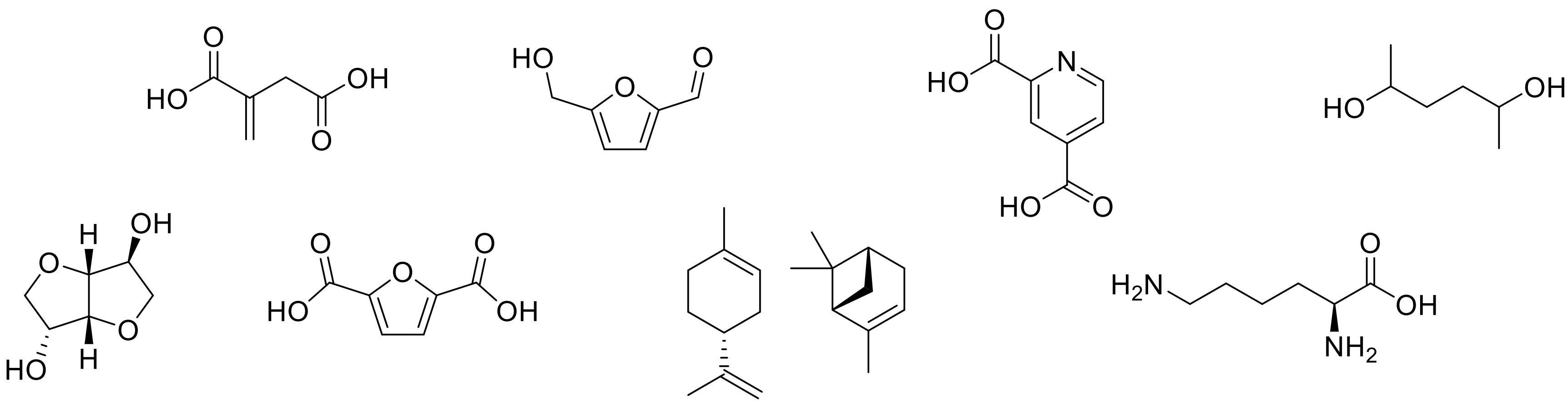
Keeping it Green in Personal Care

Platform Molecules to Polymers for Personal Care

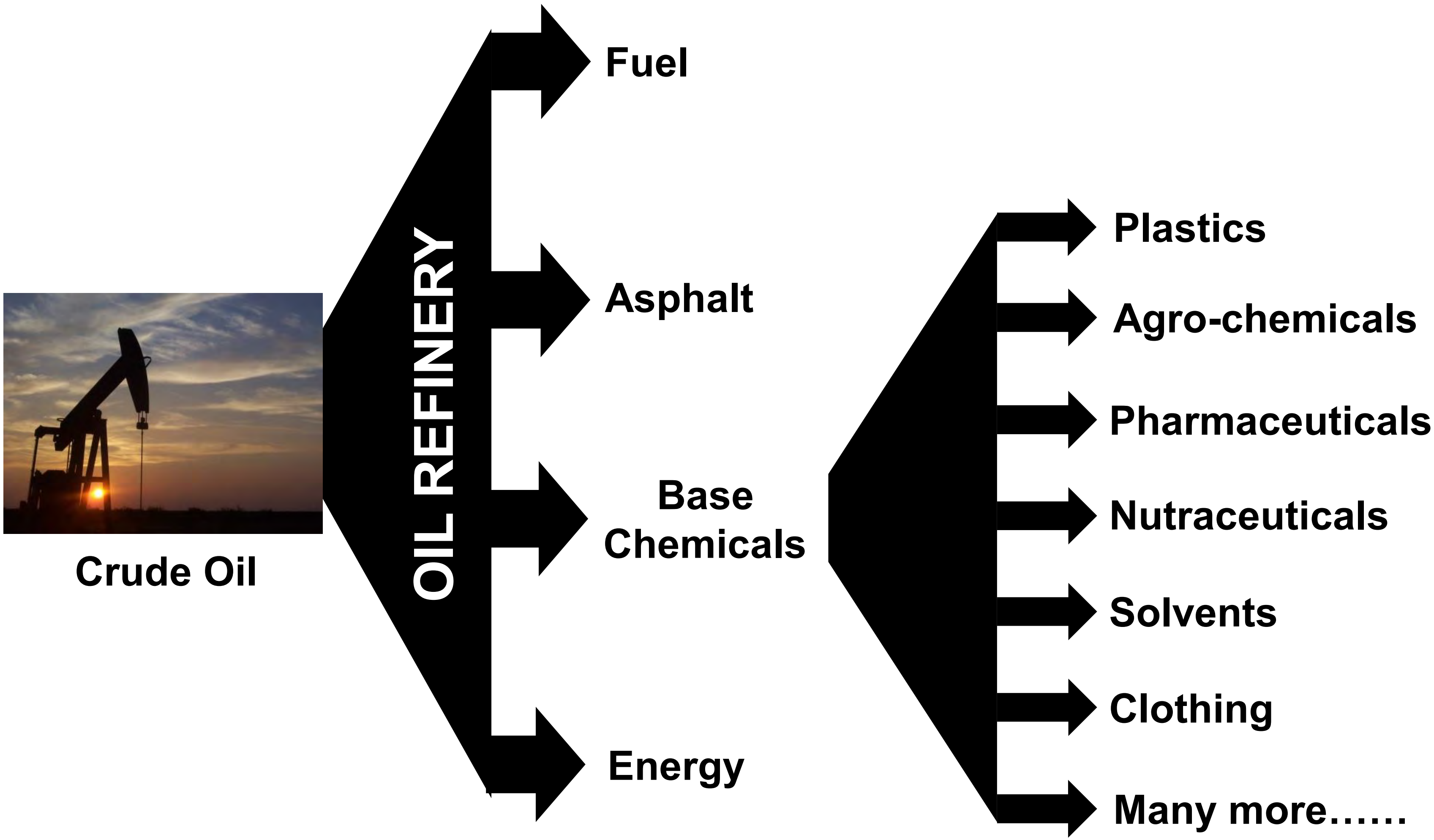


Dr Thomas Farmer

Green Chemistry Centre of Excellence, University of York

2nd March 2021

Oil Refining…



“>90% of organic chemicals are derived from non-renewable fossil resources.”

K. Kümmerer and M. Hempel, *Green and Sustainable Pharmacy*, **2010**

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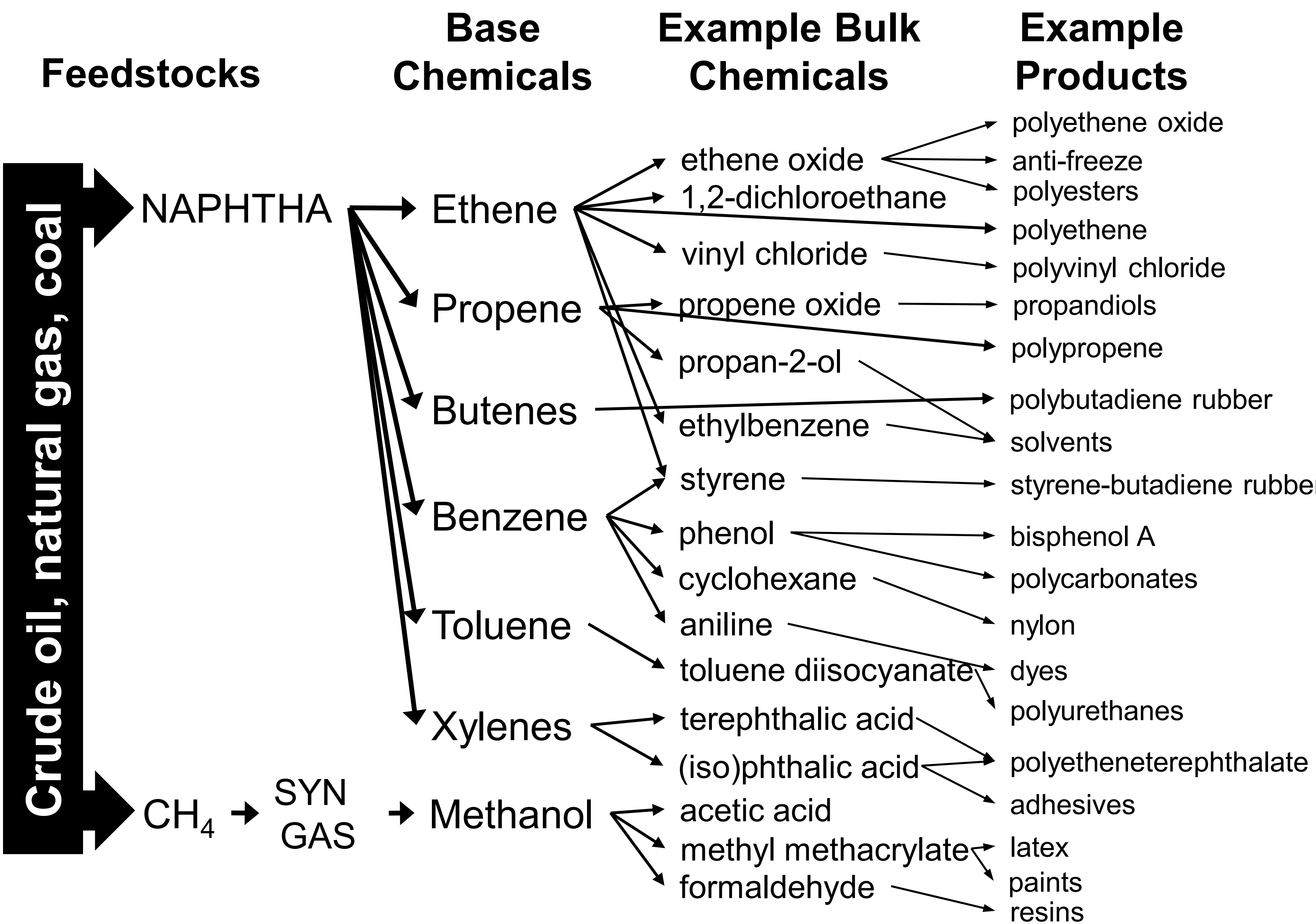
Current: Fossil-derived Base Chemicals

University of York



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Base Chemical: Scale of Production

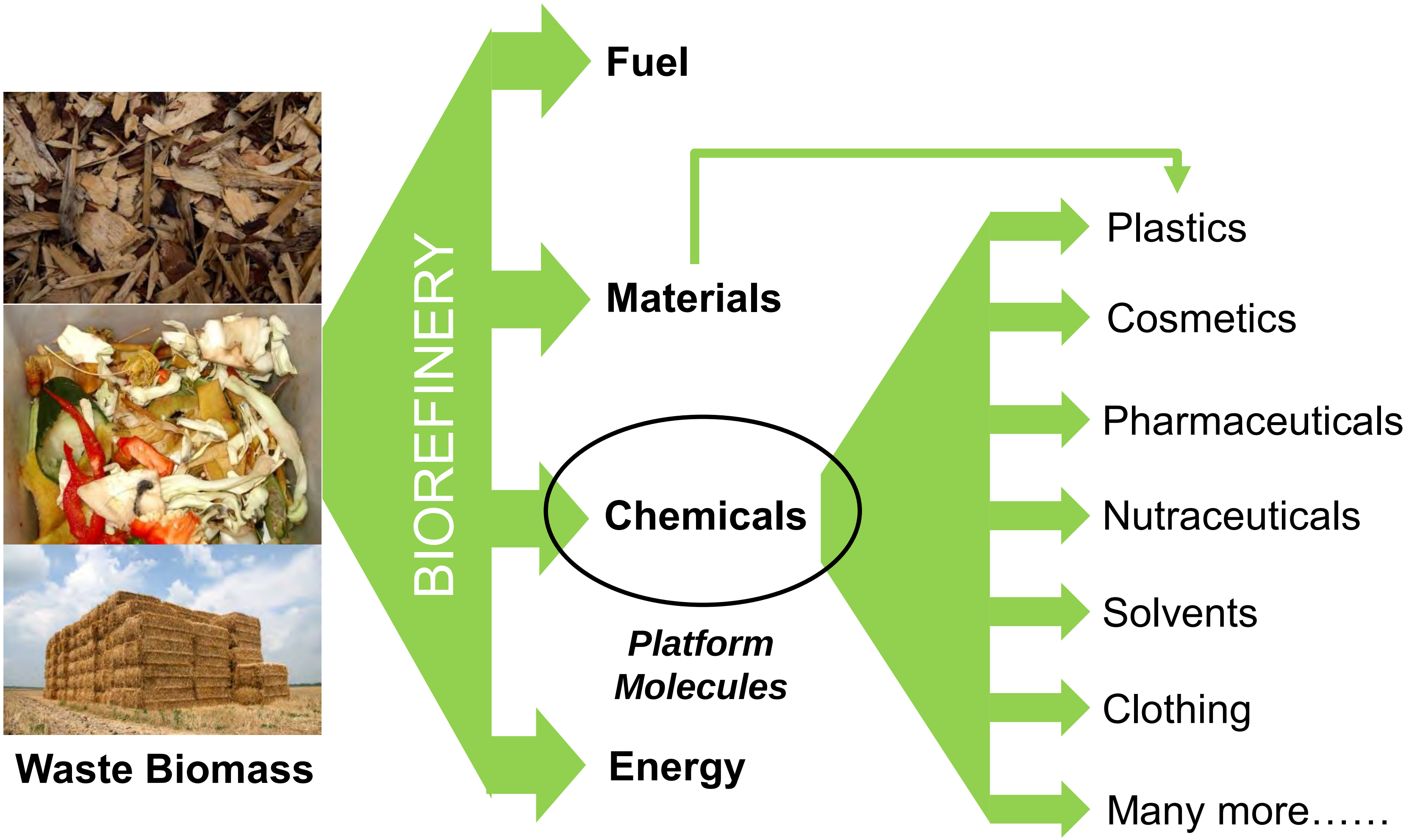
Data for 2010

Base Chemical	Predominant Feedstock	Annual production from fossil sources (tonnes annum^{-1})
ethene	oil, gas	123,300,000
propene	oil, gas	74,900,000
butadiene	oil, gas	10,200,000
benzene	oil	40,200,000
toluene	oil	19,800,000
xylenes (o-, m-, p-)	oil	42,500,000
methanol	syngas	49,100,000
TOTAL		360,030,000

~3,589,600,000 tonnes of crude oil produced in same year

Data from: Davis, S., *Chemical Economics Handbook Product Review: Petrochemical Industry Overview*, SRI Consulting, **2011**

Biorefining…



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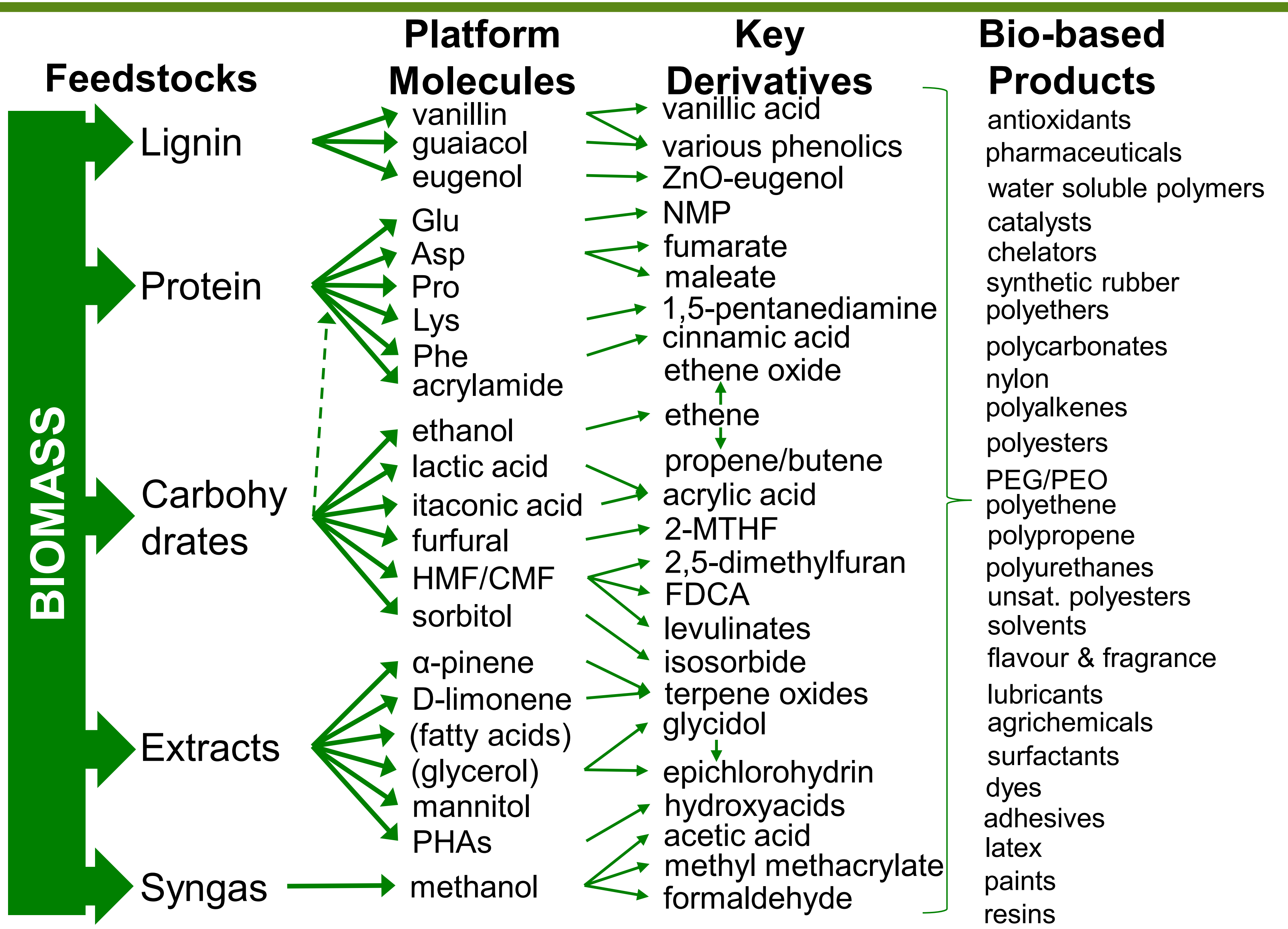
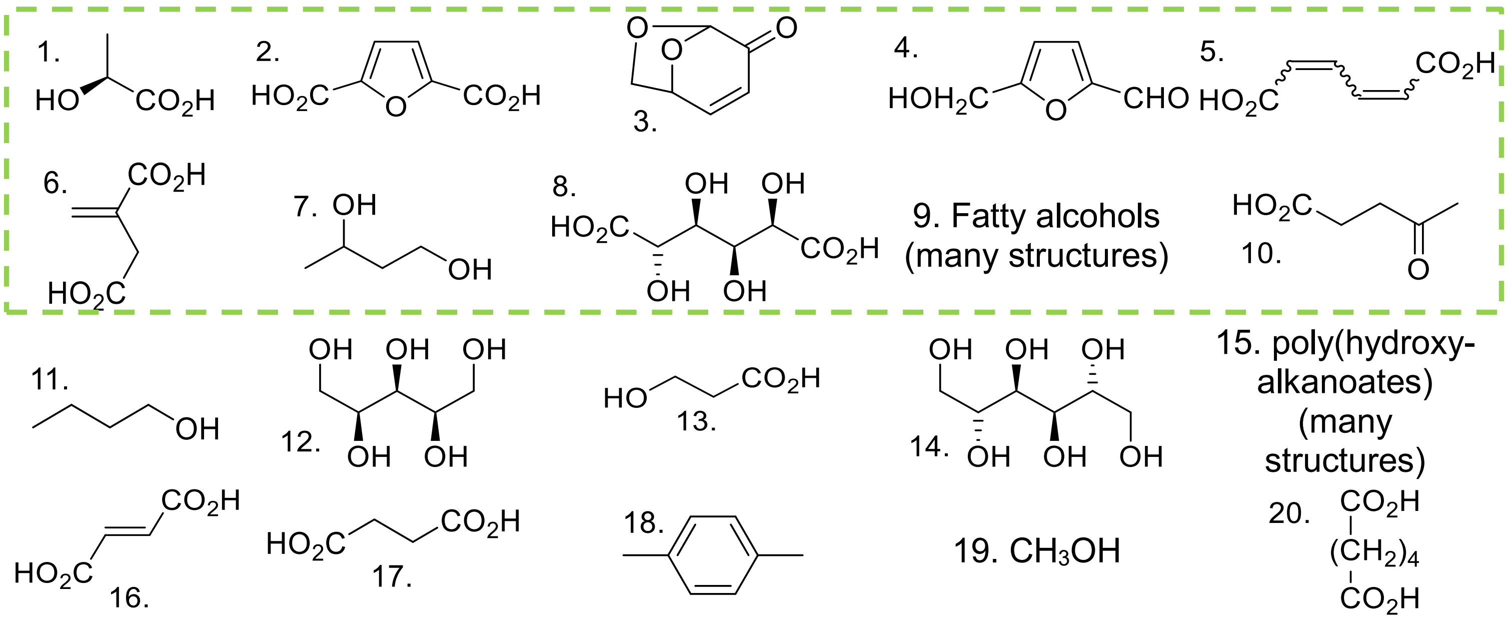
Platform Molecules replace Base Chemicals



LBNet's UKBioChem10

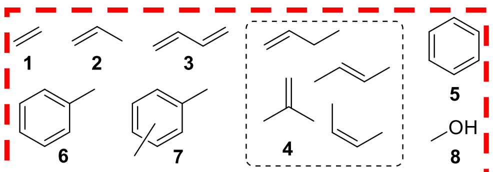
UKBioChem10 is a list of the UK's the **most promising** bio-derived building-block chemicals (platform molecules). The list contains both:

1) molecules the UK **already has a strong foothold** in
2) molecules which are **envisaged to become** very significant to industry in the future and therefore require further support in their development.



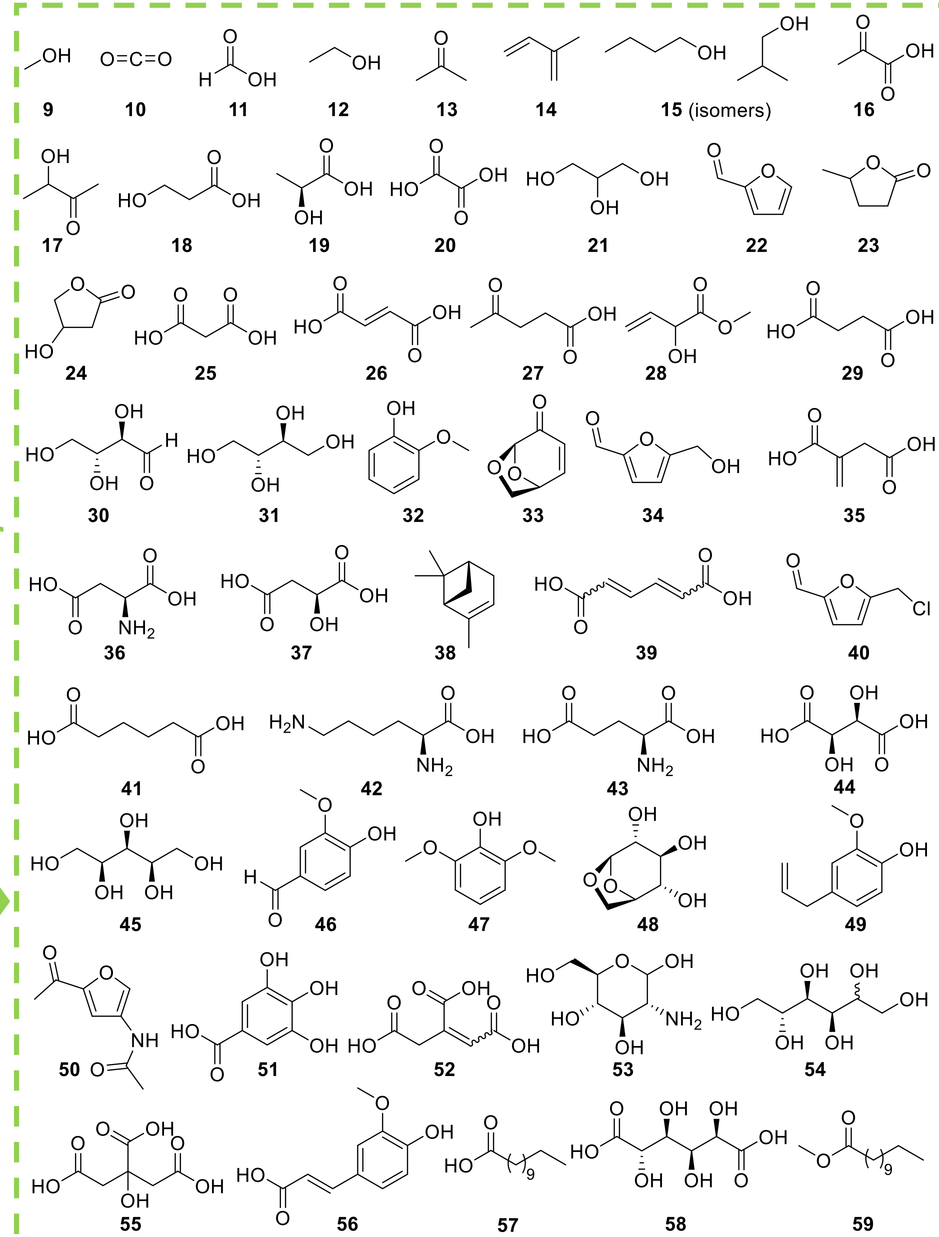
Much more info: **www.ukbiochem10.co.uk**

BioLogicTool: Plotting Heteroatom Content



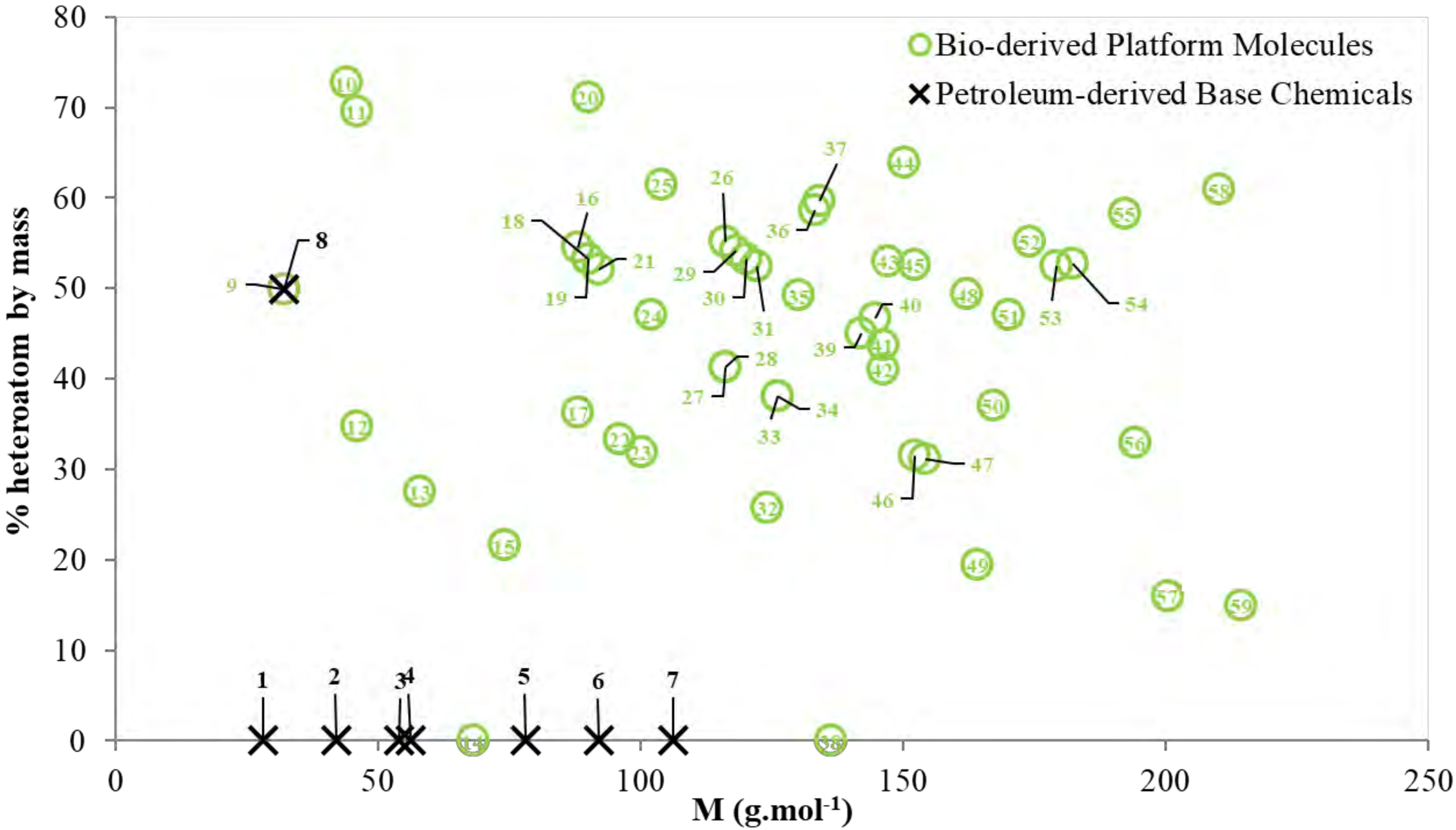
Base chemicals

Bio-based platform molecules



[1] *BioLogicTool:* A Simple Visual Tool for Assisting in the Logical Selection of Pathways from Biomass to Products Y. Lie, P. Ortiz, R. Vendamme, K. Vanbroekhoven & T. J. Farmer, *Ind. Eng. Chem. Res.* **2019,** *58*, 15945–15957

BioLogicTool: Plotting Heteroatom Content



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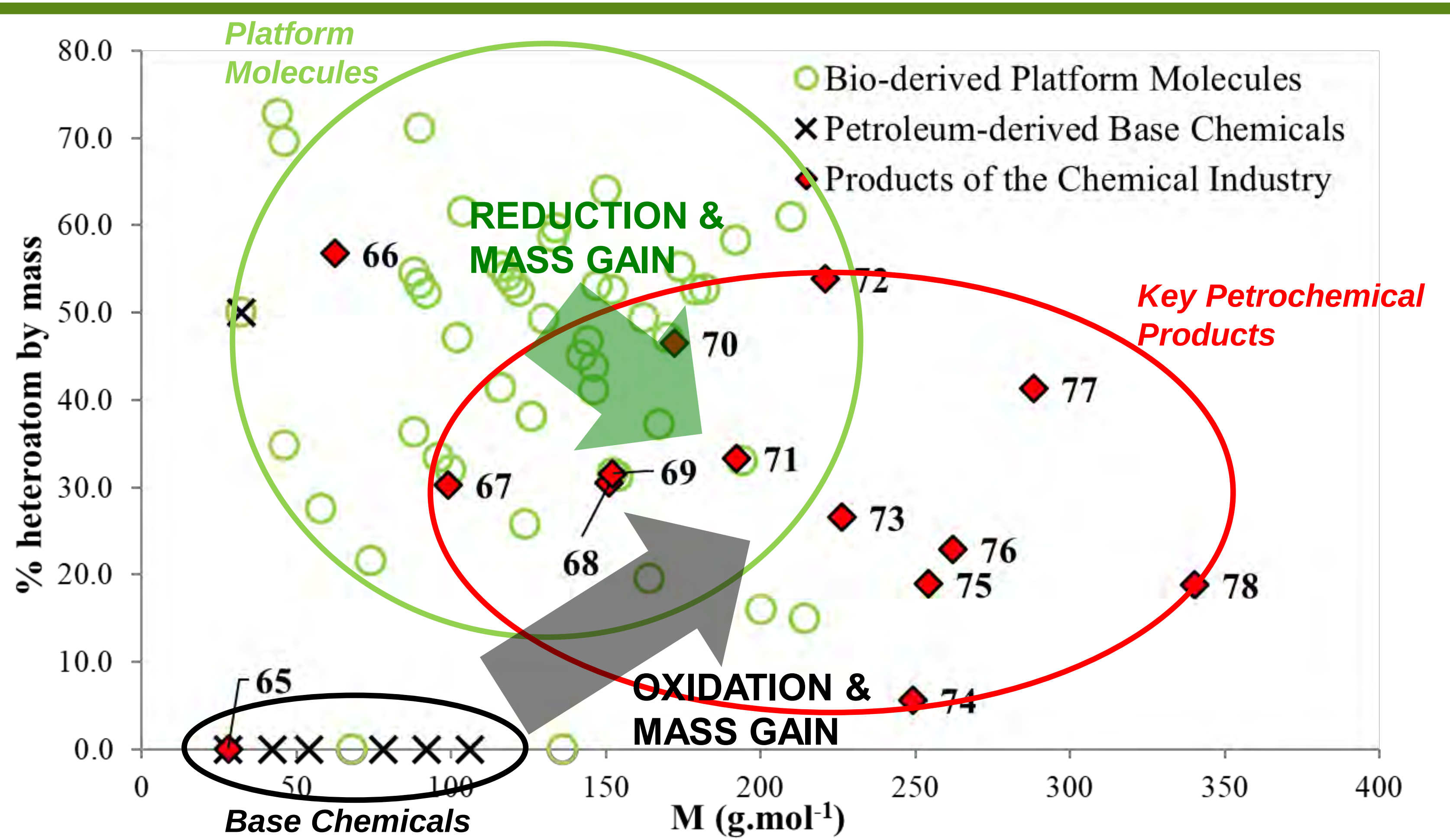

poly(ethene) **65**; poly(vinyl chloride) **66**; N-methyl-2-pyrolidone (solvent) **67**; N-acetyl-p-aminophenol (paracetamol) **68**; methyl paraben (preservative) **69**; *para*-toluenesulfonic acid (catalyst) **70**; poly(ethylene terephthalate) (polyester) **71**; 2,4-dichlorophenoxyethanoic acid (herbicide) **72**; nylon-6,6 (polyamide) **73**; 4-cyano-4'-penylbiphenyl (liquid crystal) **74**; poly(bisphenol-A) carbonate (polycarbonate) **75**; 2,2'-Bis(2,3-dihydro-3-oxoindolyliden) (indigo blue dye) **76**; sodium dodecylsulfate (surfactant) **77**; bisphenol A diglycidyl ether (resin precursor) **78**. Polymers: M = CRU mass

[1] *BioLogicTool:* A Simple Visual Tool for Assisting in the Logical Selection of Pathways from Biomass to Products
Y. Lie, P. Ortiz, R. Vendamme, K. Vanbroekhoven & T. J. Farmer, *Ind. Eng. Chem. Res.*, **2019,** *58*, 15945–15957

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…ideal for Personal Care:

- Many di/tri acids and diol/polyol → **Make polymers!**
- Many of these potential monomers have other functional groups too
- Polymers in personal care often seek an "effect", i.e. interactions between other compounds/surfaces:
    - Structuring of formulations (viscosity modifiers etc.)
    - Bringing differing polarities together
    - Aiding formulation (again mixed polarities)
    - Delivery of actives in the right place at the right time
- Also have concerns above end-of-life (what happens after use)

The high functionality and "tunability" of bio-based polymers can address all of these…

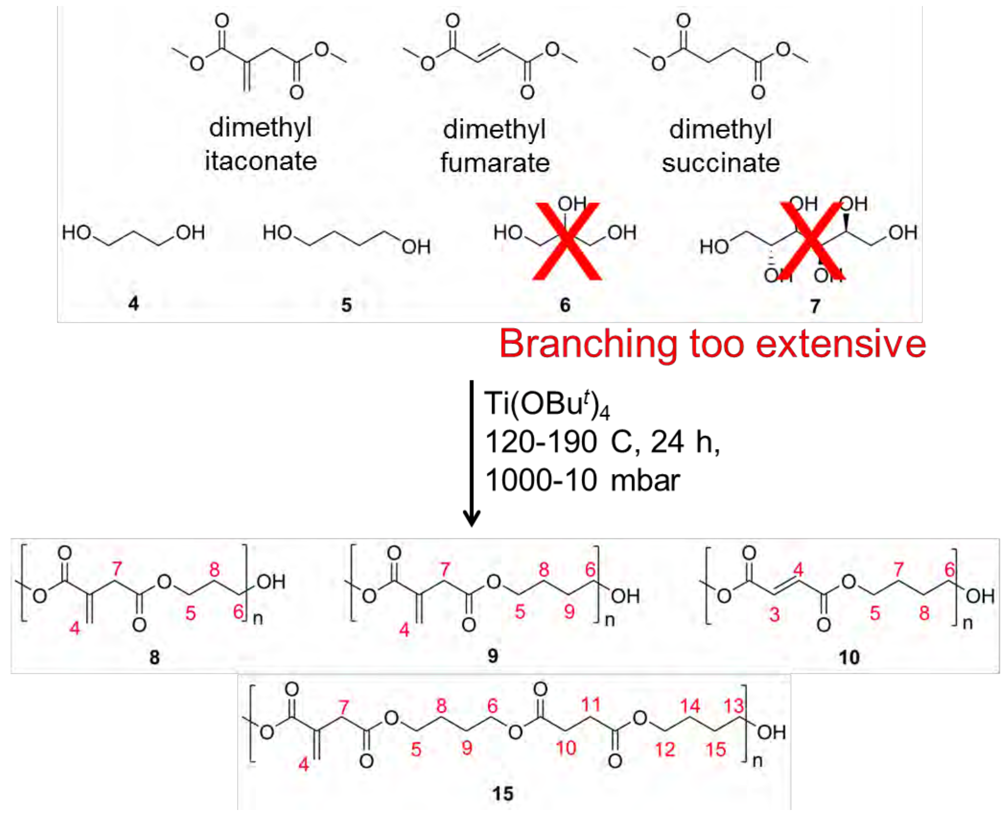
Unsaturated Polyester Resins

- Polytransesterification of maleate (MA) or itaconate (IA) diesters and various diols has been used to produce UPRs

- IA can be used as a replacement for the petrochemical derived MA:

- Since the 1960's IA has been produced industrially from the fungal fermentation of glucose (already bio-based!)

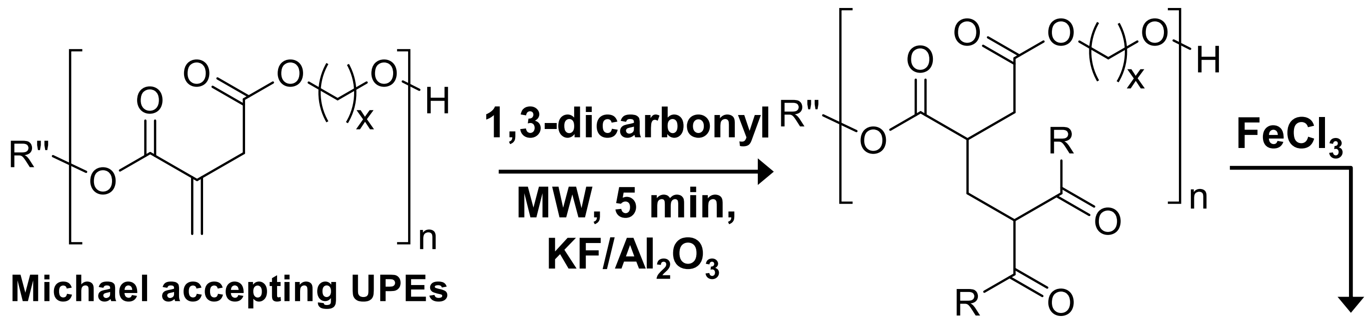
- IA can be co-polymerized with other bio-based monomers to tailor the final properties of the resin/coating

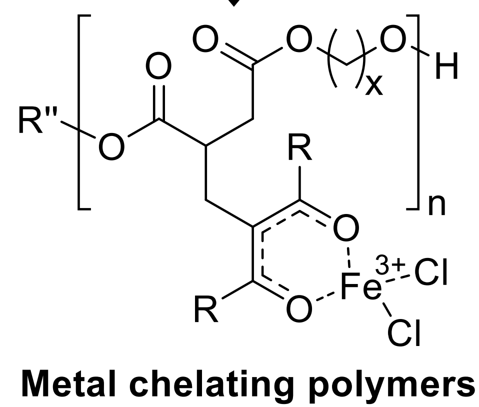


T. J. Farmer *et al.*, *Int. J. Mol. Sci.*, **2015**, 16, 14912-14932

Michael Additions to Bio-derived Unsaturated Polyesters

- Various pendants can be added to itaconate UPRs, here we added chelating dicarbonyls:

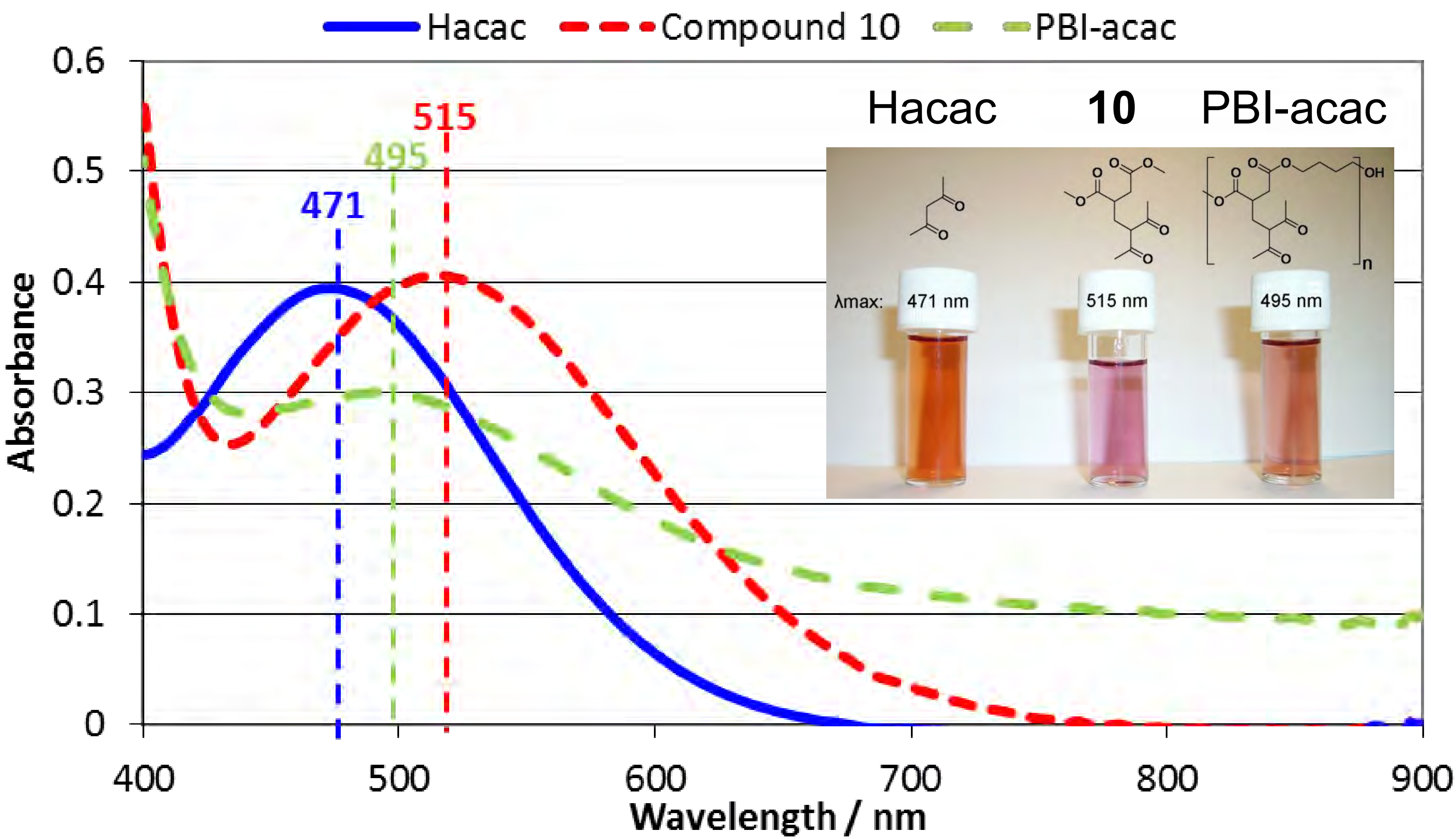




✓ Bio-derived monomers
✓ Rapid conditions for addition
✓ Solventless
✓ Heterogeneous catalyst
✓ Controllable level of addition

T. J. Farmer *et al.*, *Polymer Chemistry*, **2016**, 7, 1650-1658

Chelating Ability of Pendant Remains



400-900 nm UV-Vis absorbance spectra for Fe(III) complexes with Hacac, compound **10** and PBI-acac in ethanol. Concentration of diketone ≈ 2 mmol dm^{-3}, λ_{max} above 450 nm highlighted for each complex

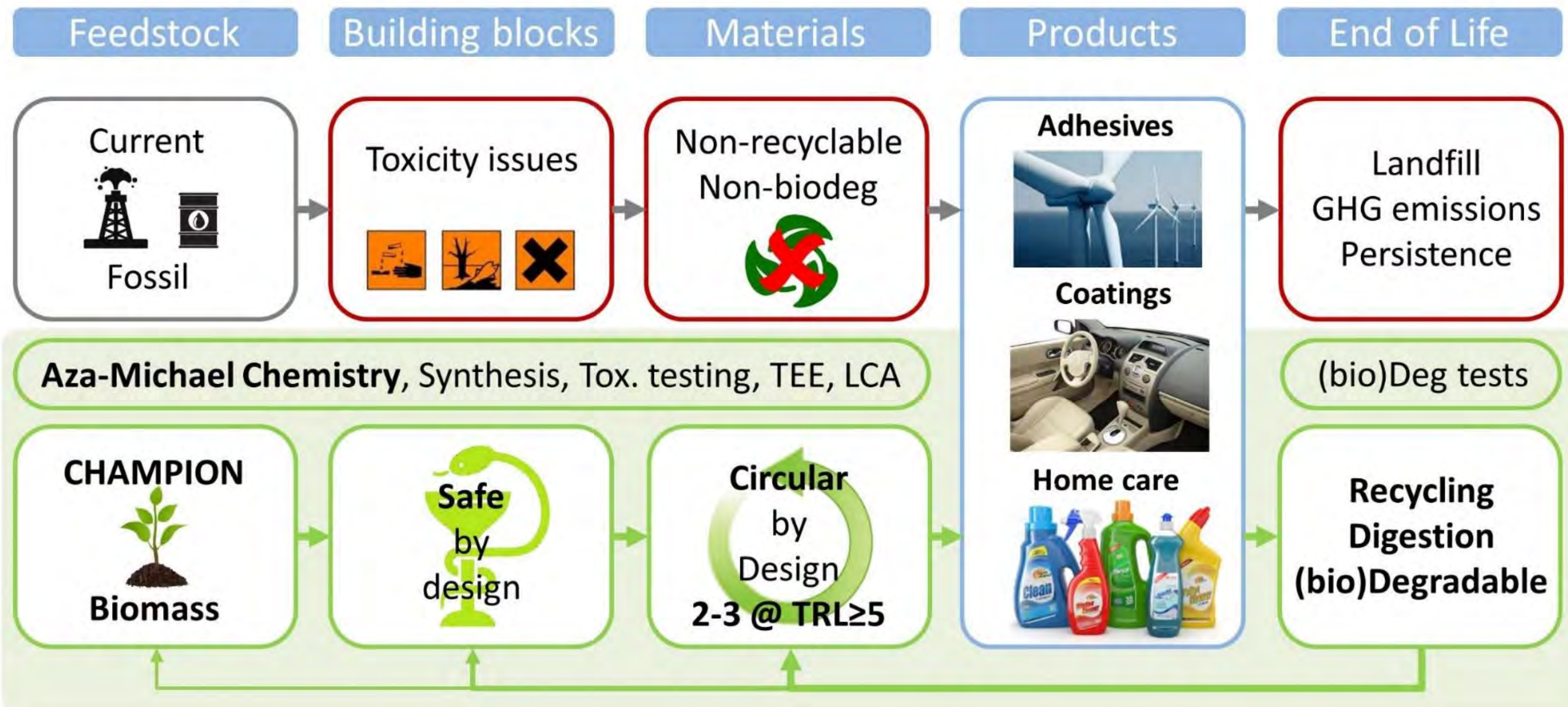
T. J. Farmer *et al.*, *Polymer Chemistry*, **2016**, 7, 1650-1658 www.champion-project.eu

Introducing the CHAMPION Project

Circular High-performance Aza-Michael Polymers as Innovative materials Originating from Nature

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement No 887398. The JU receives support from the European Union's Horizon 2020 research and innovation programme and the Bio Based Industries Consortium.

The CHAMPION Project (June 2020-November 2023):



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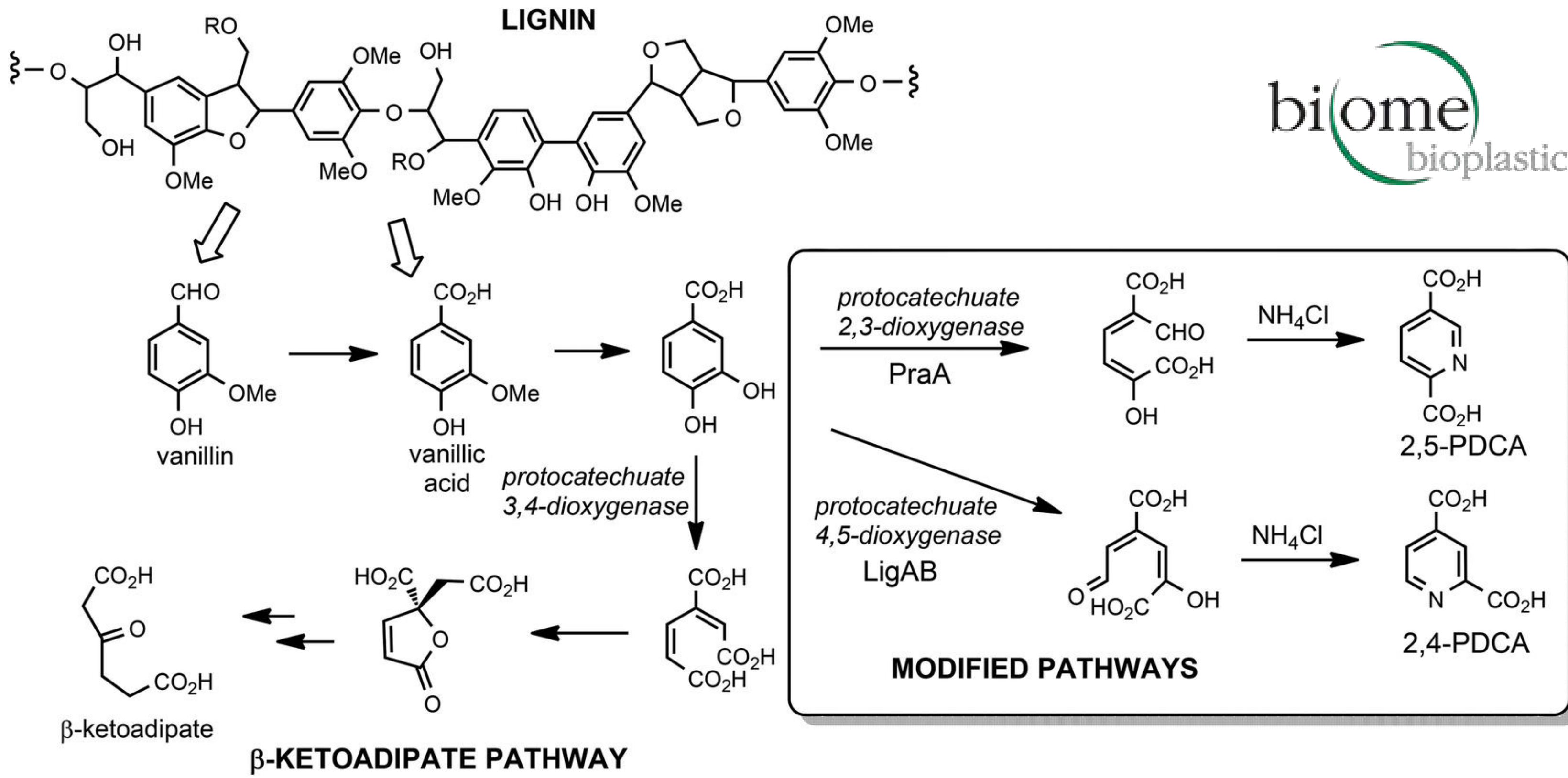
SCOTT BADER Making a positive difference
Unilever
stahl
VTT
PDC
SQ sustainable quality | consult
ORINEO original renewables
circa
BDS
OWS
CHAMPION circular bio-based polymers

Lignin-derived Pyridine Diacids

Rhodococcus jostii RHA1 aromatic degradation pathway re-routed by Bugg *et al.* showed the potential for converting lignin to pyridine diacids:



biome bioplastics

PDCA yields of 80–125 mg L^{-1} when grown on media containing 1% wheat straw lignocellulose

[1] Z, Mycroft, M. Gomis, P. Mines, P. Law, T.D.H. Bugg, *Green Chem*., **2015**, *17*, 4974-4979

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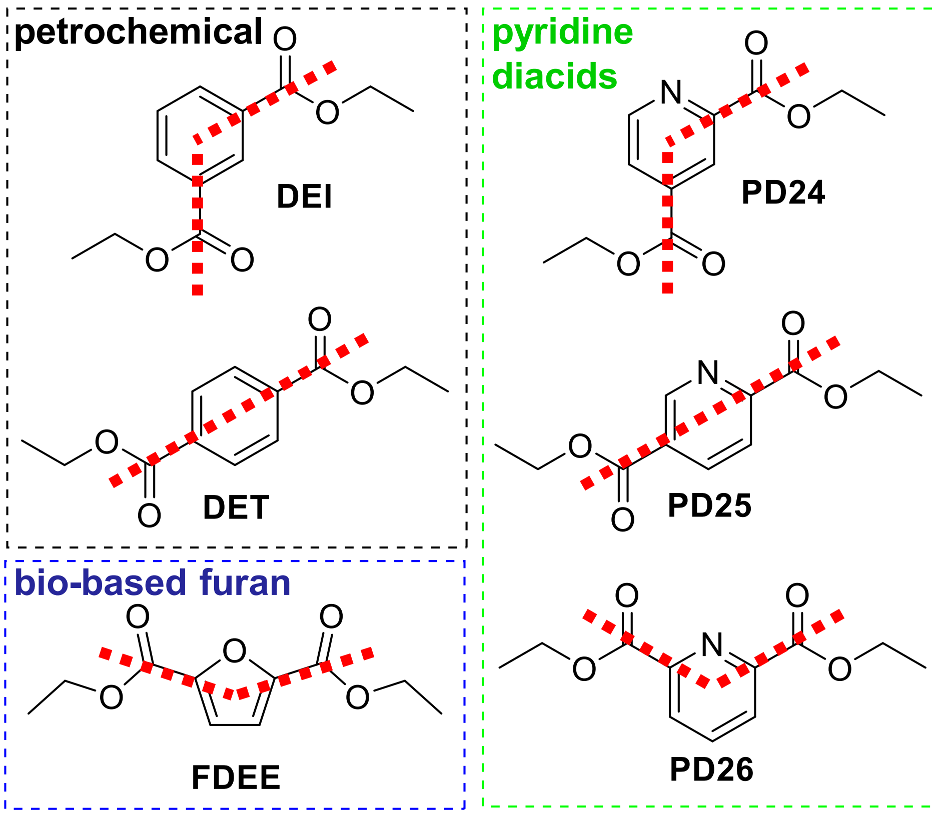
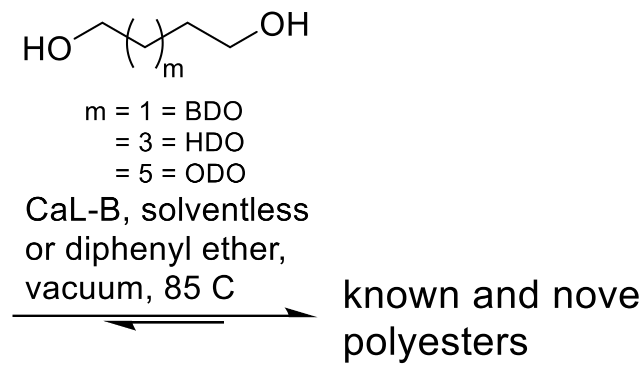
Pyridine Polyesters via Enzymatic Polycondensation

- A range of pyridine containing polyesters were prepared using enzymatic polycondensation and compared to petrochemical and furan equivalents:



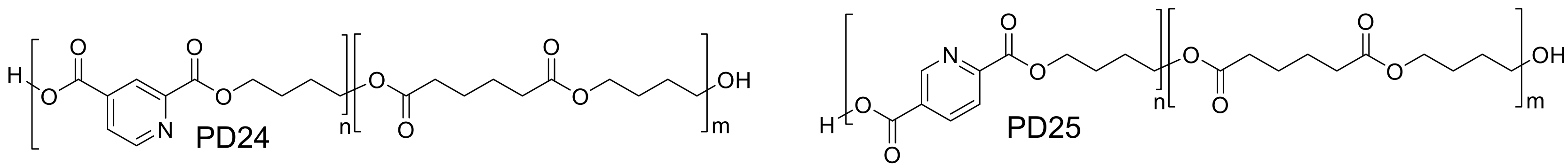


DEI and PD24 polymers were almost entirely amorphous. The others all showed clear melts
Pyridine gave higher T_gs and T_ms

A. Pellis et al. **2019**, *Nat. Commun.*, 10, 1762

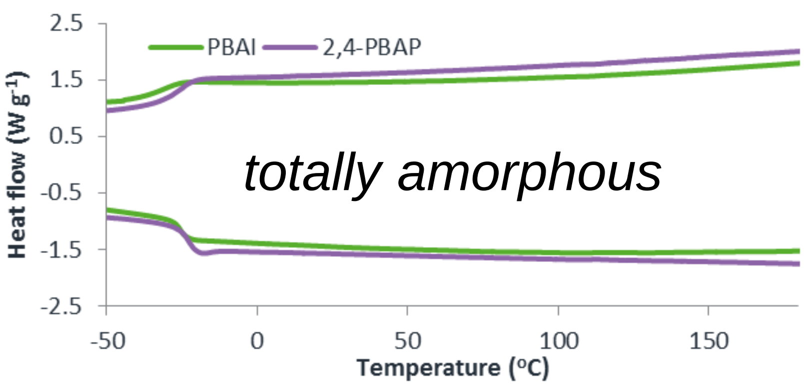
Pyridine Polyesters via Chemocatalytic Polycondensation

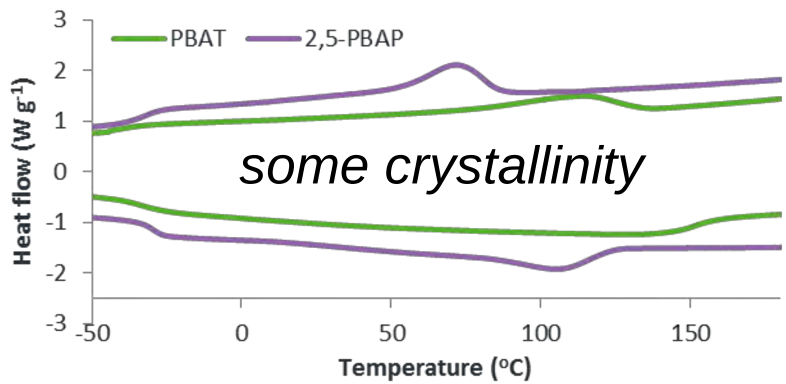
- Chemocatalysis investigated to allow for scale-up
- Adiapte co-polymer was needed to allow for increased chain-length, but this better matches PBAT and PBAF that we will replace



Polymer	Method	Ar	Bond angle	$\overline{Mn}$ (g mol^{-1})	$\overline{Mw}$ (g mol^{-1})	Đ	T_g (°C)	T_c (°C)	T_m (°C)	Tensile strength (MPa)
2,4-PBAP	1	PD24	120°	3,850	6,700	1.74	-31.0	-	-	Film too weak
2,5-PBAP	1	PD25	180°	4,400	7,300	1.65	-41.0	76.2	97.4	1.76
PBAI	2	DEI	120°	17,600	26,950	1.53	-28.3	-	-	1.79
PBAT	2	DET	180°	9,600*	15,450	1.60	-37.5	115.1	~130	5.63

Insoluble polymer





J. Comerford et al. **in preparation**

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Optimised polymerization and enzymatic hydrolysis

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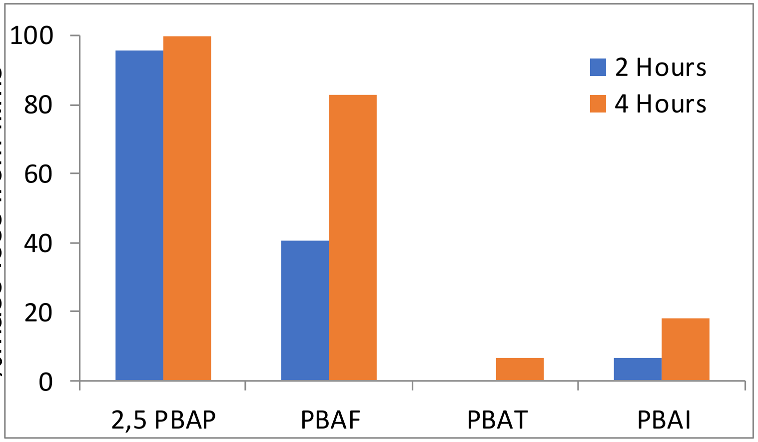
Method optimisation (reaction time, time of adipate addition, catalyst, excess diol etc.) gave much better polymers:

Increased reaction times, all adipate co-polymers

Polymer	Ar	Ar bond angle	$\overline{Mn}$ (g mol^{-1})	$\overline{Mw}$ (g mol^{-1})	Đ	T_g (°C)	T_c (°C)	T_m (°C)	Tensile strength (MPa)
2,4-PBAP	PD24	120°	**18,000**	28,000	1.56	-23.0	-	-	Weak film
2,5-PBAP	PD25	180°	**15,900**	25,100	1.58	-29.7	74.3	105.8	4.72
PBAI	DEI	120°	17,600	26,950	1.53	-28.3	-	-	1.79
PBAT	DET	180°	9,600*	15,450	1.60	-37.5	115.1	-	5.63
PBAF	FDEE	>120°	10,300	17,950	1.74	-34.4	62.5	97.4	2.67

Pyridines enhance enzymatic hydrolysis:



- Polymers films cut into precise segments
- Degradation performed in buffer
- *Humicola insolens cutinase* (*HiC*), a fungal enzyme previously reported to effectively degrade a wide array of aliphatic and aromatic polyesters

J. Comerford et al. **in preparation**

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Wholly Bio-based Self-foaming Non-isocyanate PHU

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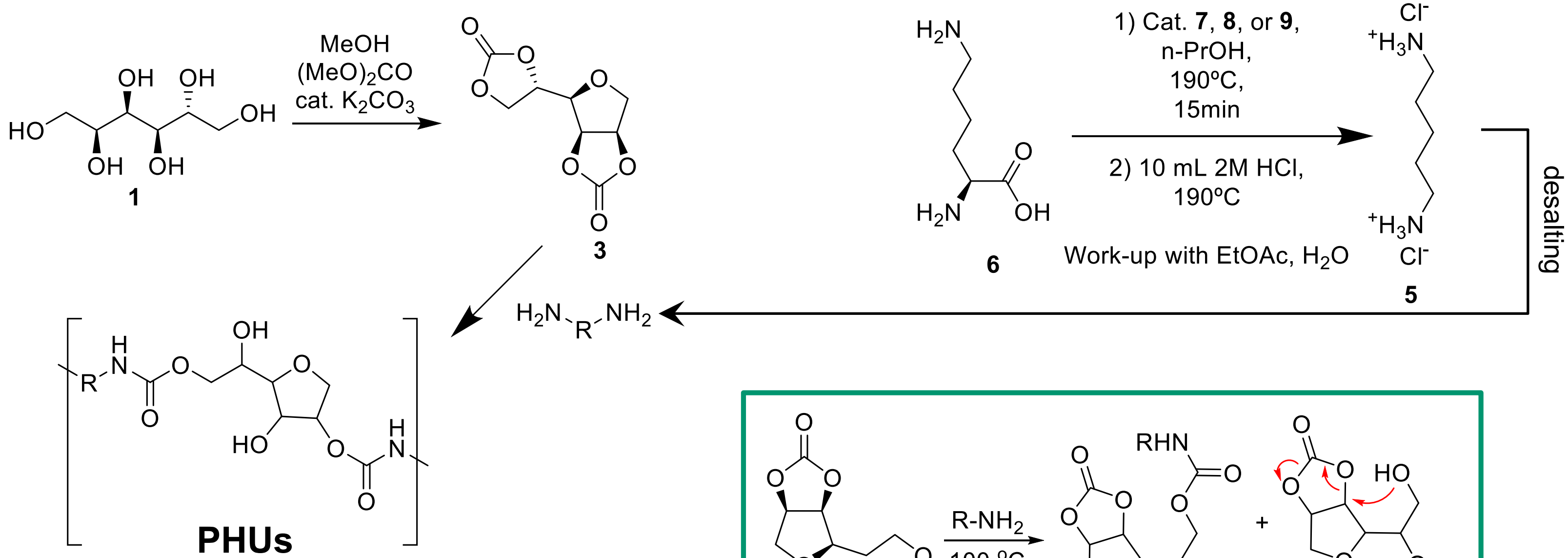
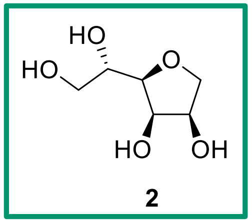
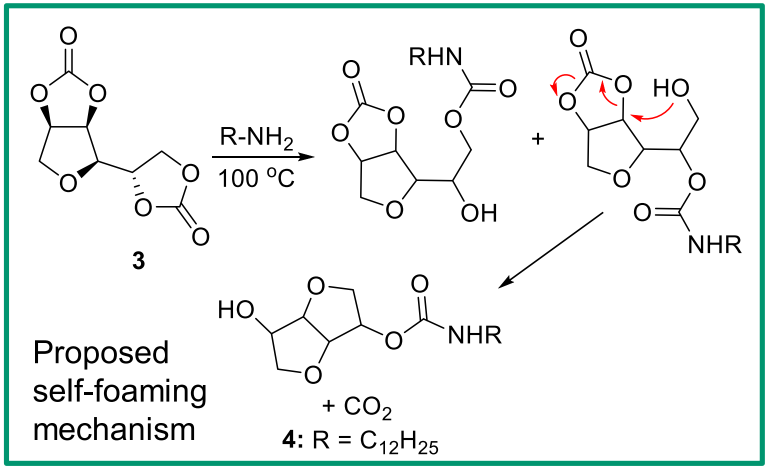
We have recently shown that 100% bio-based polyhydroxy urethanes (PHUs) can be made from the reaction of a sugar derived bis-cyclic carbonate and amino-acids derived diamine. Of note is that the PHU self-foams when the reaction is carried out in the absence of a solvent.



Sorbitan **2** not needed, can go direct from sorbitol

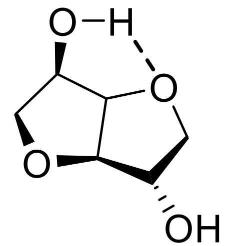




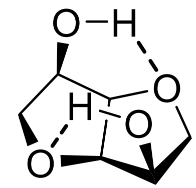
I. Ingram, M. North, T. Farmer, Y. Lie and J. Clark, *Euro. J. Org. Chem.*, **2018**, 4265–4271

The Value of Chirality

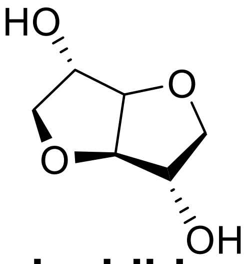
Crude oil has no chirality, biomass has lots – USE IT!



isosorbide



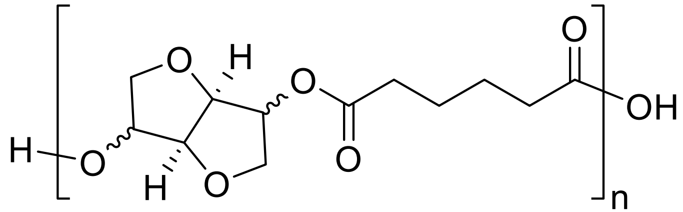
isomannide



isoidide

Feedstock:	glucose	mannose, mannitol	idose, iditol
Availability:	very abundant	fairly abundant	very rare
Designation	exo-endo	endo-endo	exo-exo
-OH reactivity	1 high, 1 low	both low	both high
Adipate polyester Tg	21 °C	28 °C	45 °C

Adipate polyester =



F.Fenouillot et al., *Progress in Polymer Science,* 35, **2010**, 578–622

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Hydrophobes?

Food (Supply Chain) Waste: promising source of hydrophobes

Use high O-content constituents for large volume applications and low O-content parts for low volume / high value products.


Waste Biomass (inc. food waste)

- **glucose, fructose**
- **cellulose, hemicellulose**
- mannitol
- **chitin**
- **protein**
- **lignin**
- anacardic acid
- triglycerides
- terpenes

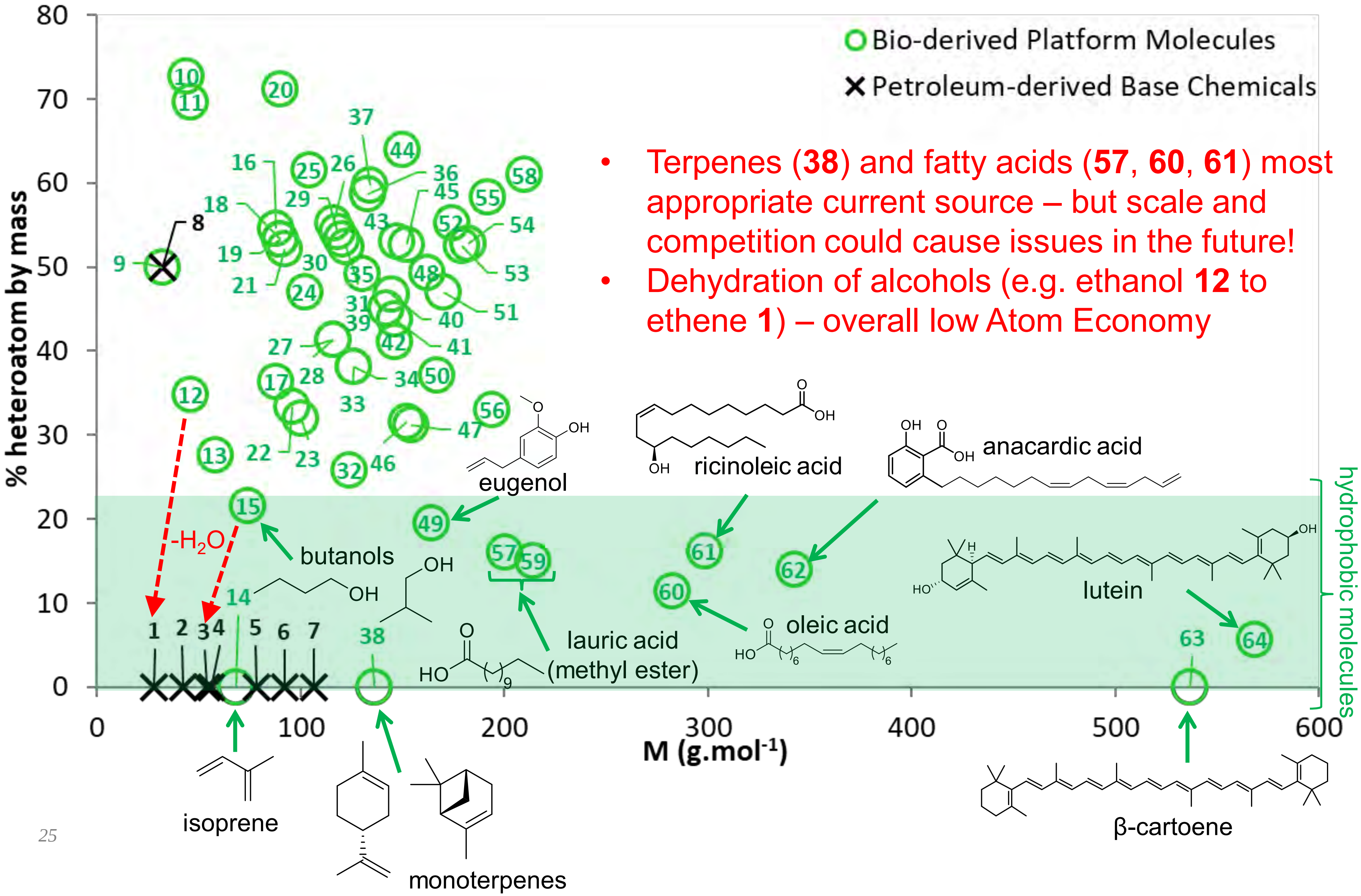
High O-content

Low O-content

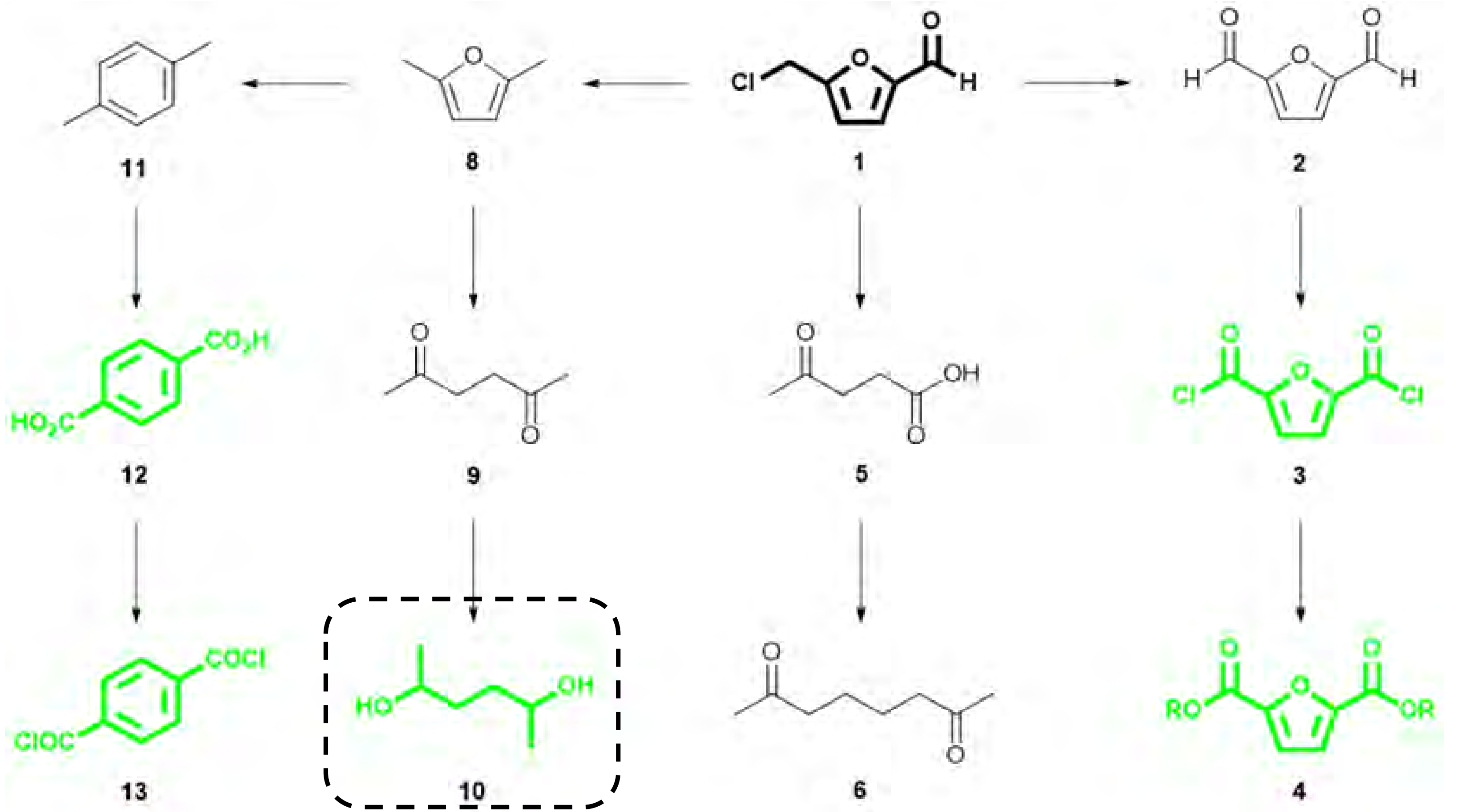
bold: high volume

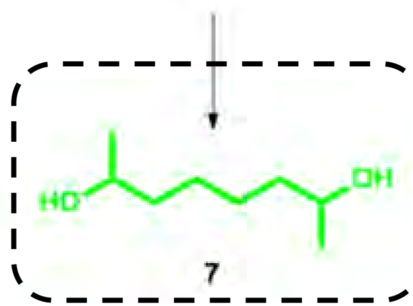
Hydrophobic Platform Molecules

- Terpenes (**38**) and fatty acids (**57**, **60**, **61**) most appropriate current source – but scale and competition could cause issues in the future!
- Dehydration of alcohols (e.g. ethanol **12** to ethene **1**) – overall low Atom Economy



CMF-based Monomers – New 2^{o} Diols





Main aim: to investigate secondary diols that have previously been hard to come by from an oil based feedstock

T. Farmer, M. Mascal *et al*., *ChemSusChem*, 2017, **10**, 166–170; T. Farmer, M. Mascal *et al.*, *Faraday Discuss.*, 2017, **202**, 61-77

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Transesterification of 2º Alcohol Diol Co-polyesters

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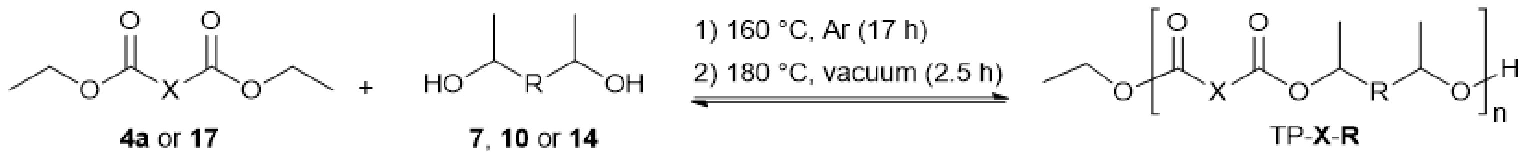

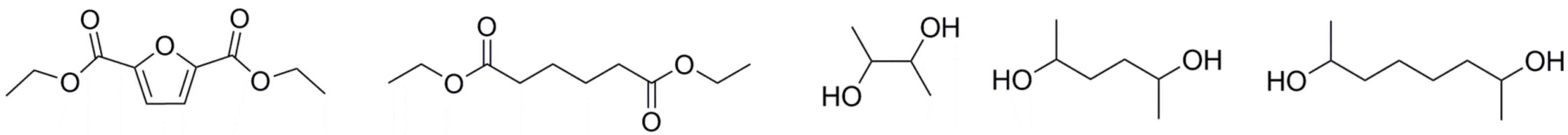

4a | 17 | 14 | 10 | 7

Entry	Polymer	X		R		% Yield	M_n (g/mol)	M_w (g/mol)	Đ	T_g (°C)
1	TP-**4a**-**14**	furan	-	-		82	830	1200	1.4	40
2	TP-**4a**-**10**	furan	-	$(CH_2)_2$		90	3300	5500	1.7	32
3	TP-**4a**-**7**	furan	-	$(CH_2)_4$		97	6400	9900	1.6	34
4	TP-**17**-**14**	-	$(CH_2)_4$	-		65	2300	3700	1.6	-43
5	TP-**17**-**10**	-	$(CH_2)_4$	$(CH_2)_2$		72	[illegible]	[illegible]	[illegible]	[illegible]
6	TP-**17**-**7**	-	$(CH_2)_4$	$(CH_2)_4$		77	[illegible]	[illegible]	[illegible]	[illegible]
7	TCP-**4a**-**17**-**10**	furan	$(CH_2)_4$	$(CH_2)_2$	2°	87	11000	16000	1.5	2
8	TCP-**4a**-**17**-**7**	furan	$(CH_2)_4$	$(CH_2)_4$	2°	73	9900	19000	2.0	-8
9	PBAF	furan	$(CH_2)_4$	BDO	1°	n/a	10300	17950	1.7	-34

2º diols increase T_g

T. Farmer, M. Mascal *et al.*, *ChemSusChem,* 2017, **10**, 166–170; T. Farmer, M. Mascal *et al.*, *Faraday Discuss.*, 2017, **202**, 61-77

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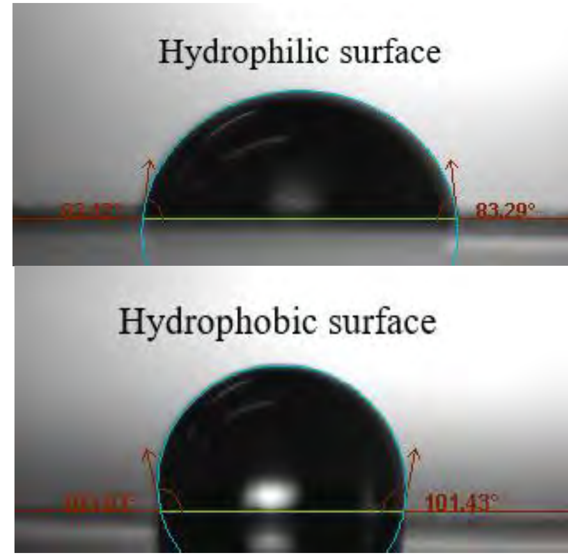
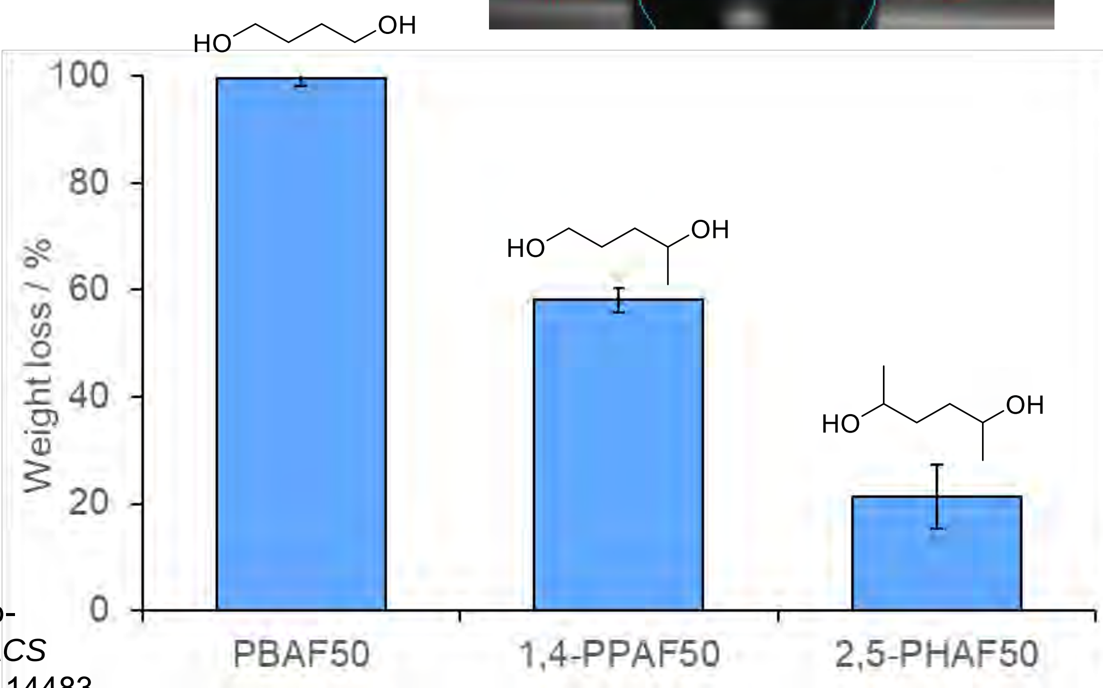
New 2º Alcohol Diols Tailor Polymer Properties

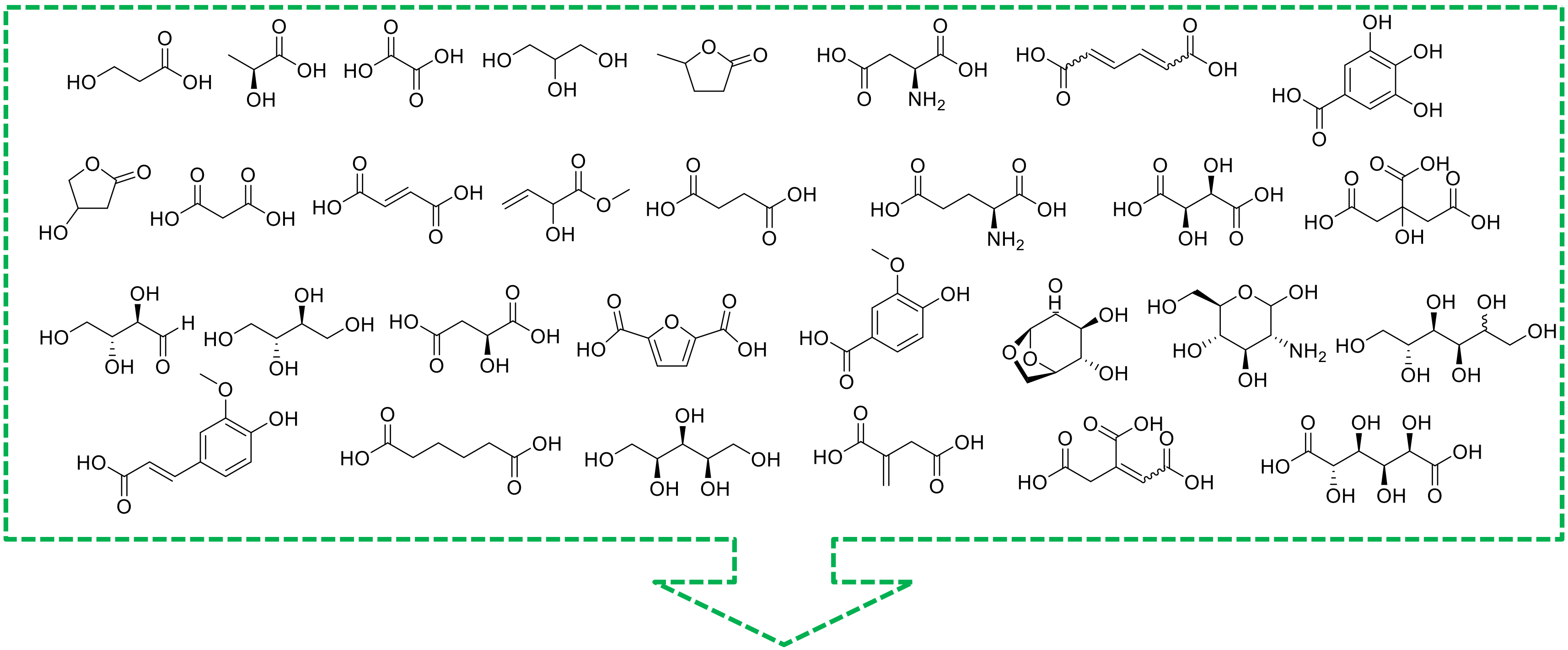
- 2º alcohol diols resulted in polyesters with a more hydrophobic surface compared to their linear equivalents
- **2º diol polyesters were totally amorphous** (stereo-irregular)
- Rate of enzymatic hydrolysis (*HiC*) was reduced by using 2º diols. Linked both to steric effects and hydrophobicity

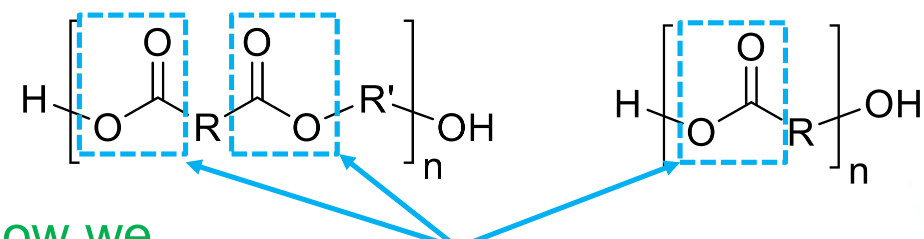




A. Little A. Pellis, J.W. Comerford, E. Naranjo-Valles, N. Hafezi, M. Mascal & T.J. Farmer, *ACS Sustainable Chem. Eng.* **2020**, 8, 38, 14471–14483

Circular Economy: Higher O-content leading to recycling and/or biodeg?





Points of attack for chemical recycling and biodegradation

✓ Our studies show we can tune biodegradation, both to make it go faster (Py) or slower (2° diols)

Concluding Remarks

- In the first instance drop-in replacements for fossil-derived monomers will be preferable (fit into current supply chains, legislation etc.)

- Longer-term we need to consider the high oxygen content of biomass as a feedstock and try to keep this in (more feedstock to product)

- The chemical diversity in platform molecules (bio-derived building blocks) brings challenges but also opportunities (new functional performance = new IP)

- Prevalence of polyesters should improve end-of-life options but may cause issues with in-use stability

- Personal Care needs both extensive functionality (lots of different effects desired) and hydrophobes – the diverse chemical functional groups in Platform Molecules are ideal for this but **hydrophobes are a challenge**.

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Thank you for your attention

Questions?

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