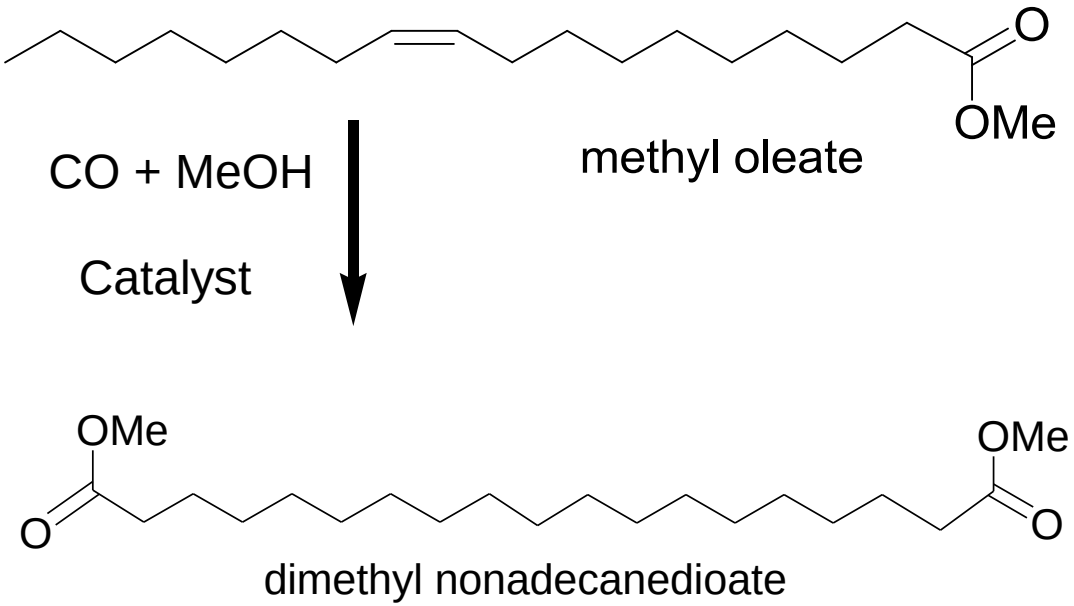


Edwin J. Routledge and John P. Sumpter **1996**, Structural Features of Alkylphenolic Chemicals Associated with Estrogenic Activity. *J. Bio. Mol.* 3280-3288

Monomers and other chemicals derived from CNS

Carbonylation

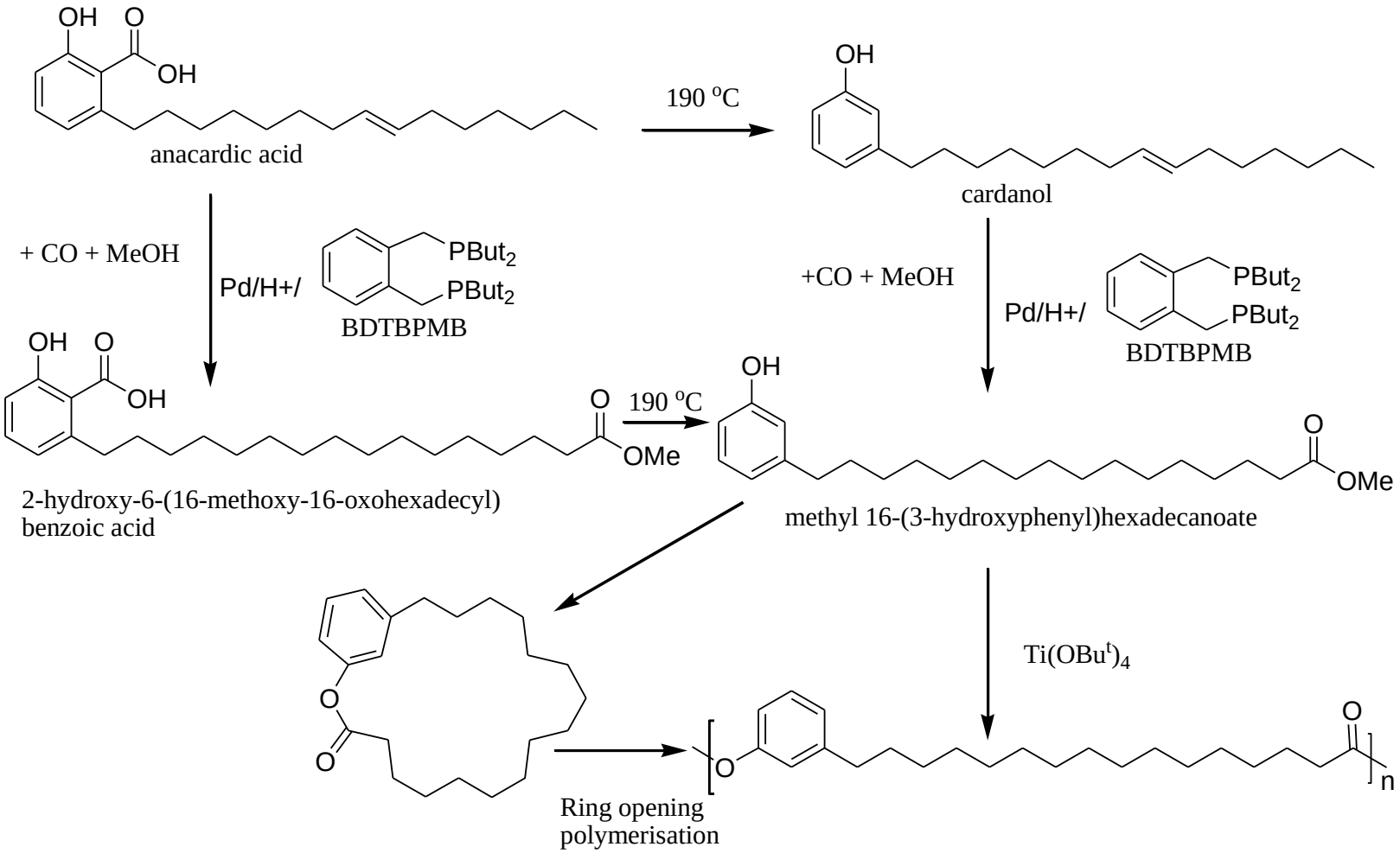
Carboxylic acids and esters can be produced from carbonylation of alkenes in the presence of H_2O or ROH



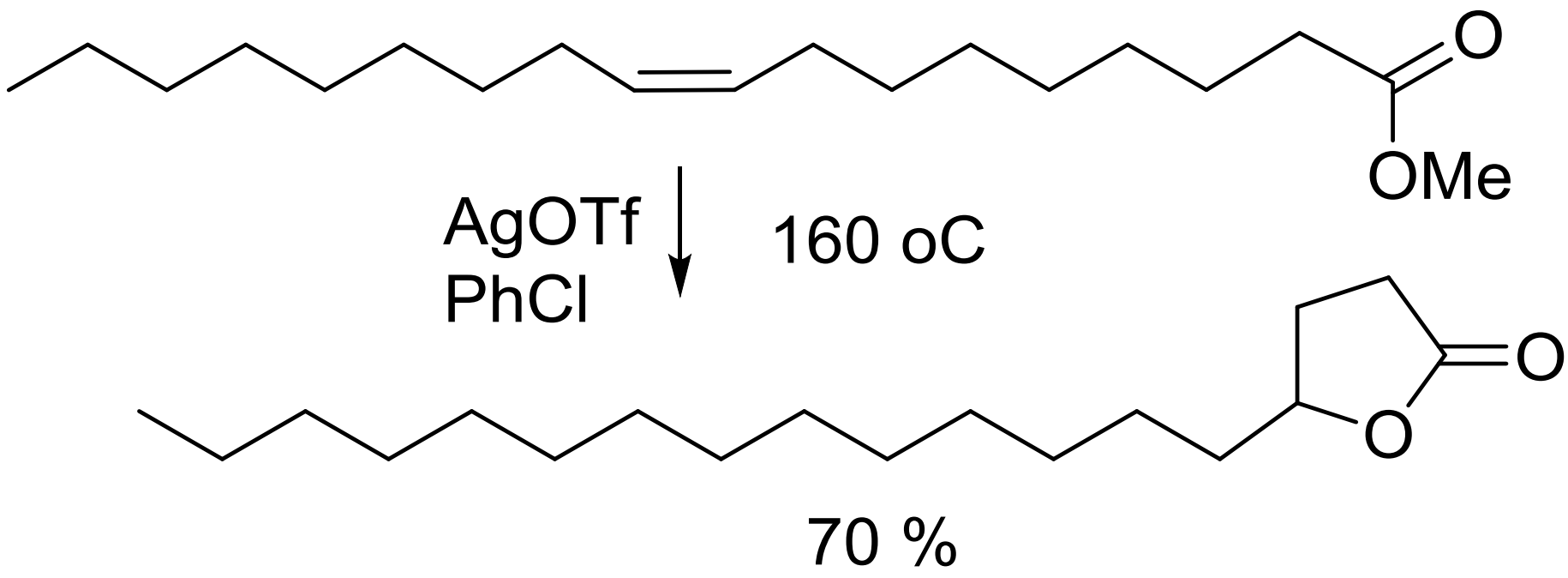
C. Jimenez-Rodriguez, G. R. Eastham and D. J. Cole-Hamilton, *Inorg. Chem. Commun.*, **2005,** *8*, 878.

Monomers for fire retardant polymers

One potential way to manufacture halogen free fire-retardant polymers is to incorporate significant amounts of aromatic groups into the polymer backbone



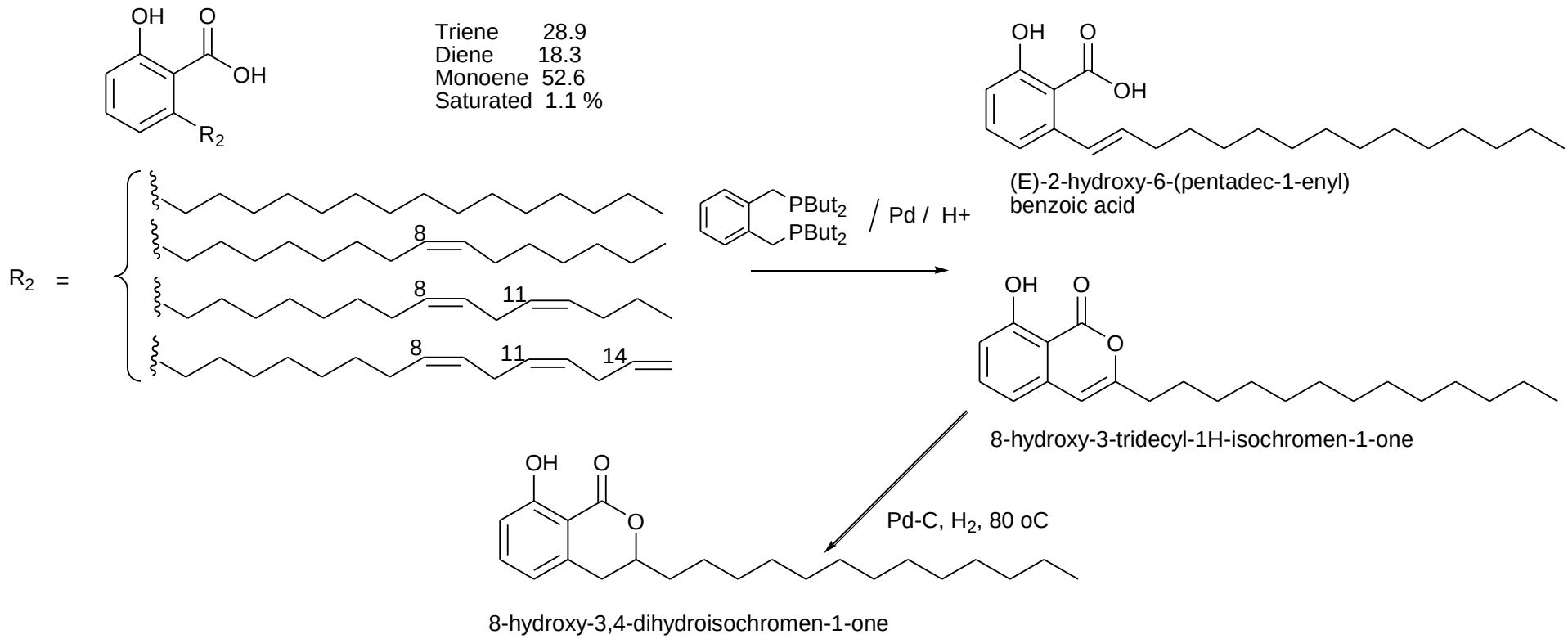
❖Based on Goossen *et al*. on trapping a double bond of oleic acid in lactone under silver triflate as an isomerization catalyst, we reasoned that this type of trapping might also be possible for anacardic acid.



Goossen, L. J., et al. Silver triflate-catalysed synthesis of gamma-lactones from fatty acids, Green Chem. 2010, 12, 197-200.

Unsaturated and saturated benzolactones from anacardic acid

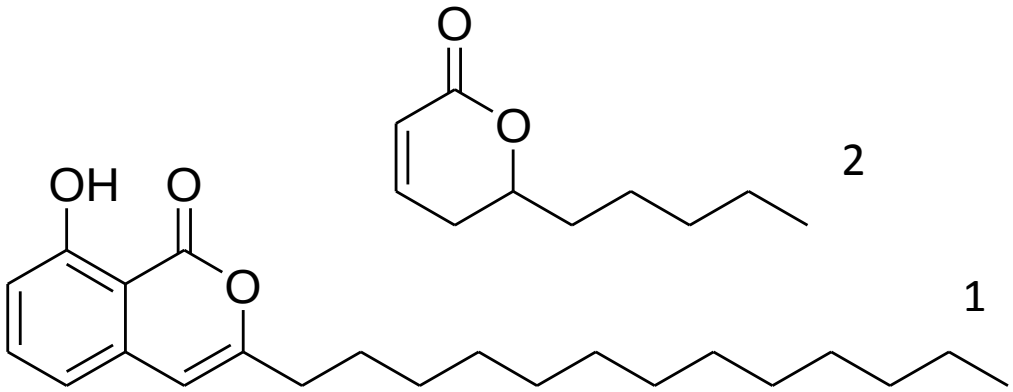
One of the product isolated during the isomerisation reaction of anacardic acid is the unsaturated benzolactone; 8-hydroxy-3-tridecyl-1H-isochromen-one



Mgaya et al. *Eur. J. Lip. Sci. Technol.*(2014**)** *Accepted*

8-hydroxy-3-tridecyl-1H-isochromen-one; medicinal value?

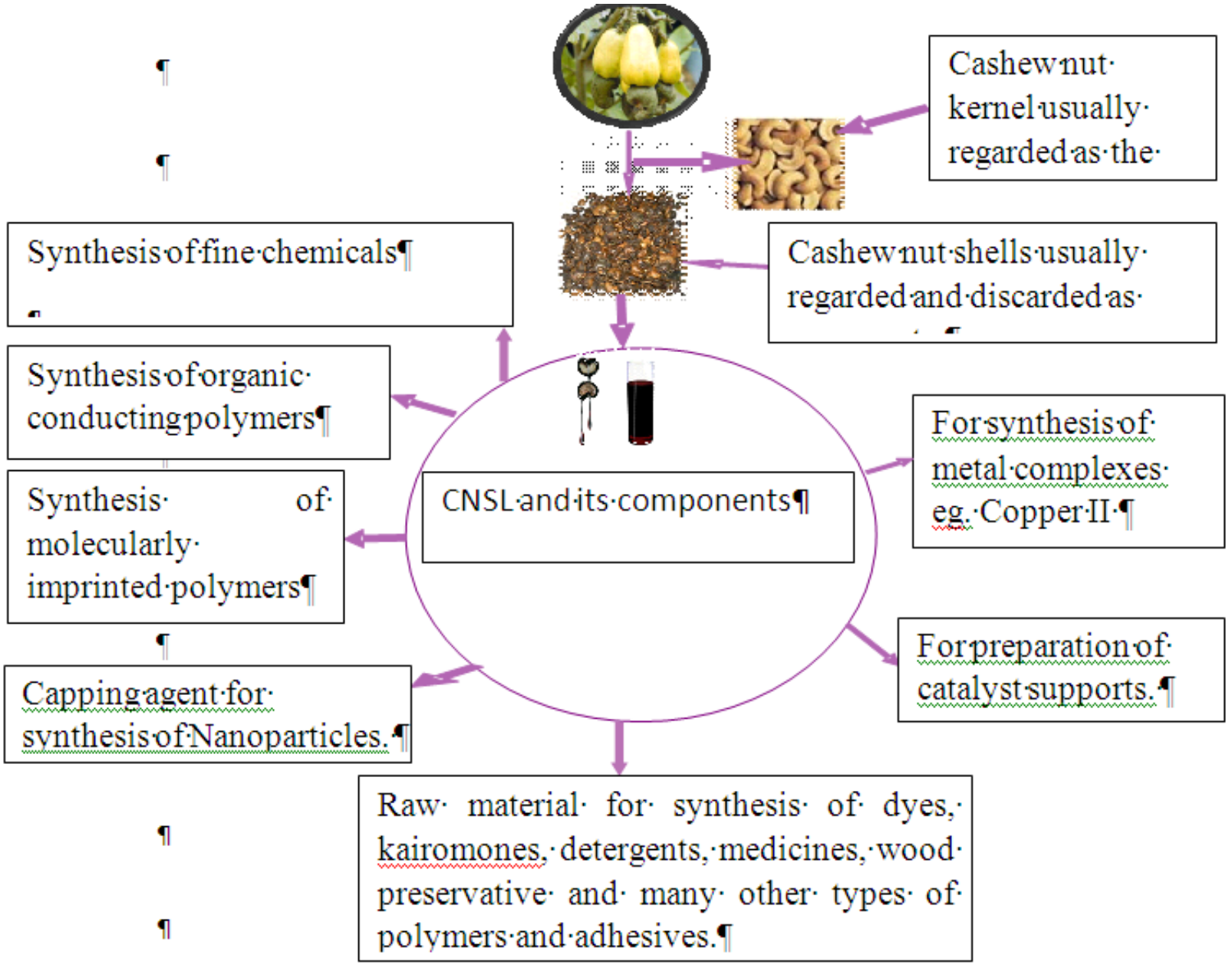
❖Unsaturated lactones often found in natural products and have medicinal value such as massoia lactone which is a constituent of native medicines.
❖Massoia lactone and analogues are known to possess good antimicrobial activity against Staphylococcus aureus, B. subtilis and E. coli.
❖They have also been reported as potential anticancer and anti-inflammatory agents.



Structural similarities between 8-hydroxy-3-tridecyl-1H-isochromen-1-one (1) and massoia lactone (2)

Barros, et al., Synthesis and evaluation of (-)-Massoialactone and analogues as potential anticancer and anti-inflammatory agents, *Eur. J. Med. Chem.* 2014, *76*, 291-300

GENERALLY, CNS ARE TREASURE-OPPORTUNITIES



Lin et al, *Biofuels, Bioproducts and Biorefining (2014)*, DOI: 10.1002/bbb.1506

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Dr. Quintino Mgani

Dr. A.Y. Makame

Dr. F. Hamad

Dr. G. Kinunda

Mr. Juma Mmongoyo

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NRF-COSTECH

THANK YOU ALL FOR LISTENING