GLYCERODENDRIMERS:

NEW TOOLS FOR SLOW RELEASE ESSENTIAL OIL BASED BIOSOURCED HERBICIDES

Chloé Maes

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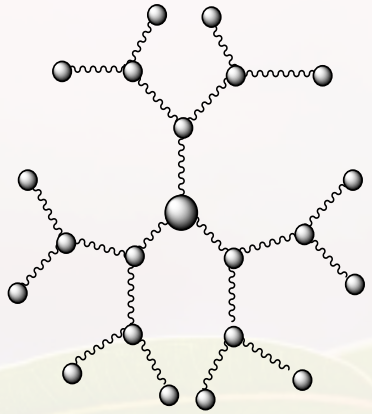
M.-L. Fauconnier



Plan

1. Context
2. Synthesis
    a) GD-PAMAM
    b) GD-PPI
    c) GAD
    d) GCD
3. Encapsulations
4. Interactions
5. Biological assays

1. Context

Essential oils are naturally bioactive (herbicides, insecticides, fungicides)

BUT they are too much volatile

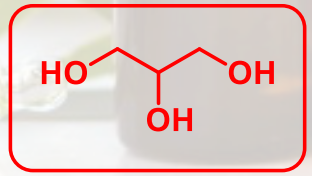
🎯 Improve performance → ***encapsulation with slow release***

EOs

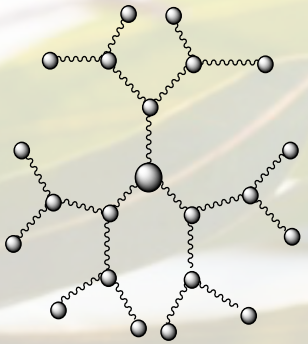
* Innovation : use of dendrimers as encapsulating matrix

* Final goal : create biosourced pesticides

* Way : dendrimer synthesis with **glycerol**



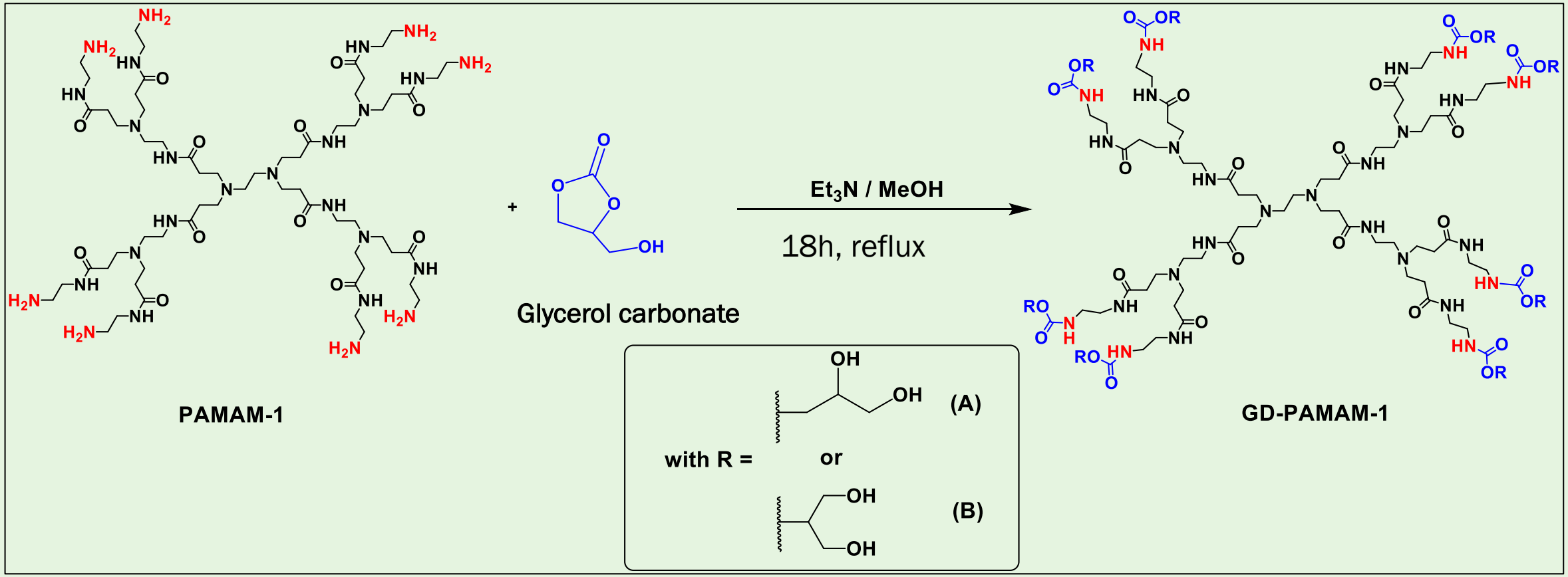
Dendrimers



2. Synthesis

a) GD-PAMAM

Commercial dendrimer decoration– PAMAM (PolyAmidoAmine)

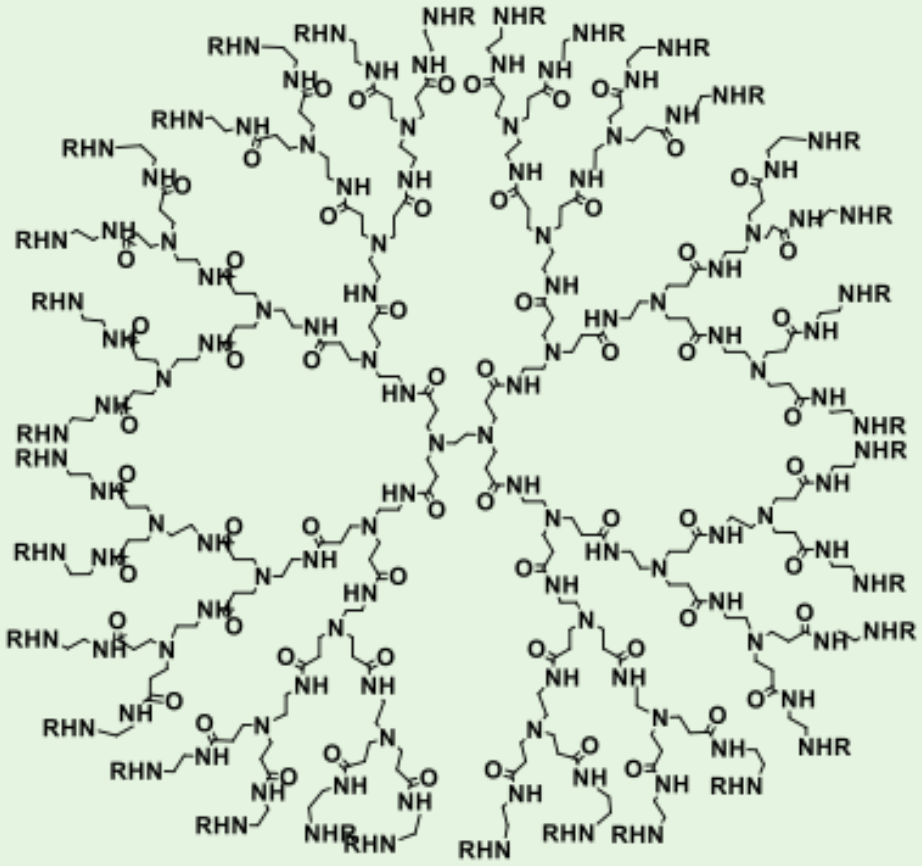


Menot, B., Stopinski, J., Martinez, A., Oudart, J. B., Maquart, F. X., & Bouquillon, S. (2015) Tetrahedron, 71(21), 3439–3446.

2. Synthesis

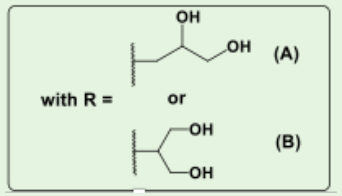
a) GD-PAMAM

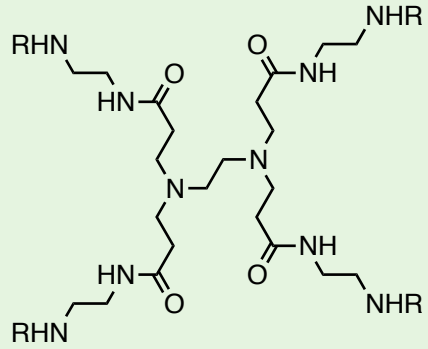
4 generations



GD-PAMAM-3

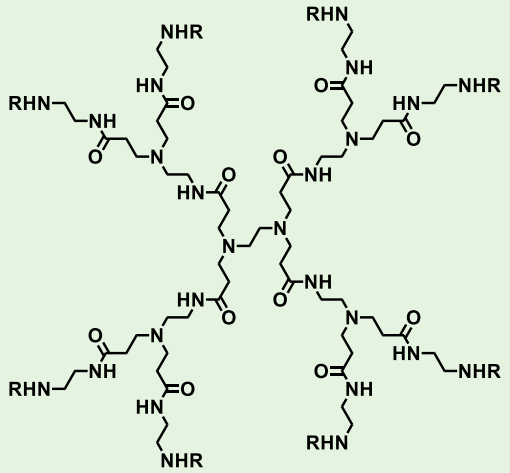
Yield: 93%





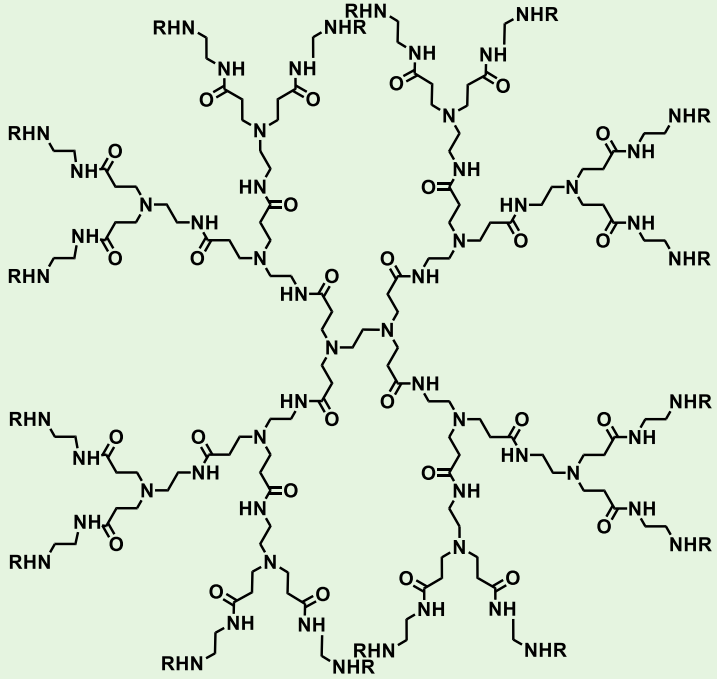
GD-PAMAM-0

Yield: 91%



GD-PAMAM-1

Yield: 92%



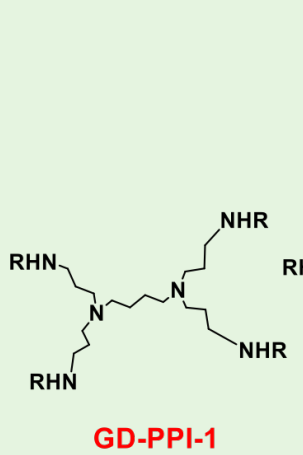
GD-PAMAM-2

Yield : 91%

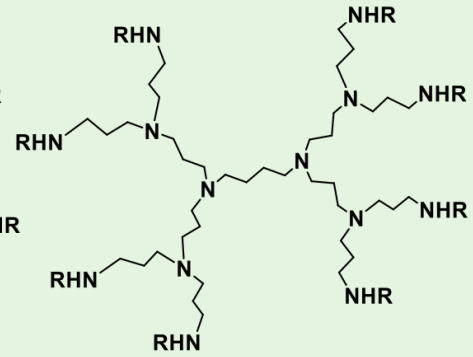
2. Synthesis

b) GD-PPI (glycerodendrimer PolyPropylenImine)

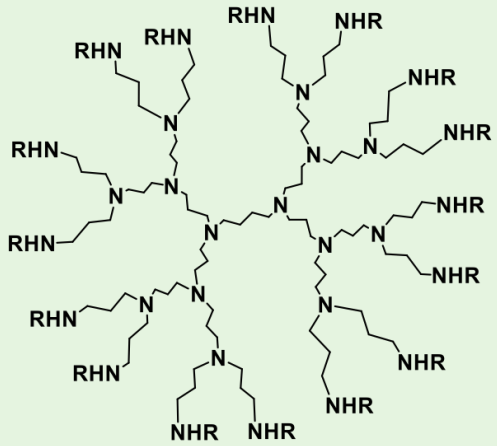
4 generations



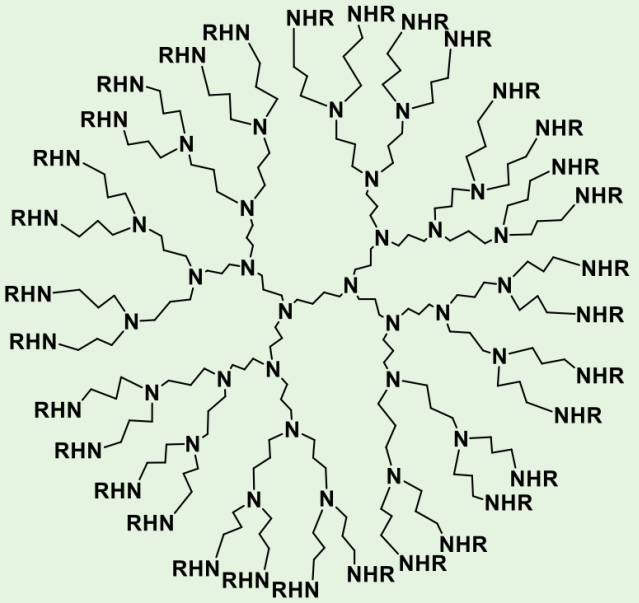
Yield: 87%



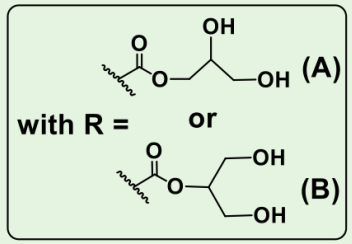
Yield: 88%



Yield: 89%



Yield: 89%

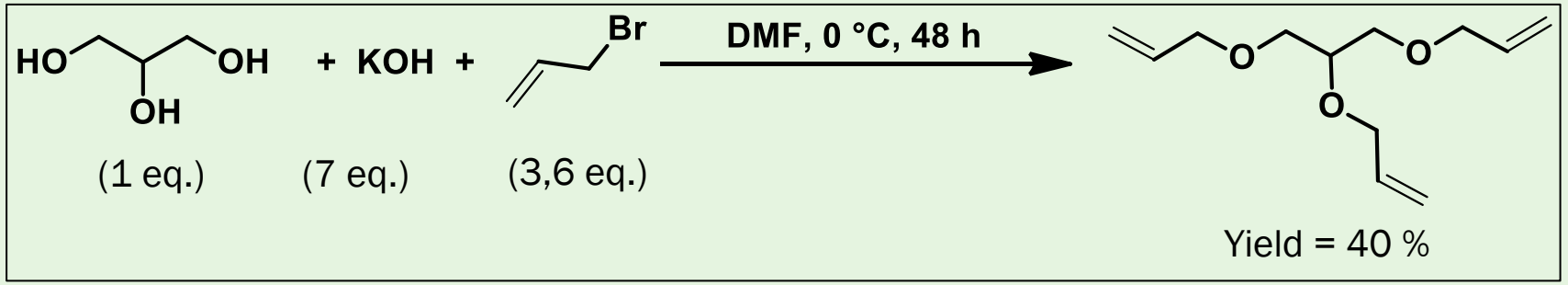


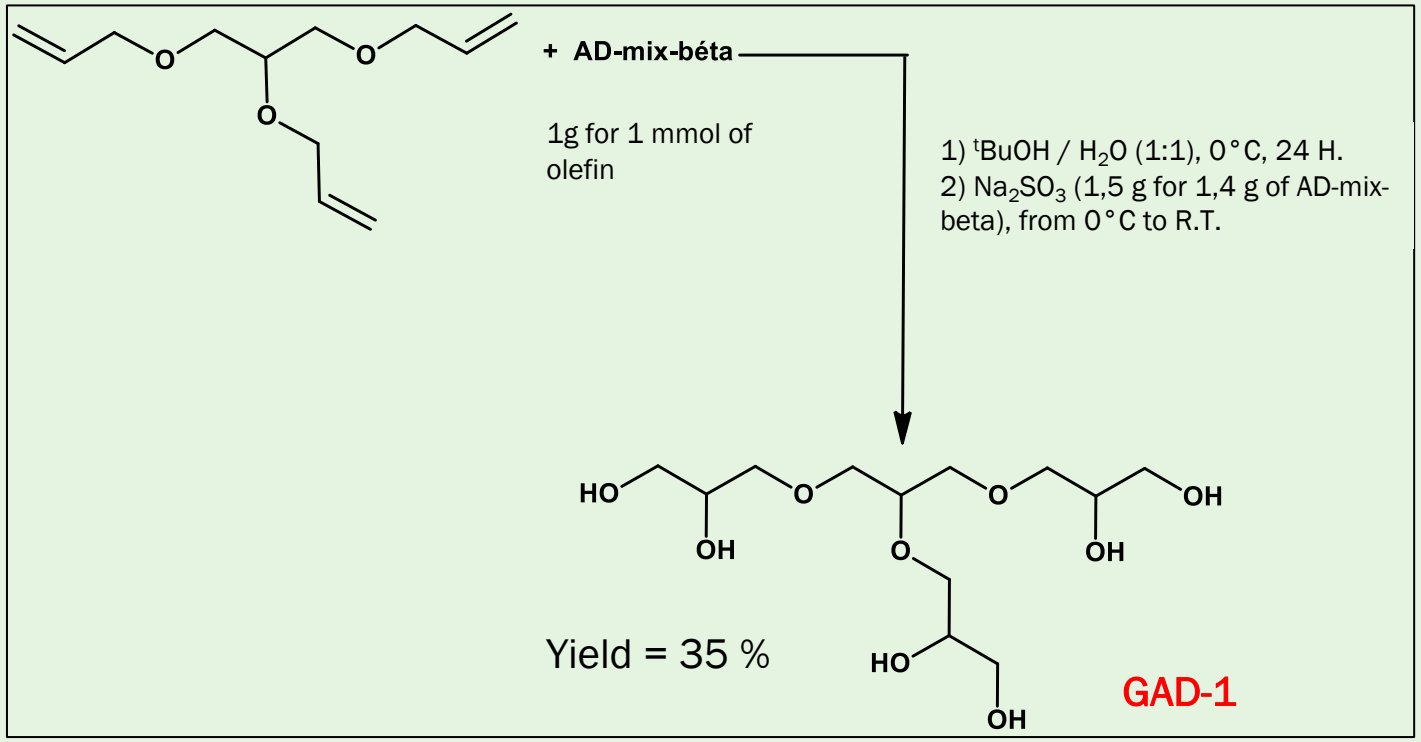
Balieu, S., Cadiou, C., Martinez, A., Nuzillard, J. M., Oudart, J. B., Maquart, F. X., Chuburu F., & Bouquillon, S. (2013) Journal of Biomedical Materials Research - Part A, 101 A(3), 613 - 621

2. Synthesis

c) Synthesis of GlycerolADendrimers (GAD)

glycerol allylation / oxidation



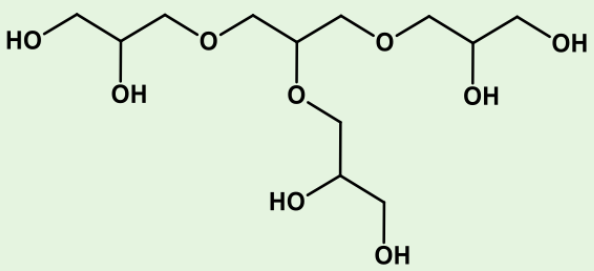


FR patent application on 26/07/2018
N°: FR1856989
Name: Université de Reims Champagne Ardenne
S. Bouquillon, S. Hayouni, B. Menot

2. Synthesis

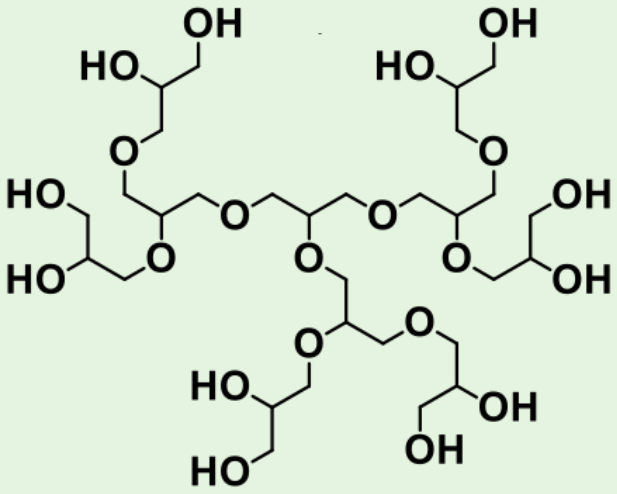
c) GlycerolADendrimers (GAD)

3 generations



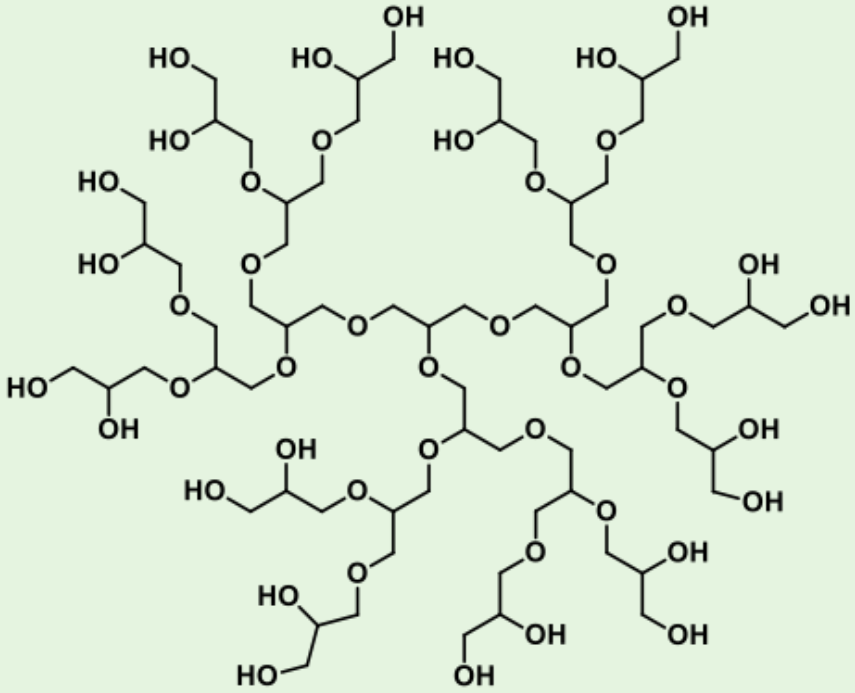
GAD-1

Yield: 40%



GAD-2

Yield: 69%



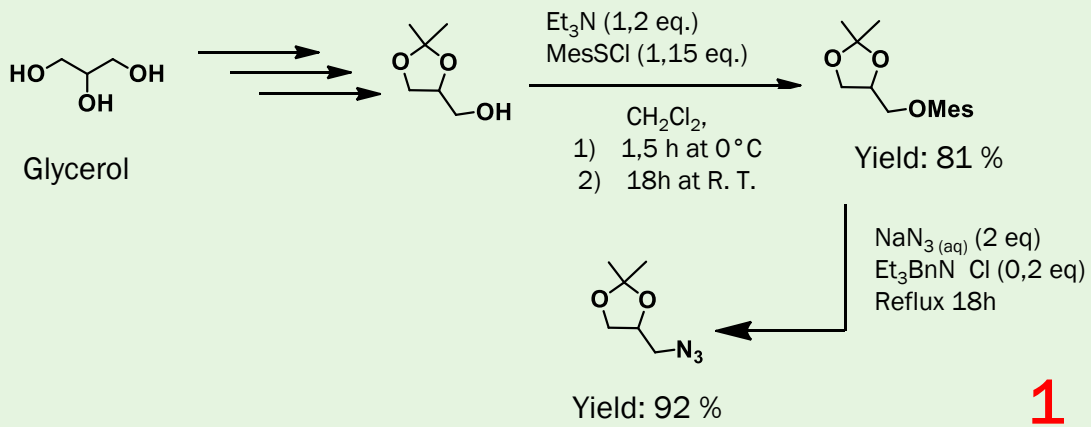
GAD-3

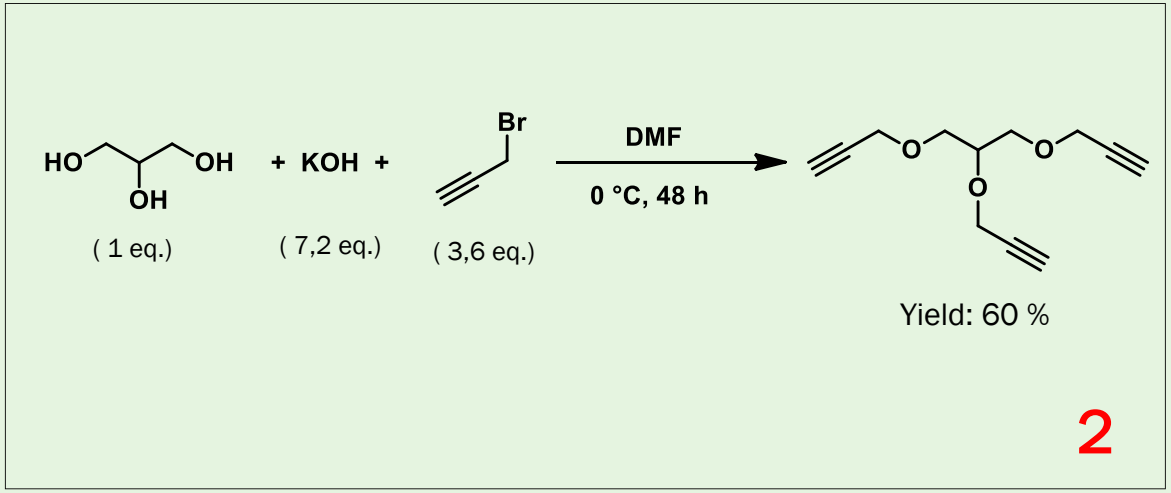
Yield: 53%

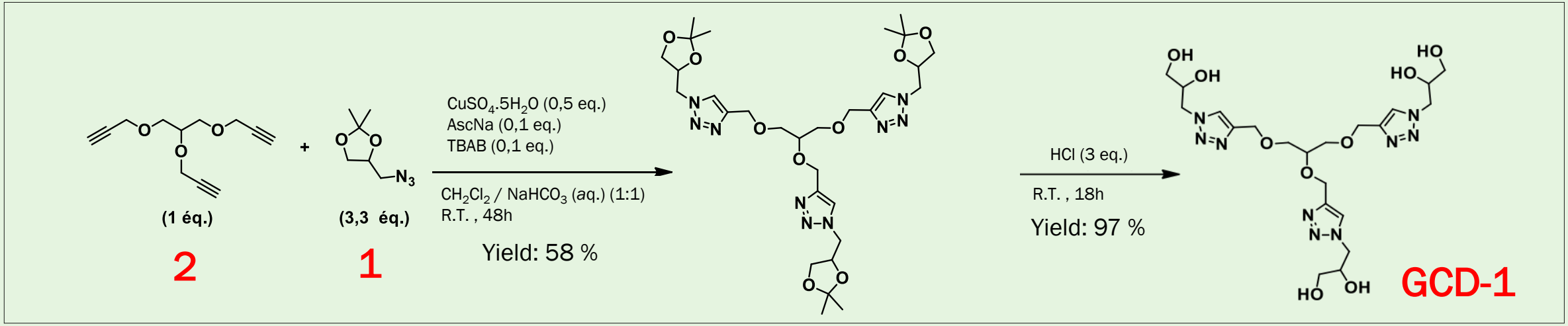
FR patent application on 26/07/2018
N°: FR1856989
Name: Université de Reims Champagne Ardenne
S. Bouquillon, S. Hayouni, B. Menot

2. Synthesis

d) GlyceroClickDendrimers (GCD) « Click chemistry»





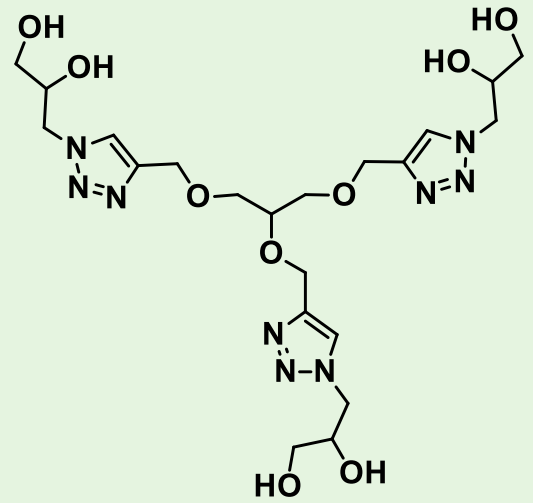


FR patent application pending on 26/07/2018
N°: FR1856990. Name: Université de Reims Champagne Ardenne. S. Bouquillon, S. Hayouni, B. Menot

2. Synthesis

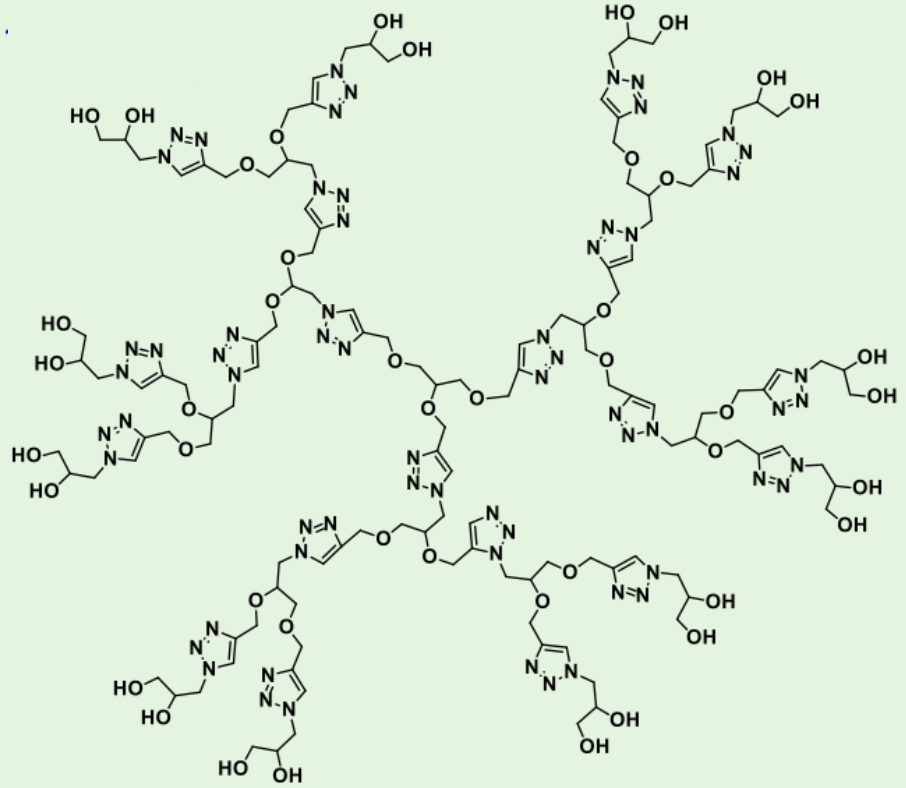
d) GlycerolClickDendrimers (GCD)

3 generations

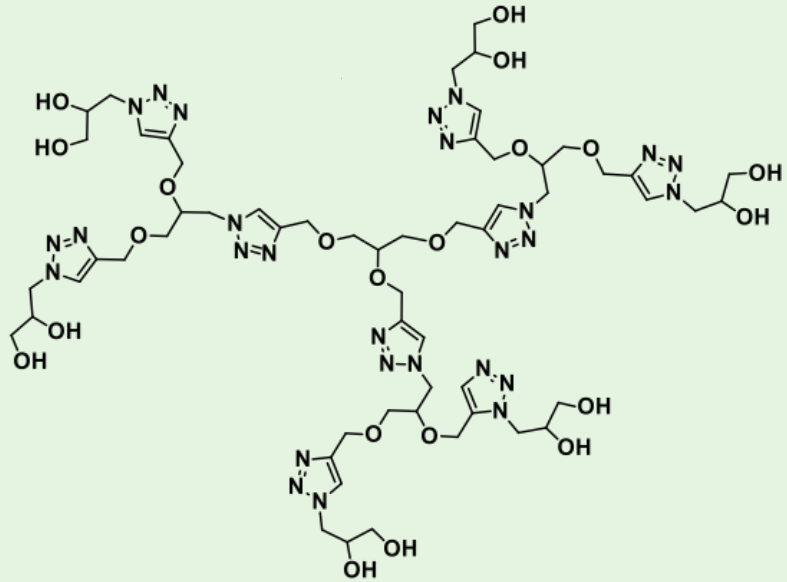


GCD-1

Yield : 58 %



GCD-3 Yield : 52 %

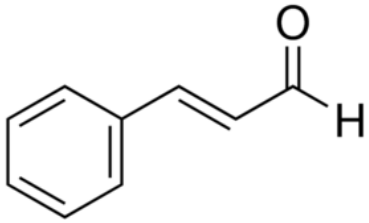
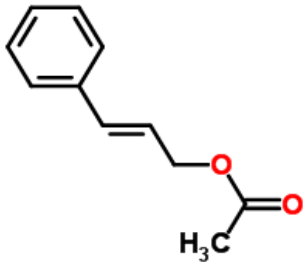


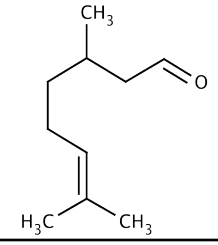
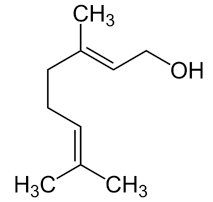
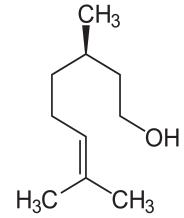
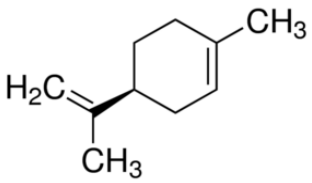
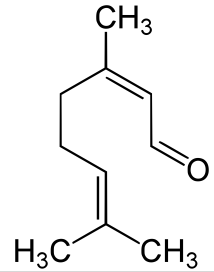
GCD-2

Yield : 72 %

FR patent application on 26/07/2018
N°: FR1856990.
Name: Université de Reims Champagne Ardenne. S. Bouquillon, S. Hayouni, B. Menot

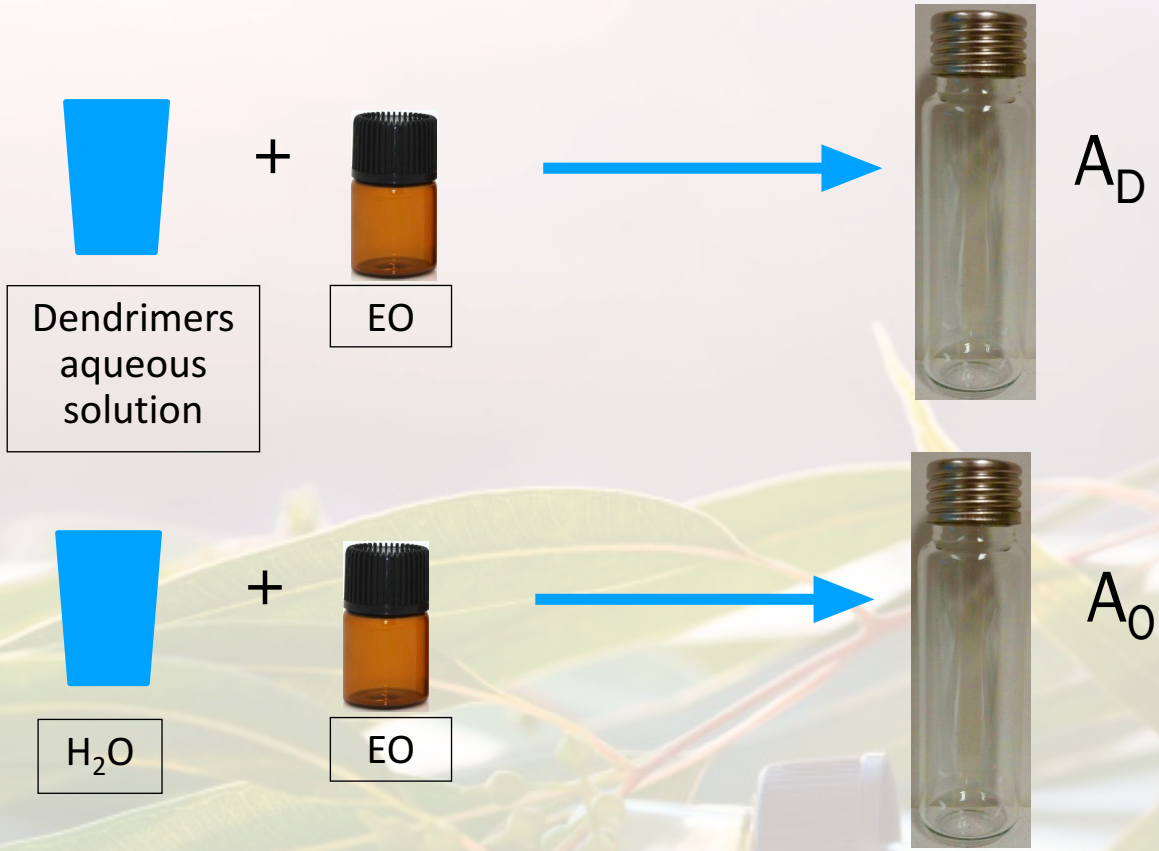
Essential oils structures

Cinnamon EO		
Trans cinnamaldehyde		85%
Cinnamyl acetate		7%

Citronella EO		
Citronellal		45%
Geraniol		30%
Citronellol		18%
Limonene		< 10%
Citral		< 10%

3. Encapsulation

Method: In solution (measure DHS-GC-MS)



DHS-GC-MS analysis :
Total retention yield:

$$r\,(\%) = \left(1 - \frac{\sum A_D}{\sum A_0}\right) \times 100$$

A_D : area under curve with dendrimers
A_0 : area under curve without dendrimers

Kfoury, M., Auezova, L., Greige-Gerges, H., & Fourmentin, S. (2015) Carbohydrate Polymers, 131, 264–272.

3. Encapsulation

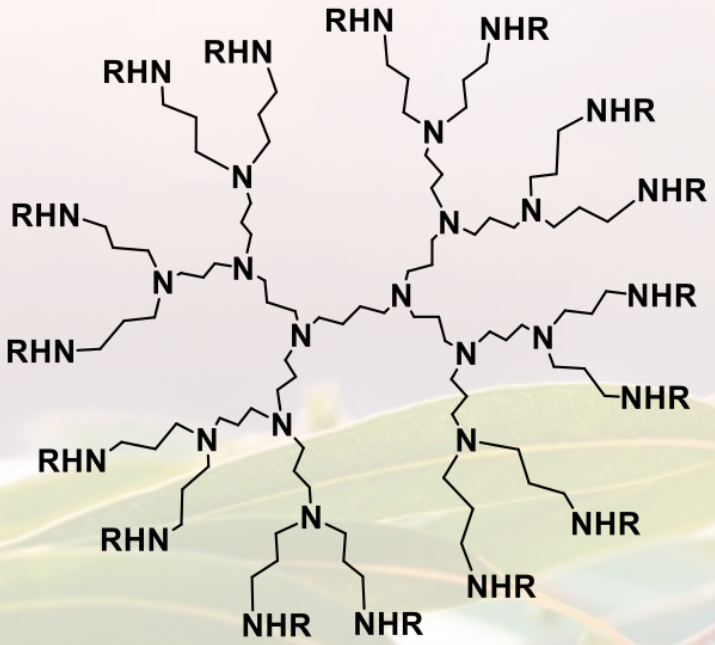
Encapsulating matrix	r. (%) - Citronella EO	r. (%) - Cinnamon EO
Dendrimers		
GD-PAMAM-0	9,83 +/- 0,44	12,17 +/- 0,41
GD-PAMAM-1	6,49 +/- 0,72	29,01 +/- 0,68
GD-PAMAM-2	24,88 +/- 4,80	38,84 +/- 0,57
GD-PAMAM-3	20,39 +/- 2,38	32,97 +/- 1,13
GD-PPI-1	/	24,35 +/- 4,23
GD-PPI-2	3,09 +/- 1,95	14,15 +/- 3,77
GD-PPI-3	26,65 +/- 5,77	25,99 +/- 4,36
GD-PPI-4	10,55 +/- 3,53	24,21 +/- 3,95
GlycéroClickdend-1	/	13,67 +/- 1,57
GlycéroClickdend-2	/	9,37 +/- 2,54
GlycéroClickdend-3	/	/
GlycéroAdend-1	3,89 +/- 1,27	16,23 +/- 5,30
GlycéroAdend-2	/	23,38 +/- 2,85
GlycéroAdend-3	8,28 +/- 1,45	/

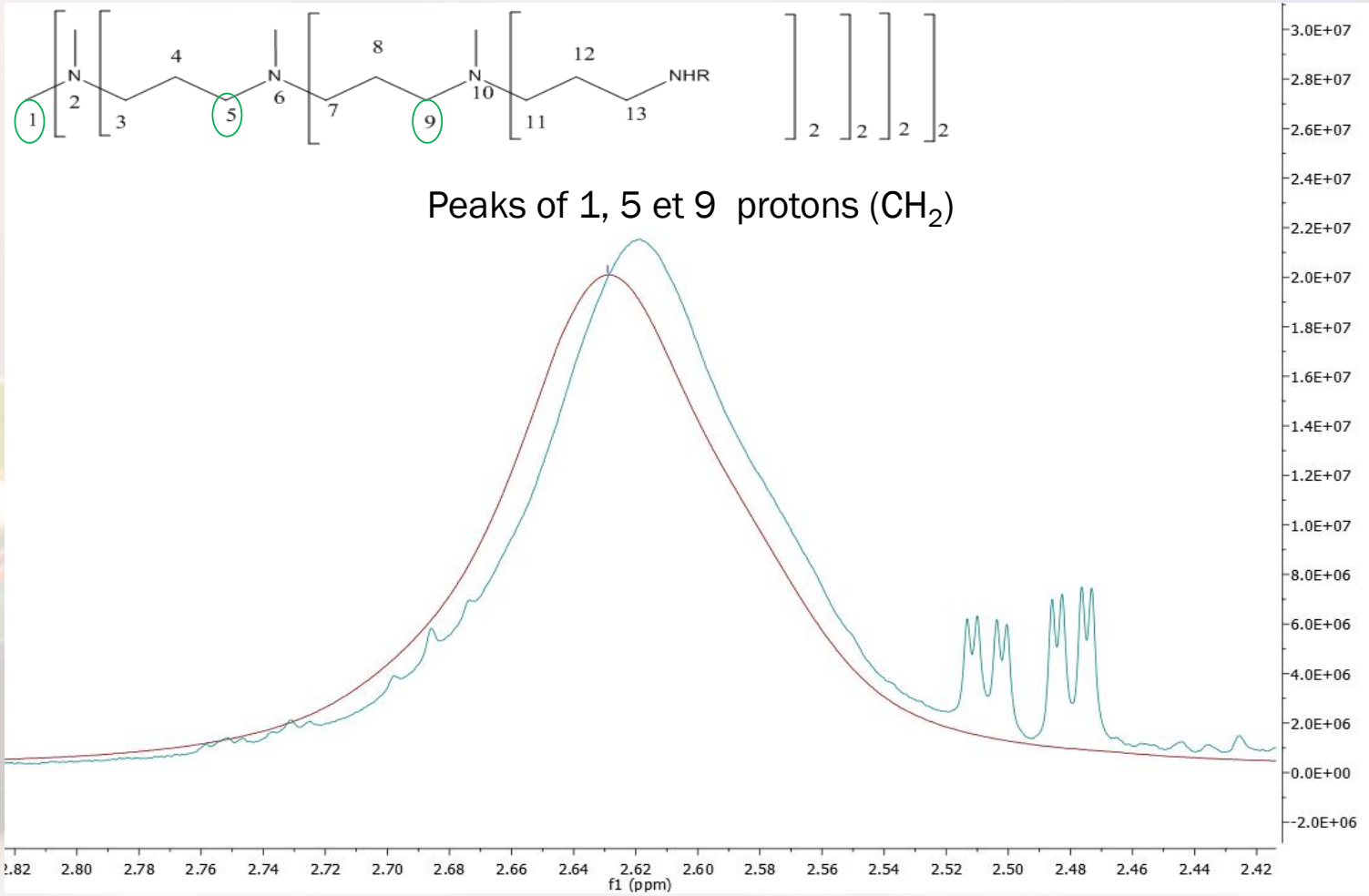
- Selection of the best candidates

4. Interactions

- NMR ^{1}H 600 MHz

GD-PPI-3 alone (red) and GD-PPI-3 with citronella EO (blue) superposition





In progress ...

5. Biological assays

- Germination inhibition of *Arabidopsis thaliana* seeds (closed space)

Modus operandi:
- In petri dishes, put paper filter then 10 *A. thaliana.* seeds
- Add 2 mL of active solution *
  ** dendrimer aqueous solution (2 mM)*
  + 1% Tween 20 (surfactant allowing Eos emulsion in water)
  + 3 mg EOs
- Close dishes hermetically and leave in a culture room (16/8 at 20°C for 5 days).

Germination inhibition (-)

Germination (+)

	A. thaliana
Citronella EO	-
Cinnamon EO	-
GD-PPI-3	+
GD-PAMAM-2	+
GD-PPI-3 + Citronella EO	-
GD-PAMAM-2 + Citronella EO	-
GD-PPI-3 + Cinnamon EO	-
GD-PAMAM-2 + Cinnamon EO	-
H_2O	+
Tween 20 (surfactant)	+

6. Conclusions et perspectives

Synthesis of 4 biosourced dendrimers

Encapsulations

Herbicide activities

Interactions analysis:

- NMR (2D, NOESY)
- IR

Optimise encapsulations

Study the release dynamics

ISGC 2019
May 13rd - 17th

Université de Reims Champagne-Ardenne

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Projet cleanup2

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MINISTÈRE
DE L'ENSEIGNEMENT
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DE LA RECHERCHE
ET DE L'INNOVATION

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Thank you

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