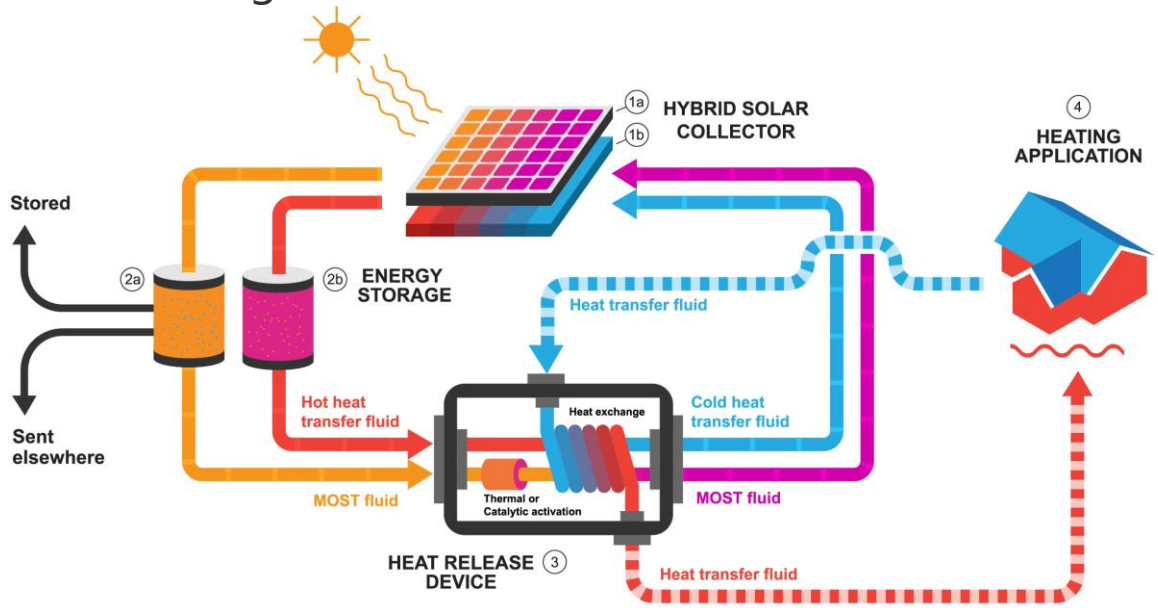
Original Heteroaryl Azobenzenes Anchored on Peptoids As Solar Thermal Fuel

Gwendal Henrard, Thomas Robert, Benjamin Tassignon, Ari Serez, Julien De Winter, Jérôme Cornil, Pascal Gerbaux

gwendal.henrard@umons.ac.be



SRC Young Chemists' Day 2024
Monday 17th May 2024

UMONS Université de Mons

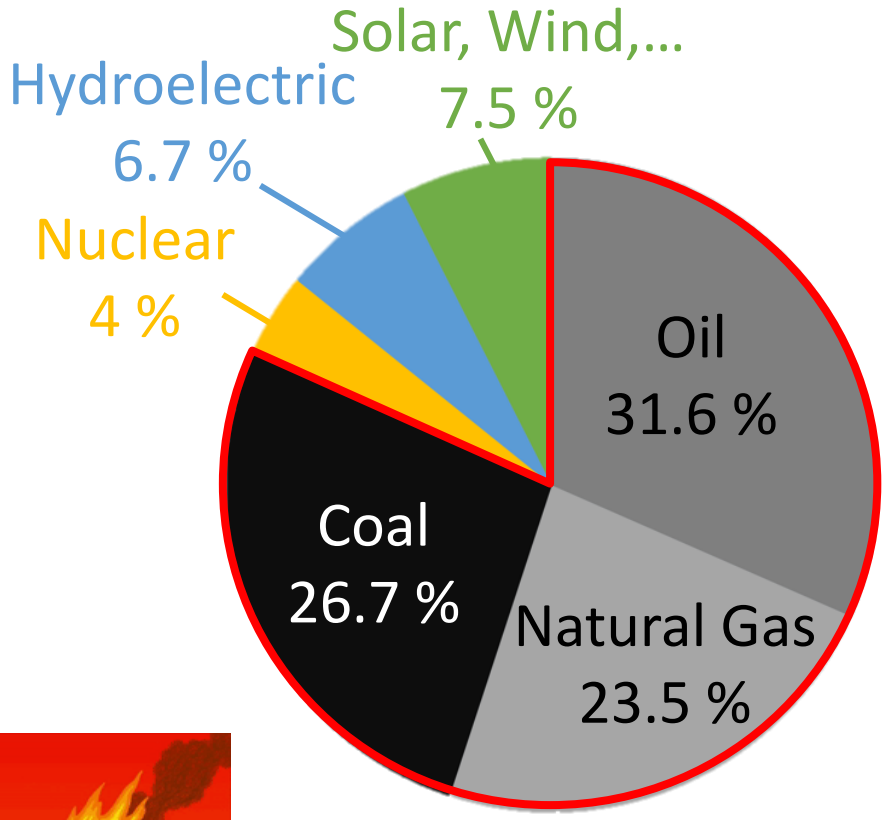
Faculté des Sciences

S²MOs

K, V. Mikkelsen (2023) "Searching the Chemical Space of Bicyclic Dienes for Molecular Solar Thermal Energy Storage Candidates

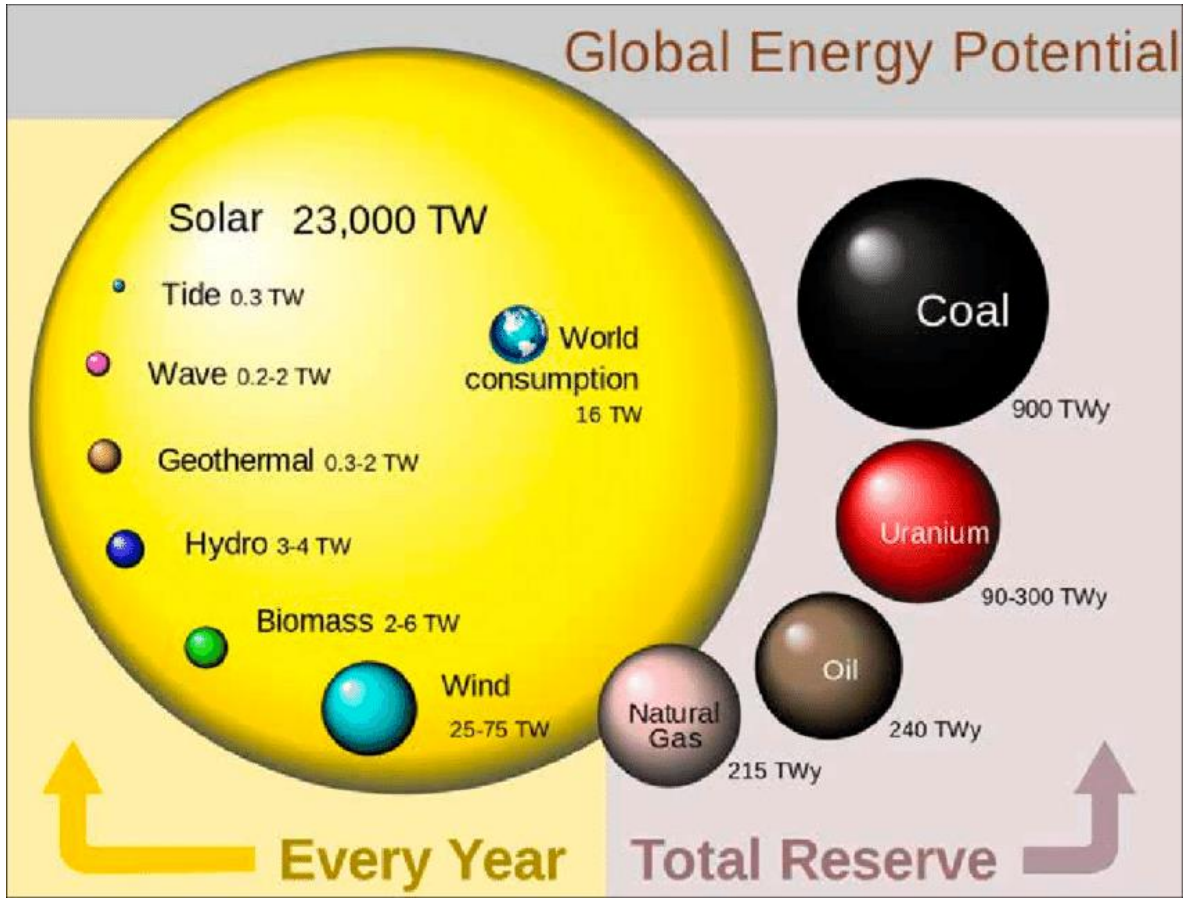
The one with energy issues

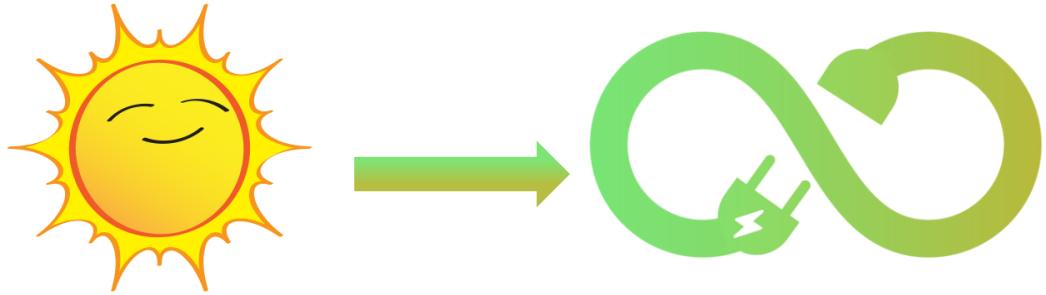
Primary global energy consumption 2022



82 % Fossil fuels

CO_2 Increases

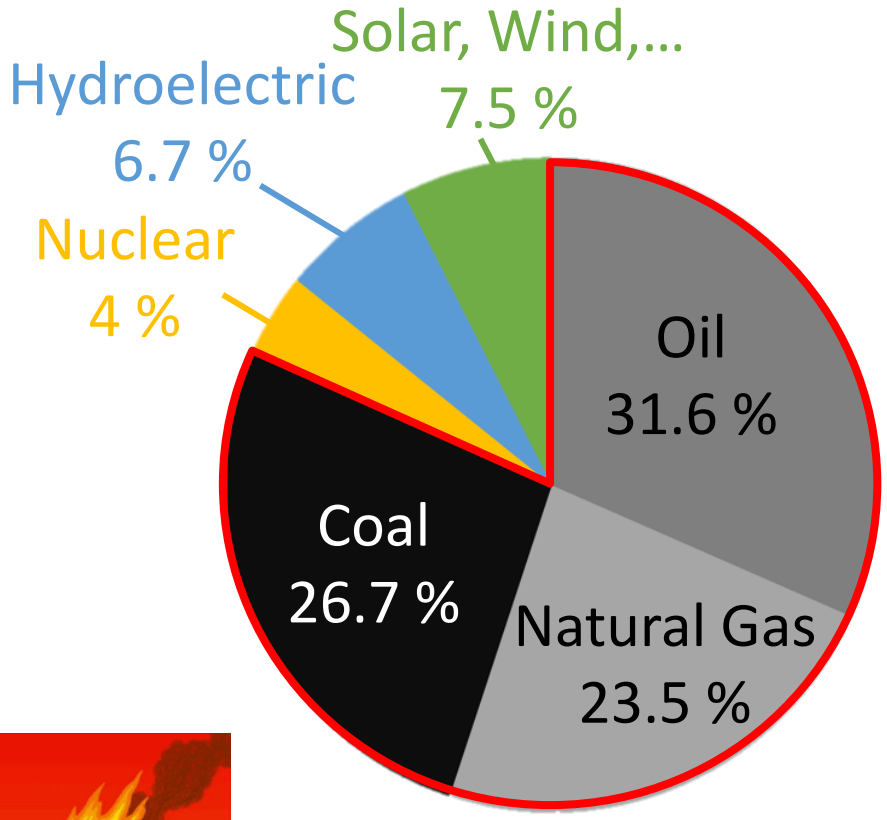




Oil and Gas Journal, **2023**, *1*, 12–19 ; *The Bridge*, **2021**, *50* (2), 134–137

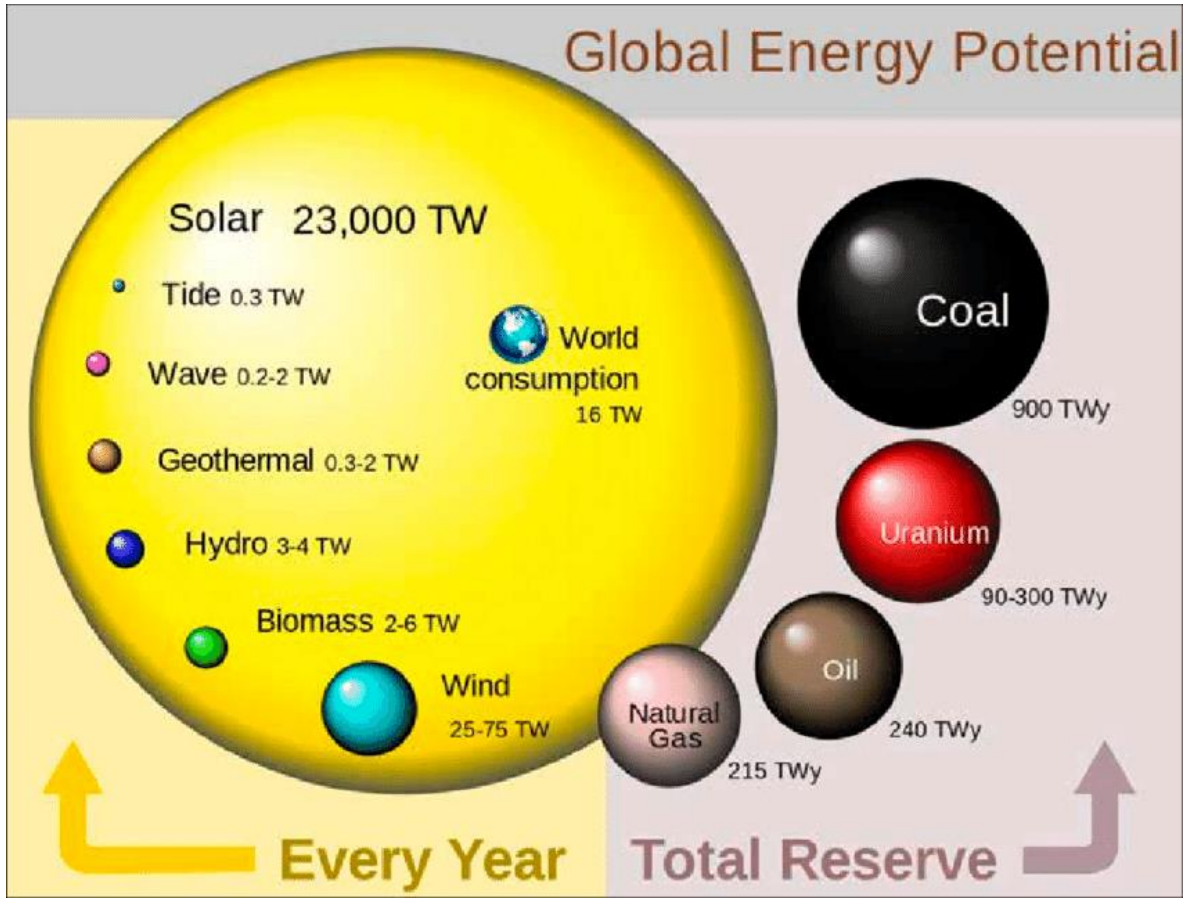
The one with energy issues

Primary global energy consumption 2022



82 % Fossil fuels

CO_2 Increases

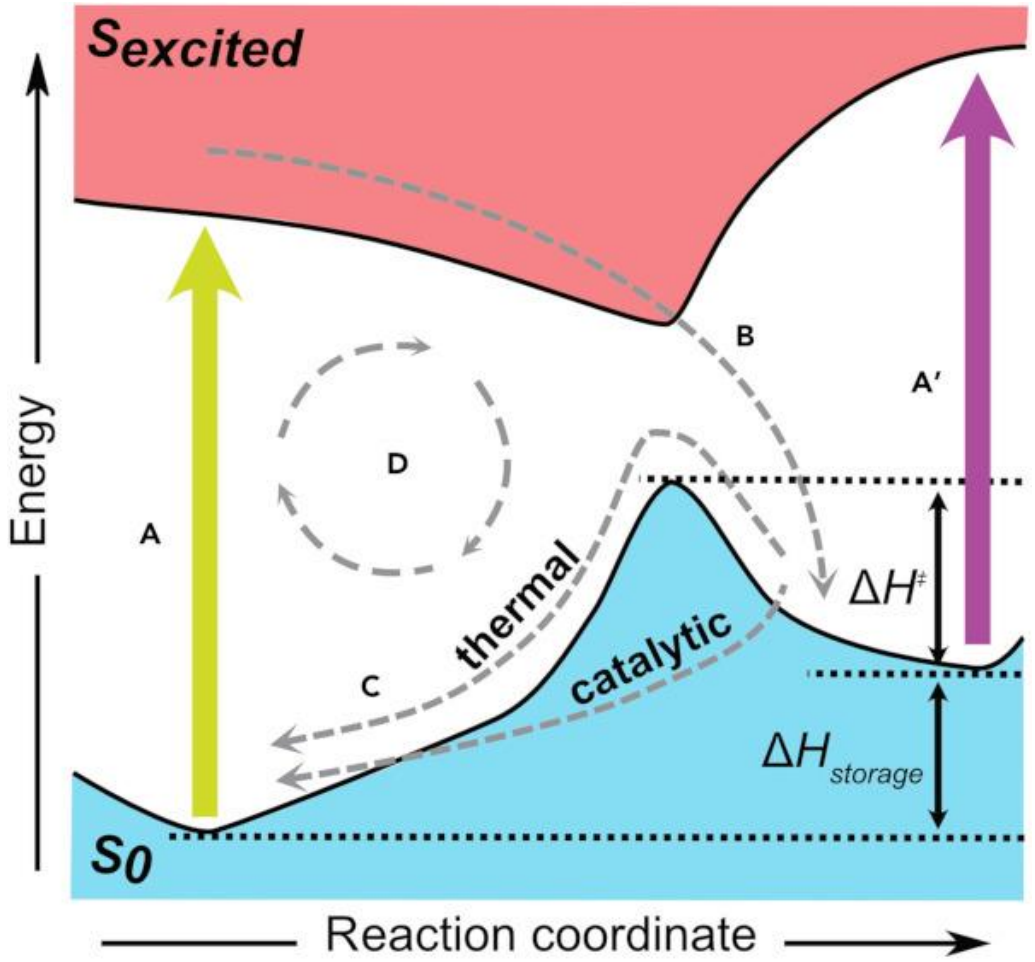


MOlecular **S**olar **T**hermal systems (**MOST**)

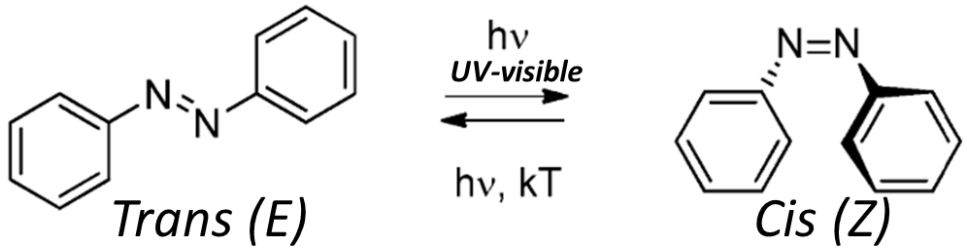
Oil and Gas Journal, **2023**, *1*, 12–19 ; *The Bridge*, **2021**, *50* (2), 134–137

The one who stores solar energy: MOST systems

Working principle



- Storage energy ⇔ ΔH
- Half-life time ($t_{1/2}$) ⇔ $\Delta H^{‡}$
- Absorbance > 400 nm



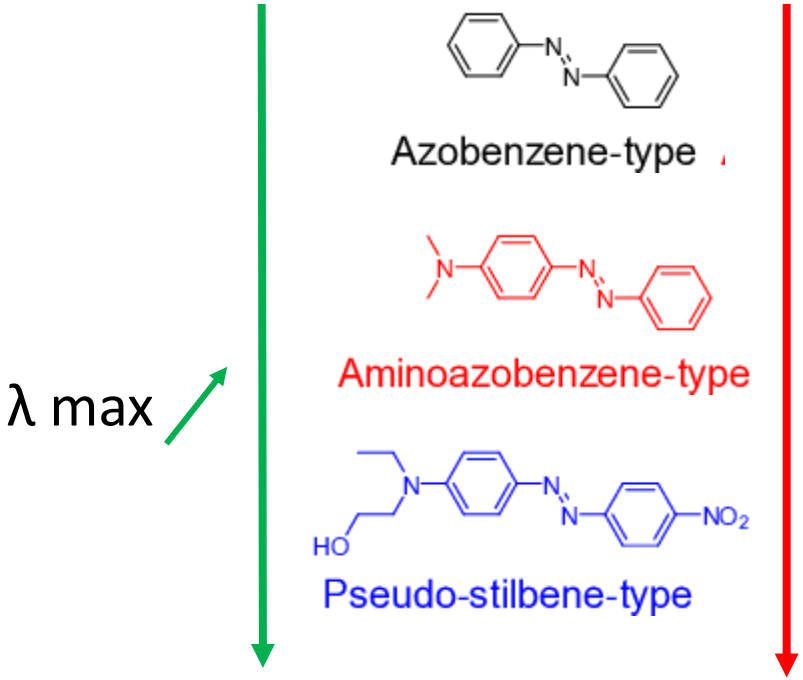
- $\Delta H = 50\ kJ.mol^{-1}$
- $t_{1/2}$ ~ 2 - 4 days
- $\lambda_{max} = 325\ nm$

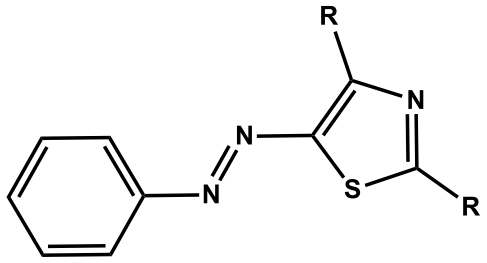
Joule **2021**, 5 (12), 3116–3136.

Energy Environ. Sci. **2011**, *4* (11), 4449–4472

The one who makes improvements

Heteroaryl azobenzene

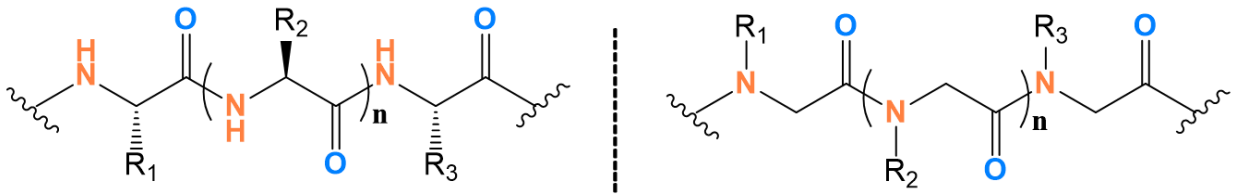




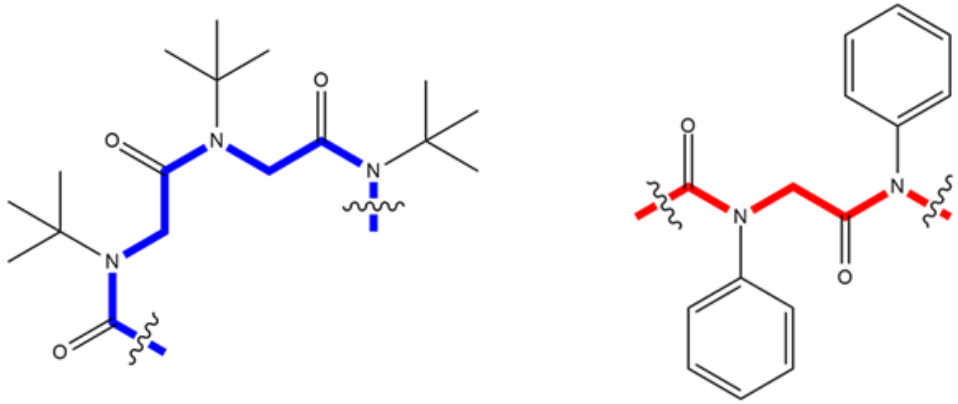
π-π* ≈ 480 – 650 nm

bathochromic shift ✓

Peptoid template



Peptides ⟷ **Peptoids**

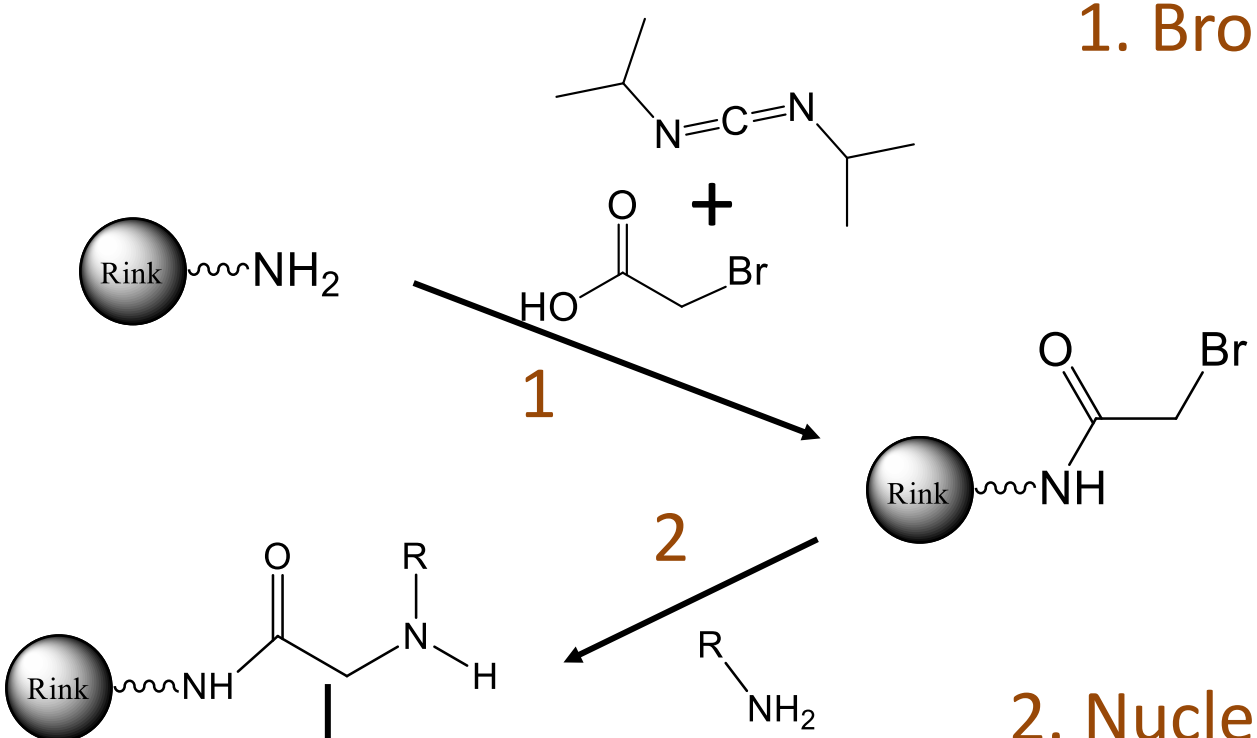


Cis/trans Amide bond → 3D structure

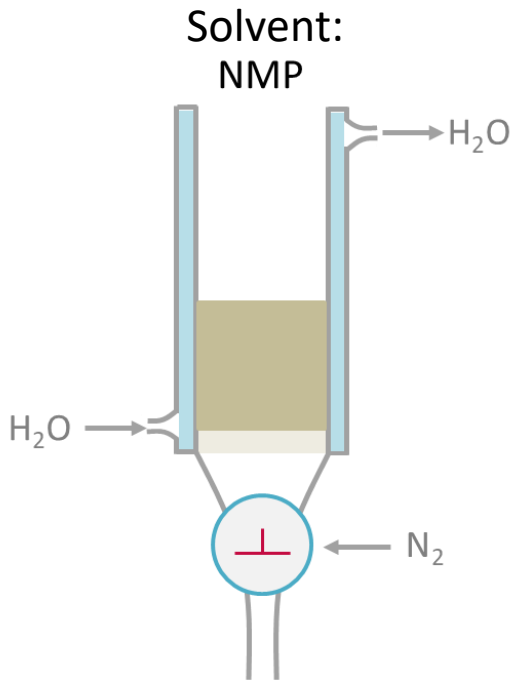
Text. Res. J. **2020**, *90* (11-12), 1396-1403

Org. Biomol. Chem, **2008**, *6*, 2516–2521.

The one who synthetizes peptoids

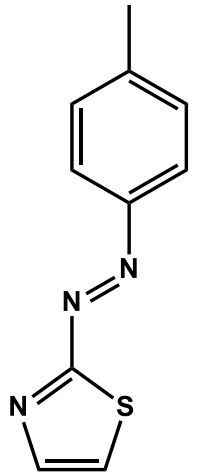


1. Bromoacetylation

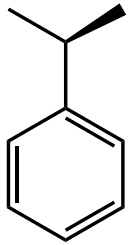


2. Nucleophilic substitution

R =

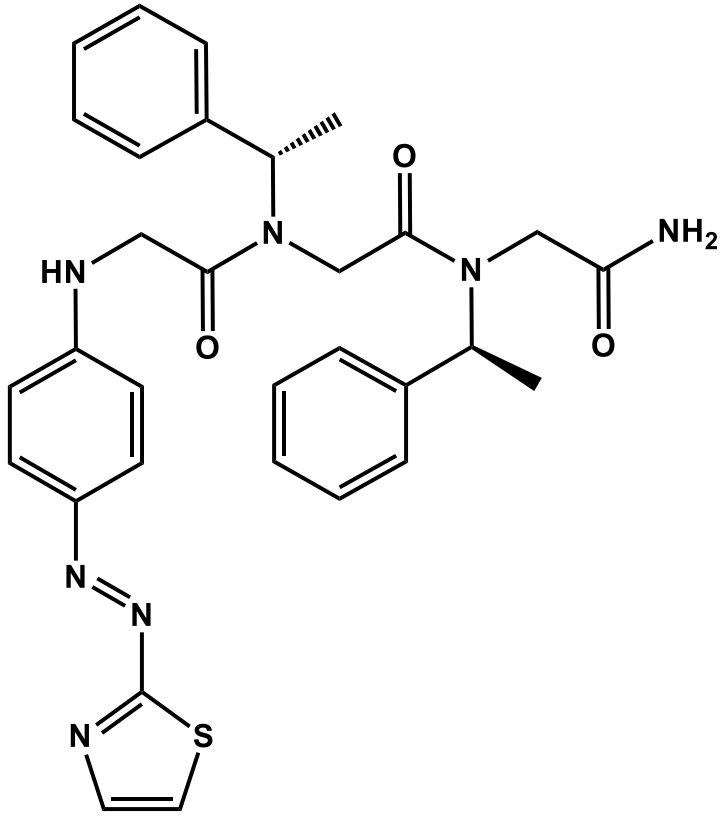


Or

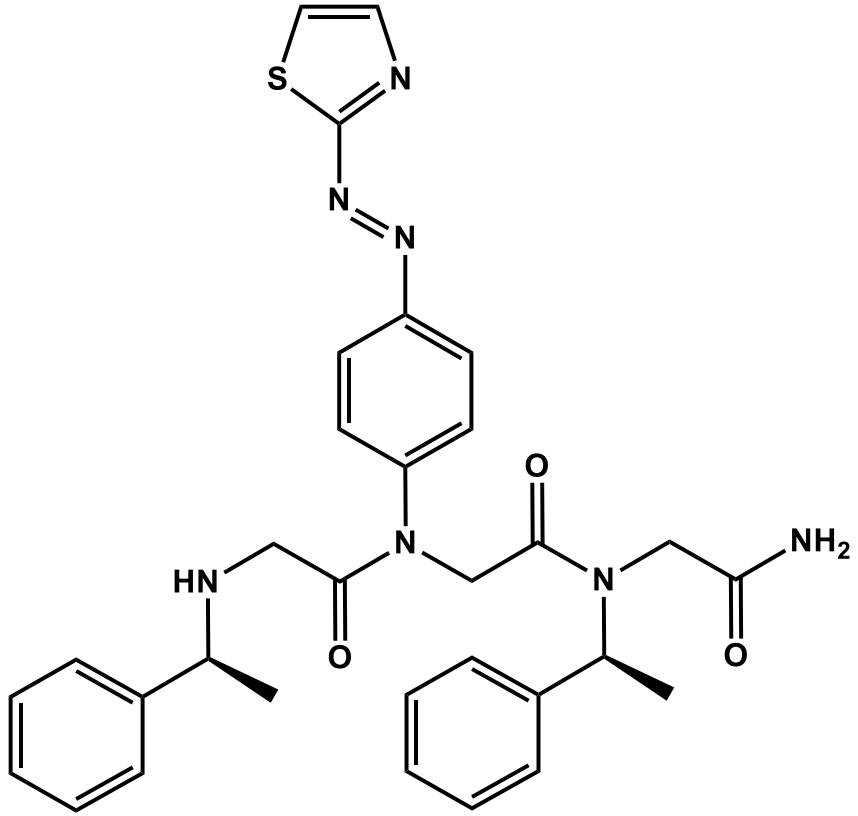


J. Am. Chem. Soc. **1992**, *114* (6), 10646–10647.

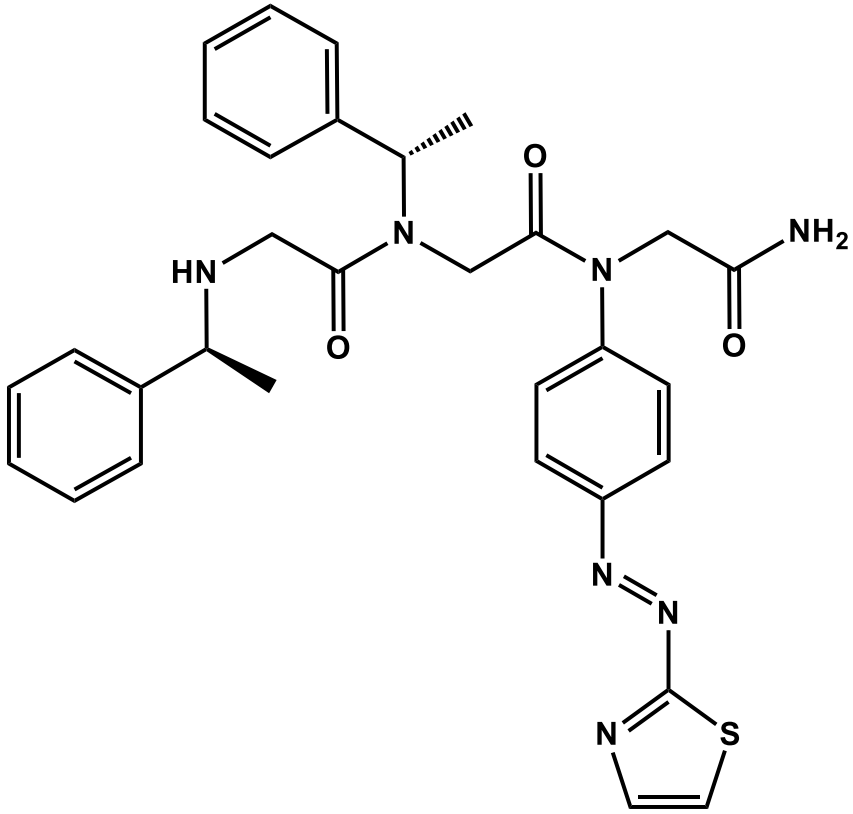
The one with 3-unit peptoids



N-ter position



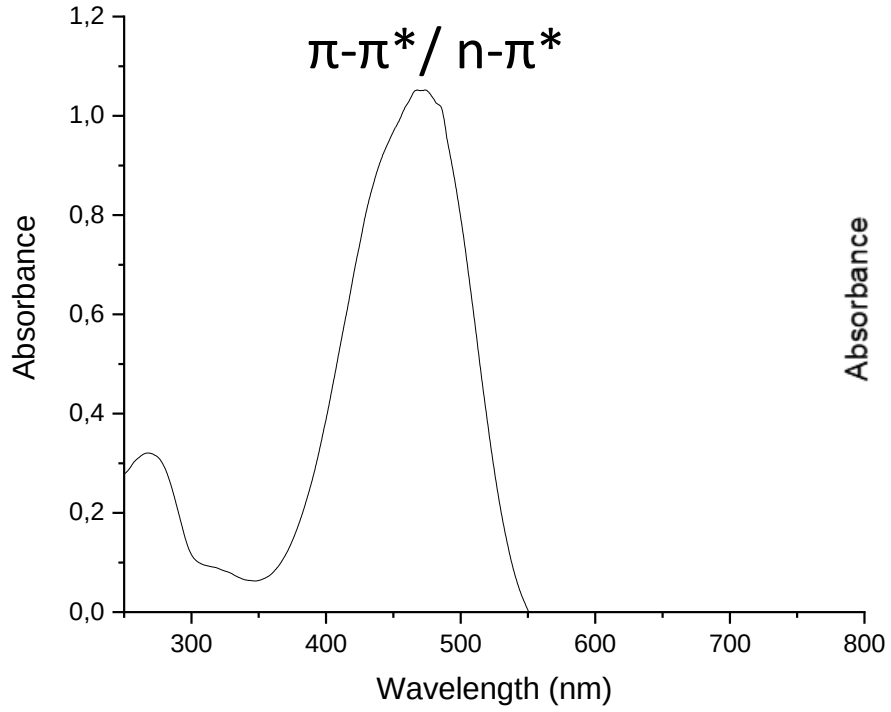
Center position

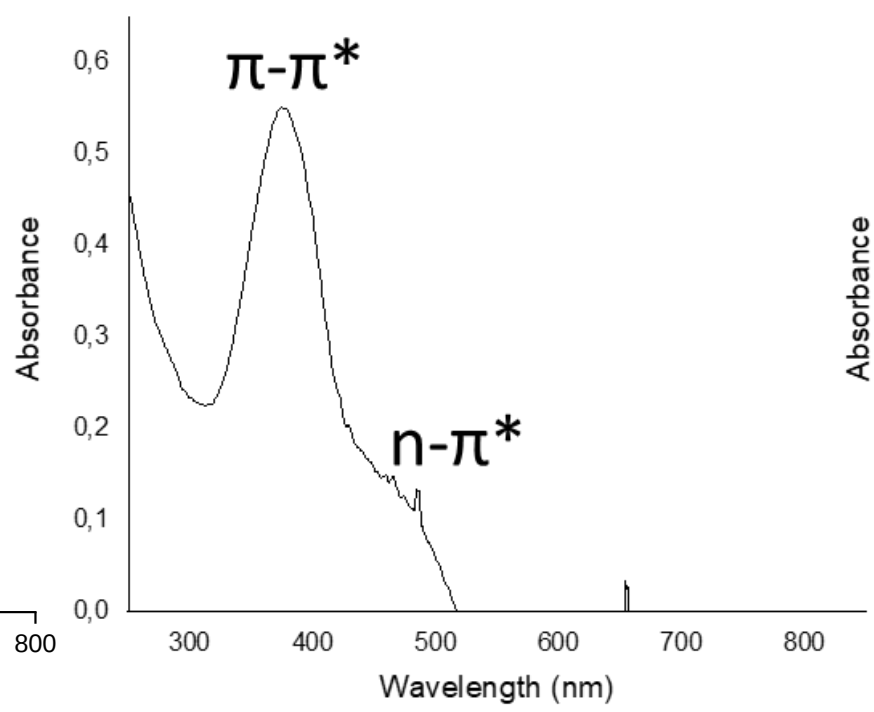


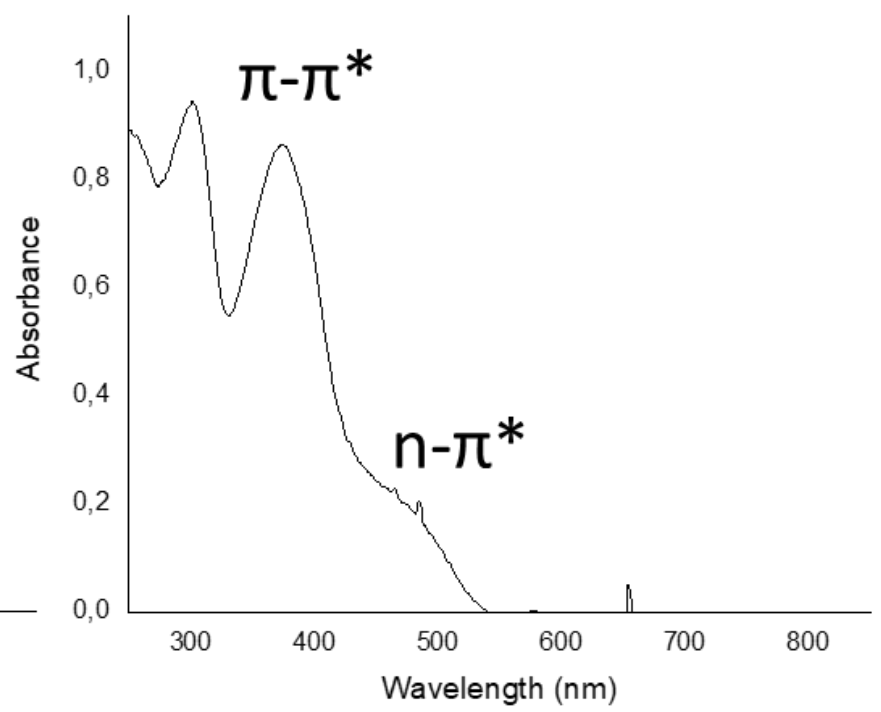
C-ter position

3 position isomers

The one with spectroscopic properties







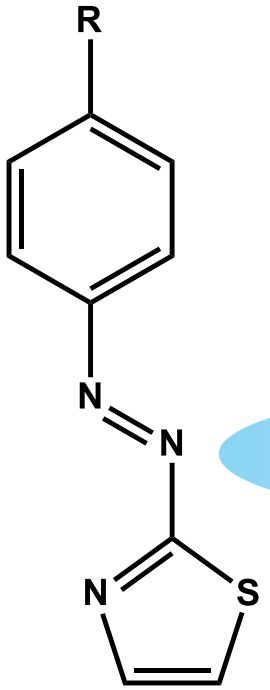
π-π* = 466 nm
n-π* = n.a

π-π* = 370 nm
n-π* = 480 nm

π-π* = 370 nm
n-π* = 480 nm

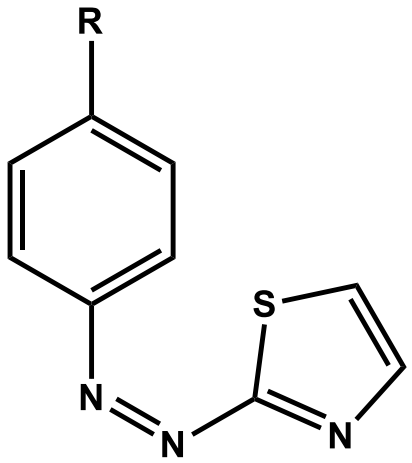
The one with LC-MS investigation

Visible lamp (ca. 350-800 nm)



Visible irradiation
Photoisomerization

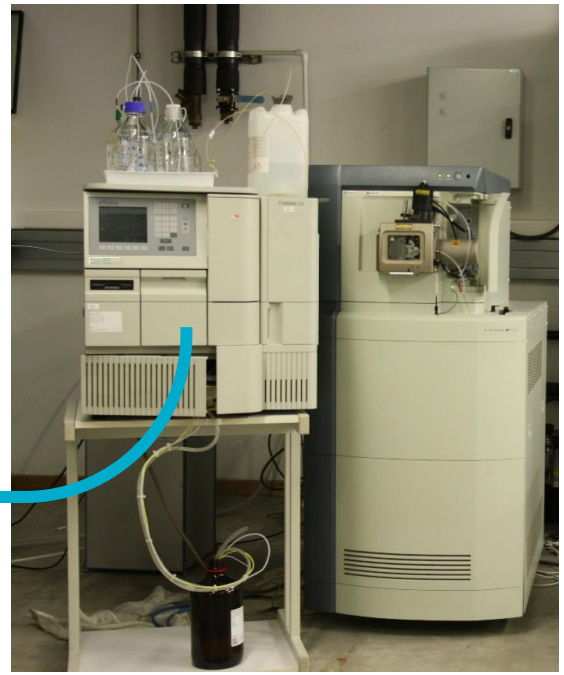
Thermal back-isomerization



LC-MS investigation

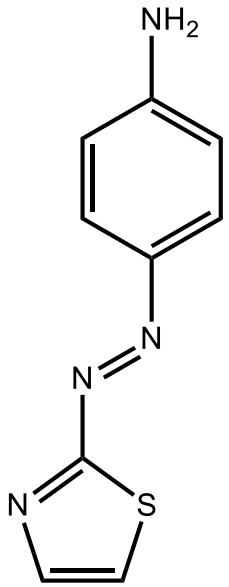
E / *Z* ratio evolution

Controlled T°
Dark storage



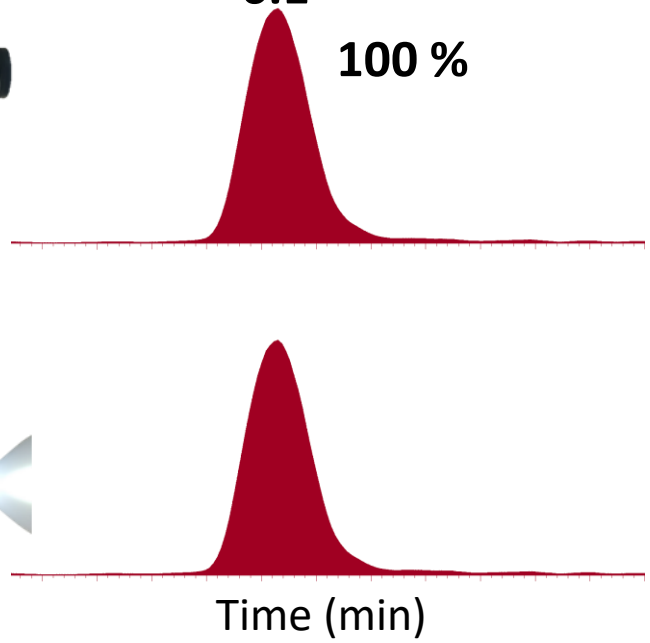
The one who performs LC-MS analyses

MeOH, 20°C



EIC *m/z* 205 [MH]⁺

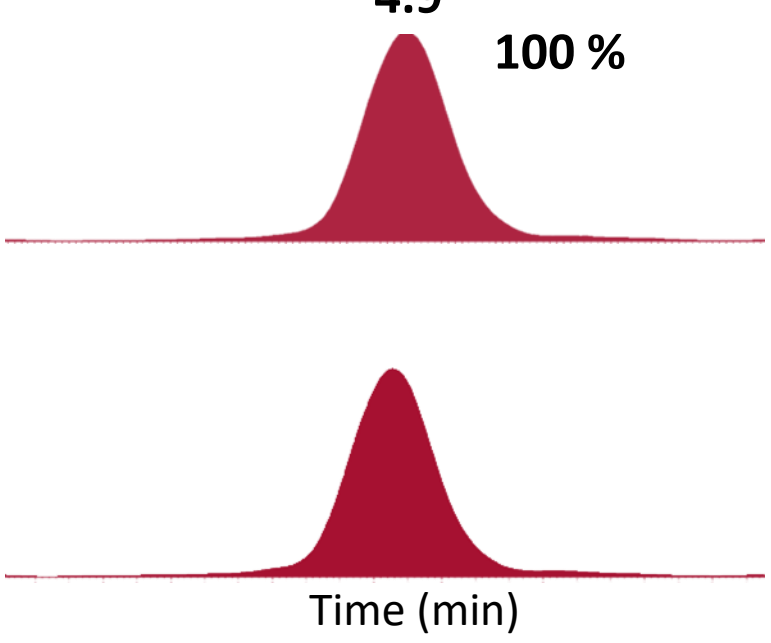
***E*-isomer**



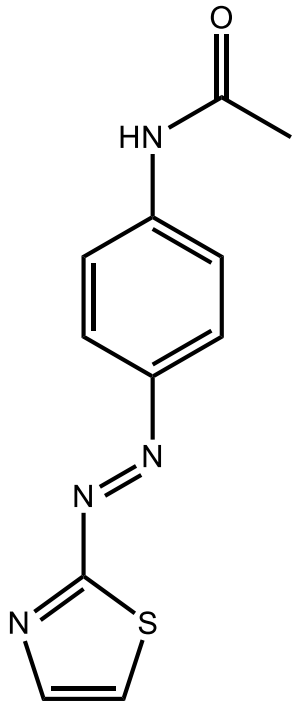
No Photoisomerization Observed

EIC *m/z* 247 [MH]⁺

***E*-isomer**

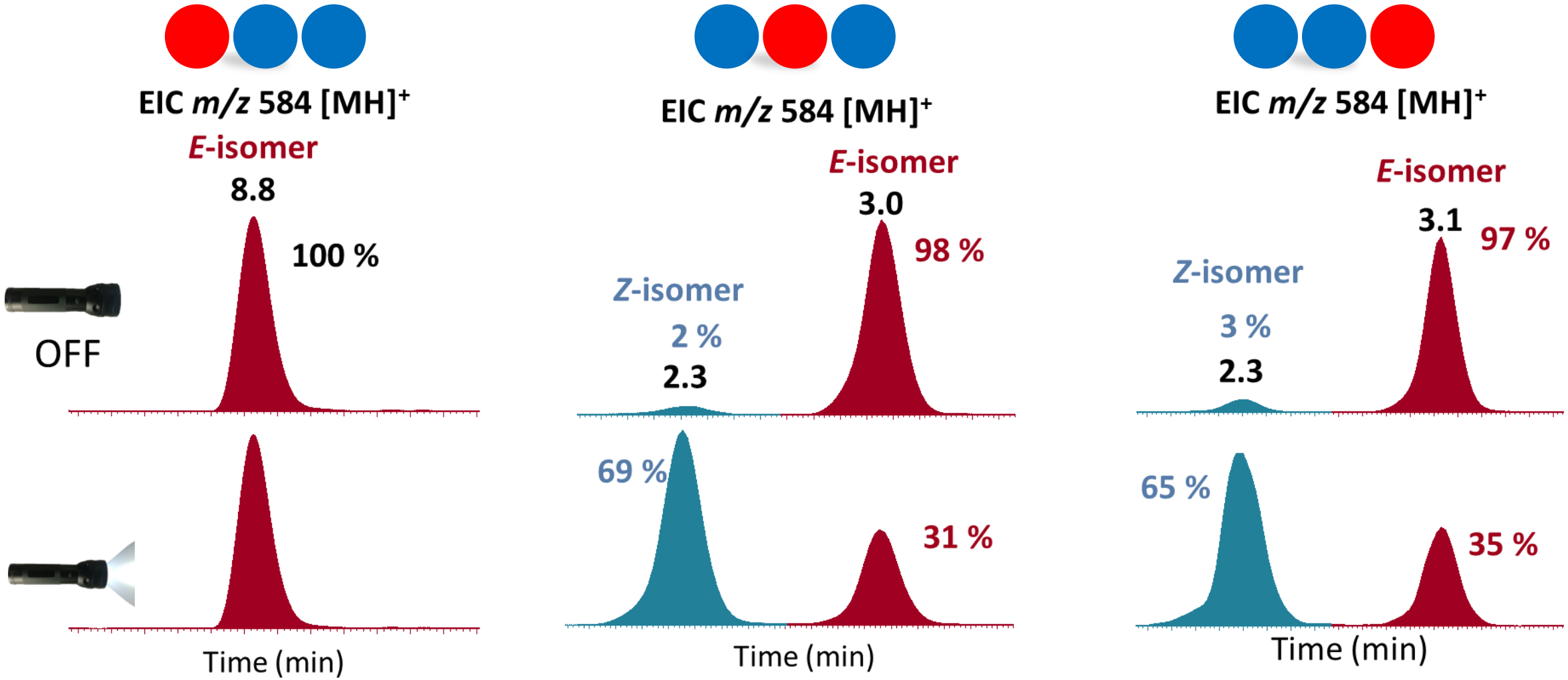


No Photoisomerization Observed



The one who performs LC-MS analyses

MeOH, 20°C



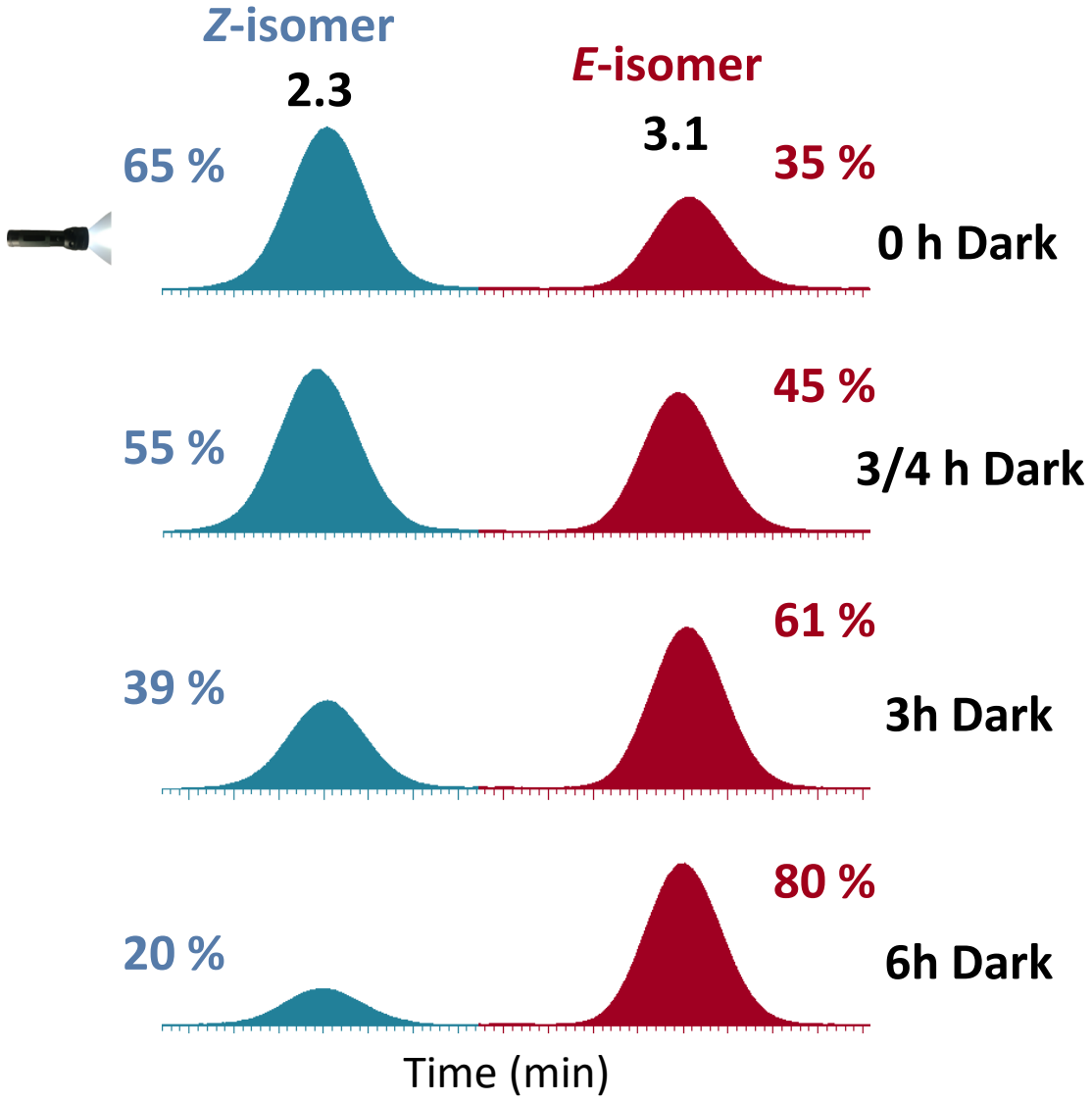
No Photoisomerization Observed

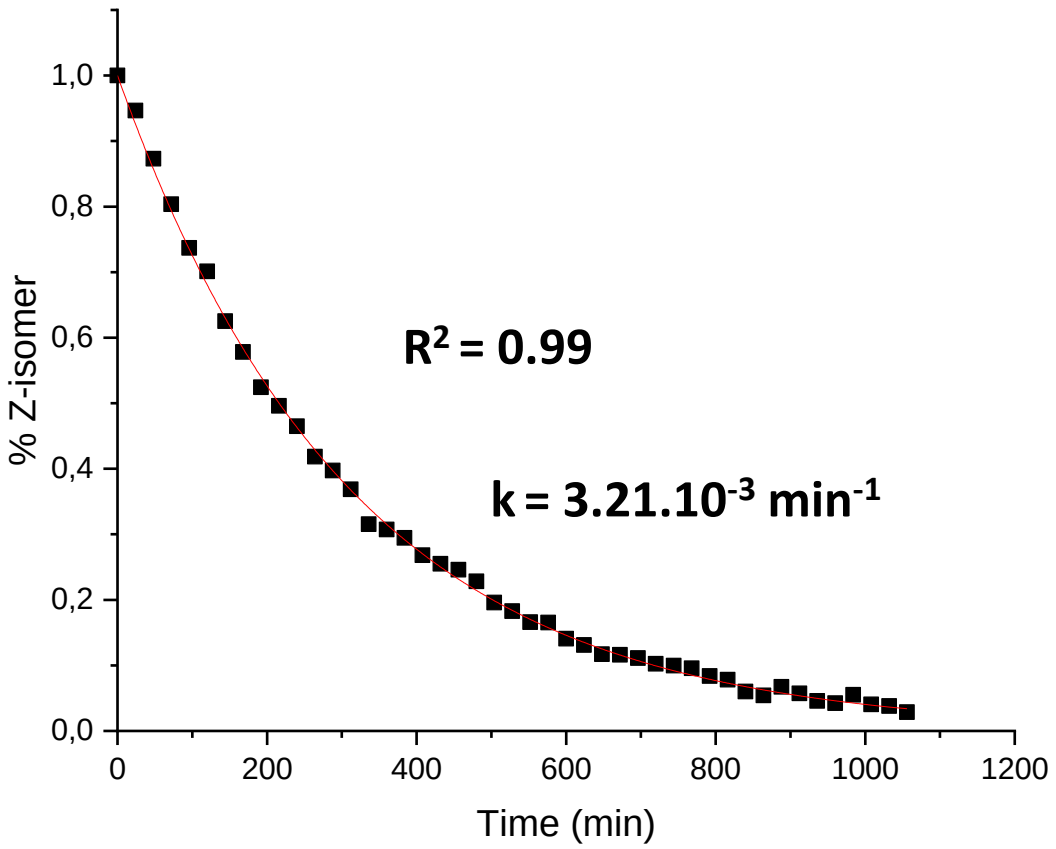
Photoisomerization Observed

Peptoid 3D structure induces cis isomer stabilization

The one who calculates the kinetic parameters

MeOH, 20°C

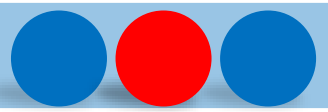




First order kinetics → $t_{1/2} = \frac{\ln 2}{k}$

$$t_{1/2} = 3.63\ h$$

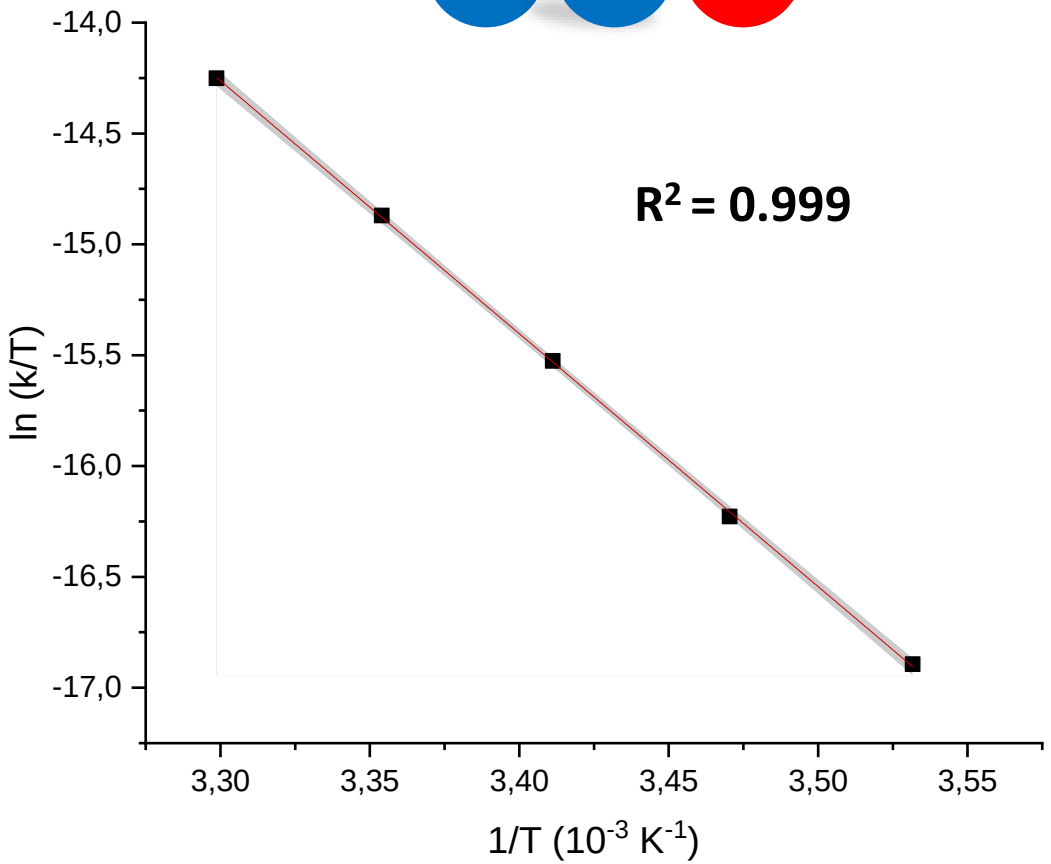
The one who calculates the kinetic parameters

				
T (°C)	k_{avg} (10^{-5} s^{-1})	$t_{1/2}$ (h)	k_{avg} (10^{-5} s^{-1})	$t_{1/2}$ (h)
10	1.57 ± 0.02	12.25 ± 0.19	1.30 ± 0.02	14.7 ± 0.22
15	3.13 ± 0.06	6.16 ± 0.12	2.58 ± 0.06	7.46 ± 0.18
20	6.14 ± 0.15	3.13 ± 0.08	5.30 ± 0.04	3.63 ± 0.03
25	12.1 ± 0.5	1.59 ± 0.07	10.4 ± 0.16	1.85 ± 0.03
30	/	/	21.3 ± 0.15	0.91 ± 0.01

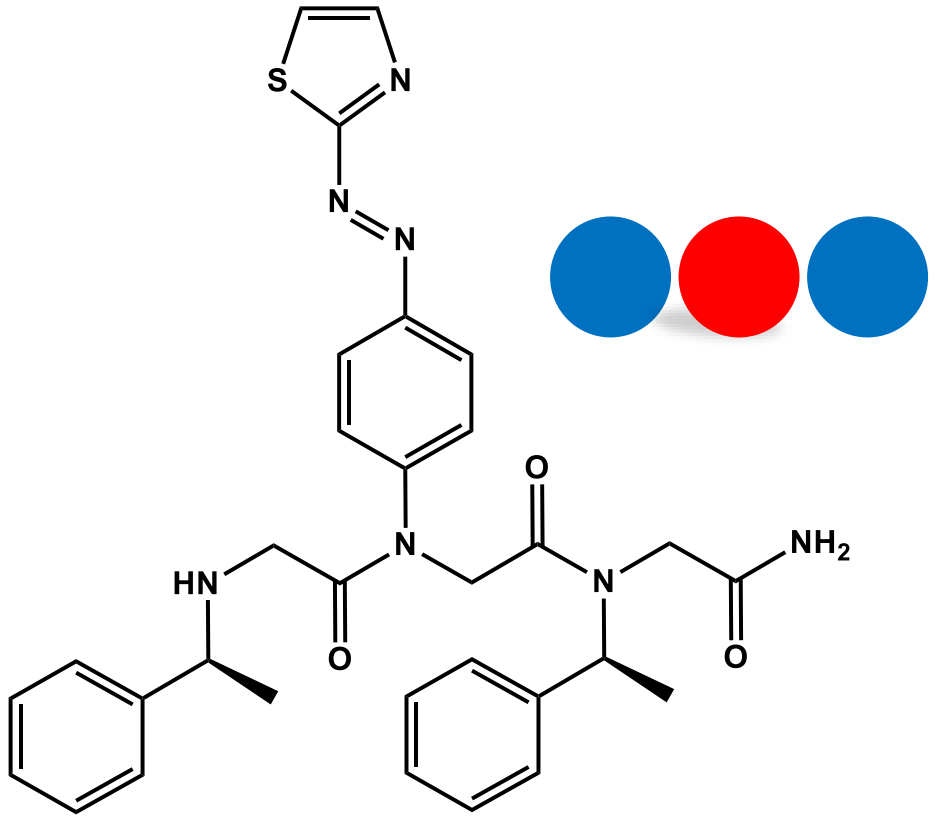
Slope Intercept

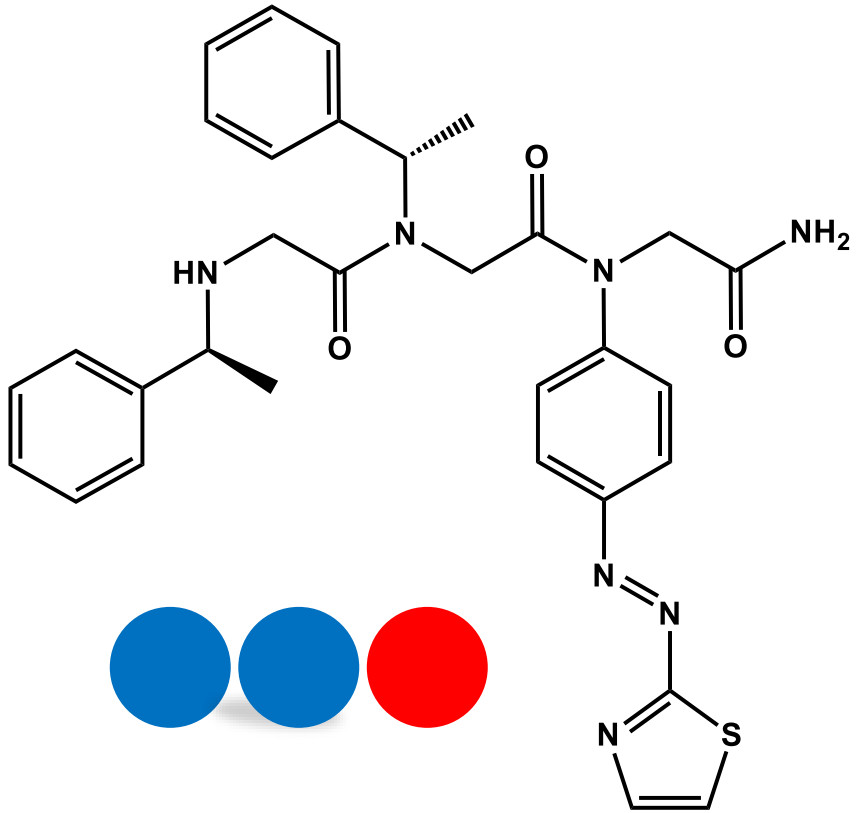
$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

Eyring plot



The one who calculates the kinetic parameters





$\Delta H^{\ddagger} = 93.10 \pm 0.85$ kJ.mol^{-1}

$\Delta S^{\ddagger} = -7.7 \pm 3$ J.mol^{-1} K^{-1}

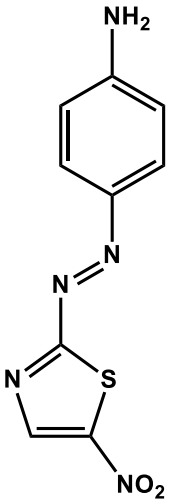
$\Delta G^{\ddagger}$ (20°C) = 95.36 ± 1.72 kJ.mol^{-1}

$\Delta H^{\ddagger} = 94.85 \pm 0.68$ kJ.mol^{-1}

$\Delta S^{\ddagger} = -3.1 \pm 2.3$ J.mol^{-1} K^{-1}

$\Delta G^{\ddagger}$ (20°C) = 95.76 ± 1.37 kJ.mol^{-1}

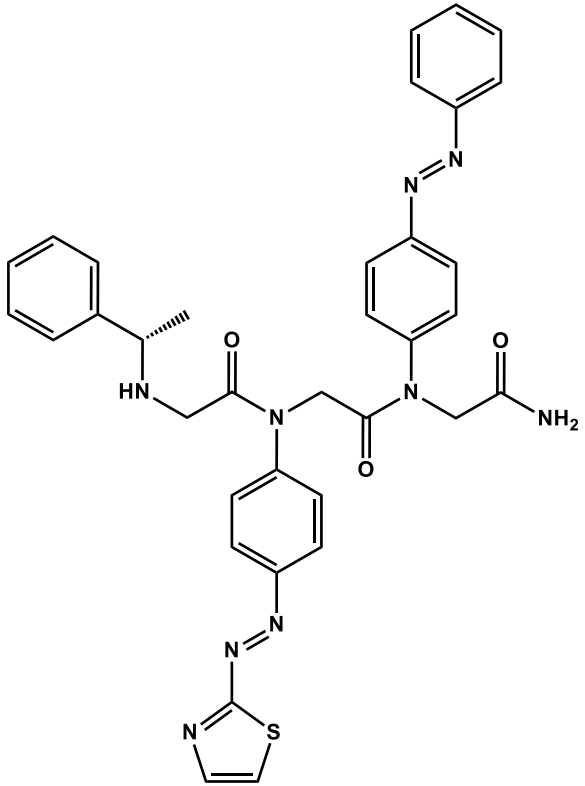
The one with conclusions and perspectives



- Heteroaryl azobenzene and peptoids successfully synthesized
- Spectroscopic properties: absorption close to visible wavelengths

  → Add nitro group
- Peptoids stabilize *cis*-azobenzene

  → Theoretical modelling
- Successfully determined the kinetic parameters
- Synthetize peptoids with different azobenzenes



The one with Acknowledgements

The S²MOs & CMN team :

Pascal Gerbaux
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Ari Serez
Quentin Duez
Paul Gueben
Sarajit Naskar
…

Special thanks to the organizers

and you for your attention !

UMONS Université de Mons

S²MOs

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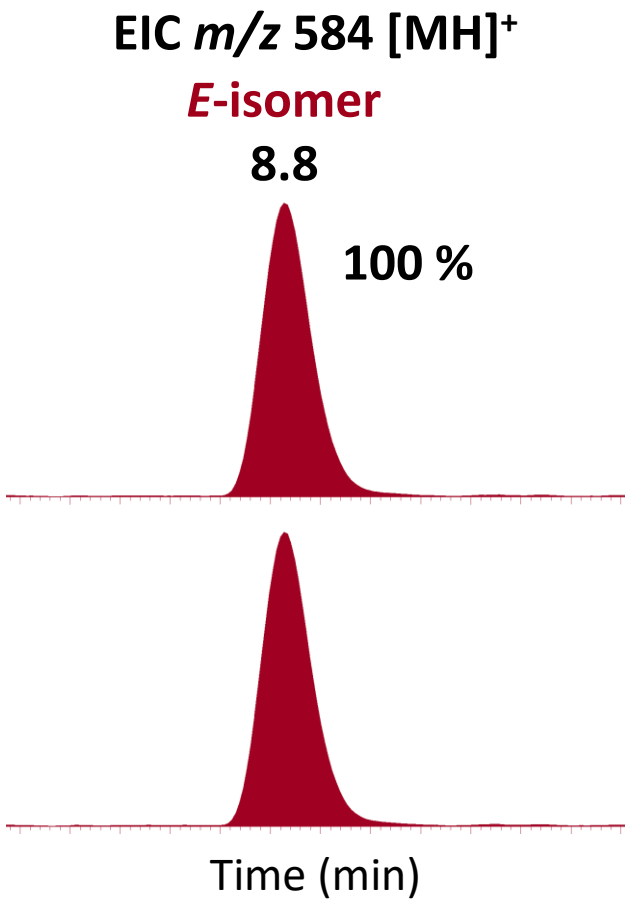
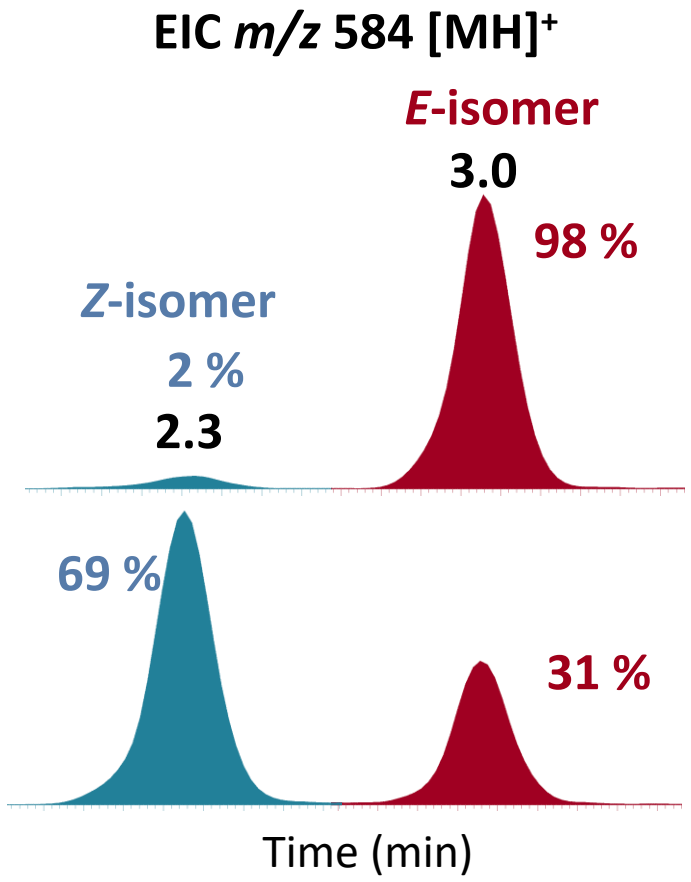
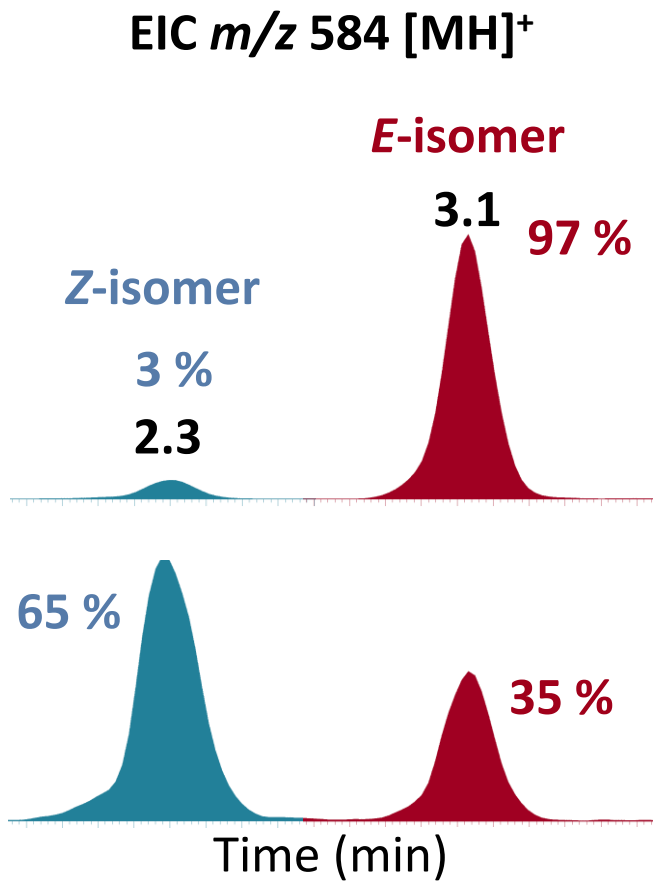
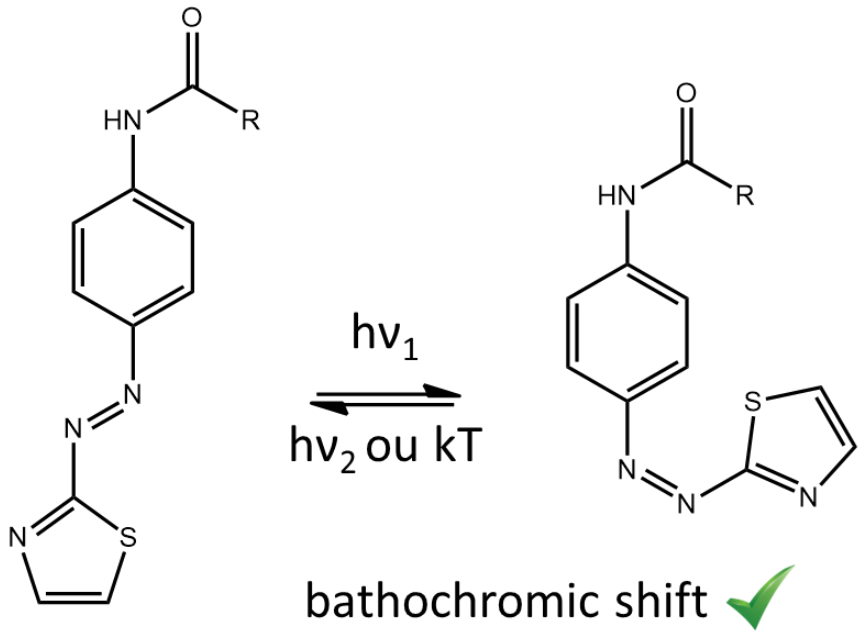
CMN


EIC *m/z* 584 [MH]+
E-isomer
8.8
100 %
Time (min)

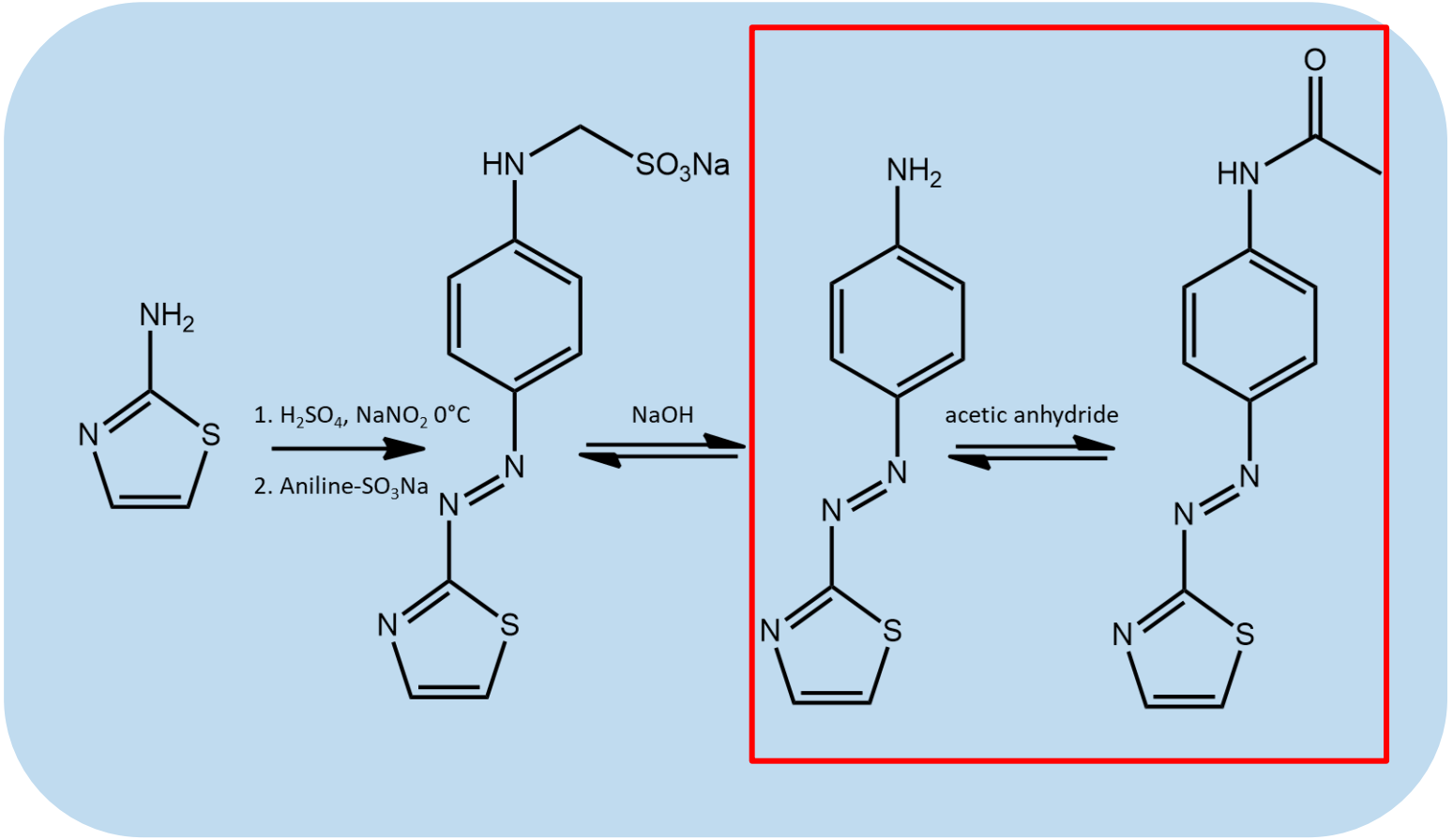

EIC *m/z* 584 [MH]+
E-isomer
3.0
98 %
Z-isomer
2 %
2.3
69 %
31 %
Time (min)


EIC *m/z* 584 [MH]+
E-isomer
3.1
97 %
Z-isomer
3 %
2.3
65 %
35 %
Time (min)

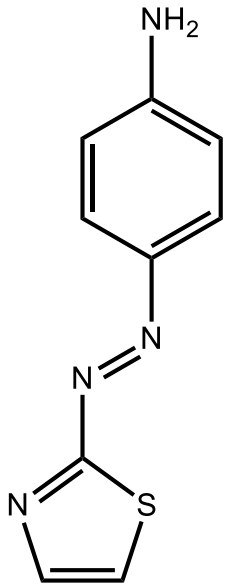
The one who synthetizes heteroaryl azobenzene

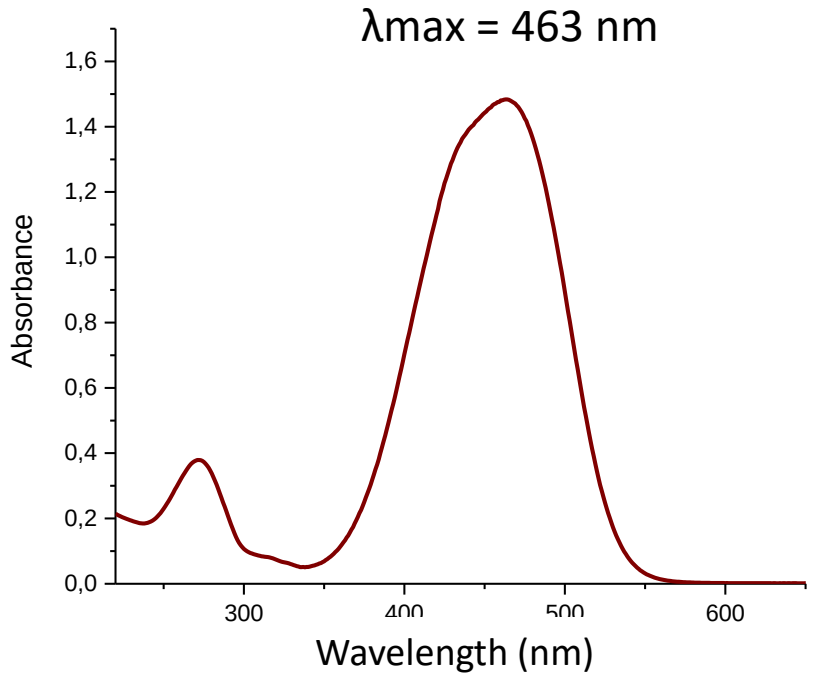


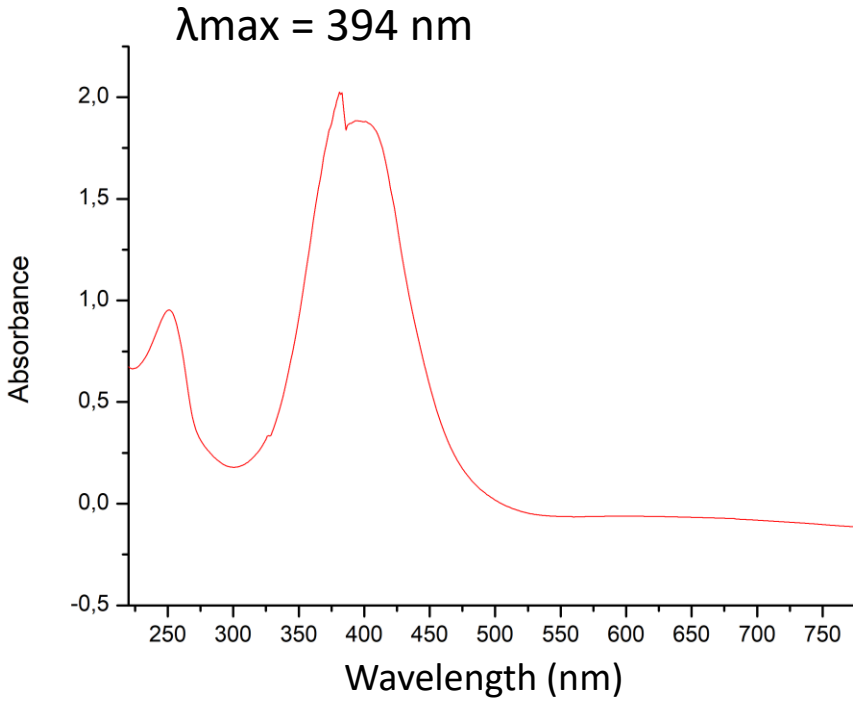
bathochromic shift ✓

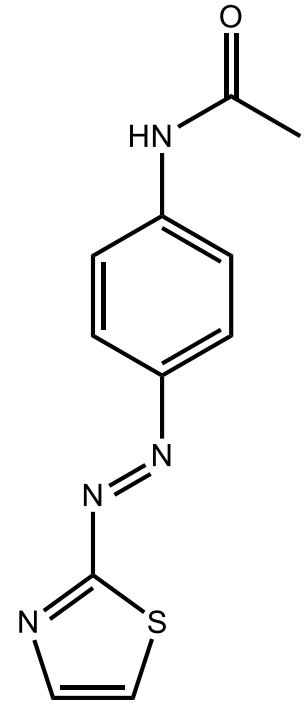


The one with spectroscopic spectra









π-π* = 463 nm
n-π* = n.a

π-π* = 394 nm
n-π* = n.a

- π-π* and n-π* recovering
- π-π* in the visible wavelength

Thank you for your attention