17 JANVIER 2023

HÉTÉROGÉNÉISATION DE PHOTOCATALYSEURS PROCÉDÉS DE PHOTO-OXYDATION EN FLUX CONTINU

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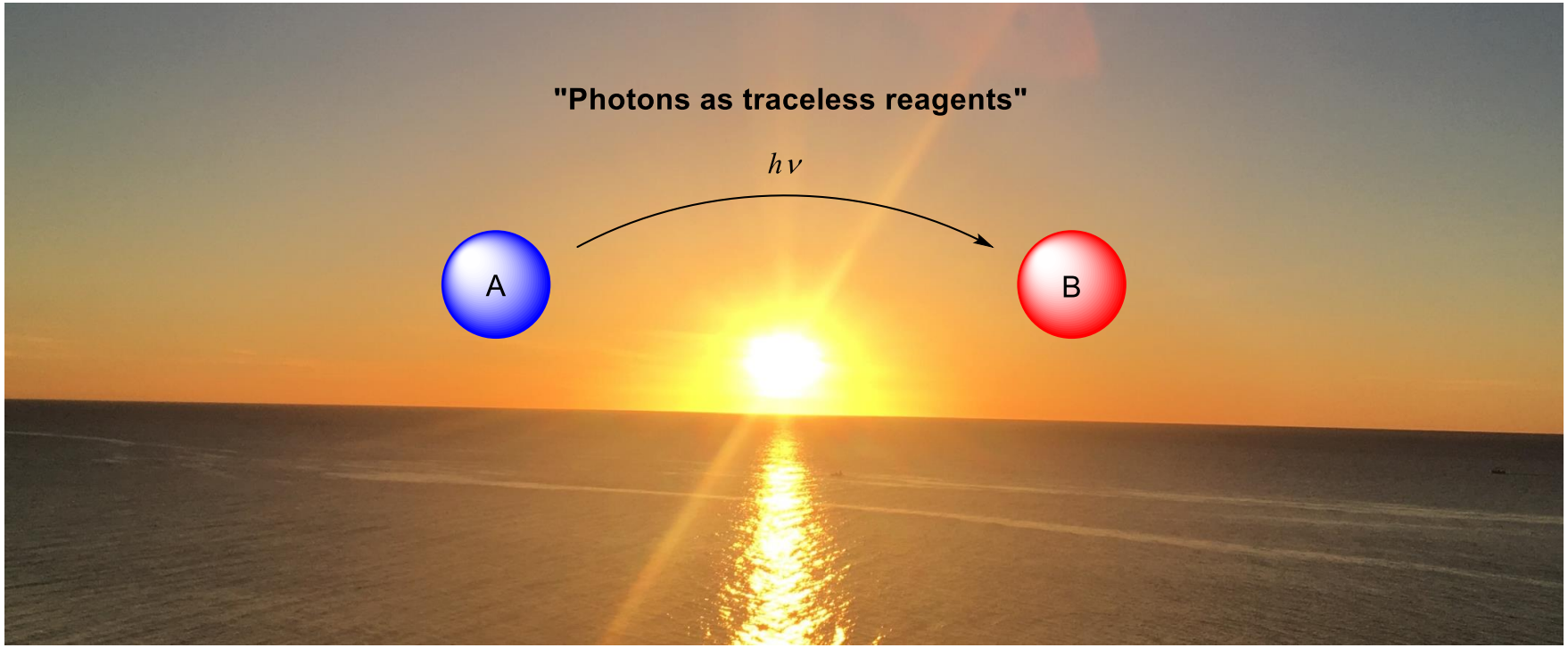
CONSERVATOIRE NATIONAL DES ARTS ET METIERS

Photochemistry



To date:

- *Over 8000 photochemical reactions reported since 1975*
- *Huge potential in CO_2 to MeOH conversion*

However:

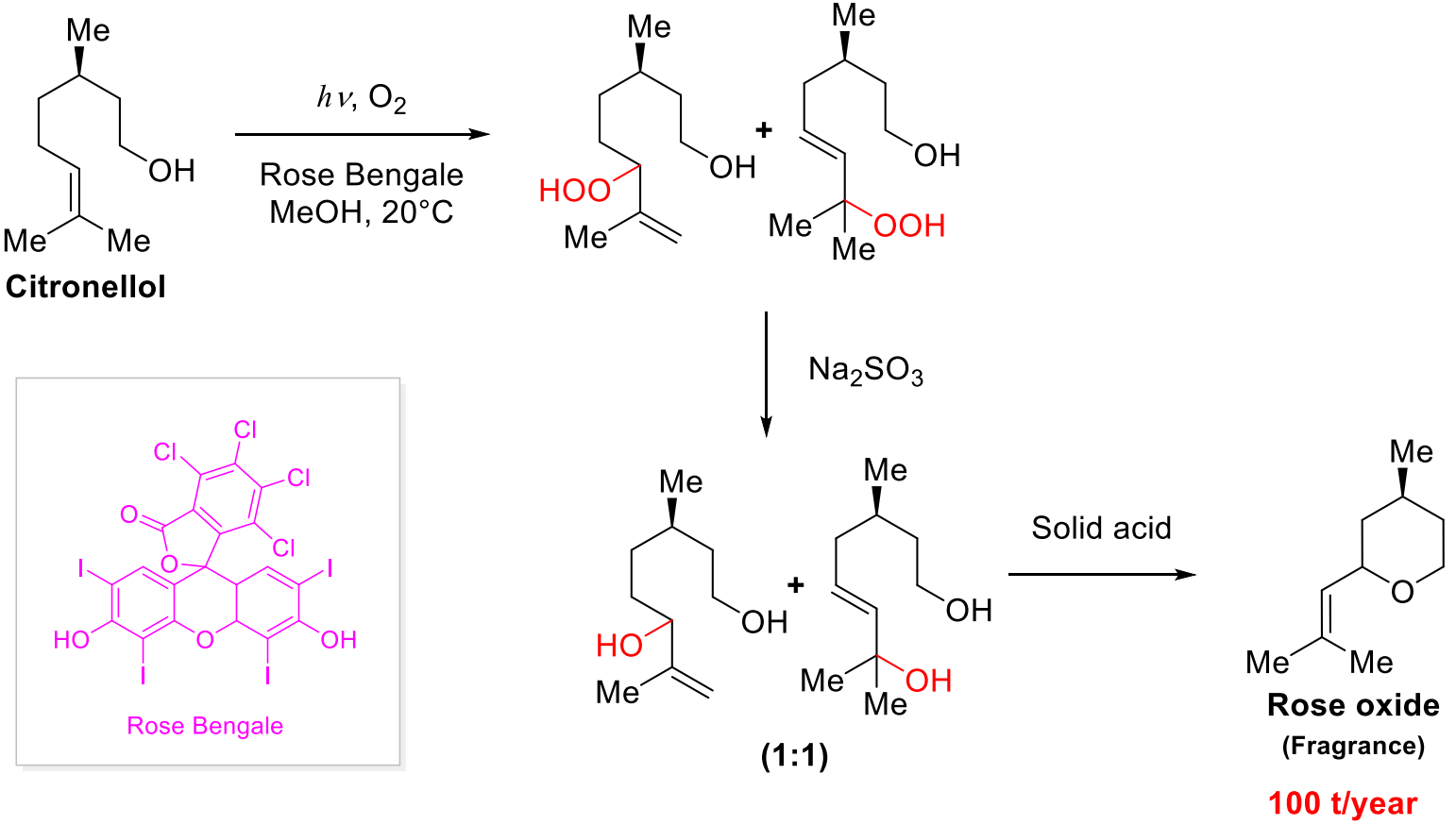
- *5 industrial applications in wastewater treatment*
- *4 industrial applications in organic chemistry*

Leblebici, *Beilstein J. Org. Chem*. **2020**, *16*, 2484–2504

Industrial Photochemistry

Synthesis of Rose Oxide

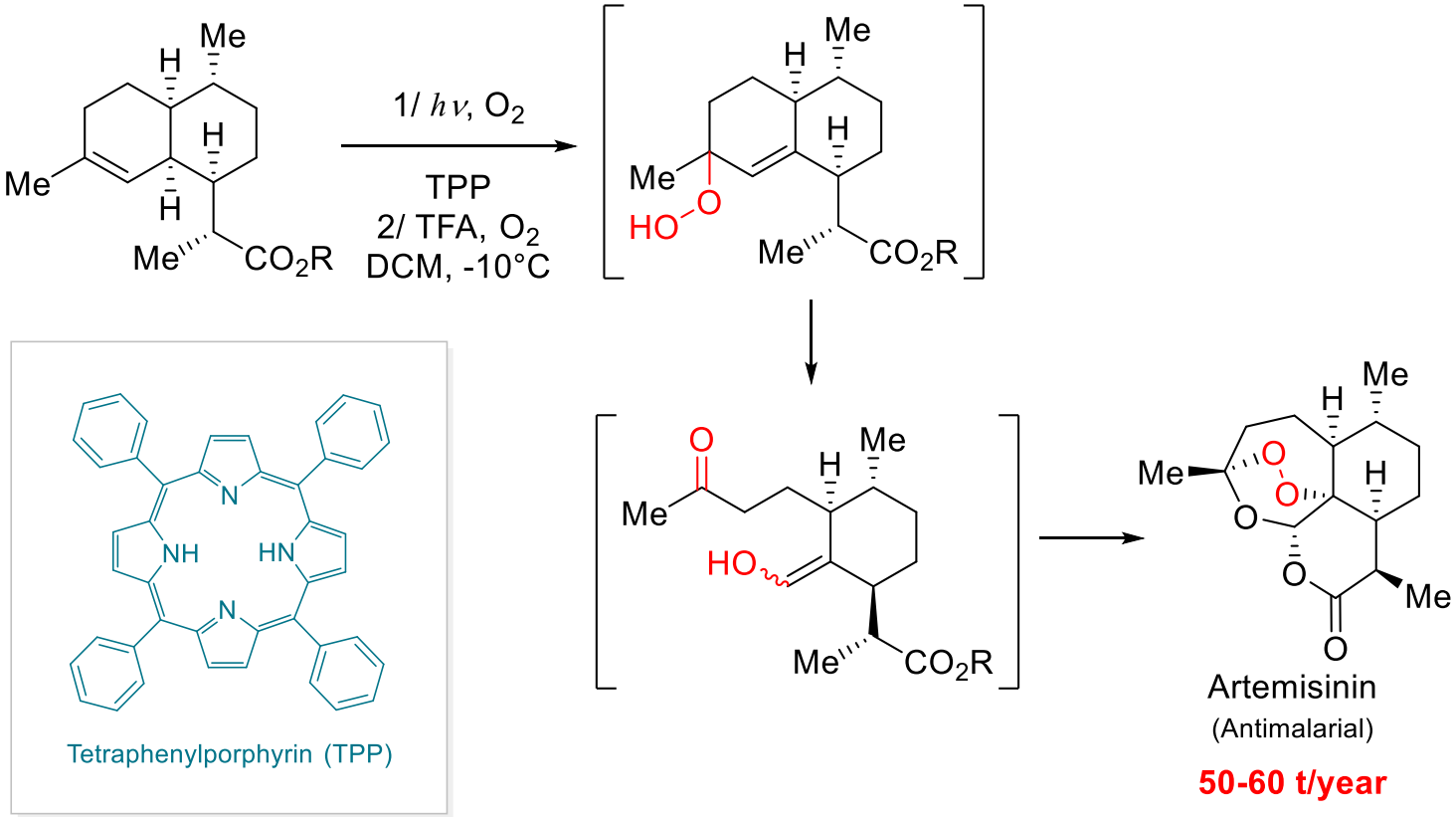
Industrial photoreactor operated by Dragoco/Symrise



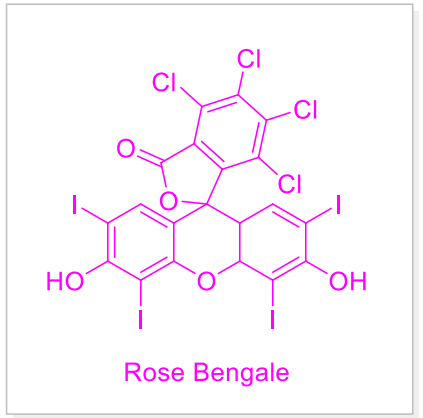
Industrial Photochemistry

Synthesis of Artemisinin

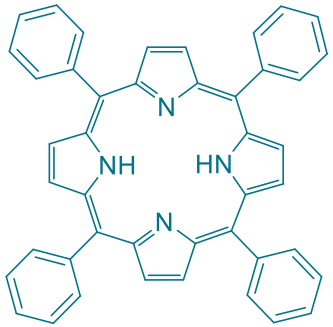
Industrial photoreactor operated by Sanofi
(synthesis of artemisinin)



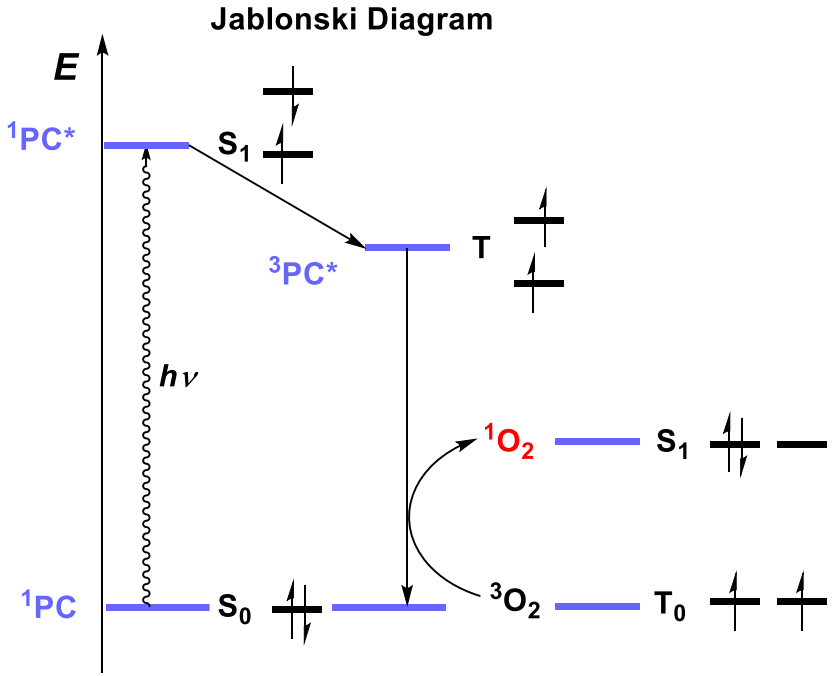
Singlet Oxygen Photochemistry

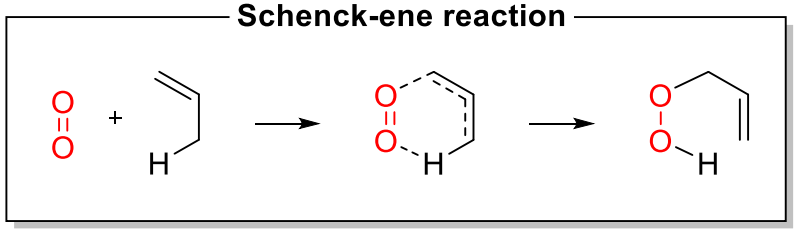


Rose Bengale

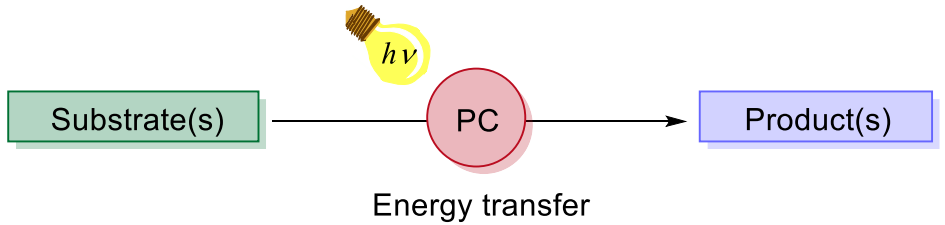


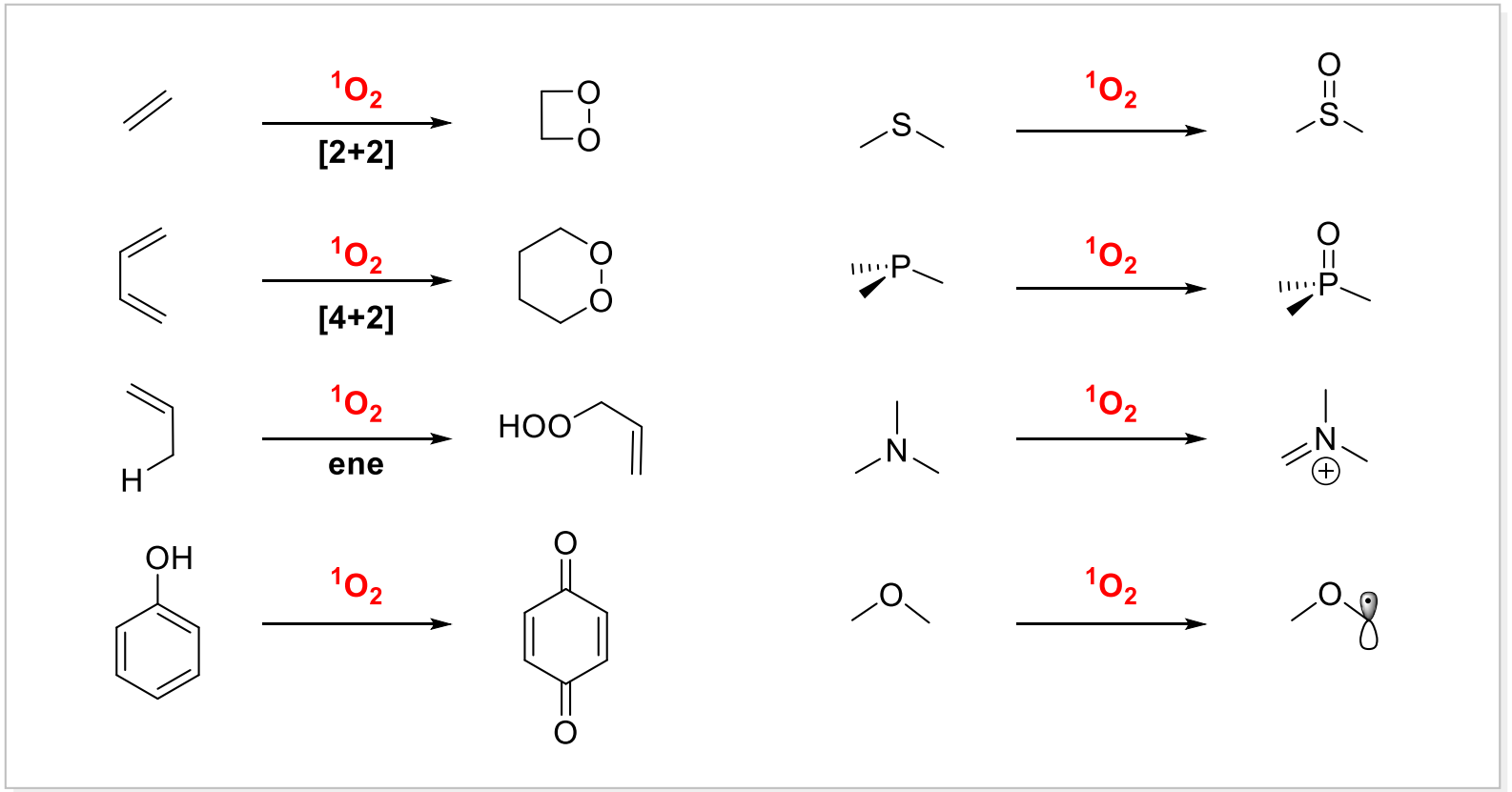
Tetraphenylporphyrin (TPP)





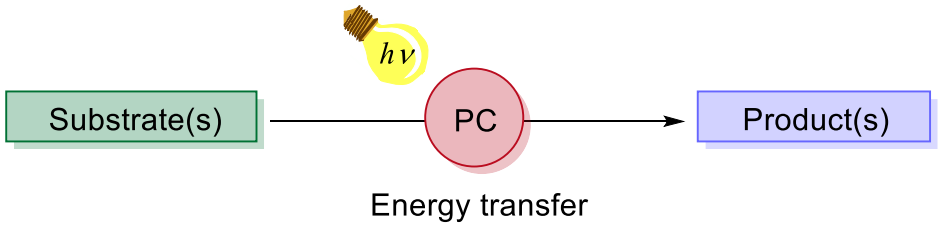
Singlet Oxygen Photochemistry



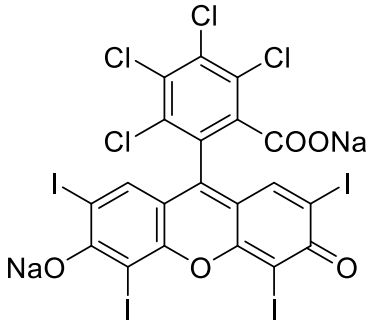


Ghogare, Greer, *Chem Rev.*, **2016**, *116*, 9994-10034

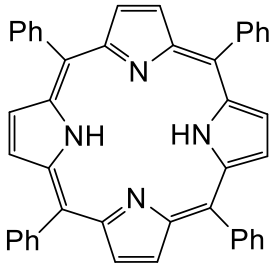
Photocatalysis



Organic PCs



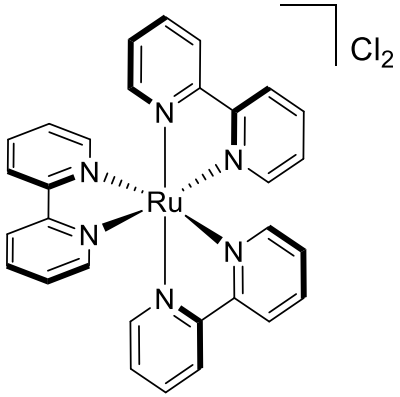
Rose Bengale



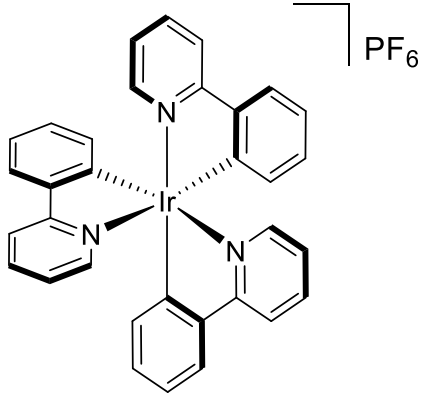
Tetraphenylporphyrin

Unstable

Organometallic PCs



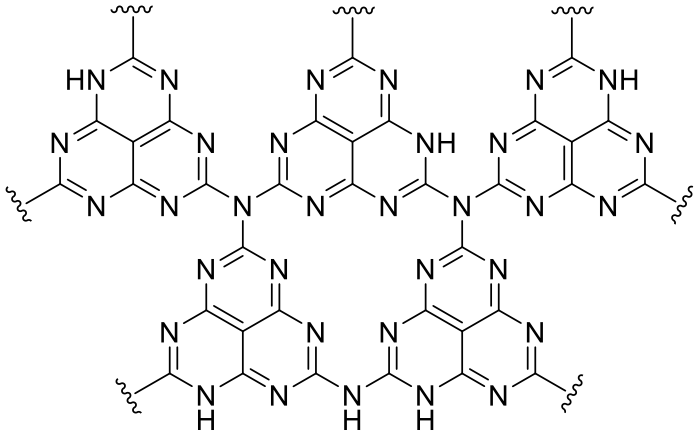
$Ru(bpy)_3Cl_2$



$Ir(ppy)_3PF_6$

Precious metals

Solid PCs (Organic or Inorganic)



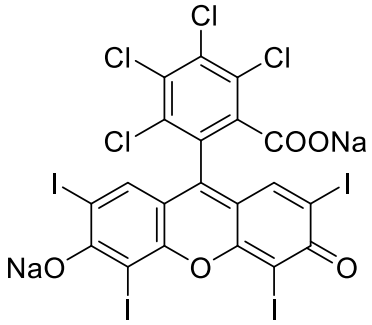
$g\text{-}(C_3N_4)$

Not efficient for energy transfer processes

Photocatalysis: Current Drawbacks

How to enhance stability ?
How to separate & recycle ?
How to solve potential solubility issues ?

Organic PCs



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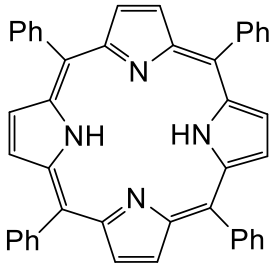

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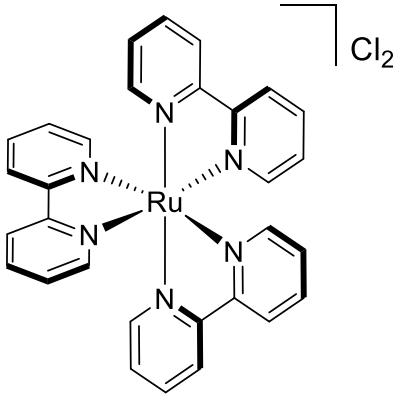

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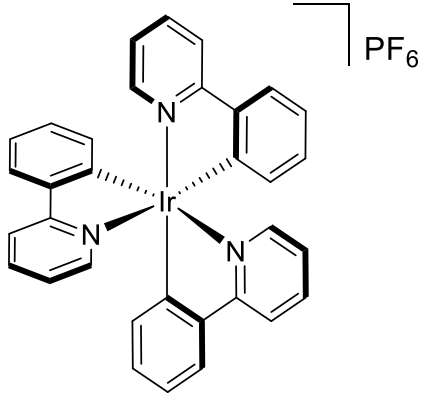

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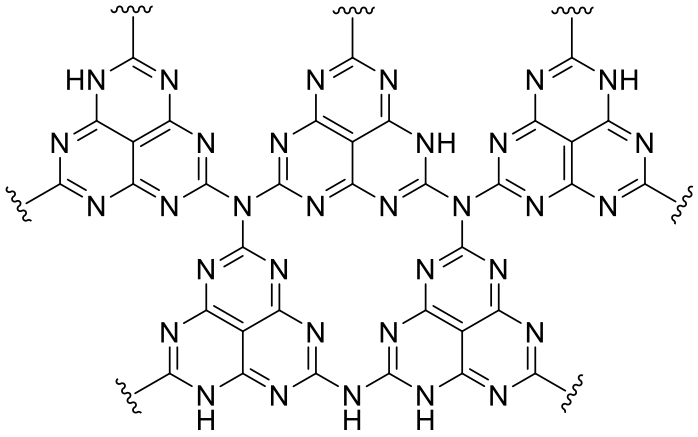

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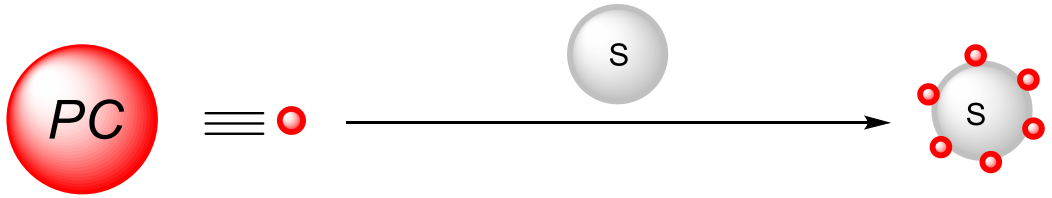
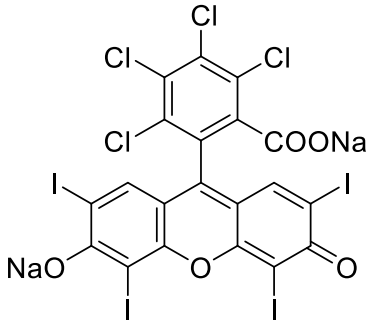
Photocatalysis: *Potential Solutions*

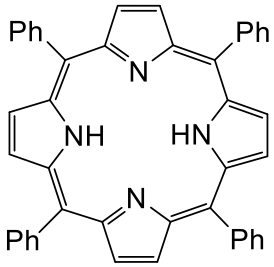


Homogeneous Photocatalyst **Supported Photocatalyst**

Organic PCs



Rose Bengale



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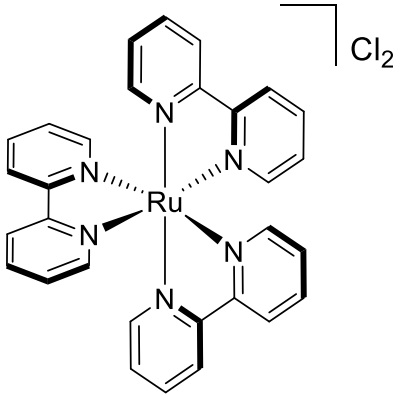

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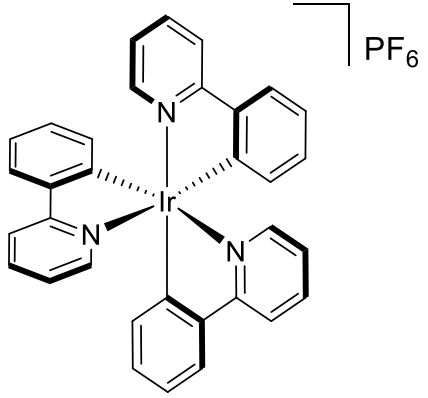

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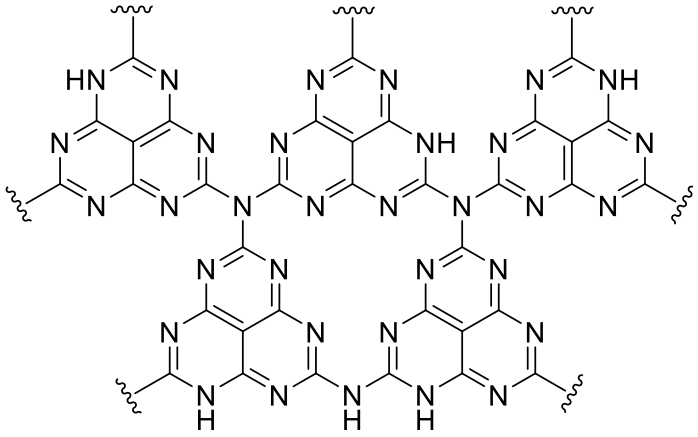

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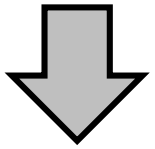
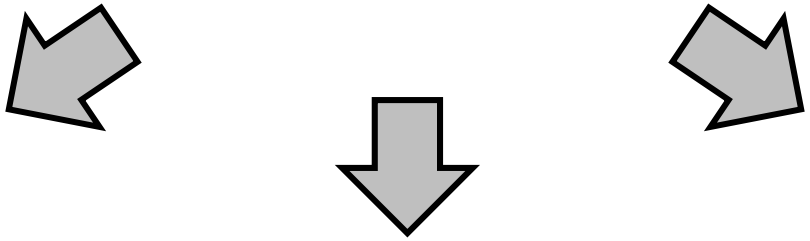
Not efficient for energy transfer processes

Research Projects @ Cnam

Focus on Green Chemistry



More Environmentally Friendly Photochemical Processes



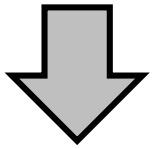
Design of Recyclable Photocatalytic Systems

Study of New Photocatalysts

Investigation of New Photochemical Routes

Research Projects @ Cnam

Focus on Green Chemistry



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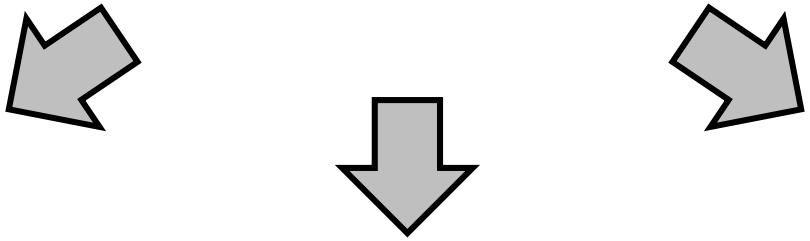

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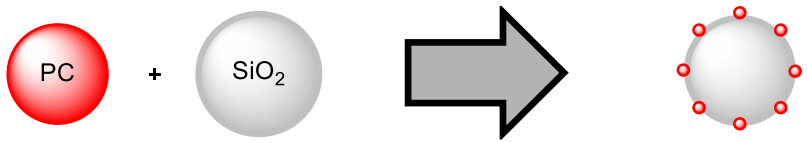
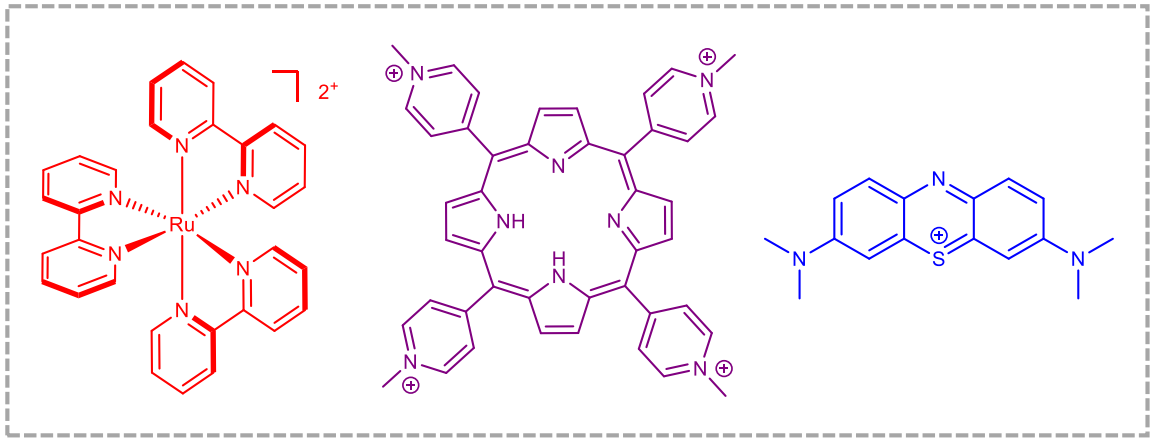


SiO_2@PC

Immobilization of cationic photocatalysts (organic & organometallic)

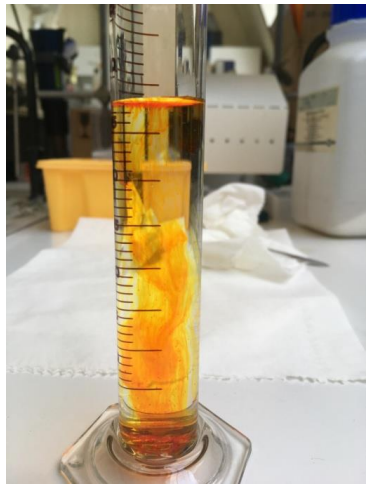
Heterogenized Photocatalysts

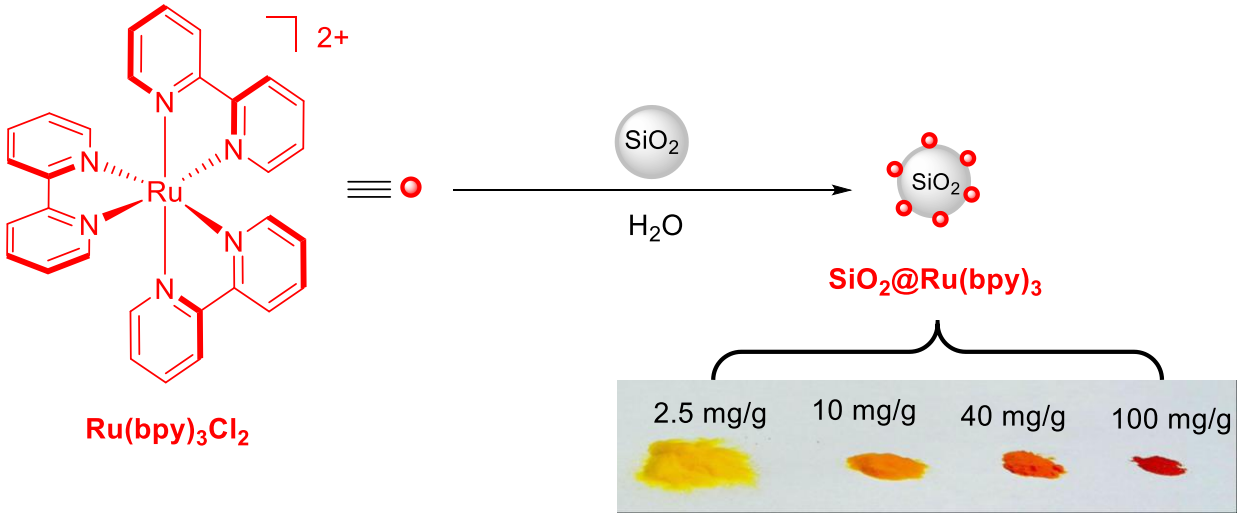


Objective = solve generic problems in photocatalysis

- ***Low stability of PC***
- ***Low process performances***
- ***No recyclability of homogeneous PC***

Immobilization of Cationic Photocatalysts on Silica

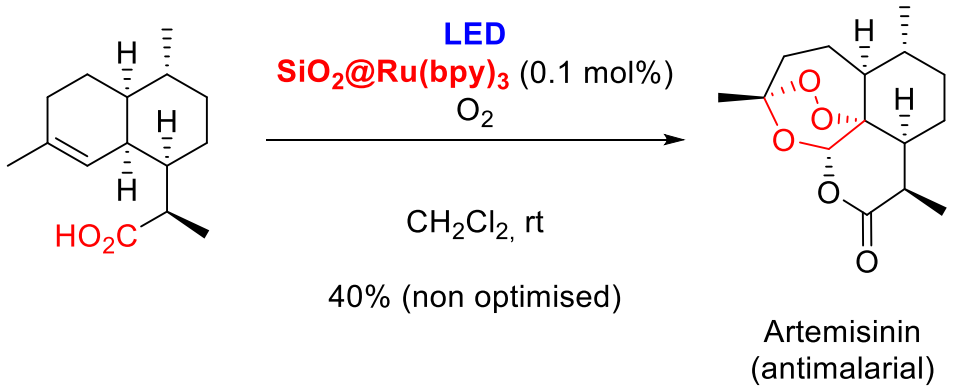




Ru(bpy)$_3$Cl$_2$

Tambosco, Segura, Seyrig, Cabrera, Port, Ferroud, Amara, *ACS Catal.* **2018**, *8*, 4383-4389

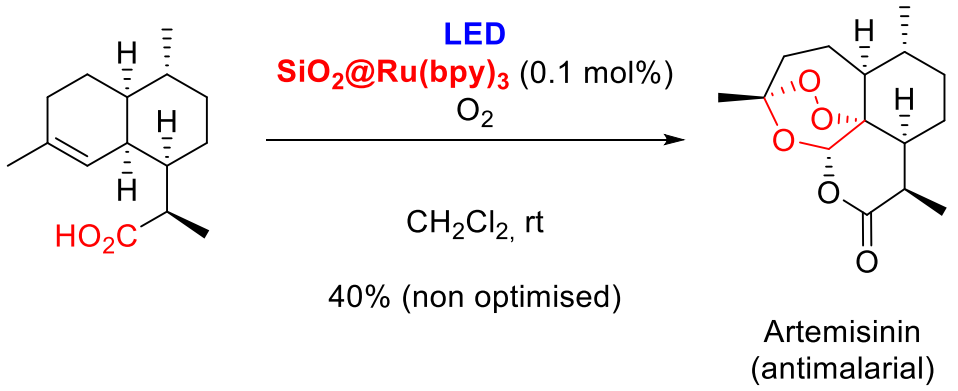
Application in Synthesis



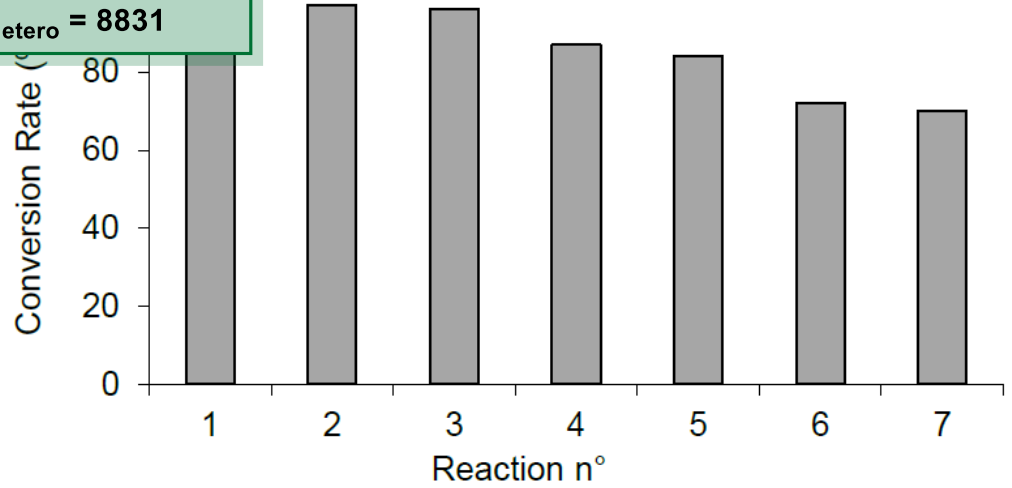
Sanofi/Amyris
50-60 tons/year
(55% yield with TPP
TFA @ -10°C)

Tambosco, Segura, Seyrig, Cabrera, Port, Ferroud, Amara, *ACS Catal.* **2018**, *8*, 4383-4389

Application in Synthesis



Under Catalytic Stress
$tTON_{homo}$ = 2089
$tTON_{hetero}$ = 8831



Tambosco, Segura, Seyrig, Cabrera, Port, Ferroud, Amara, *ACS Catal.* **2018**, *8*, 4383-4389

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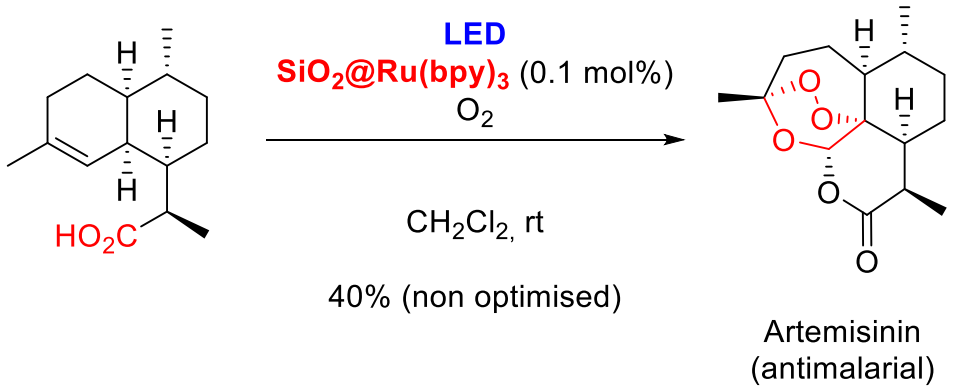

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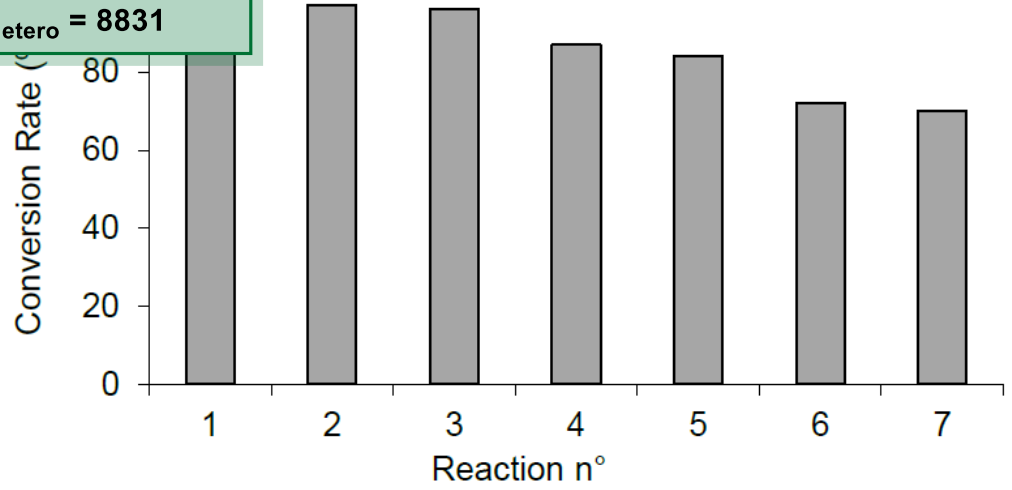
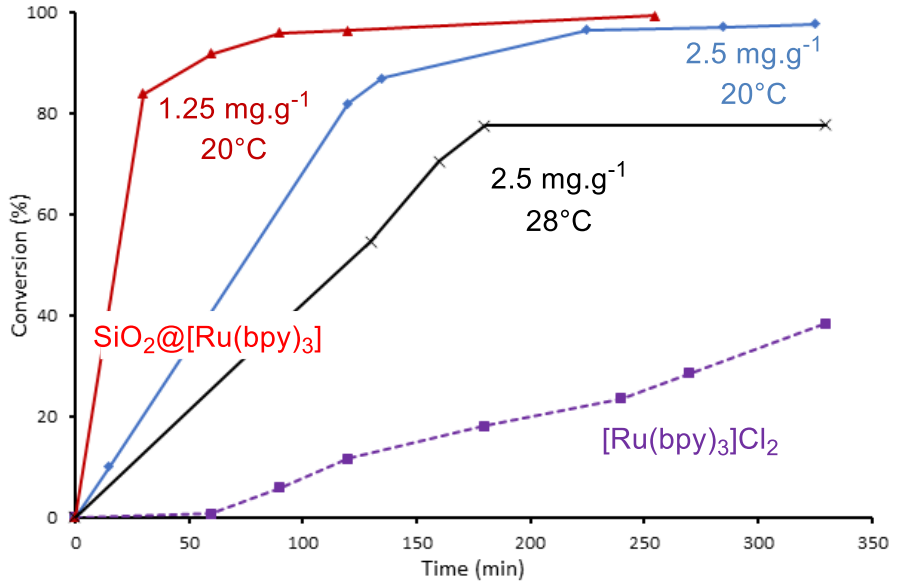
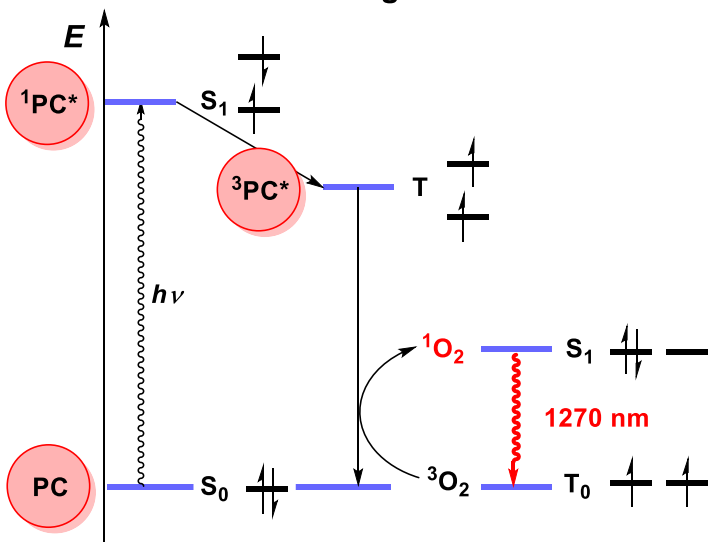




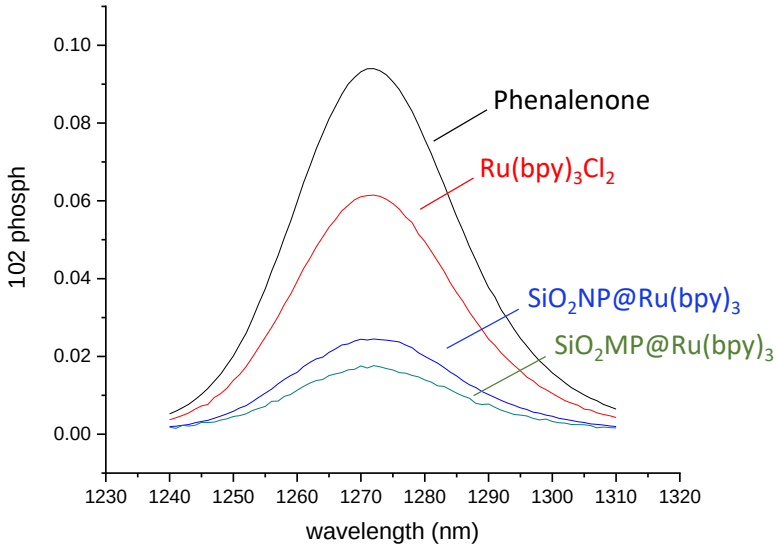
Tambosco, Segura, Seyrig, Cabrera, Port, Ferroud, Amara, *ACS Catal.* **2018**, *8*, 4383-4389

Spectroscopic characterizations

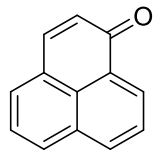
Jablonski Diagram



Experimental measurements

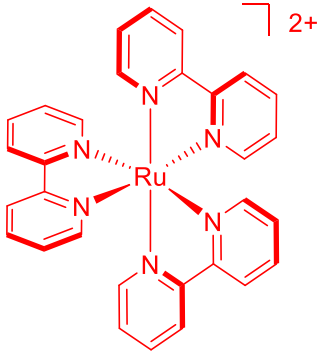


Solvant	τ_Δ
H_2O	4 µs
CH_3CN	81 µs
CH_2Cl_2	99 µs
$scCO_2$	5100 µs



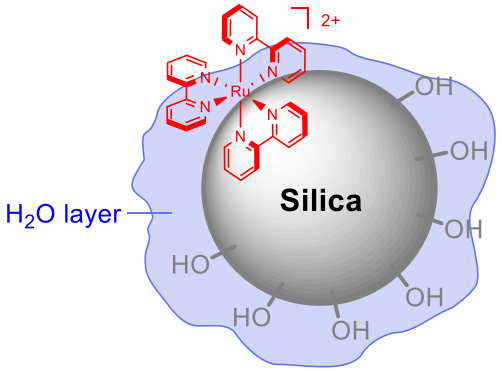
Phenalenone

Φ_Δ = 0.95



Ru(bpy)$_3$Cl$_2$

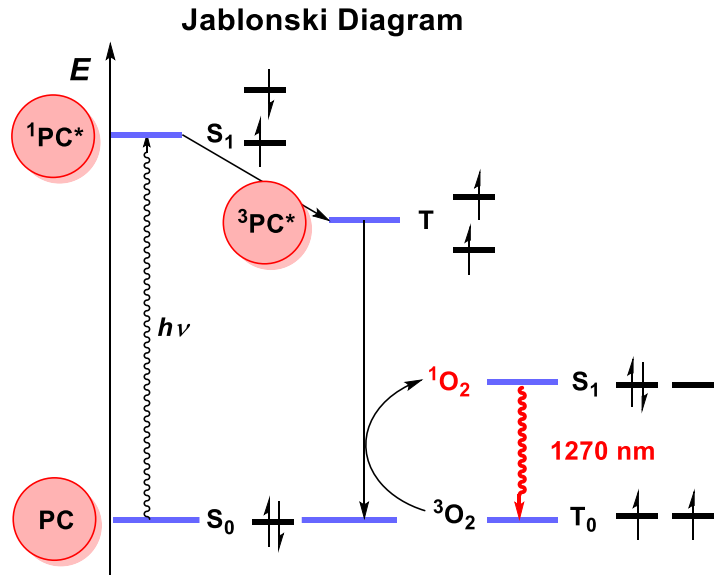
Φ_Δ = 0.62

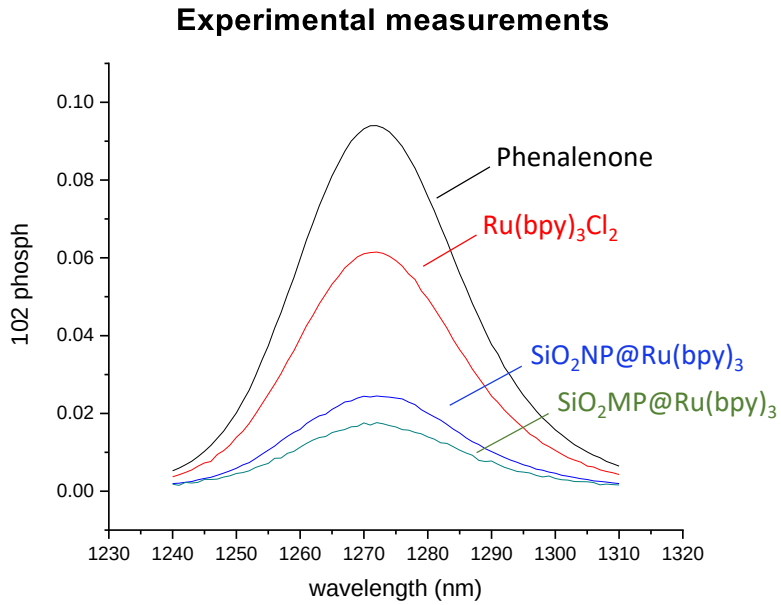


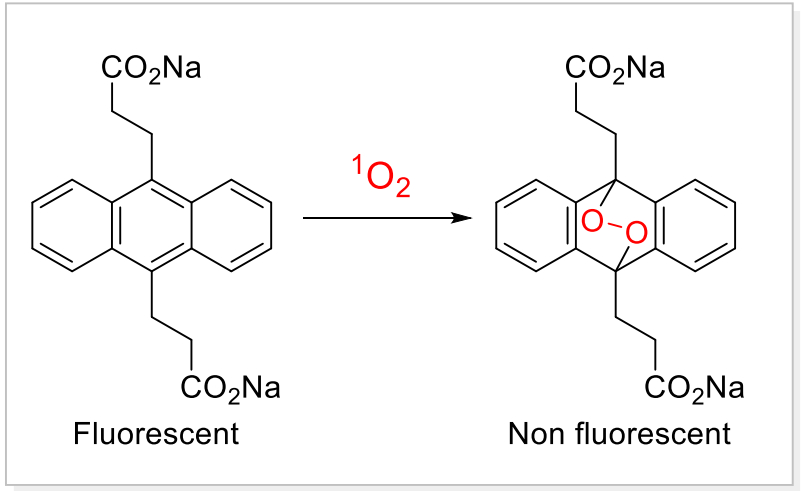
SiO$_2$@Ru(bpy)$_3$Cl$_2$

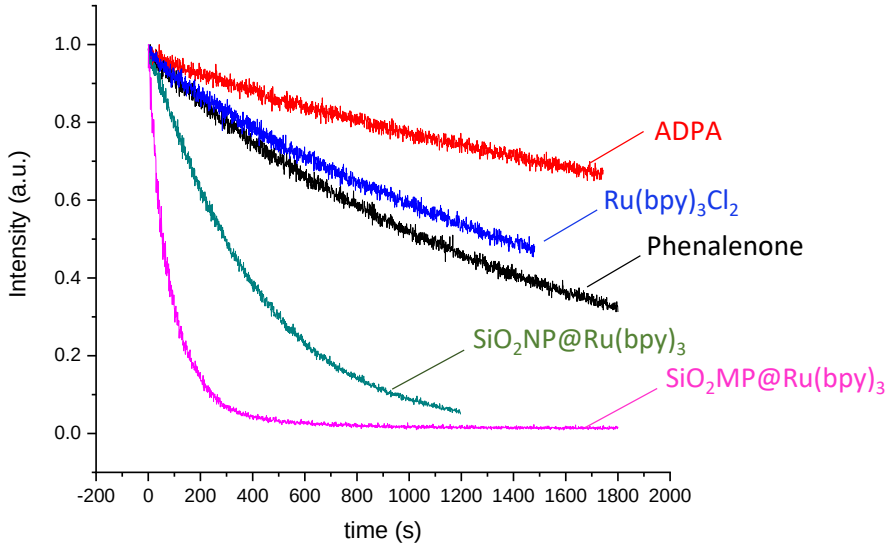
Manuscript under preparation

Spectroscopic characterizations



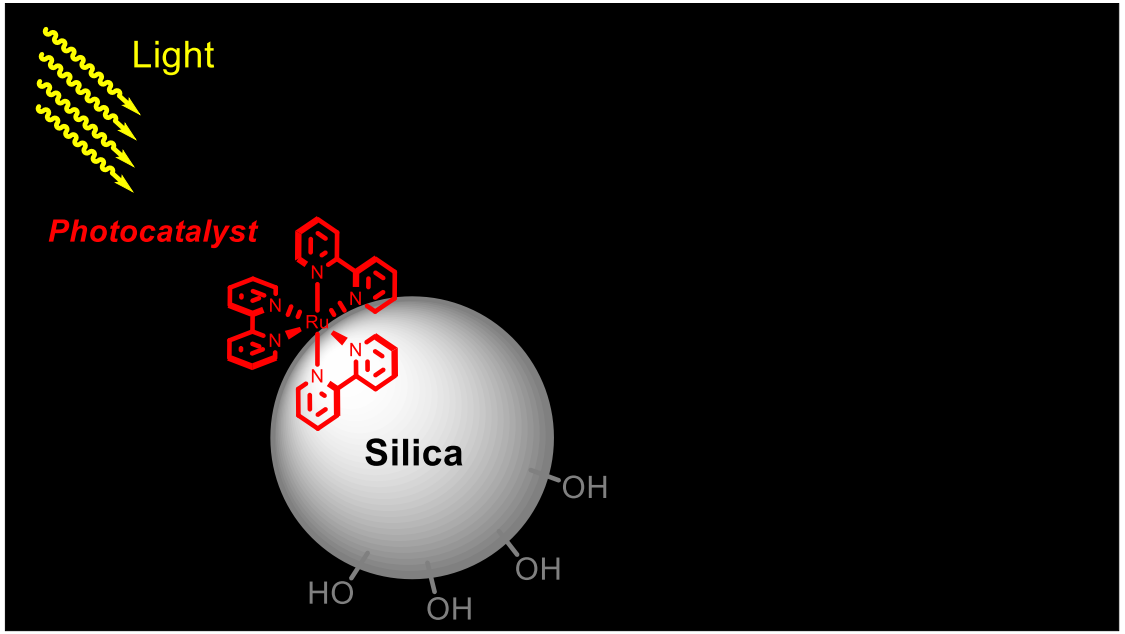






Manuscript under preparation

Mecanistic proposal



Tambosco, Segura, Seyrig, Cabrera, Port, Ferroud, Amara, *ACS Catal.* **2018**, *8*, 4383-4389

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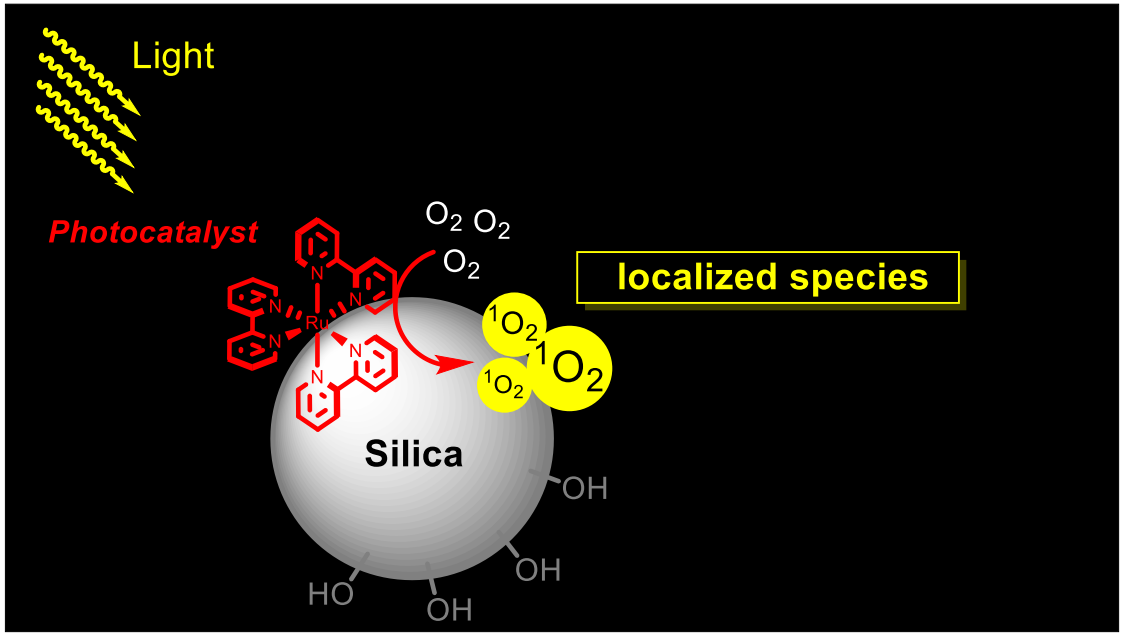

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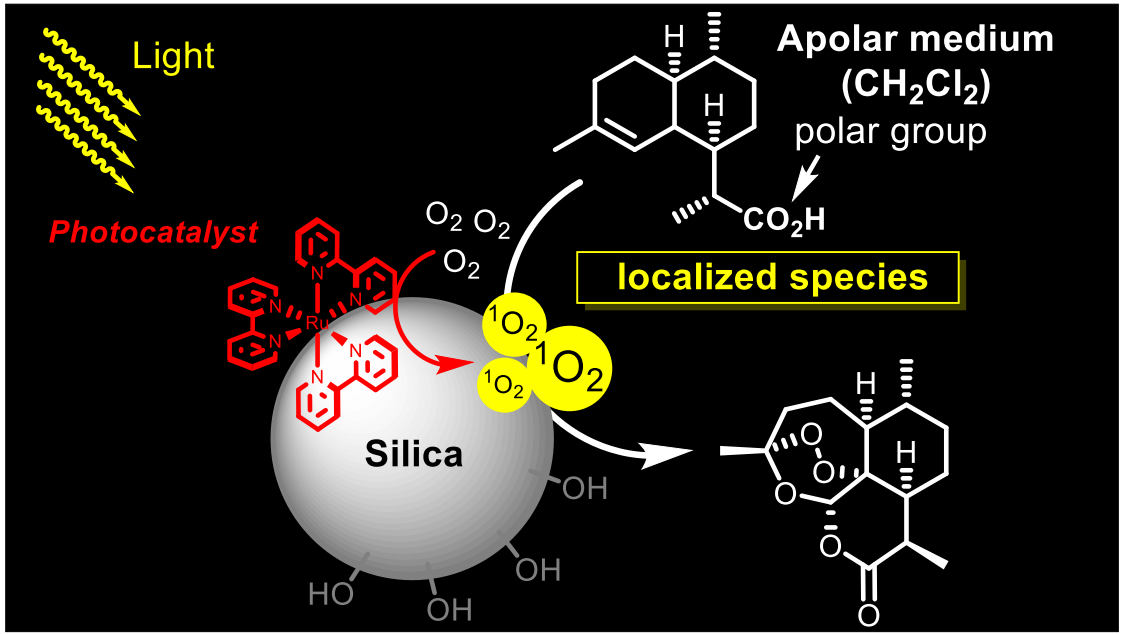

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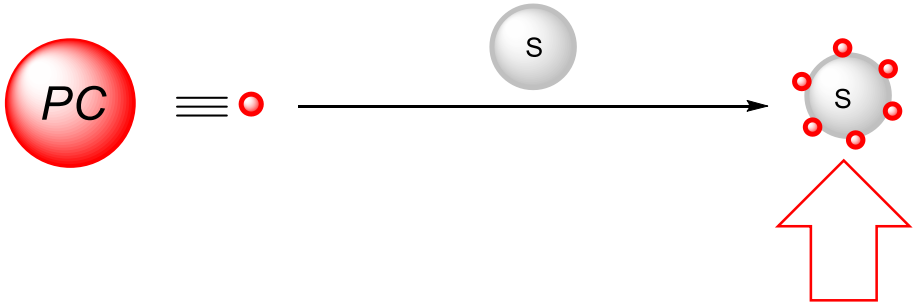
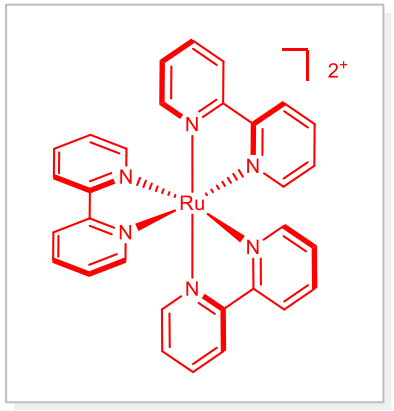
Towards New Synergies

Initial Approach

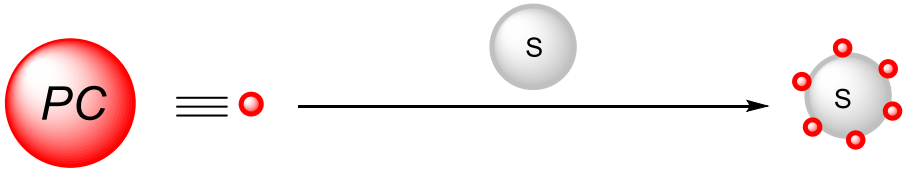


Can we introduce new functionalities?

Towards New Synergies

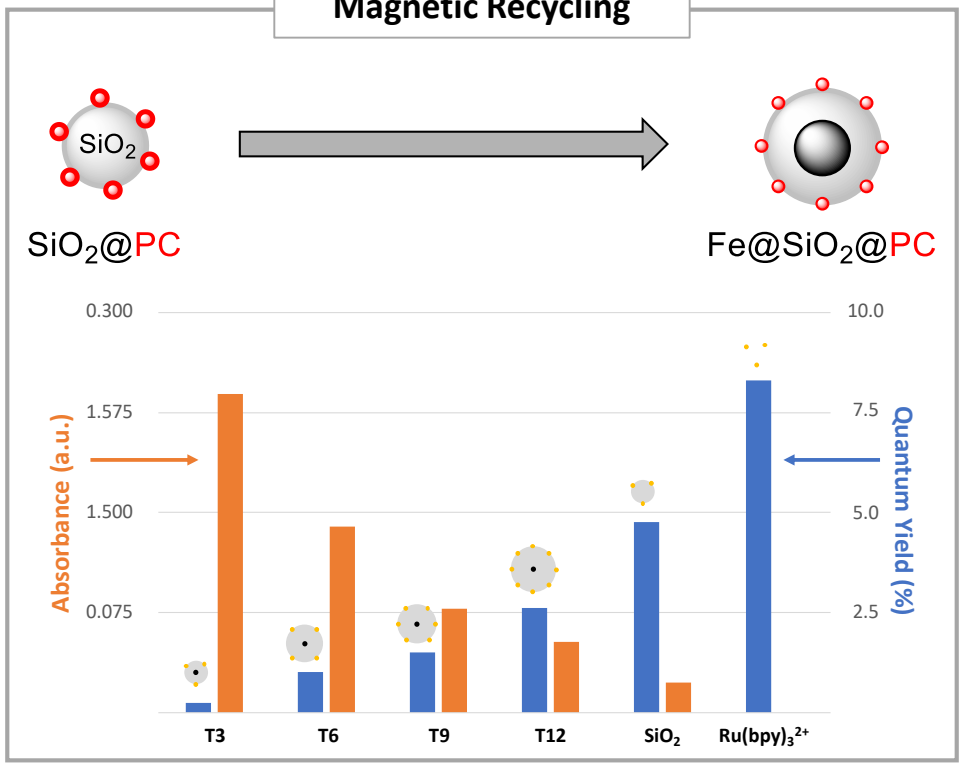


Initial Approach

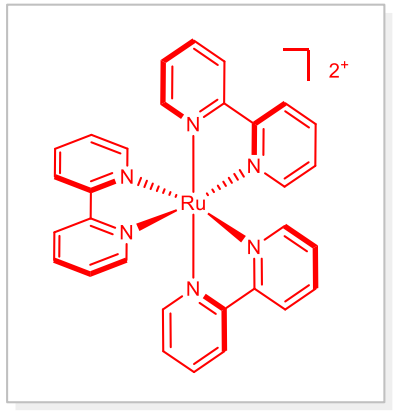


New Approaches

Magnetic Recycling



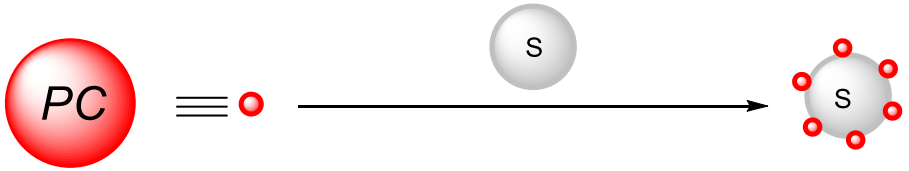
Terra, Desgranges, Monnereau, Sanchez, De Toro, Amara, Moores, *ACS Appl. Mater. Interfaces*, **2020**, *12*, 24895–24904



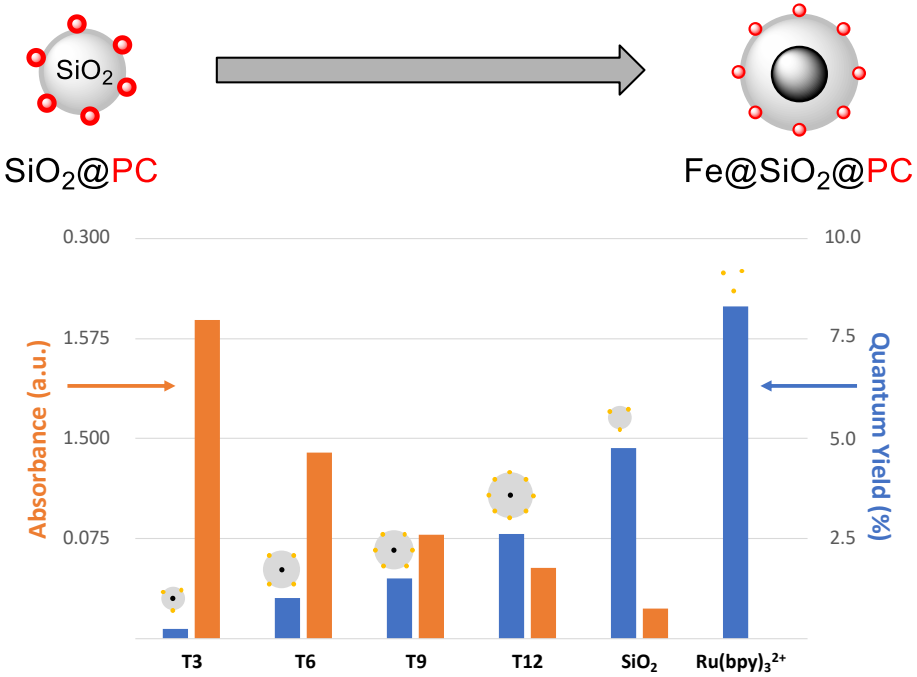
Vers de nouvelles approches nanoparticulaires

McGill

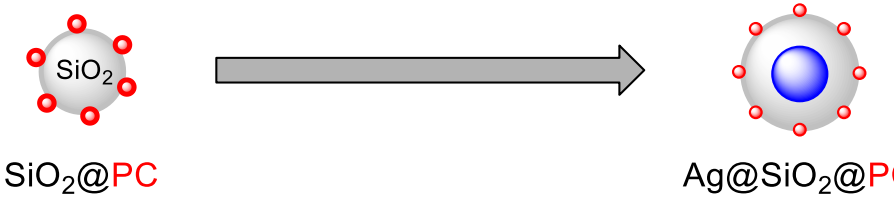
Stratégie initiale



Magnetic Recycling

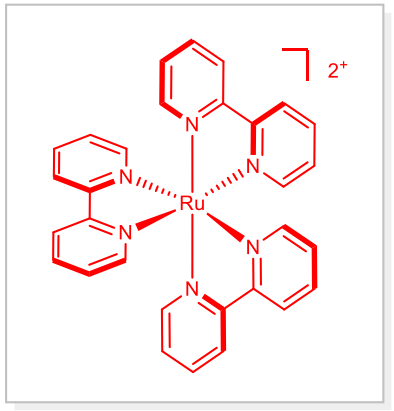


Plasmonic Enhancement

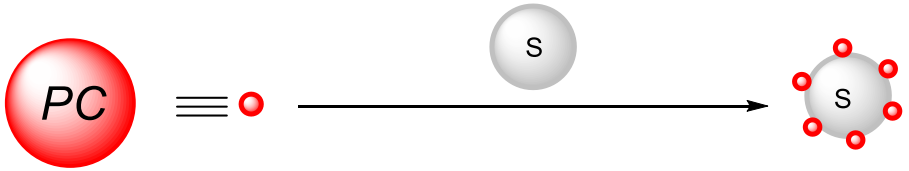


Gellé, Price, Voisard, Brodusch, Gauvin, Amara, Moores, *ACS App. Mat. Interfaces*, **2021**, *13*, 35606-35616

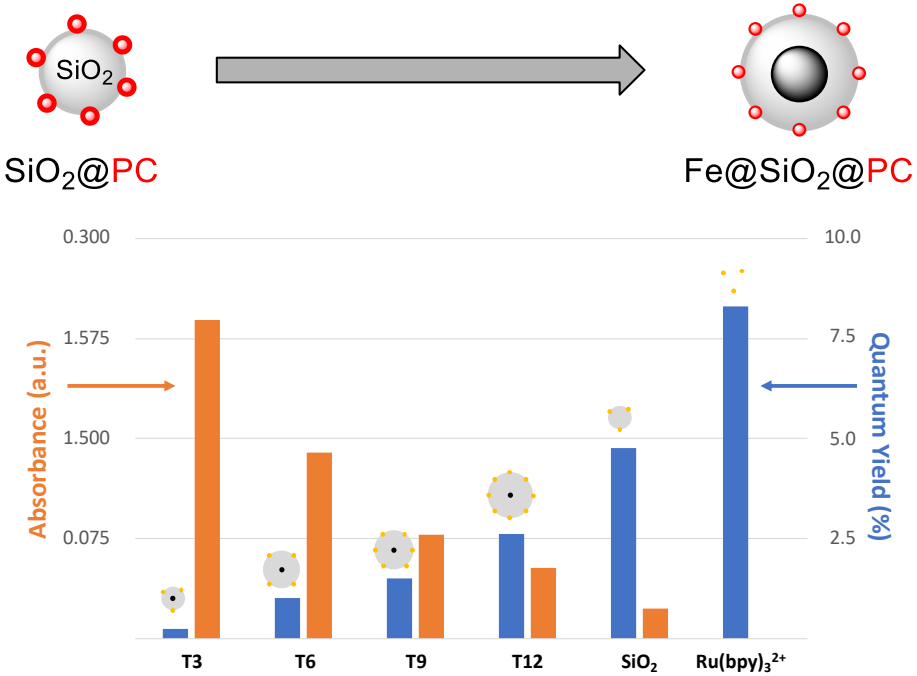
Vers de nouvelles approches nanoparticulaires



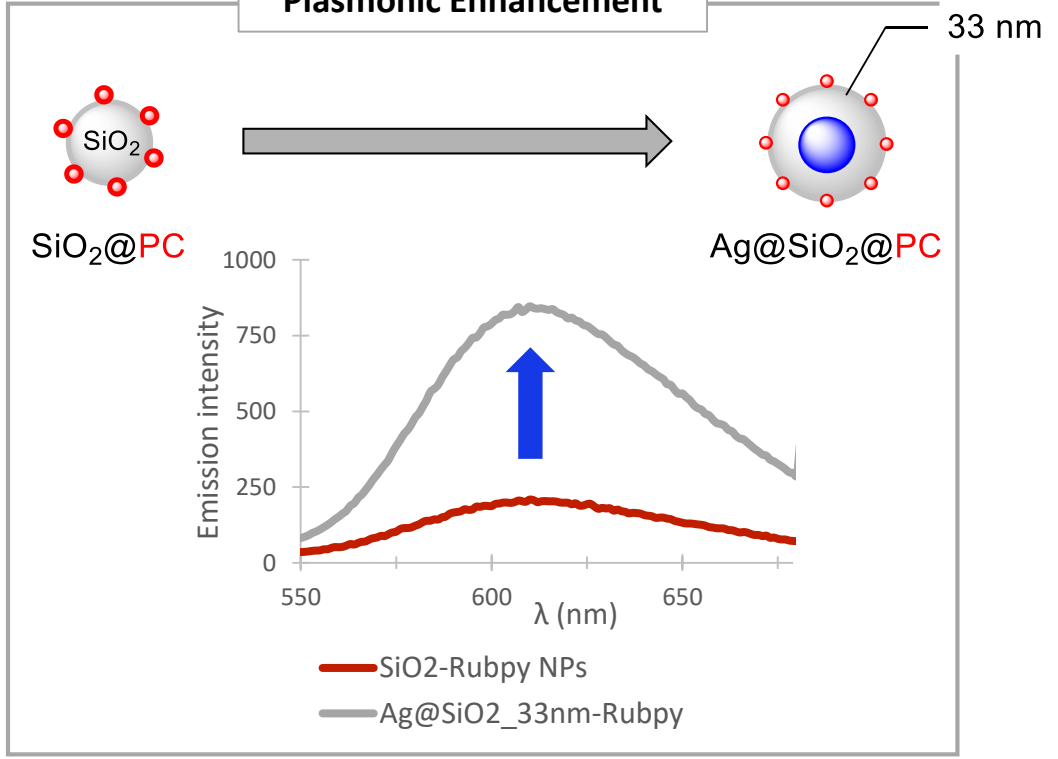
Stratégie initiale



Magnetic Recycling

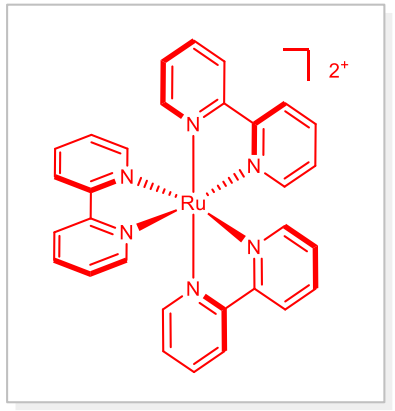


Plasmonic Enhancement

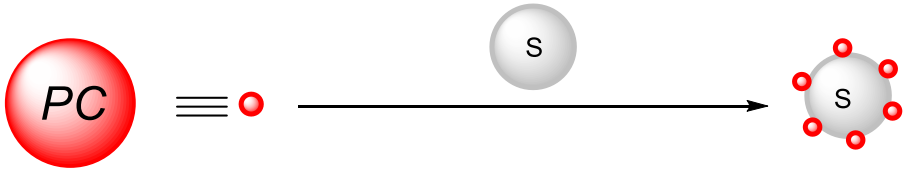


Gellé, Price, Voisard, Brodusch, Gauvin, Amara, Moores, *ACS App. Mat. Interfaces*, **2021**, *13*, 35606-35616

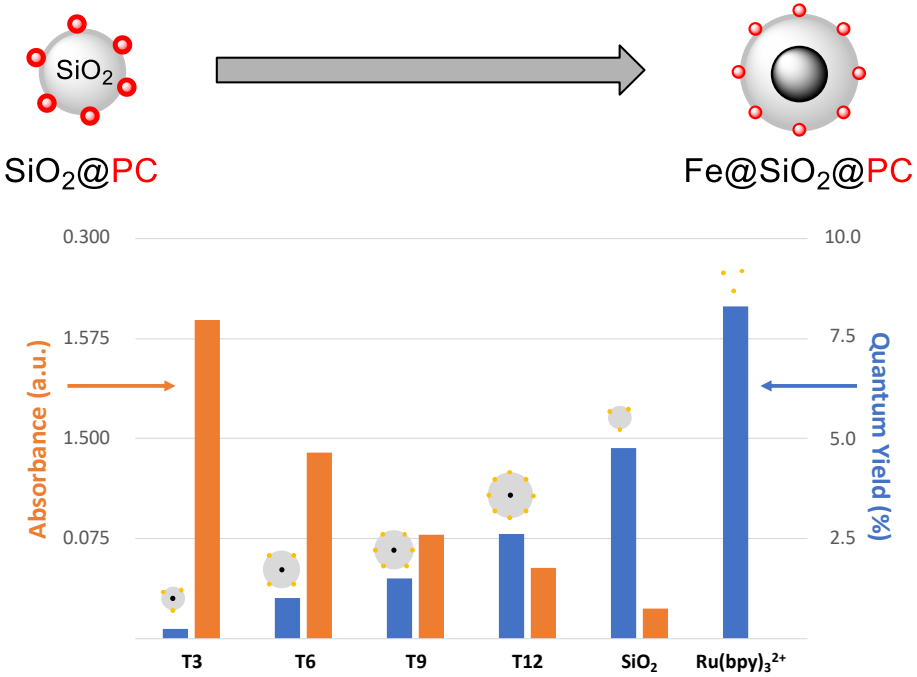
Vers de nouvelles approches nanoparticulaires



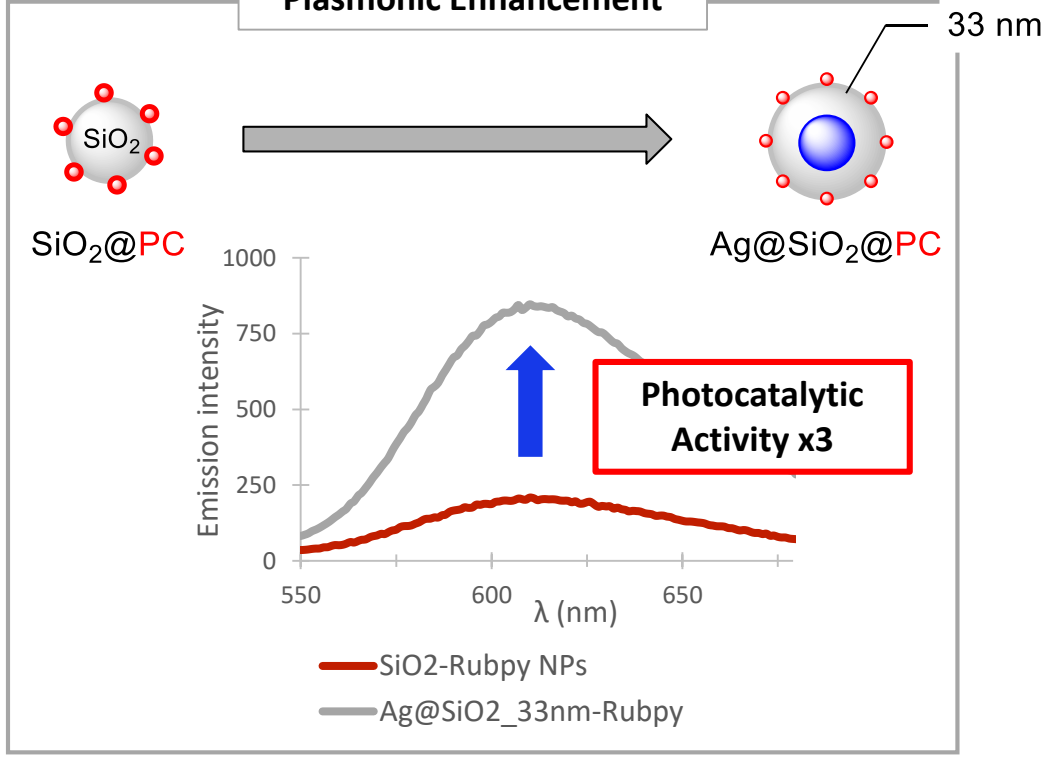
Stratégie initiale



Magnetic Recycling

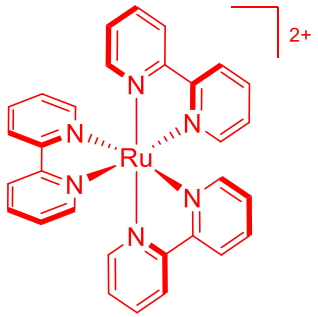


Plasmonic Enhancement

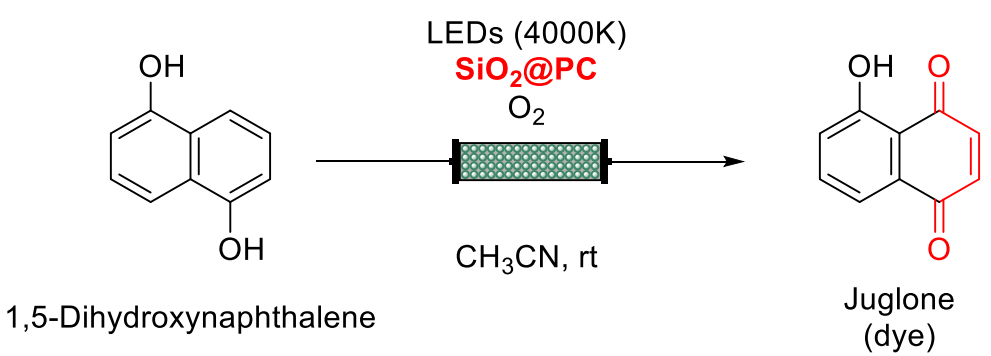


Gellé, Price, Voisard, Brodusch, Gauvin, Amara, Moores, *ACS App. Mat. Interfaces*, **2021**, *13*, 35606-35616

Transposition in Continuous Flow Reactors



$Ru(bpy)_3^{2+}$



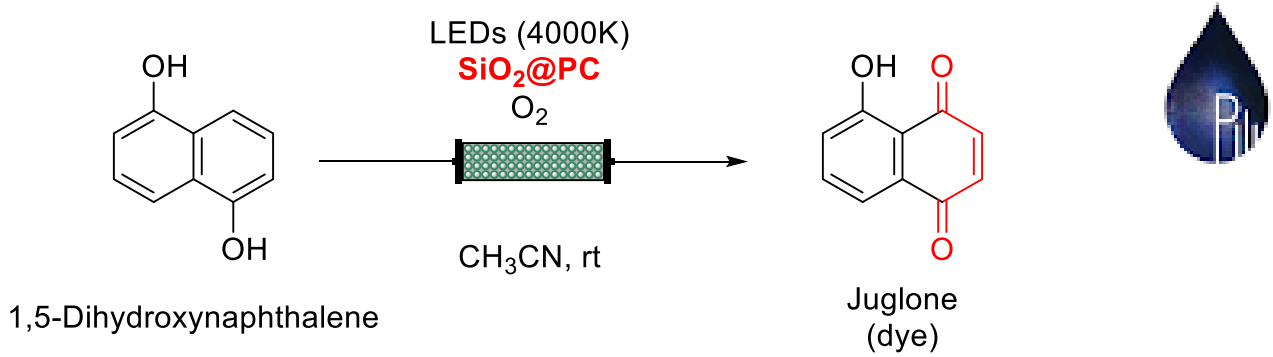
1,5-Dihydroxynaphthalene

Juglone
(dye)

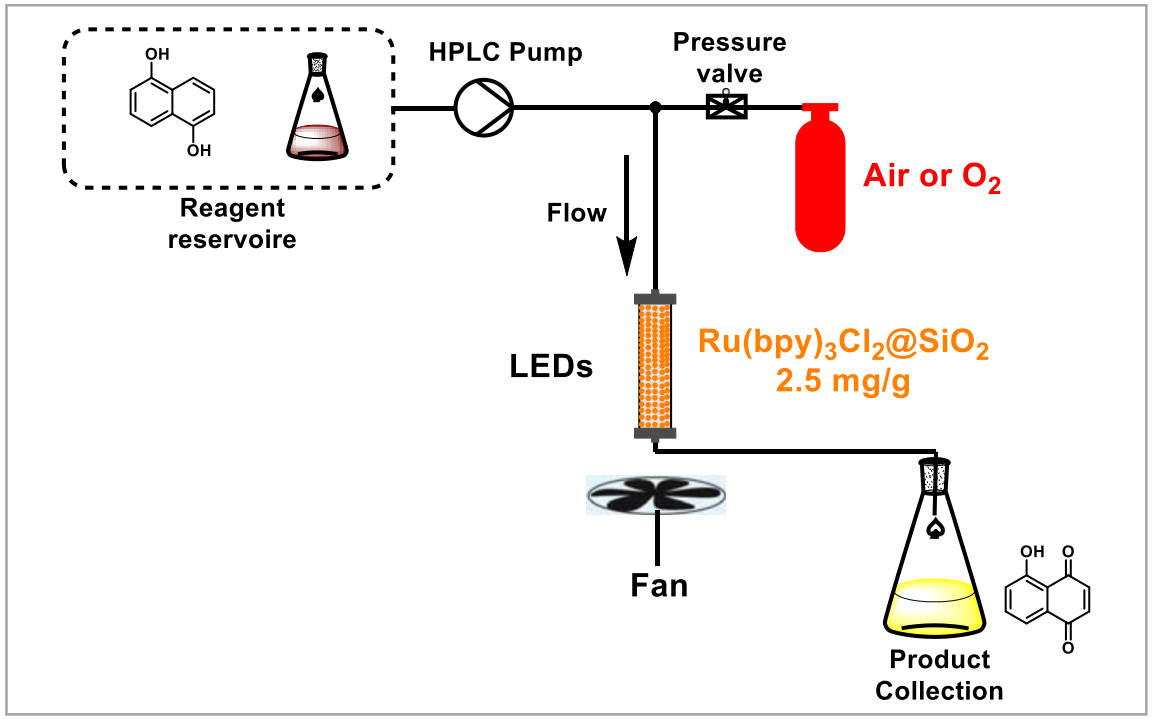
Fixed catalytic bed in a transparent tubing

Blanchard, Asbai, Cottet, Boissonnat, Port, Amara, *Org. Process Res. Dev.*, **2020**, *24*, 822–826 *(Collaboration with PILI)*

Transposition in Continuous Flow Reactors

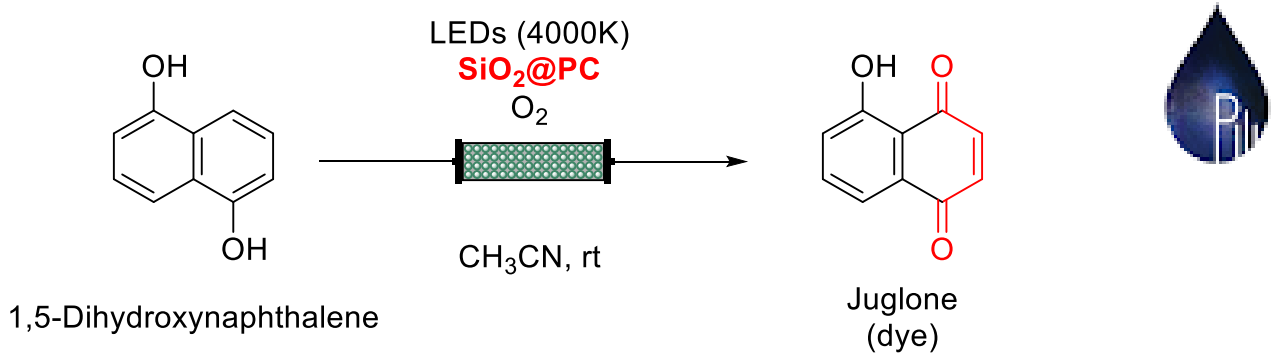


Fixed catalytic bed in a transparent tubing

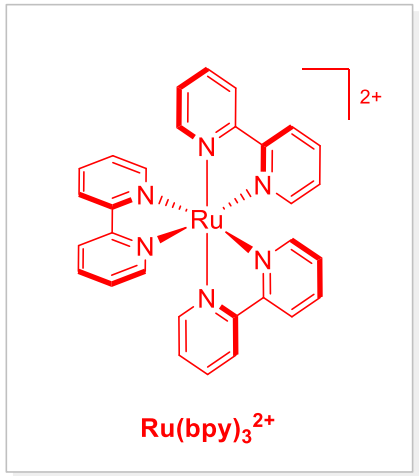


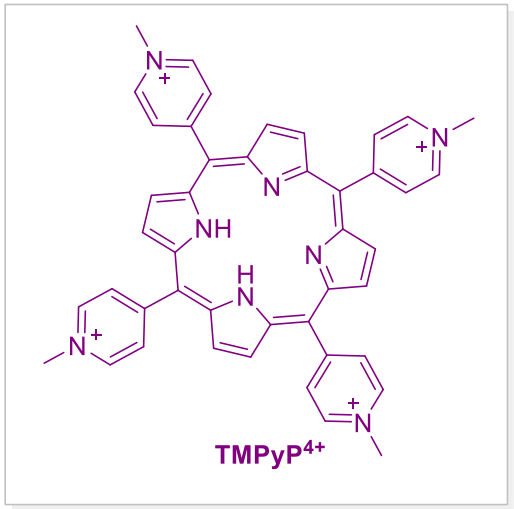
Blanchard, Asbai, Cottet, Boissonnat, Port, Amara, *Org. Process Res. Dev.*, **2020**, *24*, 822–826 *(Collaboration with PILI)*

Transposition in Continuous Flow Reactors



Fixed catalytic bed in a transparent tubing



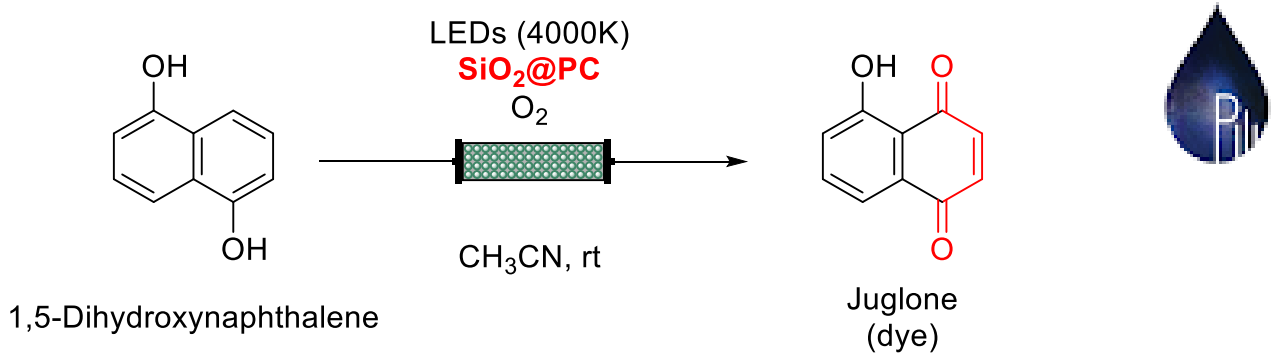


Catalyst	Quantity	Yield (% GC-MS)
$Ru(bpy)_3$	1,3 g	45
TMPyP	1,3 g	77

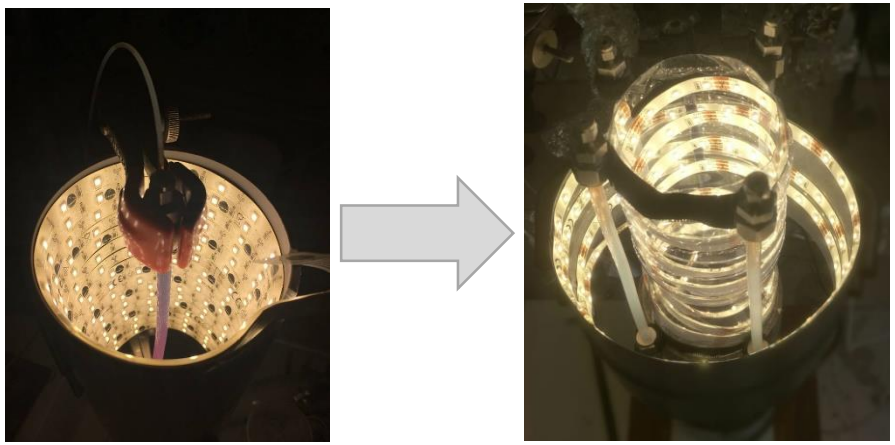
Fixed parameters: Substrate concentration [0,01 M];
Organic flow rate = 0,1 mL·min$^{-1;}$ O_2 flow rate = 0,2 mL·min^{-1}

Blanchard, Asbai, Cottet, Boissonnat, Port, Amara, *Org. Process Res. Dev.*, **2020**, *24*, 822–826 *(Collaboration with PILI)*

Transposition in Continuous Flow Reactors



Fixed catalytic bed in a transparent tubing



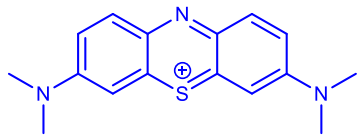
Batch → tTOF ? tTON ? STY **x24** → Flux

Catalyst	Quantity	Yield (% GC-MS)
$Ru(bpy)_3$	1,3 g	45
TMPyP	1,3 g	77
$Ru(bpy)_3$	2,6 g	78
TMPyP	2,6 g	100

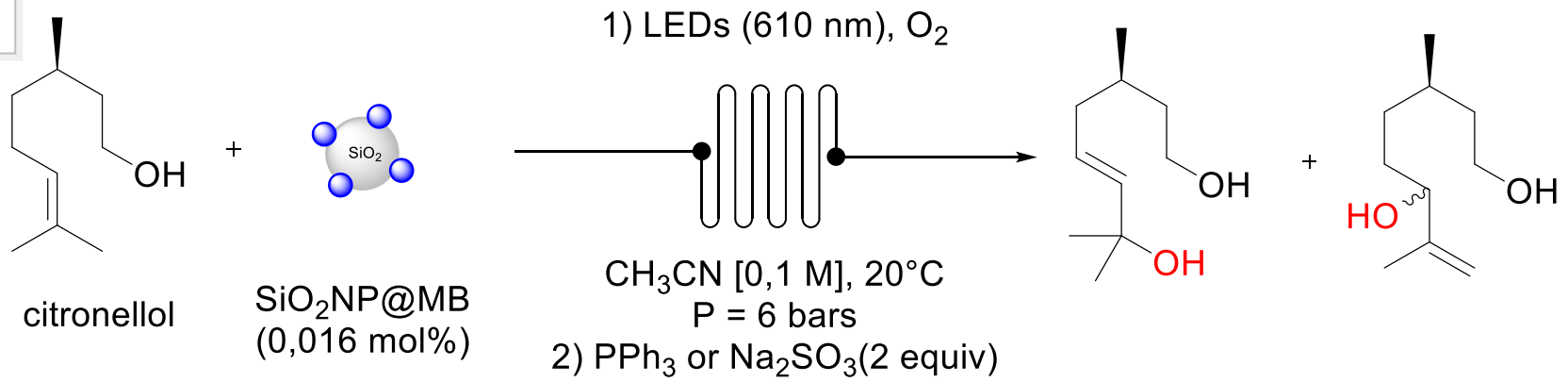
No Catalyst Deactivation after 12h

Fixed parameters: Substrate concentration [0,01 M];
Organic flow rate = 0,1 mL·min$^{-1;}$ O_2 flow rate = 0,2 mL·min^{-1}

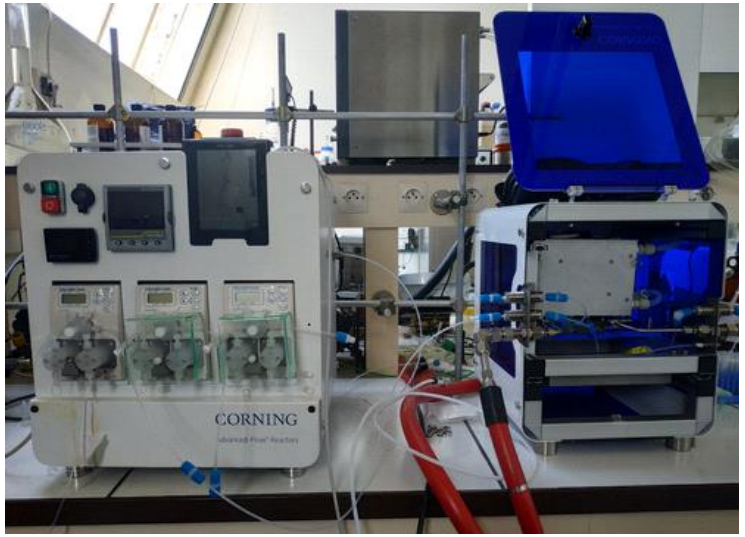
Blanchard, Asbai, Cottet, Boissonnat, Port, Amara, *Org. Process Res. Dev.*, **2020**, *24*, 822–826 *(Collaboration with PILI)*

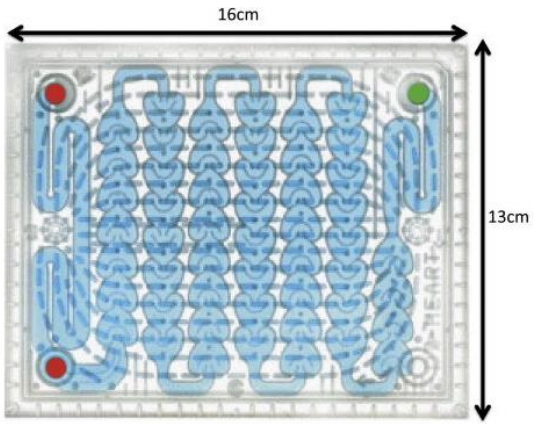


Transposition in Continuous Flow Reactors



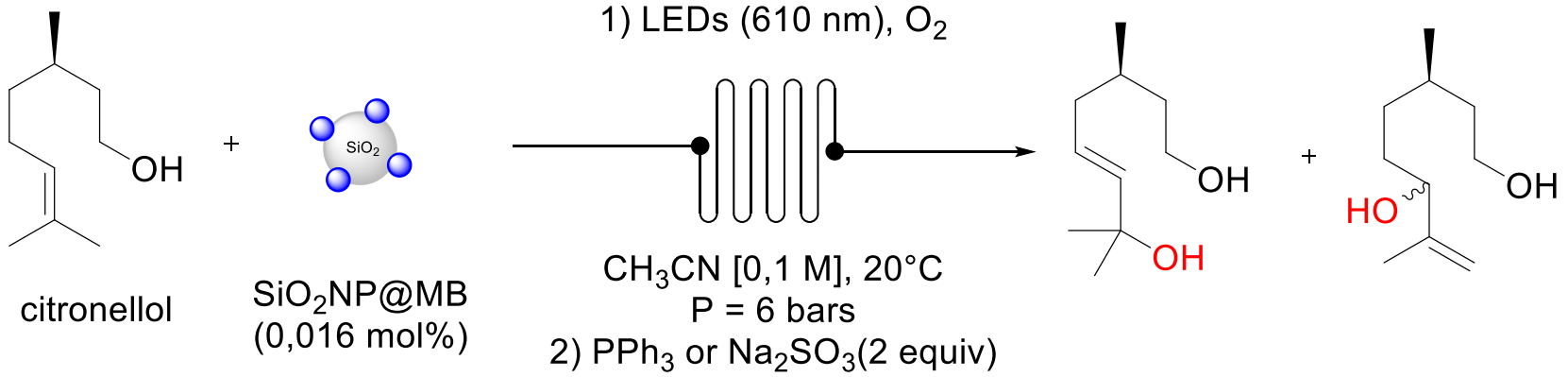
CORNING



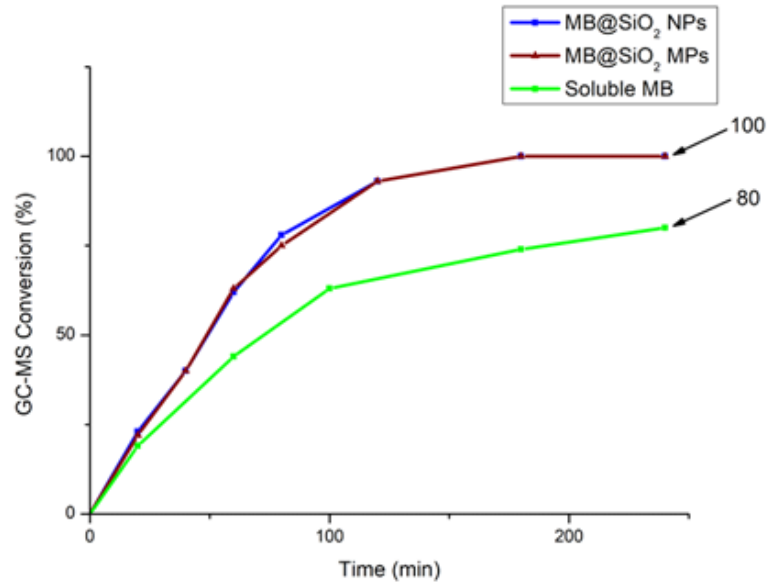


Lancel, Gomez, Port, Amara, *Front. Chem. Eng.*, **2021**, *3*, 752364 *(Collaboration with Corning)*

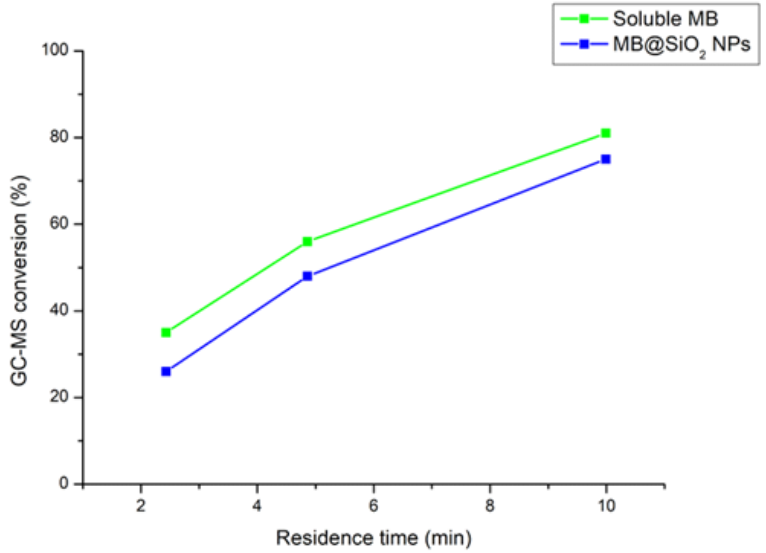
Transposition in Continuous Flow Reactors



Batch reactor



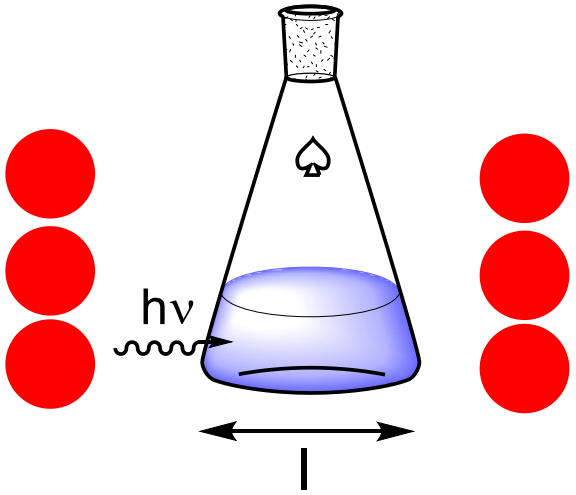
Flow reactor



Lancel, Gomez, Port, Amara, *Front. Chem. Eng.*, **2021**, *3*, 752364 *(Collaboration with Corning)*

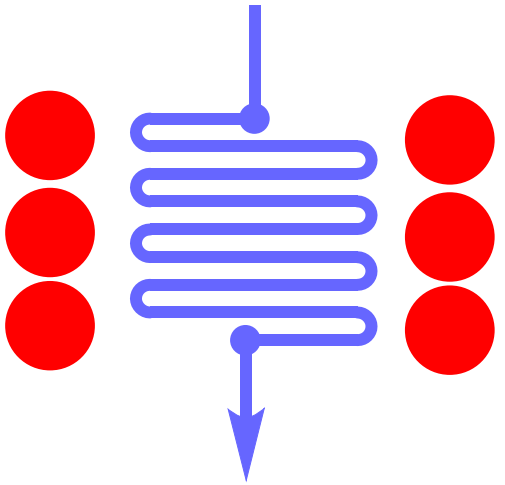
Transposition in Continuous Flow Reactors

Batch photochemical process



- Long residence time
- Longer exposition to light
- Higher PC deactivation
- **Performances $Mb_{supported} > MB_{homogeneous}$**

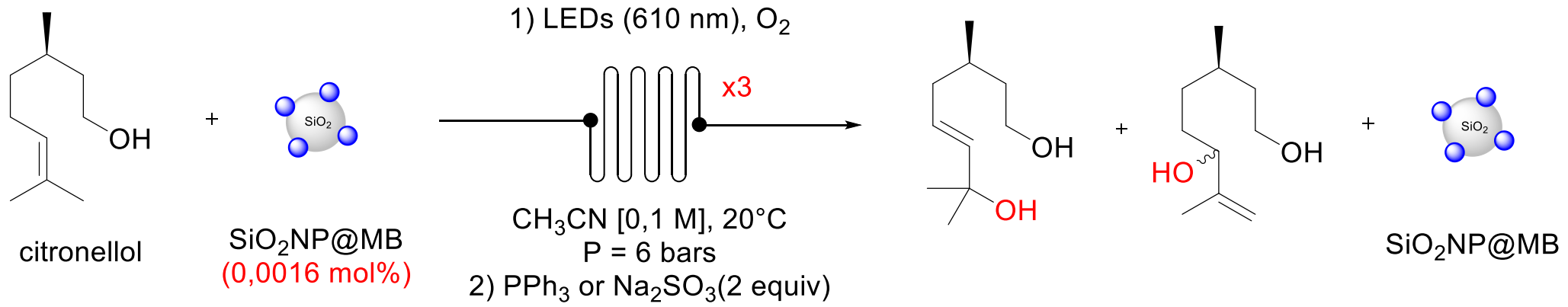
Flow photochemical process



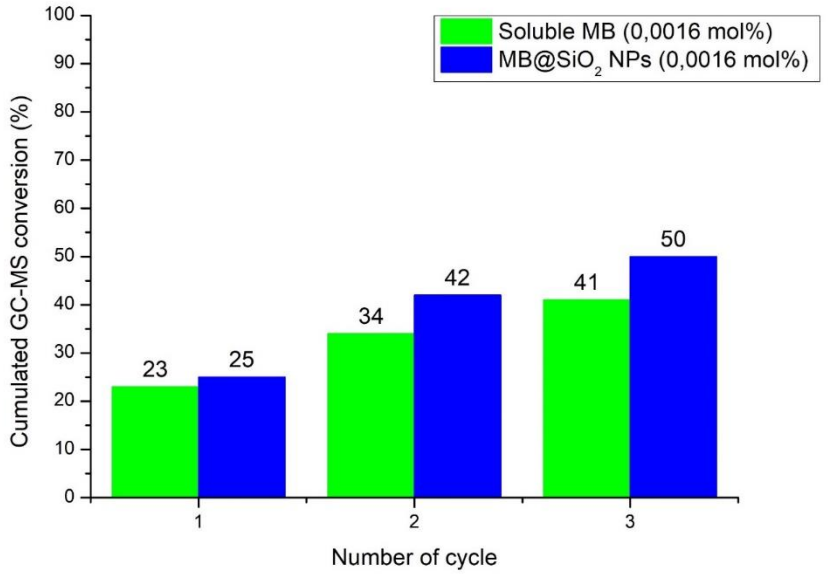
- Short residence time
- Shorter exposure to light
- PC deactivation is no longer a limiting factor
- **Performances $MB_{supported} < MB_{homogeneous}$**

Lancel, Gomez, Port, Amara, *Front. Chem. Eng.*, **2021**, *3*, 752364 *(Collaboration with Corning)*

Transposition in Continuous Flow Reactors



Stressed Catalytic Conditions

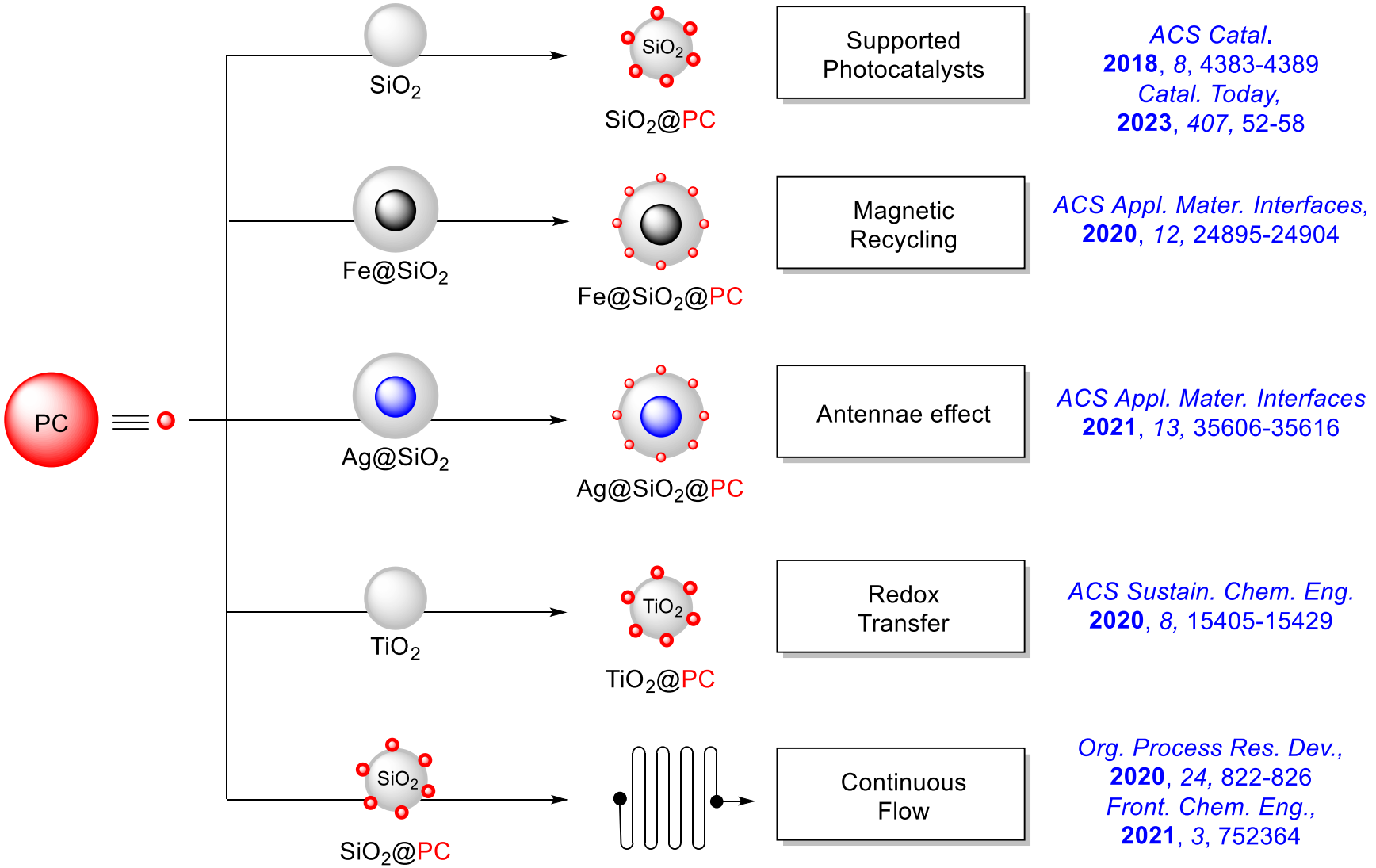


Batch → tTOF x3, tTON x5, STY x14 → Flux

- Short residence time
- Shorter exposure to light
- **PC deactivation is a limiting factor**
- **Performances $MB_{supported}$ > $MB_{homogeneous}$**

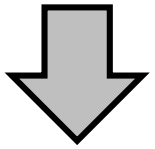
Lancel, Gomez, Port, Amara, *Front. Chem. Eng.*, **2021**, *3*, 752364 *(Collaboration with Corning)*

Conclusions

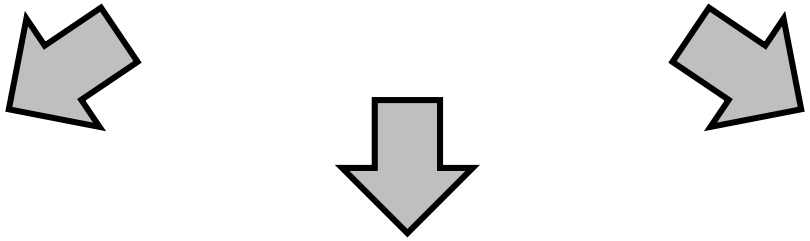


Research Projects @ Cnam

Focus on Green Chemistry



More Environmentally Friendly Photochemical Processes

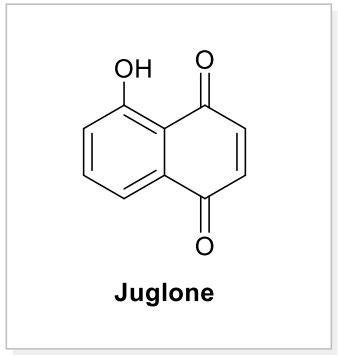


Design of Recyclable Photocatalytic Systems

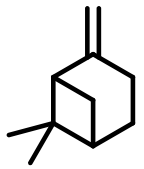
Study of New Photocatalysts

Investigation of New Photochemical Routes

Juglone: an Environmentally Benign Photocatalyst



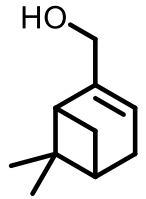
Walnuts (*Juglans nigra)*
"le brou de noix"



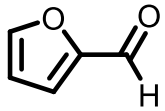
β-pinène

1) **Juglone (0.5 mol%)**
460 nm, 6 hours
CH_3CN [0.02 M], O_2

2) Reduction

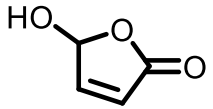


Yield: 56 %

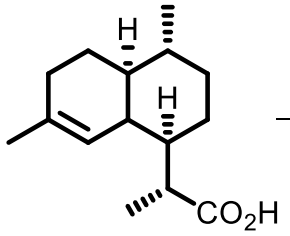


Furfural

Juglone (0.5 mol%)
460 nm, 6 hours
EtOH [0.02 M], O_2

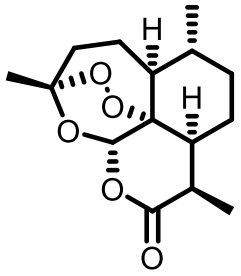


Yield: 75 %



Dihydroartemisinic acid

Juglone (1 mol%)
460 nm, 6 hours
CH_3CN [0.01 M], O_2, TFA



Artemisinine
Yield: 25 %
(Unoptimised)
Industrial Yield: 50 %

Lancel, Zimberlin, Gomez, Port, Khrouz, Monnereau, Amara, *Manuscript under revision*

Research Projects @ Cnam

Focus on Green Chemistry

More Environmentally Friendly Photochemical Processes

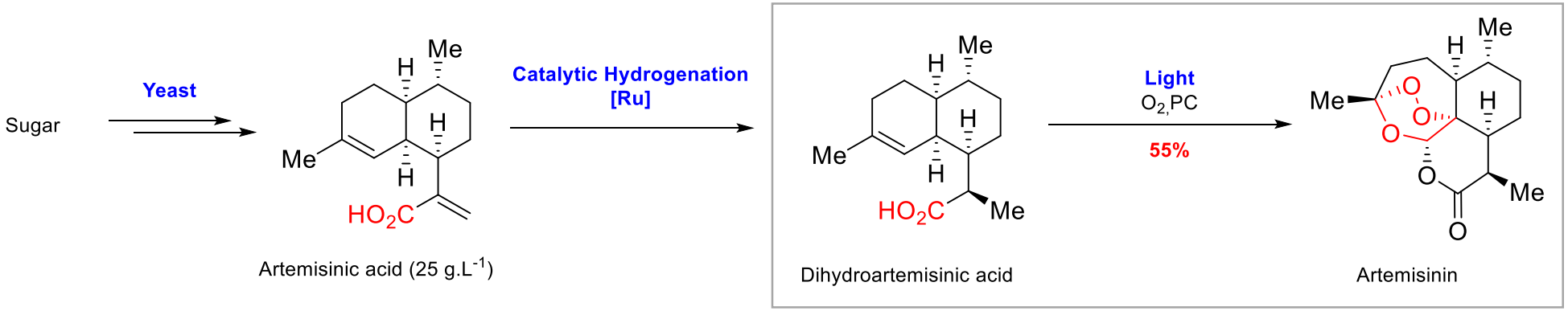
Design of Recyclable Photocatalytic Systems

Study of New Photocatalysts

Investigation of New Photochemical Routes

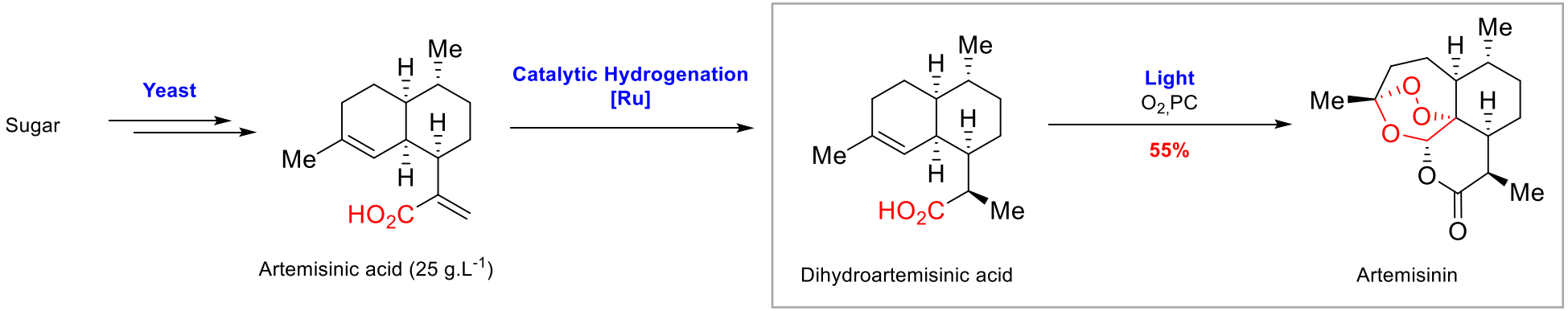
Artemisinin Production : Challenge and Inspiration

Sanofi/Amyris Process - 50 tons/year



Artemisinin Production : Challenge and Inspiration

Sanofi/Amyris Process - 50 tons/year

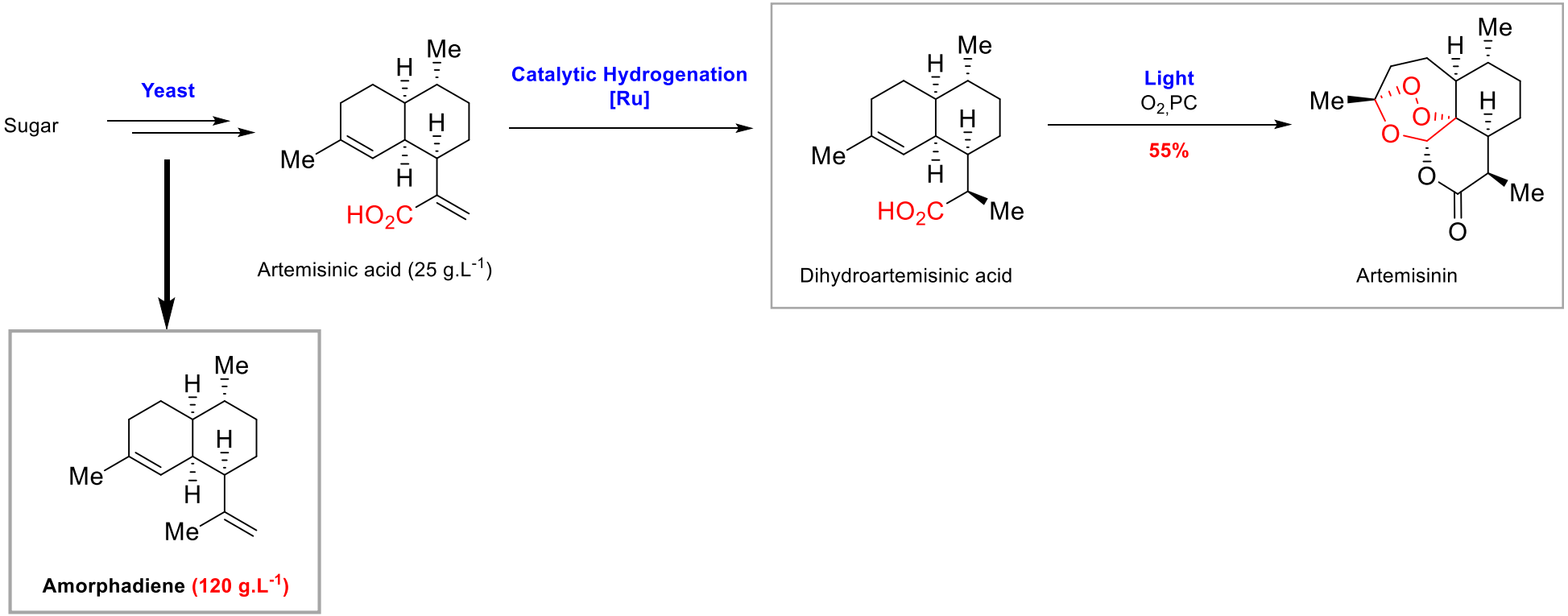


How to really decrease costs?

Start from Cost-Competitive Starting Material

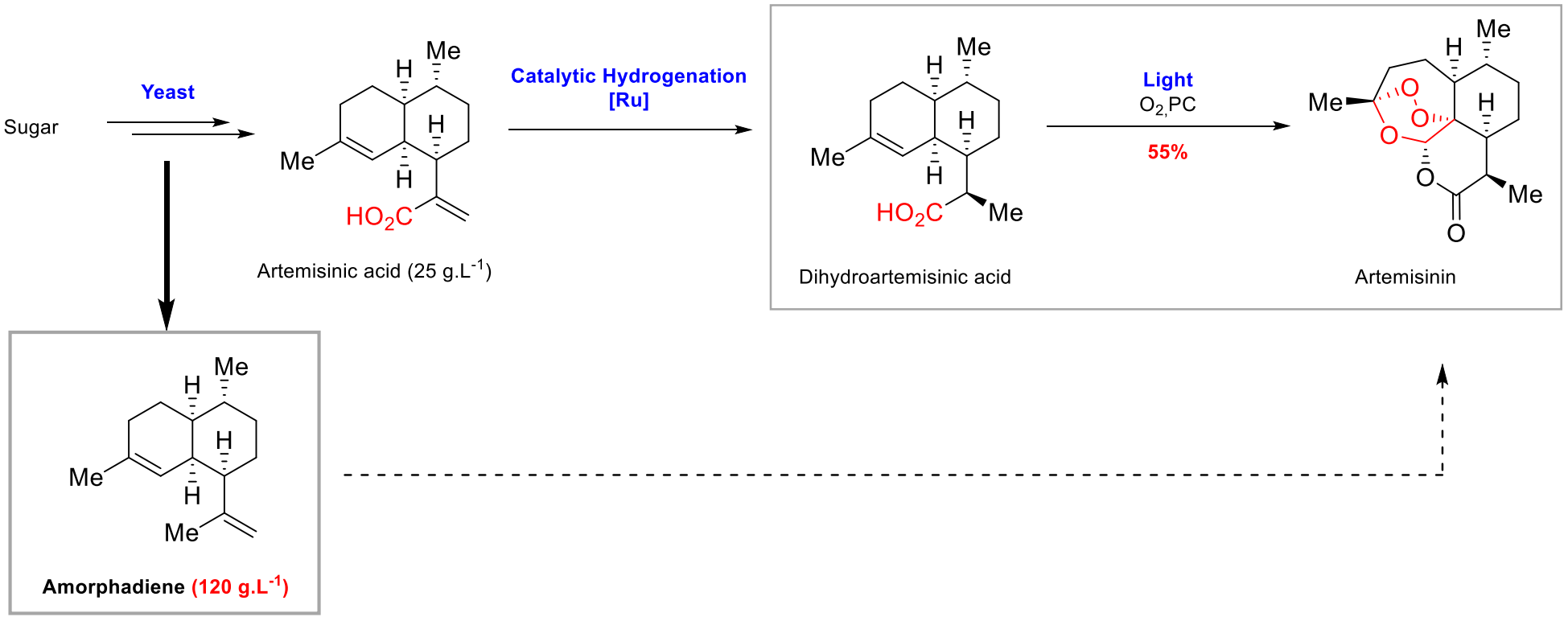
Artemisinin Production : Challenge and Inspiration

Sanofi/Amyris Process - 50 tons/year

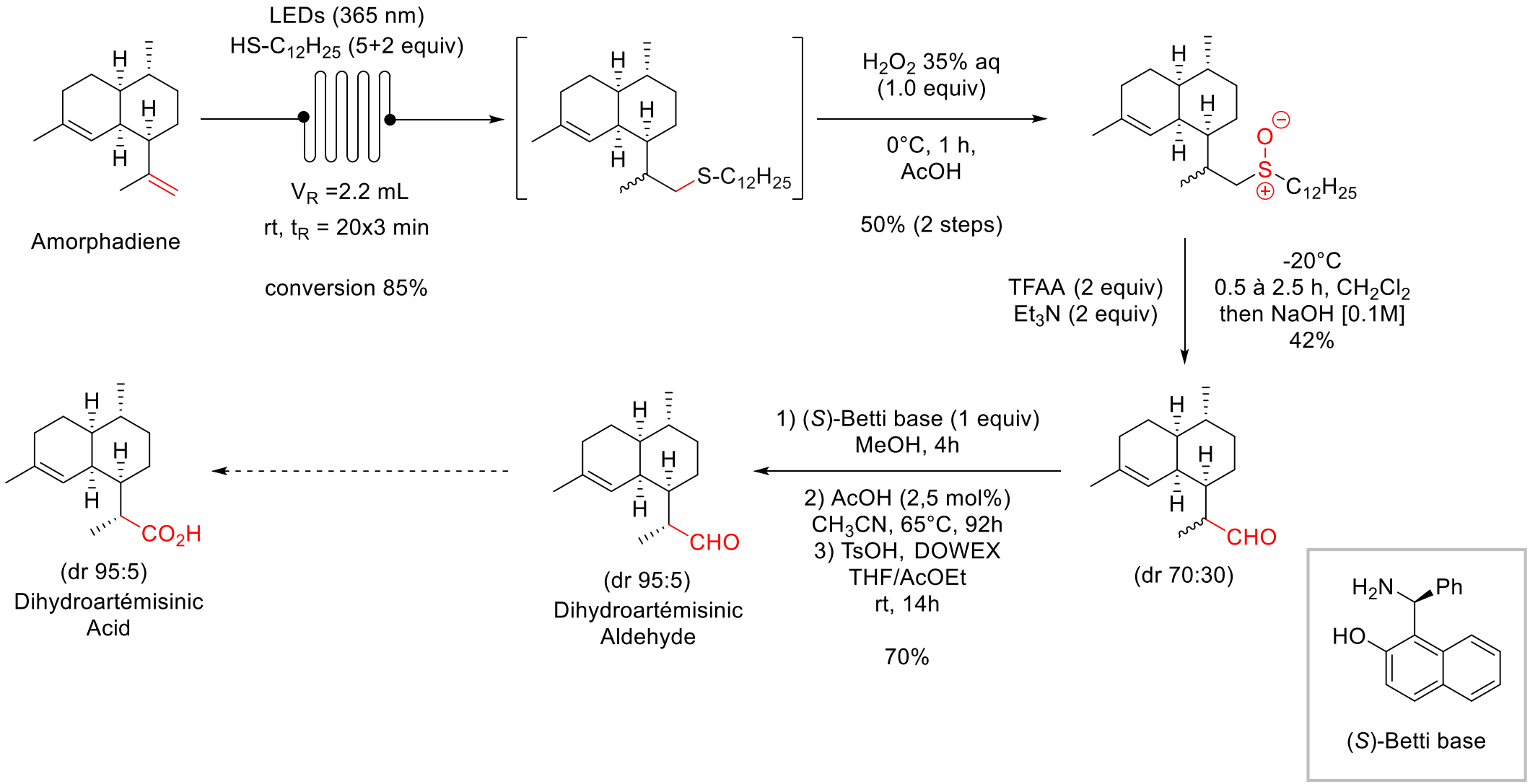


Artemisinin Production : Challenge and Inspiration

Sanofi/Amyris Process - 50 tons/year



Application to a Telescoped Process



Gomez Fernandez, Nascimento de Oliveira, Zanetti, Schwertz, Cossy, Amara, *Org.Lett.* **2021**, *23*, 5593-5598

Zanetti, Chaumont-Olive, Schwertz, Nascimento de Oliveira, Gomez Fernandez, Amara, Cossy, *Org. Process Res. Dev.*, **2020**, *24*, 850–855

Research Projects @ Cnam

Focus on Green Chemistry

More Environmentally Friendly Photochemical Processes

Design of Recyclable Photocatalytic Systems

Study of New Photocatalysts

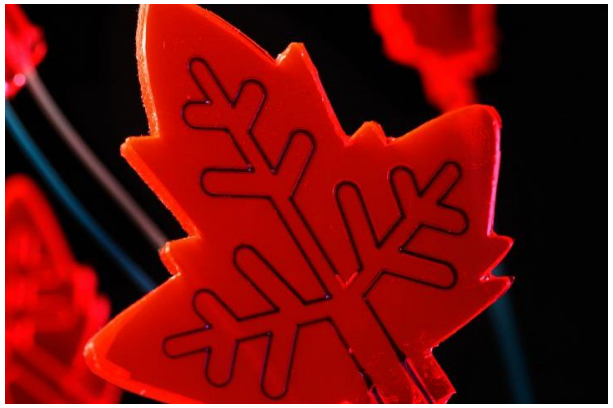
Investigation of New Photochemical Routes

Photochemistry

“Allgemeine Photochemie” 1936

Plotnikow predicted that photochemical syntheses on an industrial scale would be limited to a few special cases, i.e. to the production of particularly expensive specialties. He justified this statement by pointing out that light reactions generally require irradiation of large surface areas which would incur very high costs. In Plotnikow’s opinion, a tree is an ideal photochemical factory; its leaves present a maximum absorption area for a minimum volume. He urgently warned against any, necessarily imperfect, imitation of Nature.

Fisher, Industrial Applications of Photochemical Syntheses, *Angew. Chem. Int. Ed.* **1978**, *17*, 16-26



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