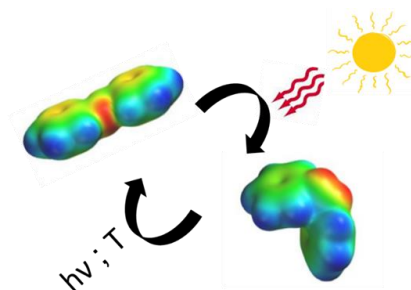


Original Heteroaryl Azobenzene derivatives As Solar Thermal Fuel Candidates : a Mass Spectrometry and UV-vis Spectrophotometry Investigation

Gwendal Henrard, Thomas Robert, Benjamin Tassignon, Ari Serez, Julien De Winter, Jérôme Cornil, Pascal Gerbaux
gwendal.henrard@umons.ac.be

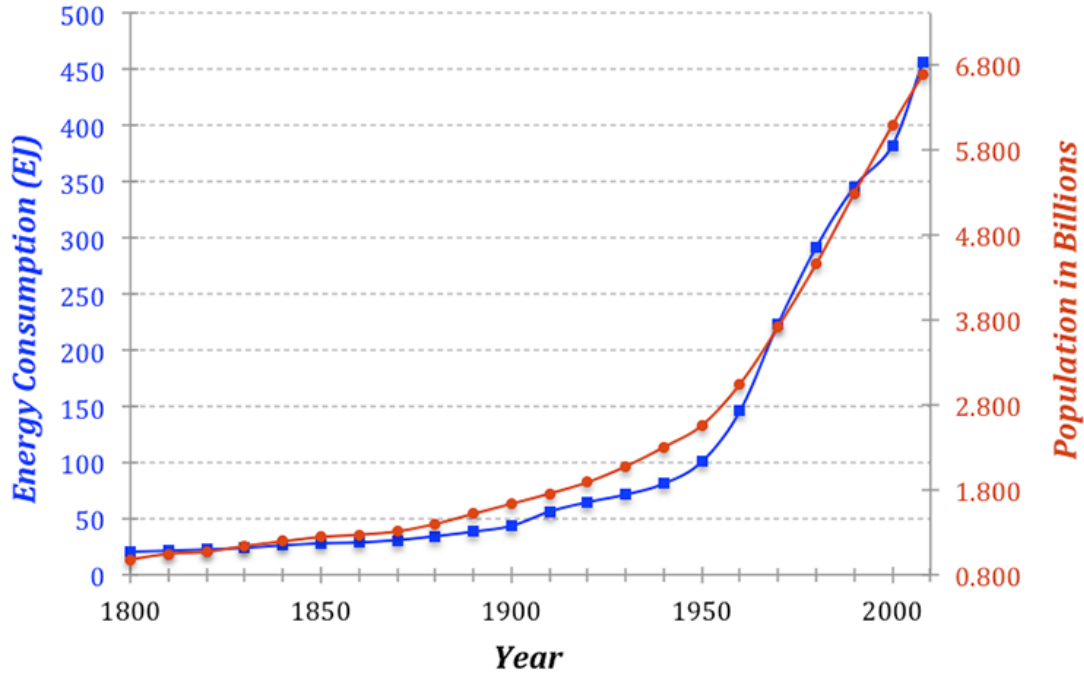
SRC Young Chemists' Day 2023
Monday 22nd May 2023



S²MOs

Energy issue

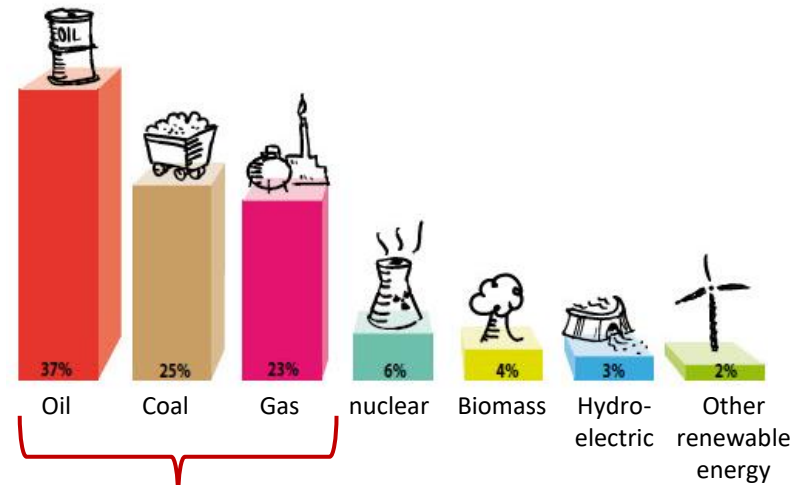
Energy Consumption and Population



World Population Increase



Energy consumption Increase



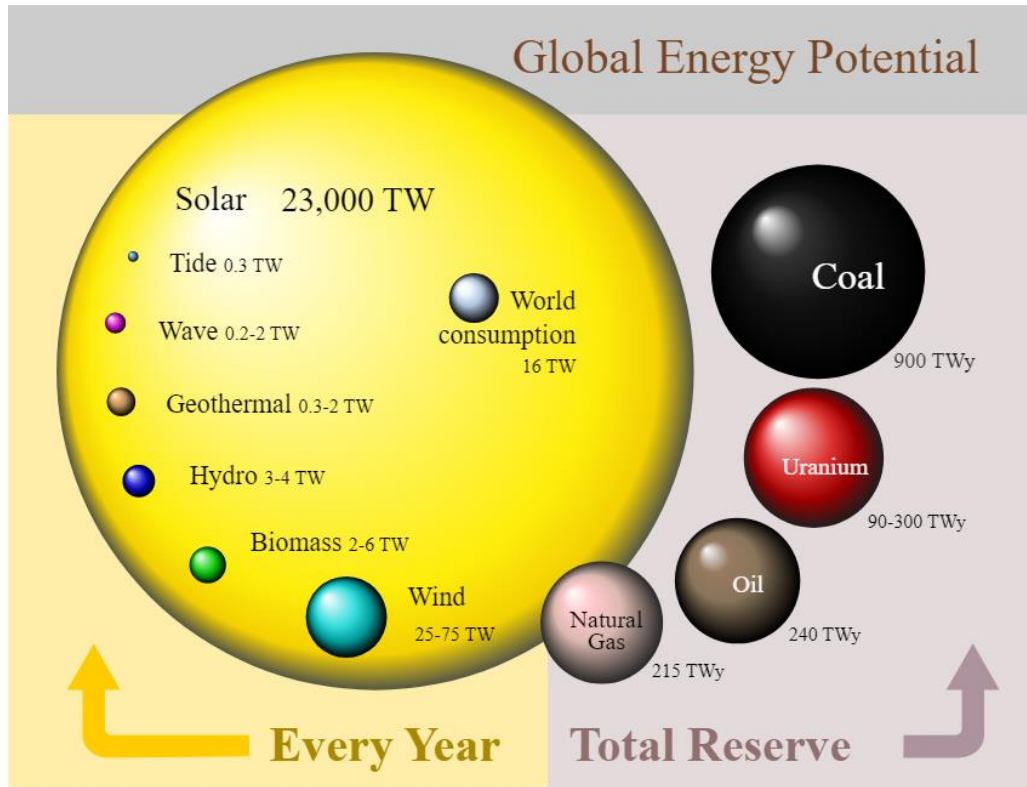
Fossil fuels



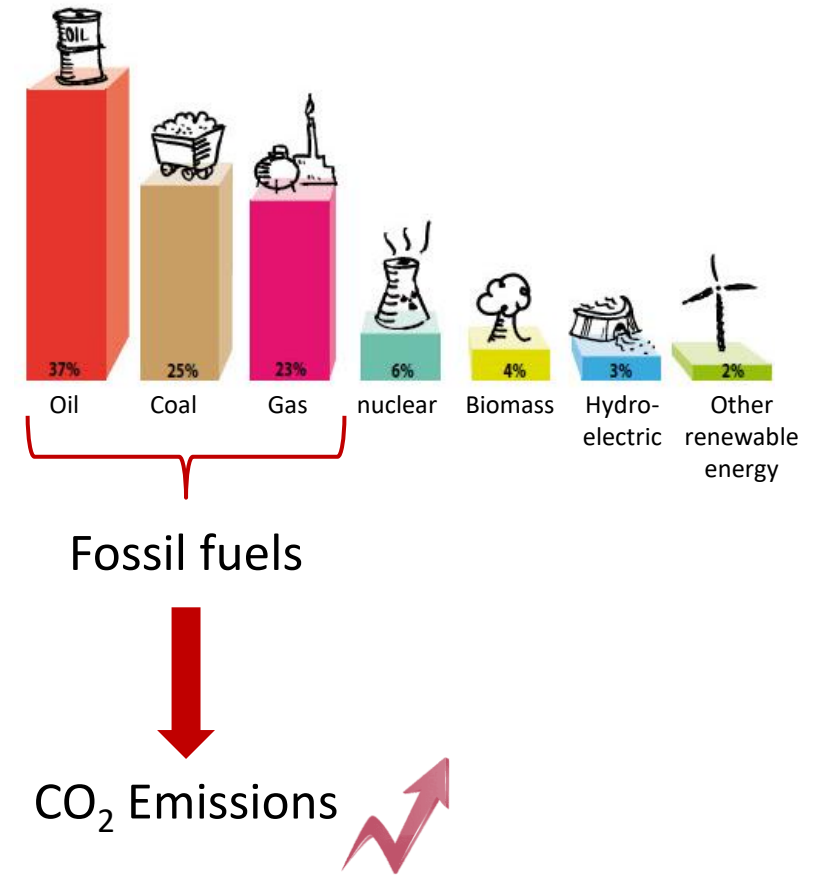
CO₂ Emissions



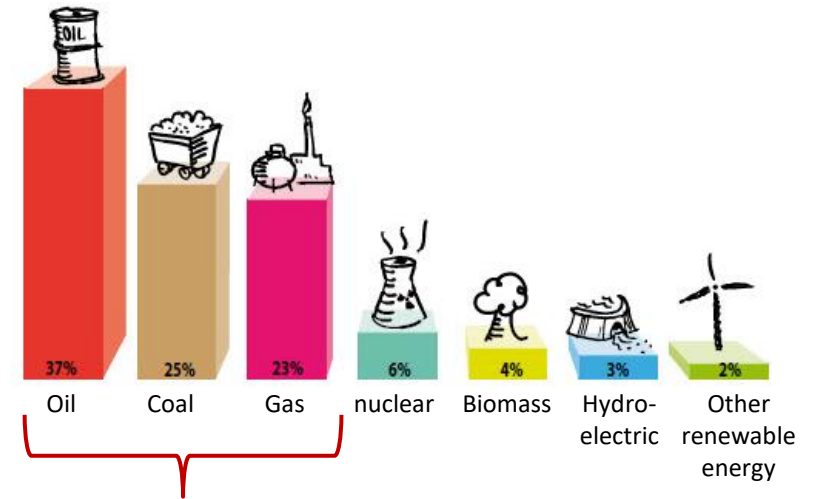
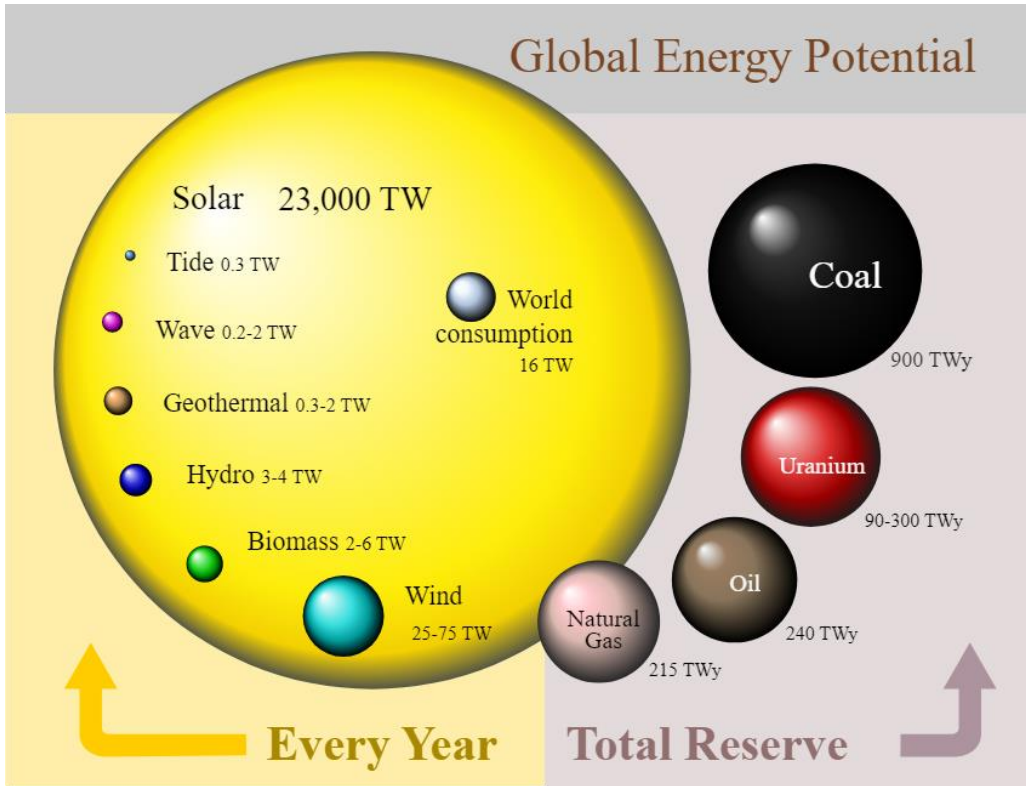
Energy issue



Sun energy potential / years > 1000 X World consumption



Energy issue



Fossil fuels

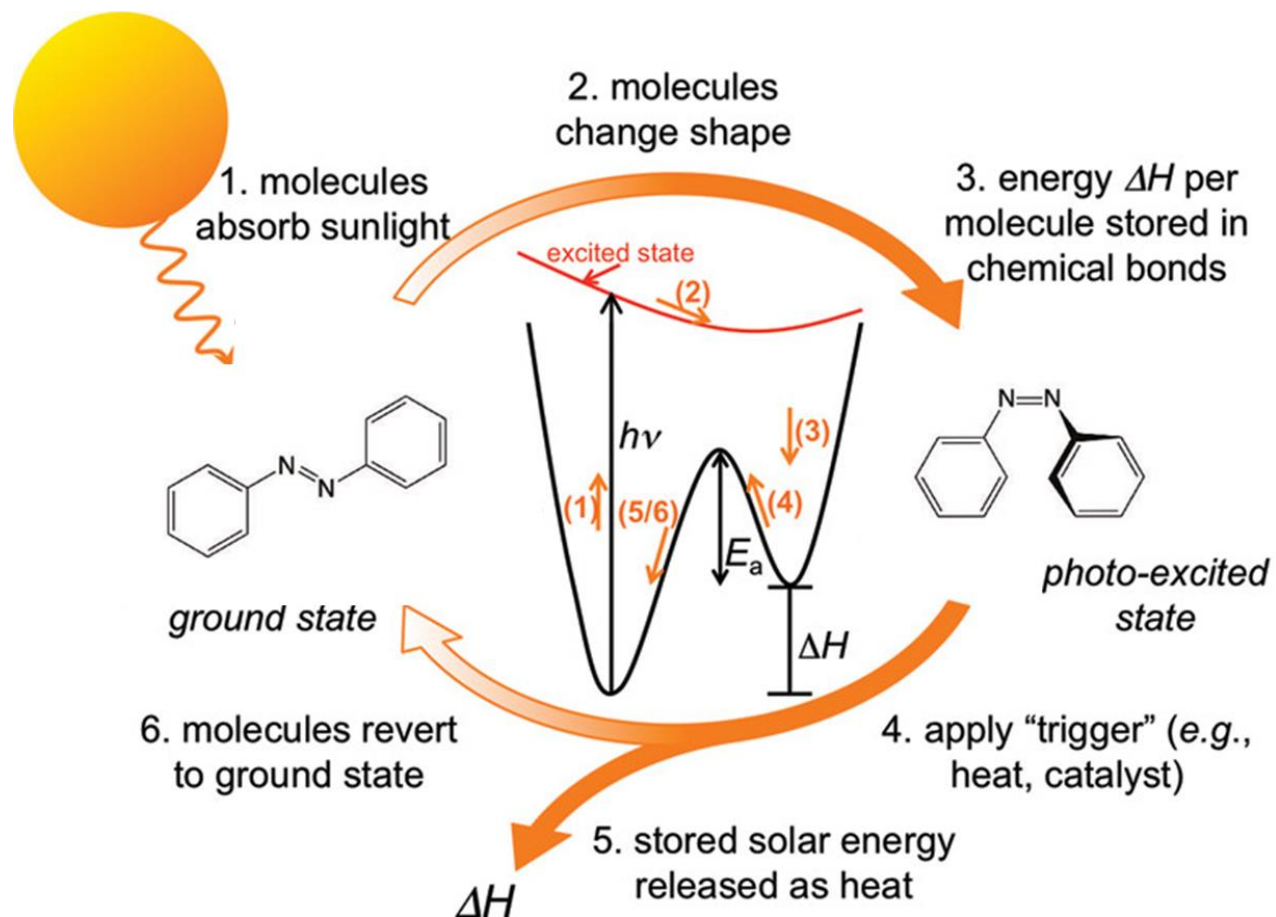
CO₂ Emissions

Sun energy potential / years > 1000 X World consumption

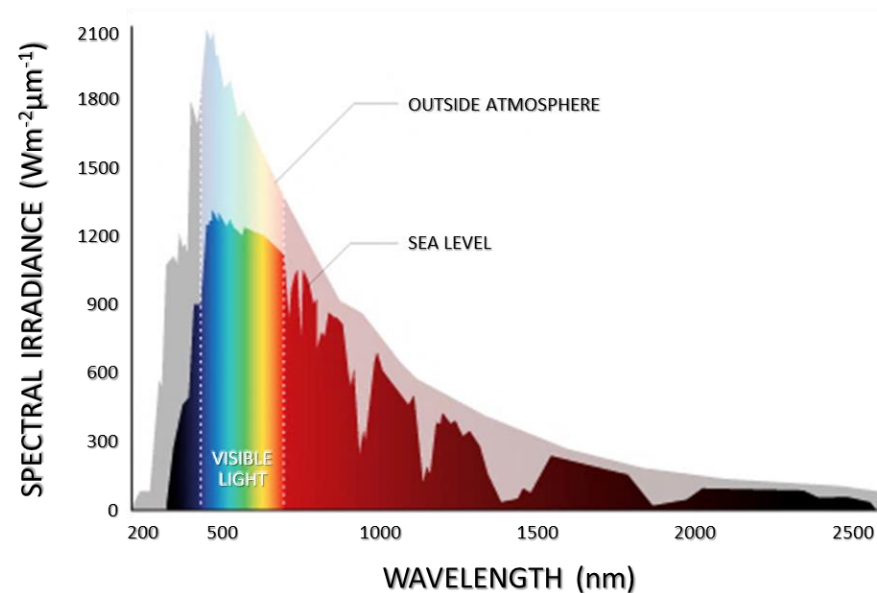


MOlecular Solar Thermal systems (MOST)

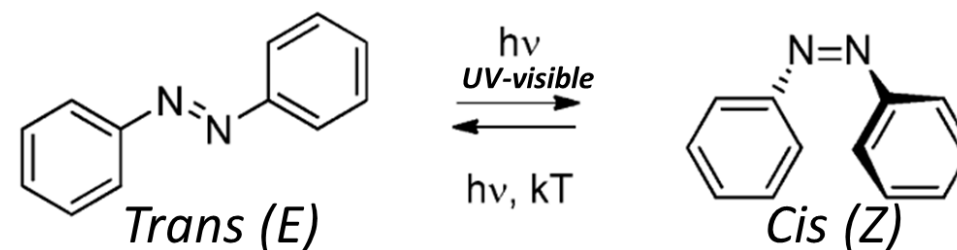
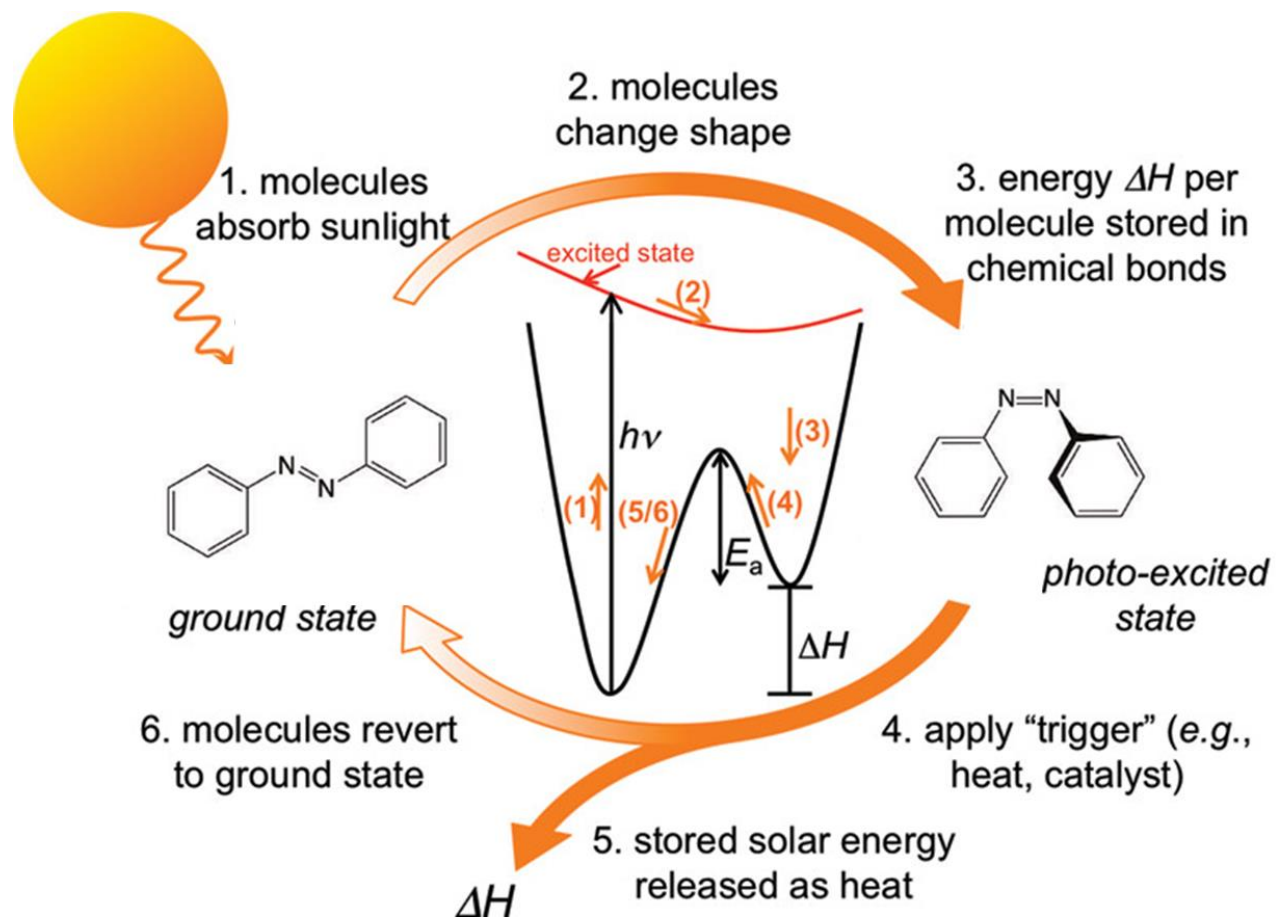
What is a MOlecular Solar Thermal systems ?



- Storage energy $\leftrightarrow \Delta H$
- Half-life time ($t_{1/2}$) $\leftrightarrow E_a$
- Absorbance > 400 nm



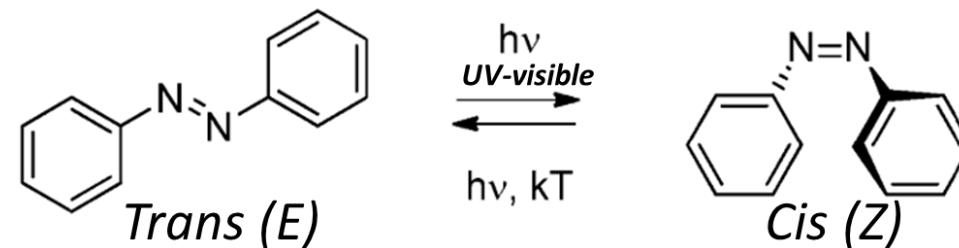
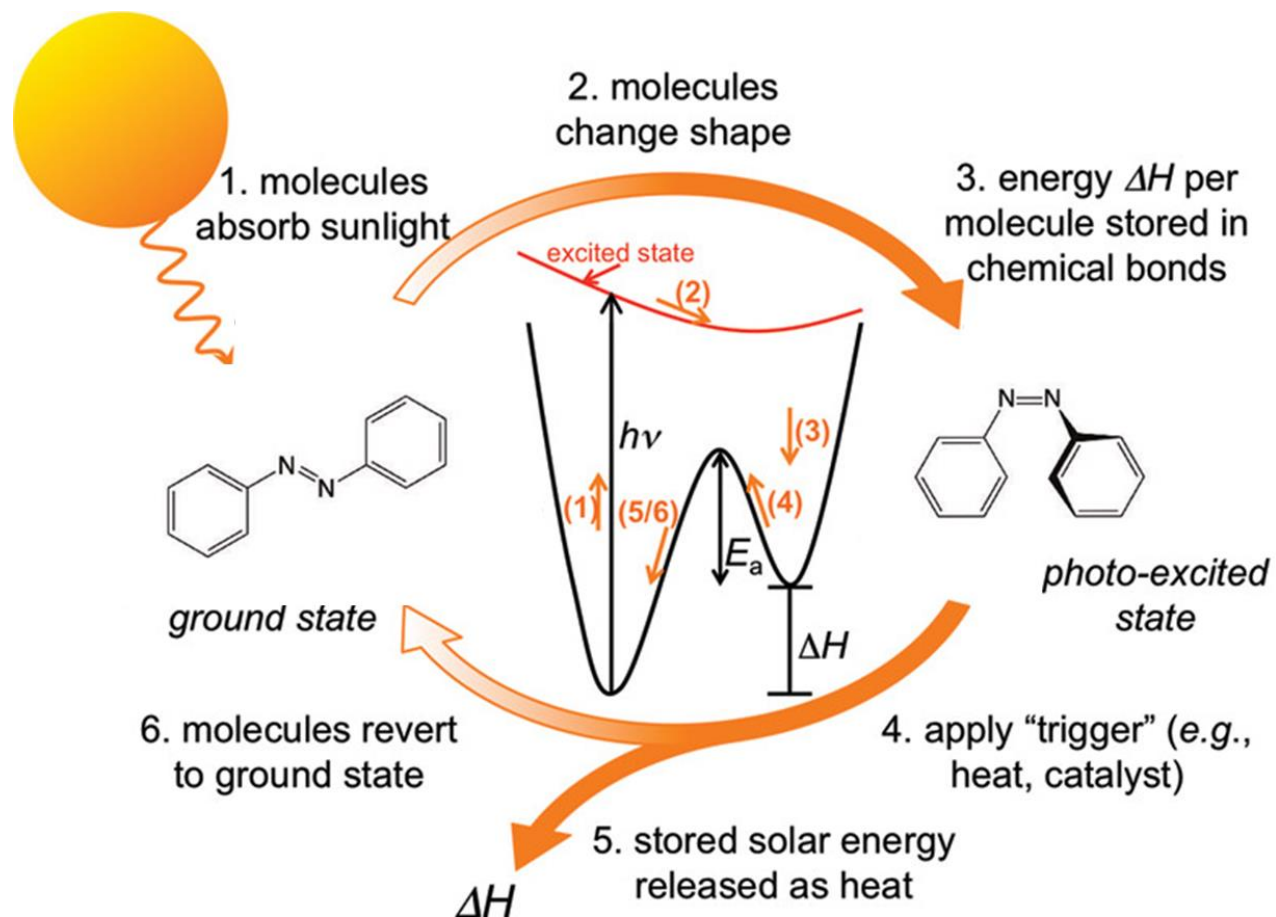
What is a MOlecular Solar Thermal systems ?



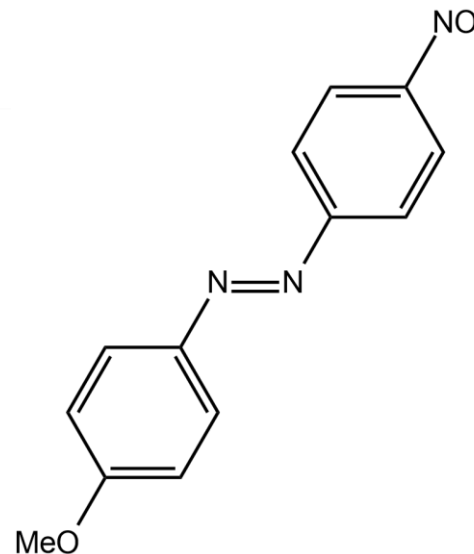
- Storage energy $\leftrightarrow \Delta H$
- Half-life time ($t_{1/2}$) $\leftrightarrow E_a$
- Absorbance > 400 nm

- $\Delta H = 50 \text{ kJ.mol}^{-1}$
- $t_{1/2} \sim 24\text{h}$
- $\lambda_{\text{max}} = 325 \text{ nm}$

What is a MOlecular Solar Thermal systems ?



Push-Pull systems

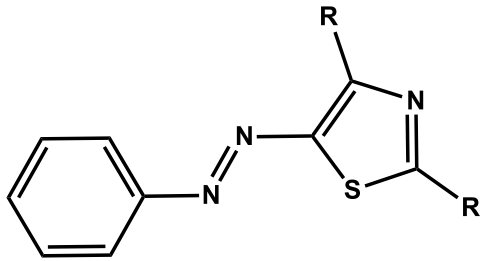


$\pi-\pi^*$: 370 nm
 $n-\pi^*$: 460 nm

$t_{1/2} \approx 10^{-4} \text{ s}$

MOST Property Improvement

Spectroscopic properties Improvement



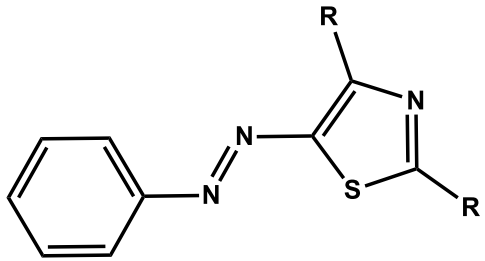
$\pi-\pi^* \approx 480 - 650 \text{ nm}$

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

Half-life time improvement

MOST Property Improvement

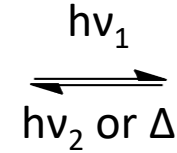
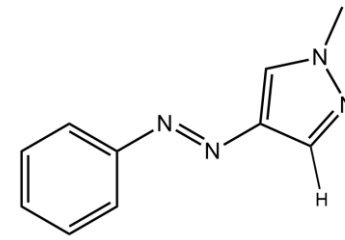
Spectroscopic properties Improvement



$\pi-\pi^* \approx 480 - 650 \text{ nm}$

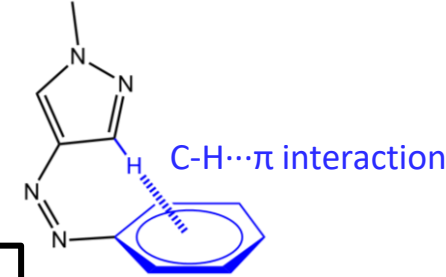
Text. Res. J. **2020**, *90* (11-12), 1396-1403

Half-life time improvement



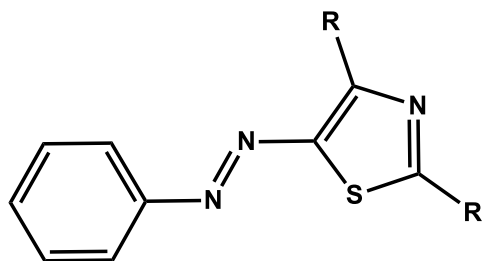
$t_{1/2} \approx 1000 \text{ days}$

Nat Rev Chem, **2019**, *3*, 133–146; 1



MOST Property Improvement

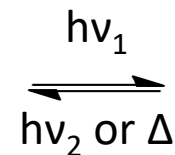
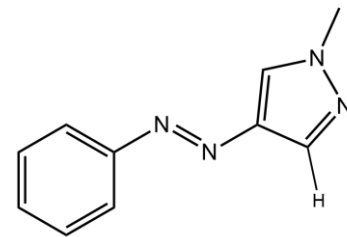
Spectroscopic properties Improvement



$\pi-\pi^* \approx 480 - 650 \text{ nm}$

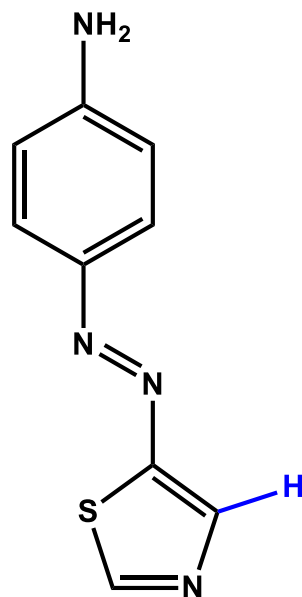
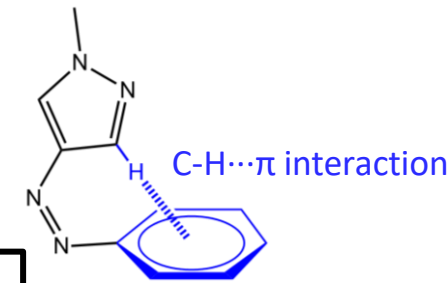
Text. Res. J. **2020**, *90* (11-12), 1396-1403

Half-life time improvement



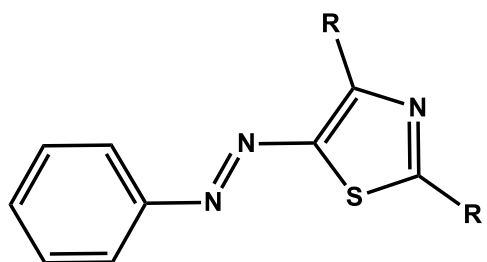
$t_{1/2} \approx 1000 \text{ days}$

Nat Rev Chem, **2019**, *3*, 133–146; 1



MOST Property Improvement

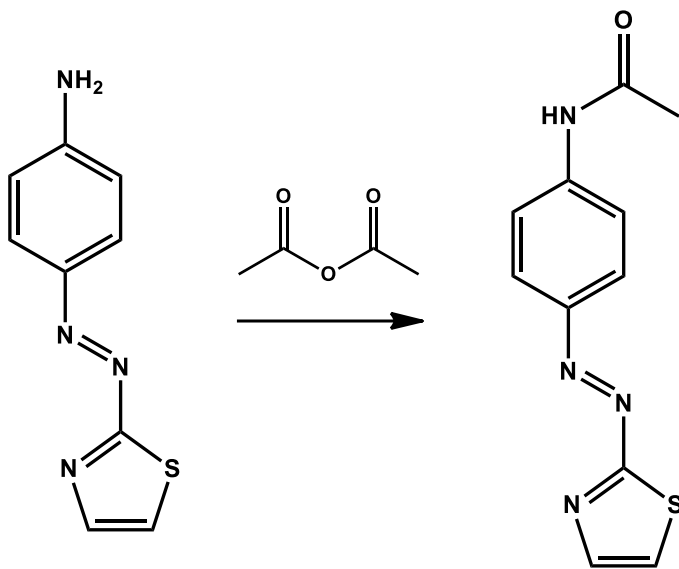
Spectroscopic properties Improvement



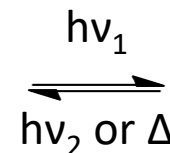
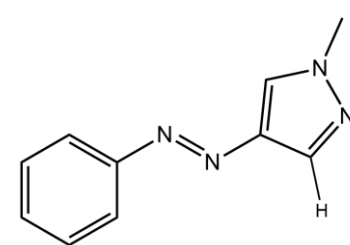
$\pi-\pi^* \approx 480 - 650 \text{ nm}$

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

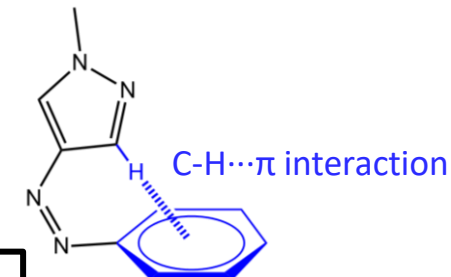
Synthesized molecules



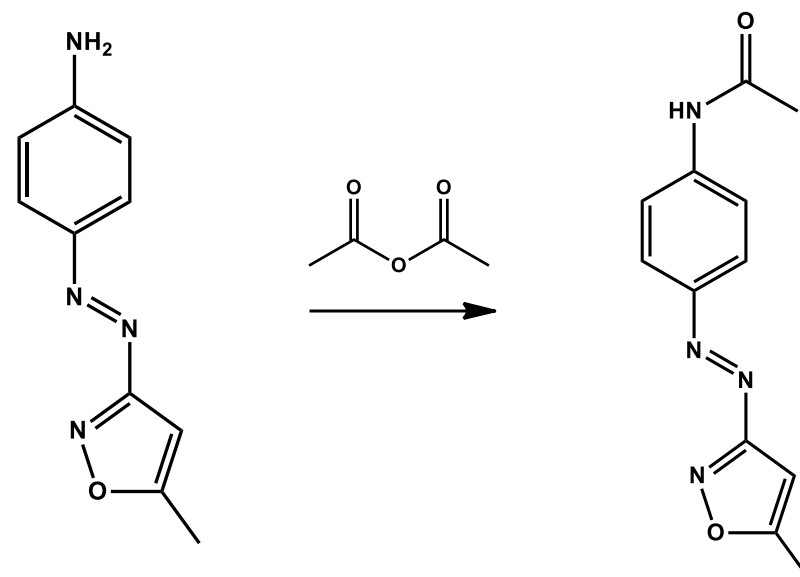
Half-life time improvement



$t_{1/2} \approx 1000 \text{ days}$

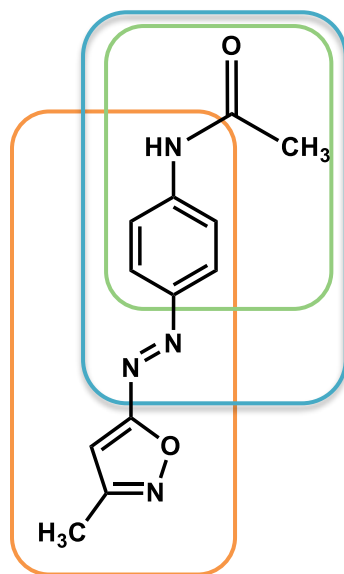


Synthesized molecules



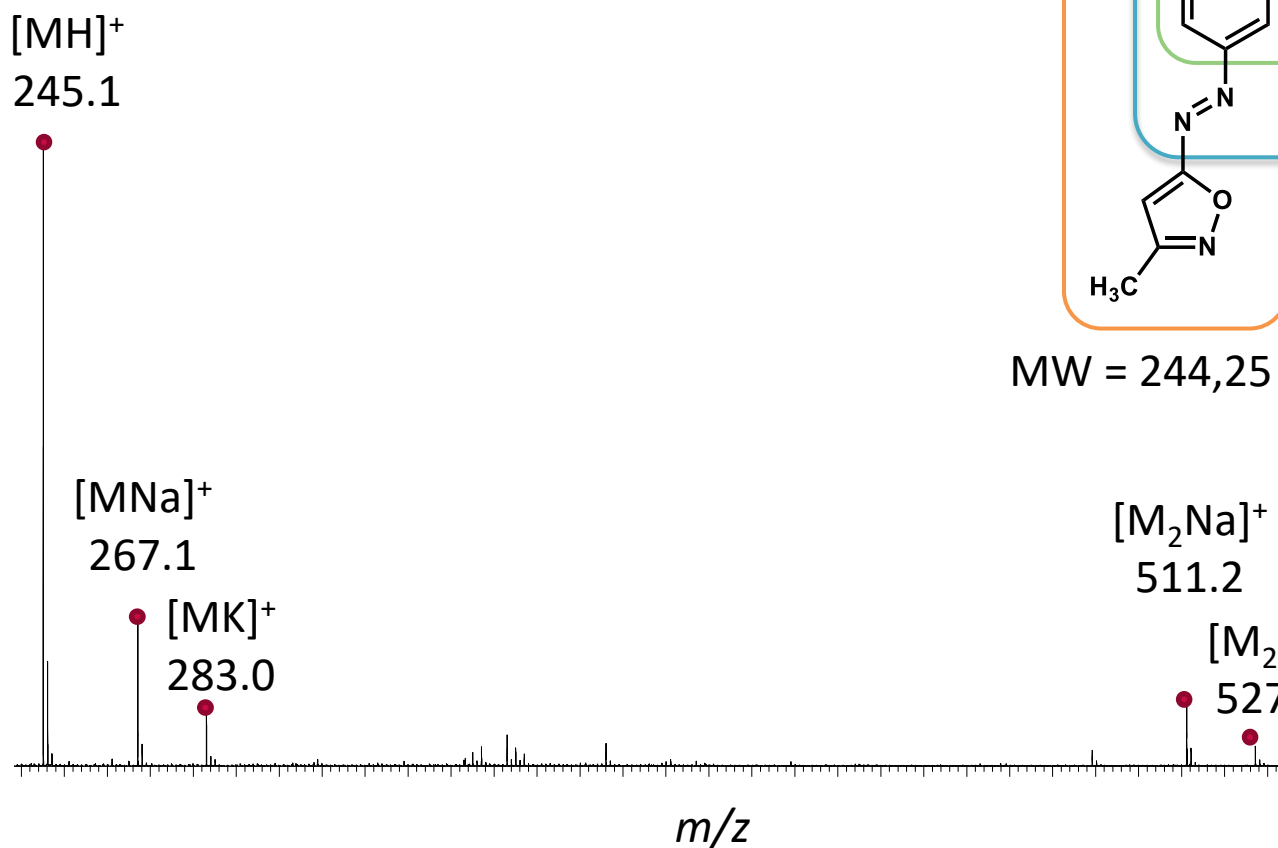
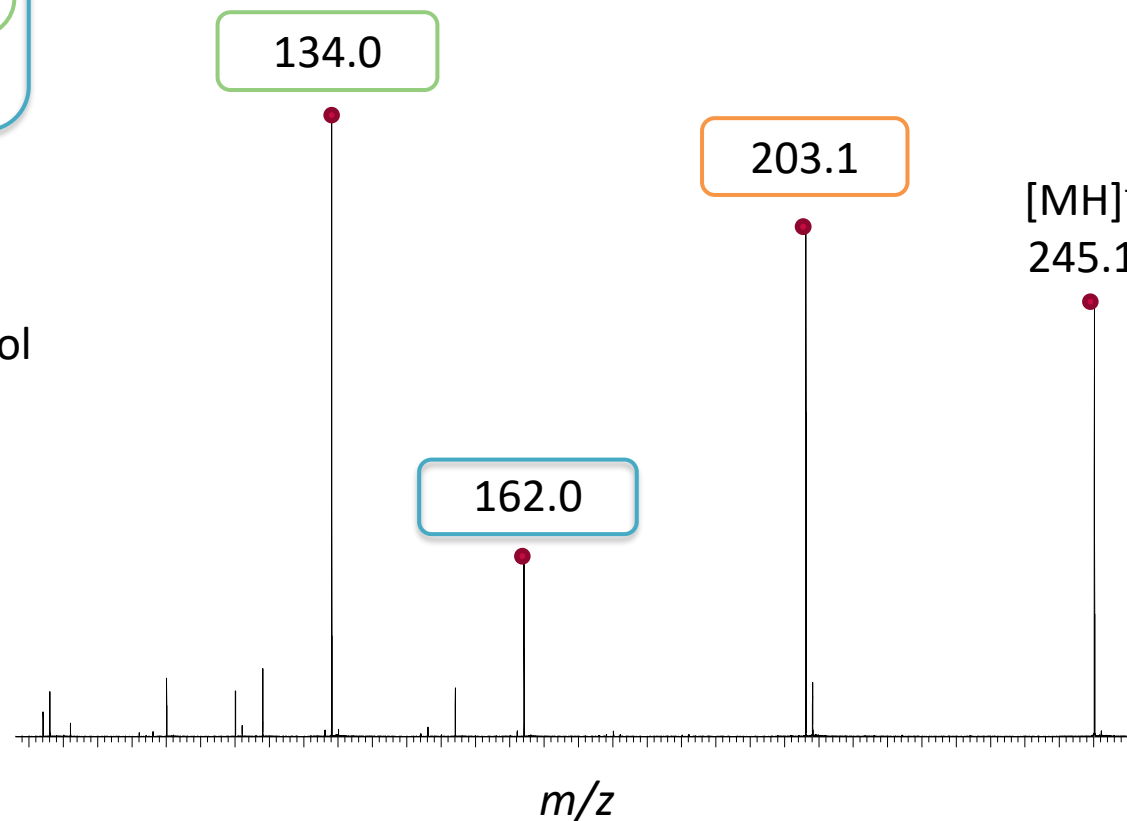
Structural Characterization

ToF MS ESI (+)

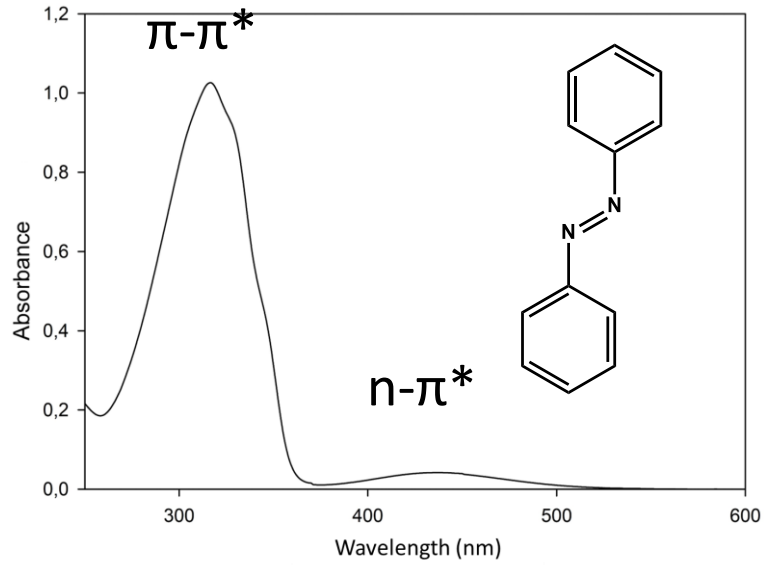


MW = 244,25 g/mol

ToF MS-MS ESI (+)



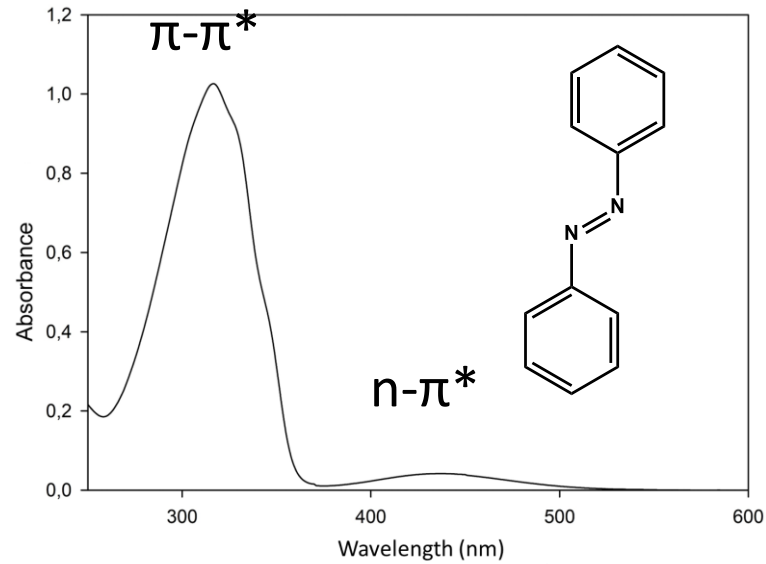
Spectroscopic properties



MeOH HPLC, $C \approx 5 \cdot 10^{-5}$ M

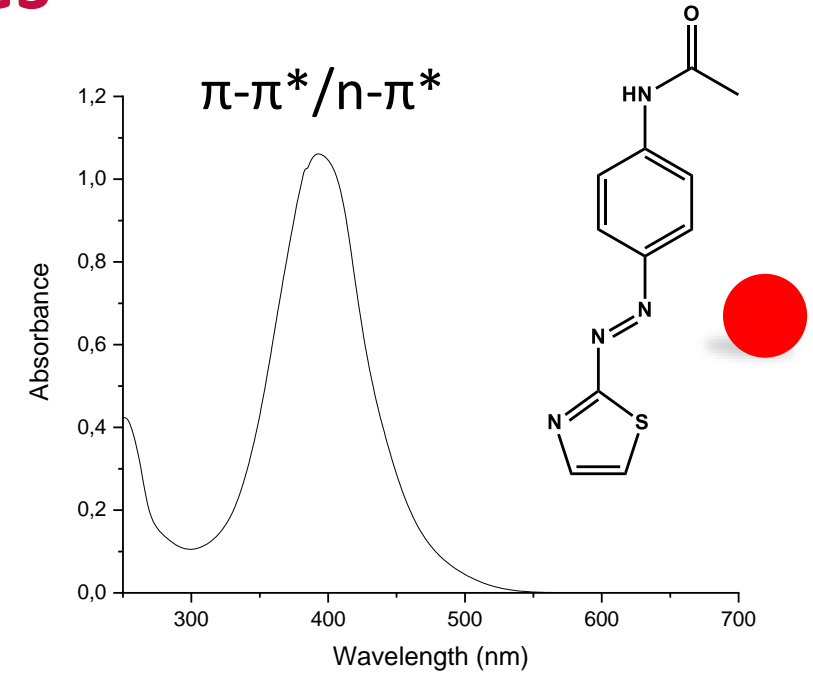
	$\pi-\pi^*$ (nm)	$n-\pi^*$ (nm)
Azo	315	440

Spectroscopic properties

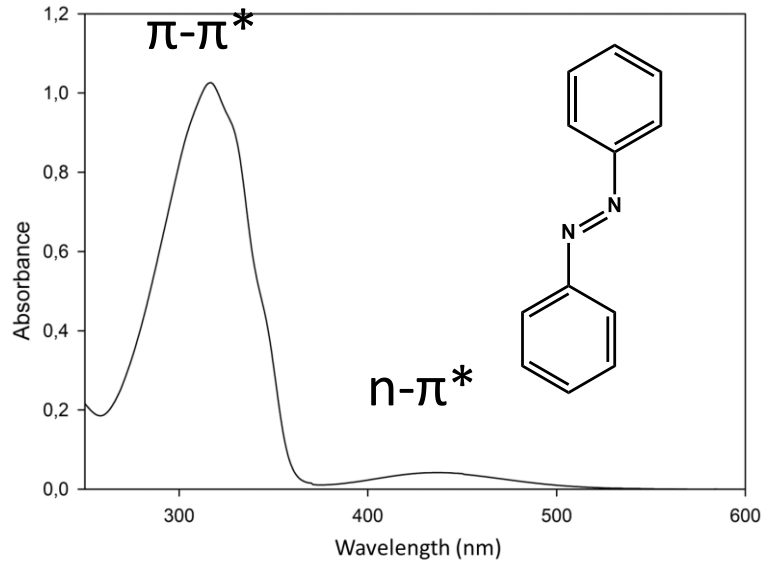


MeOH HPLC, $C \approx 5 \cdot 10^{-5}$ M

	π - π^* (nm)	n- π^* (nm)
Azo	315	440
Azo- ●	394	na

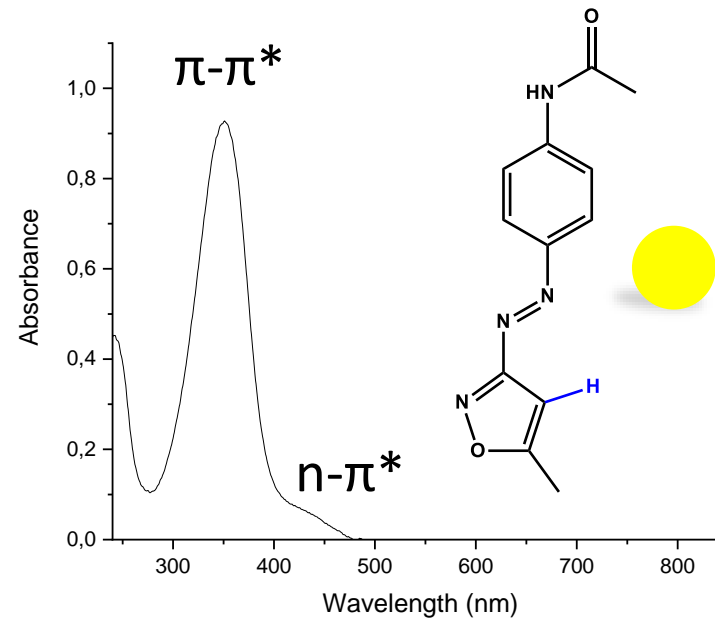
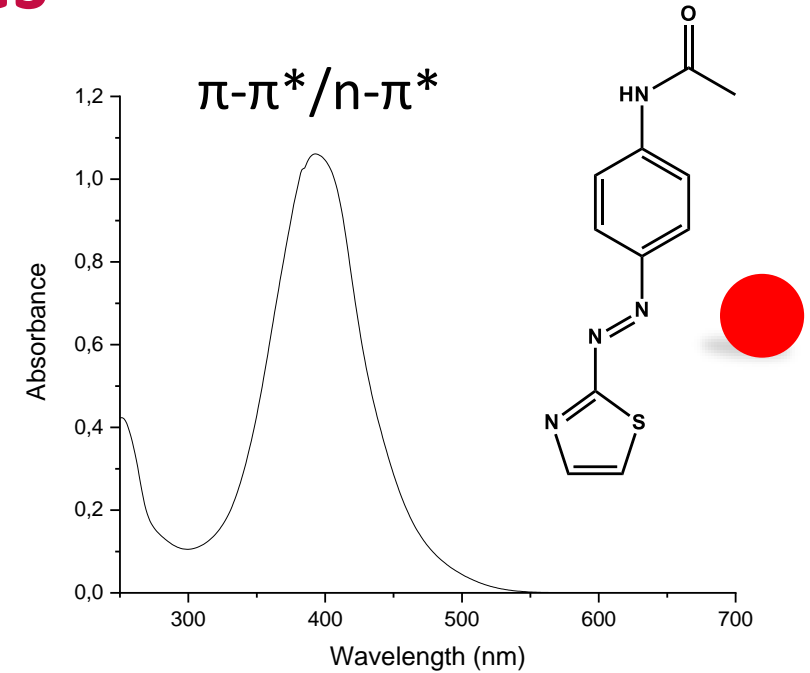


Spectroscopic properties



MeOH HPLC, C ≈ 5.10⁻⁵ M

	π-π* (nm)	n-π* (nm)
Azo	315	440
Azo- ●	394	na
Azo- ●	350	430



Photoisomerization materials and methods

Inducing photoisomerization



E and Z isomers



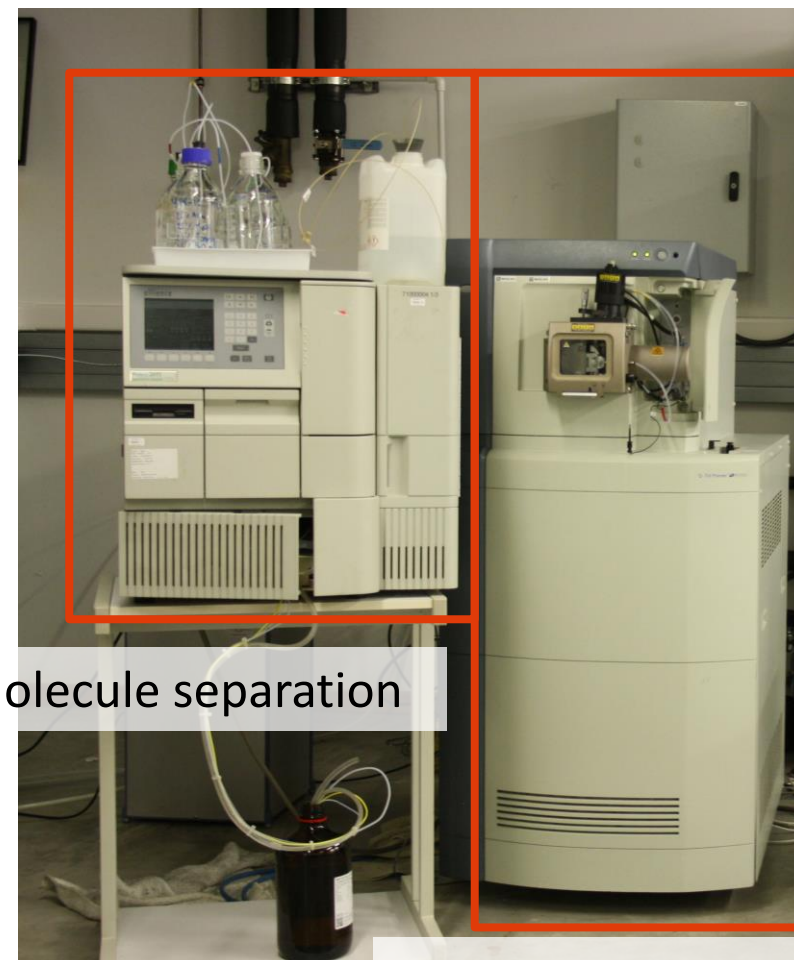
LC-MS Analyses



Visible lamp (ca. 400-800 nm)



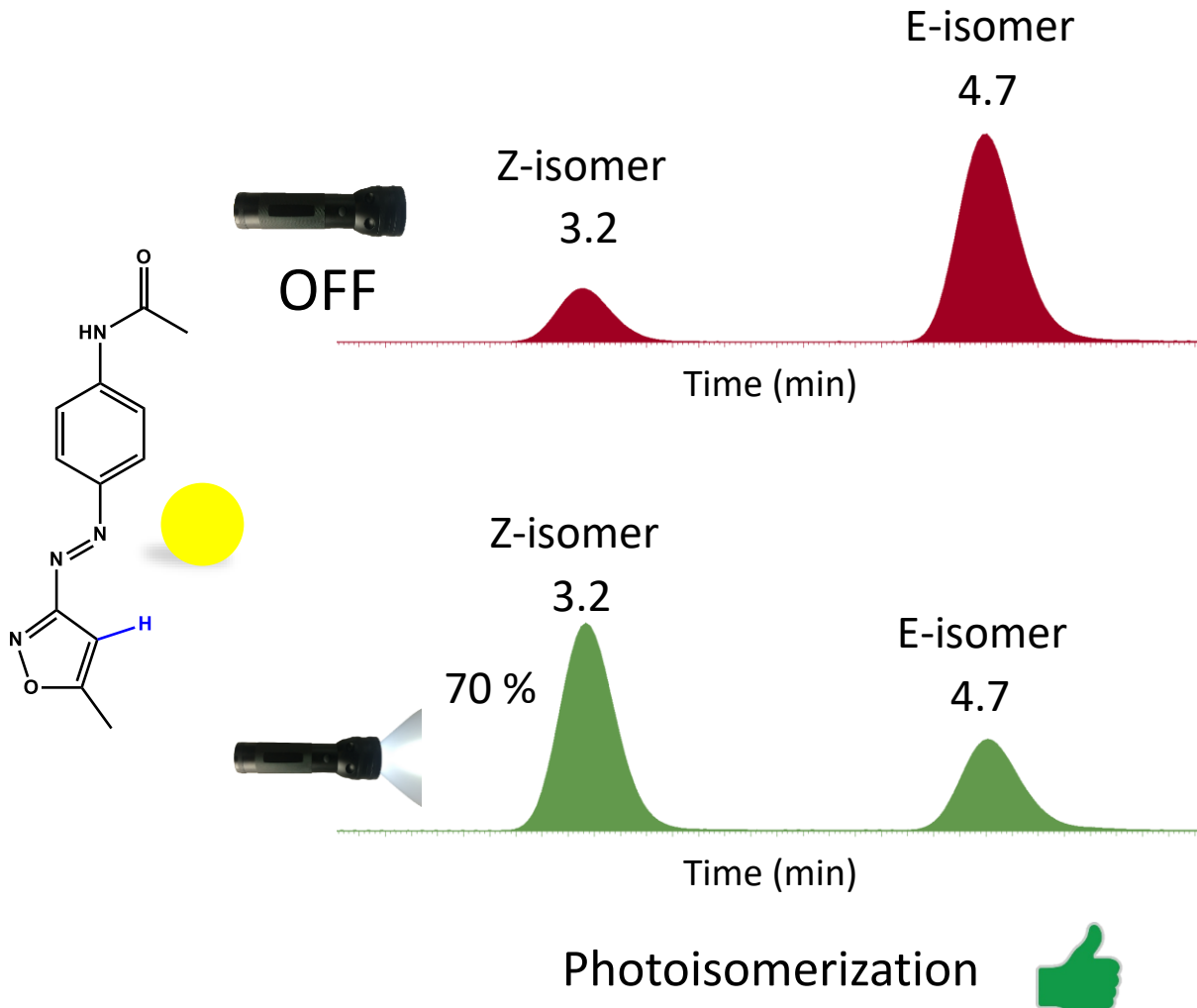
UV lamp (ca. 220 - 400 nm)



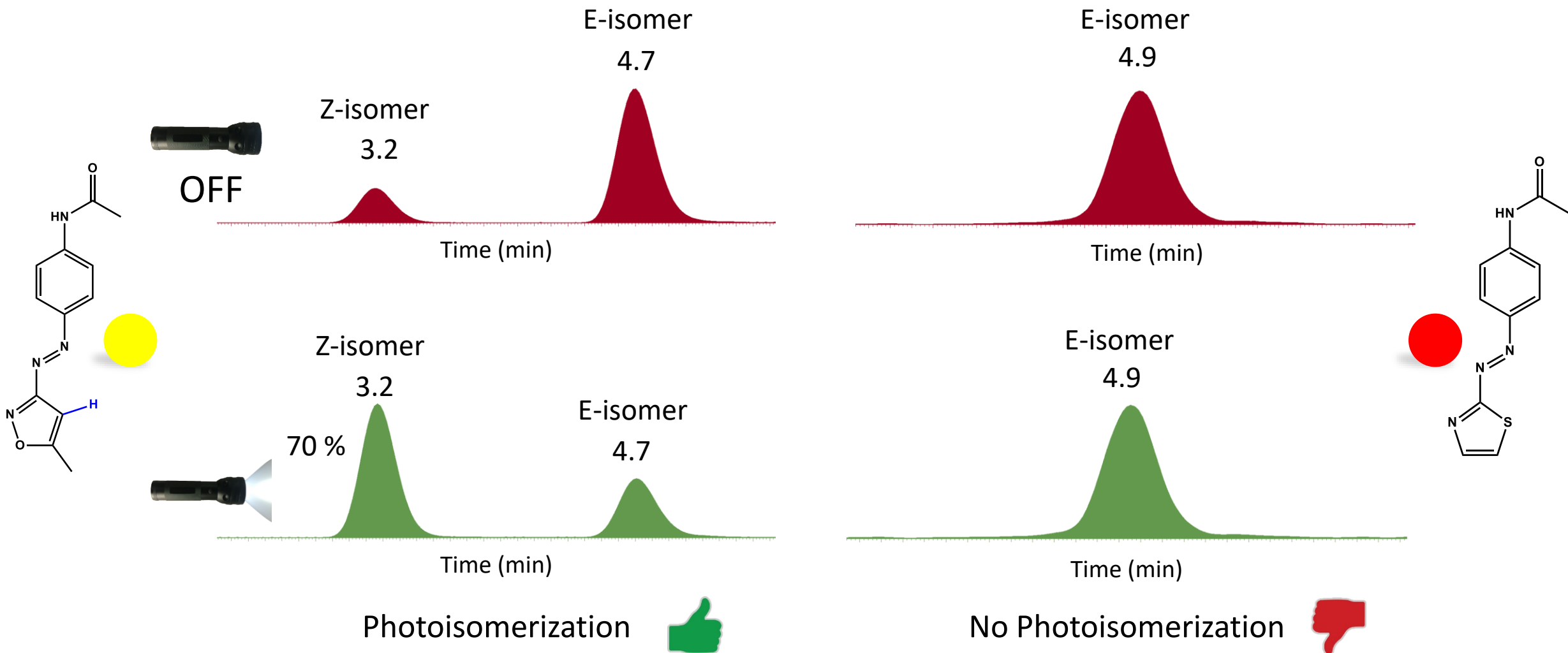
Molecule separation

Ion detection

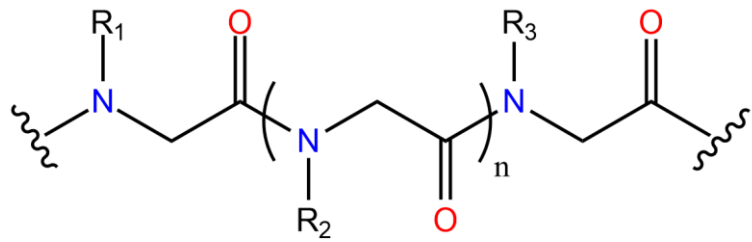
Photoisomerization LC-MS analyses



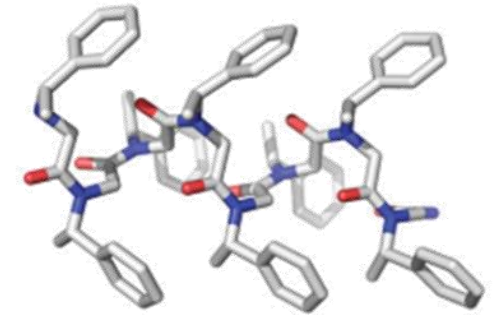
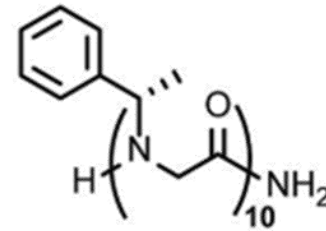
Photoisomerization LC-MS analyses



Grafting on macromolecules



3D Structure

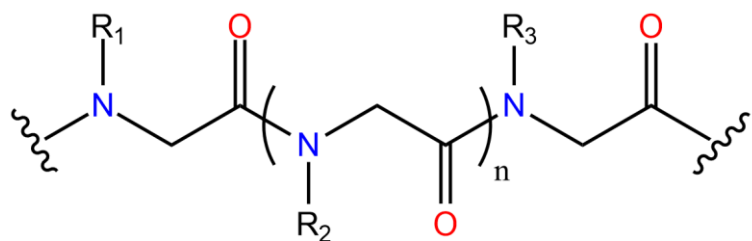


Inter-residue interaction

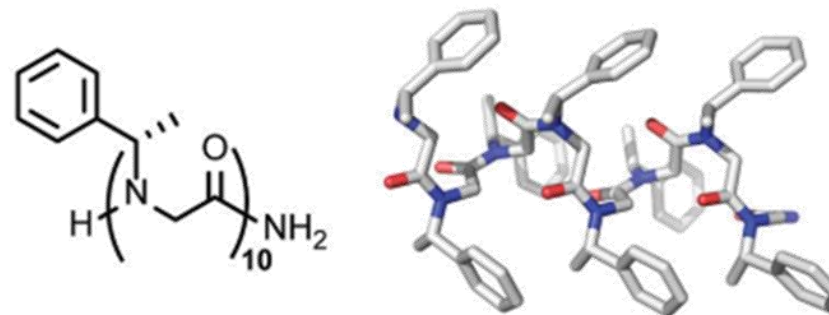


$t_{1/2}$ and ΔH improvement

Grafting on macromolecules



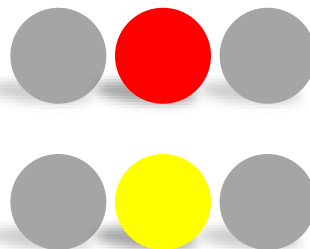
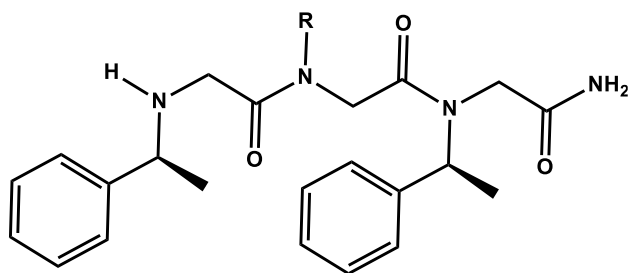
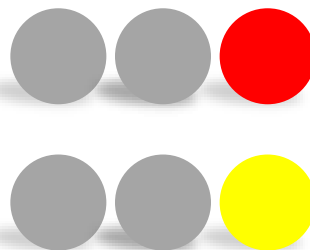
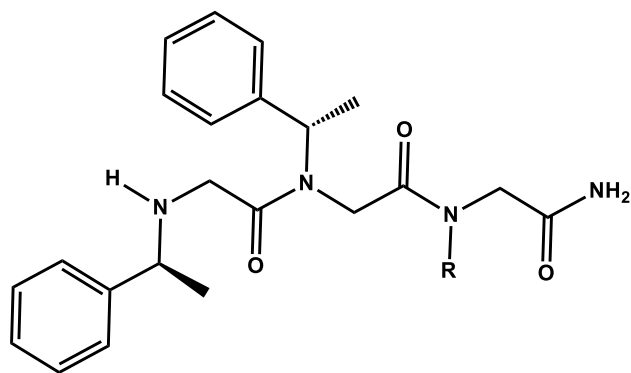
3D Structure



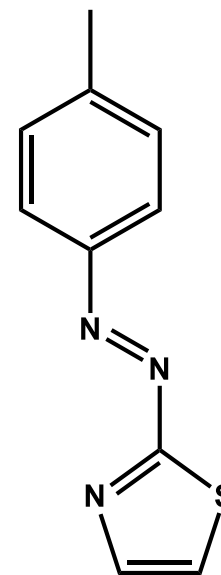
Inter-residue interaction



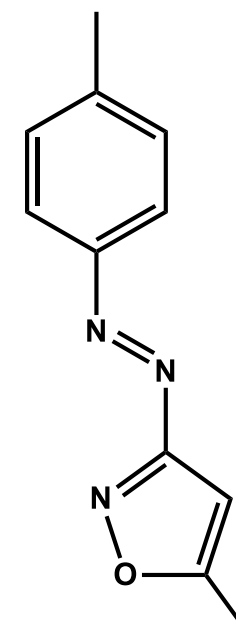
$t_{1/2}$ and ΔH improvement



R =

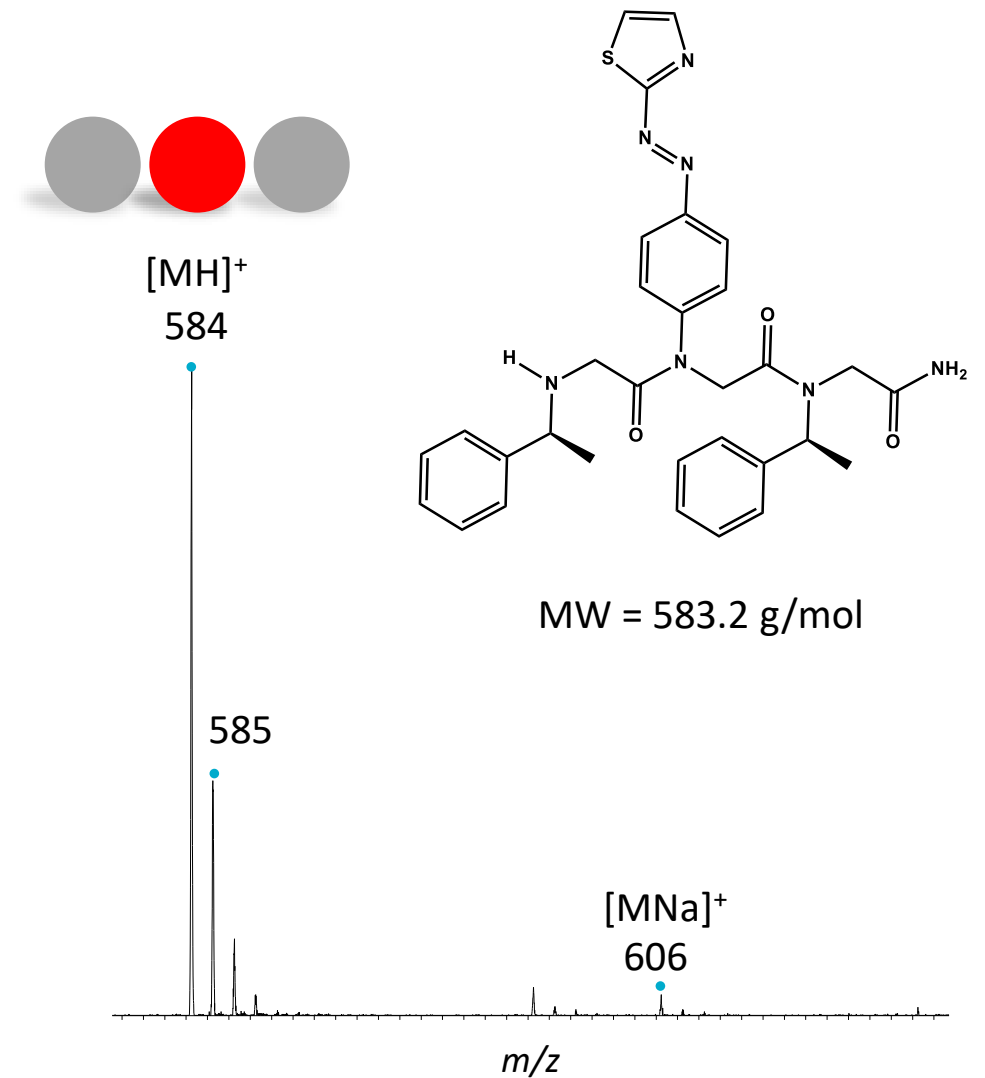
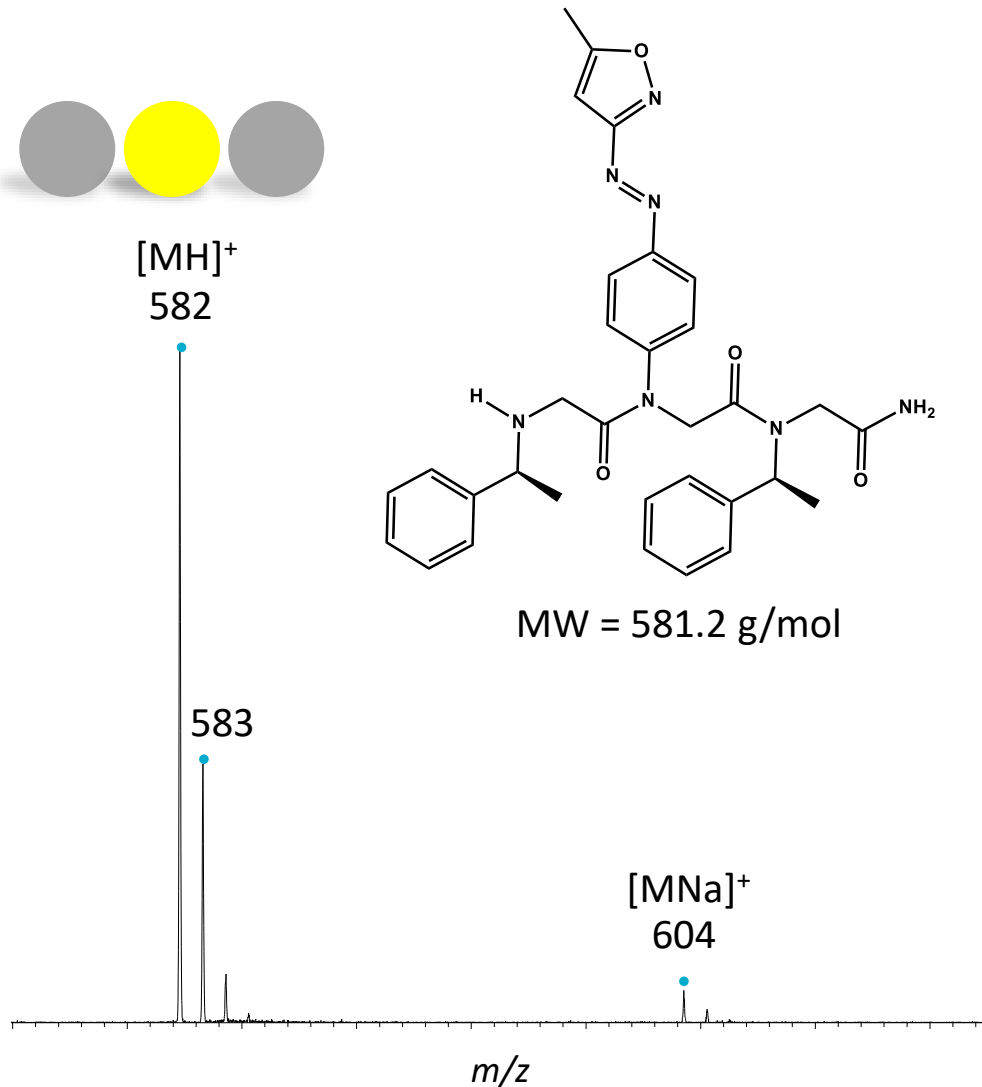


or

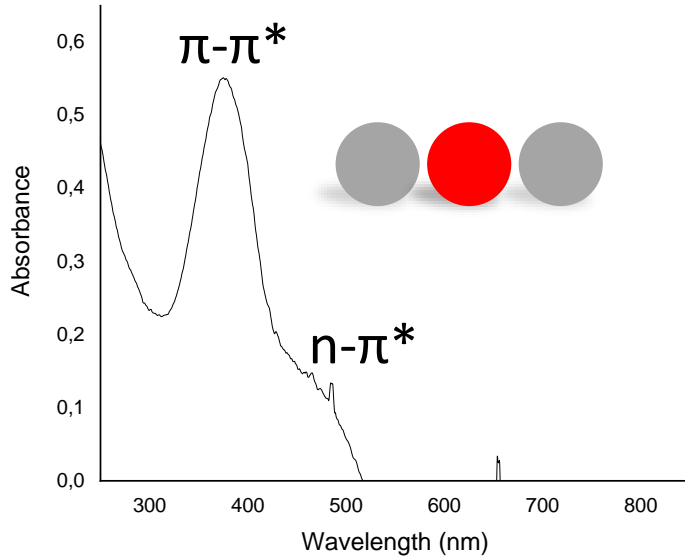


Structural Characterization



ToF MS ESI (+)

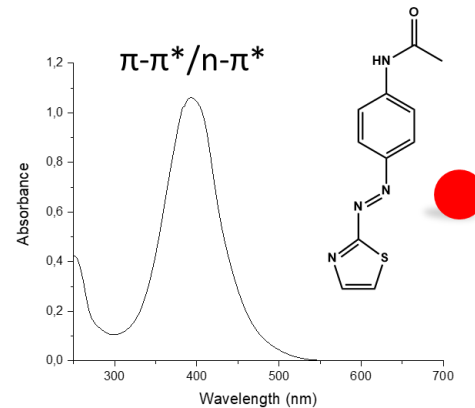
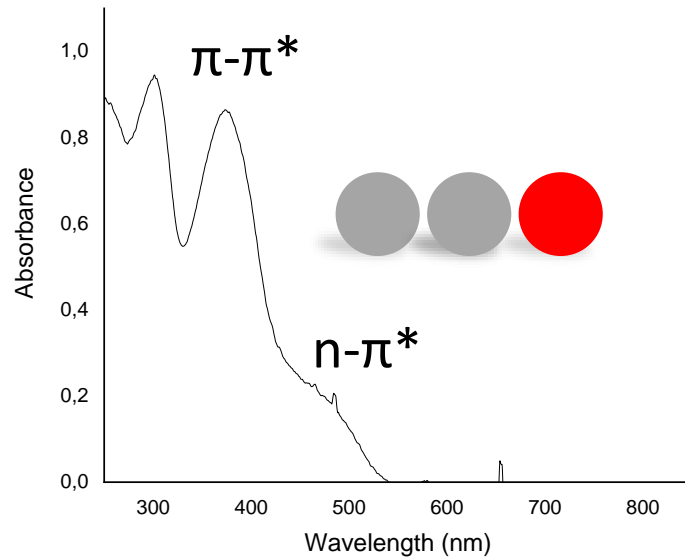


Spectroscopic properties

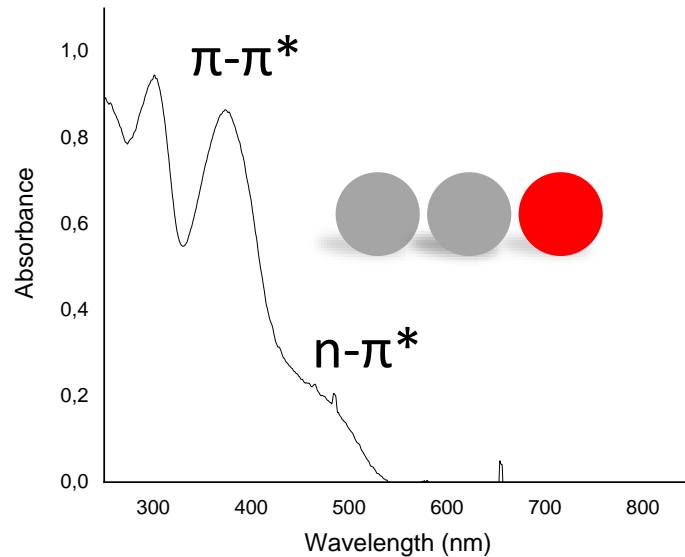
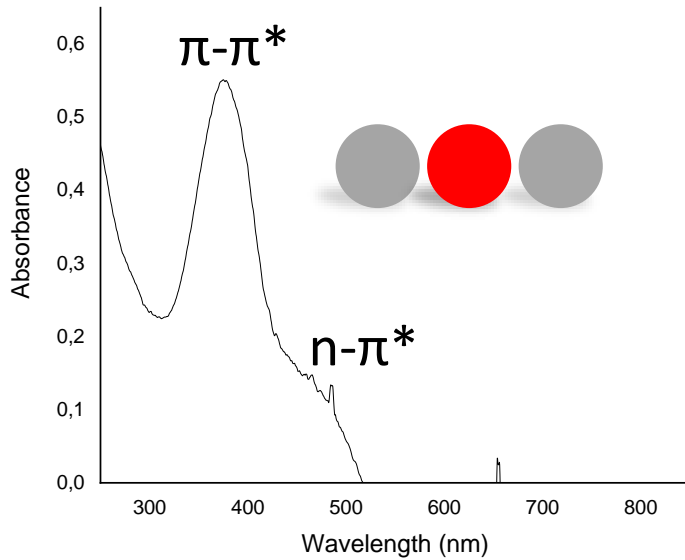


MeOH HPLC, $C \approx 5.10^{-5}$ M















	π-π* (nm)	n-π* (nm)
Azo	315	440
Azo- 	394	na
  	370	480
  	370	480
Azo- 	350	430

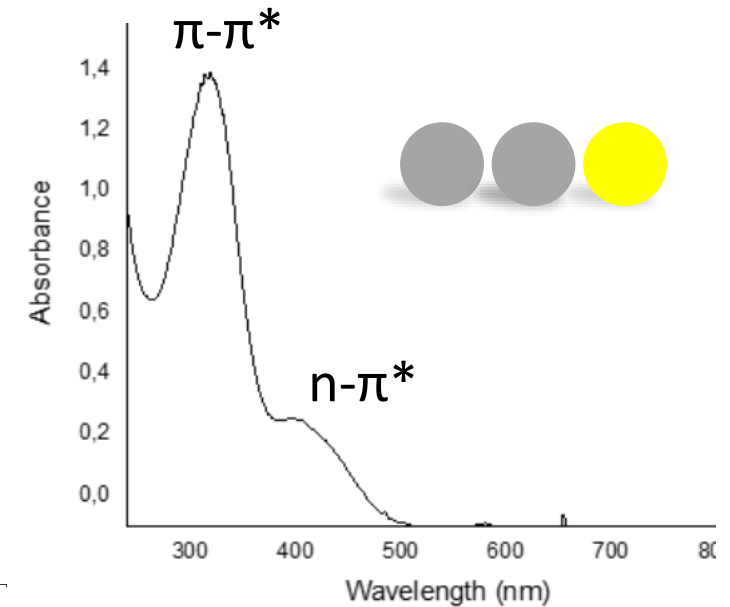
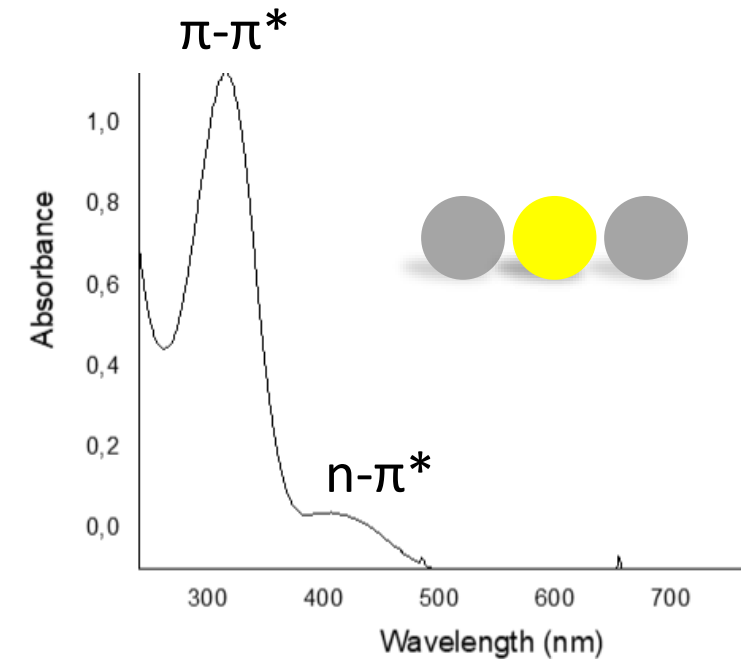
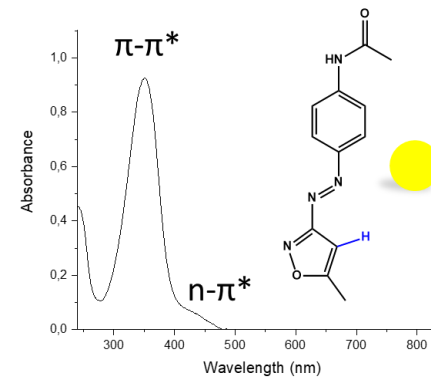
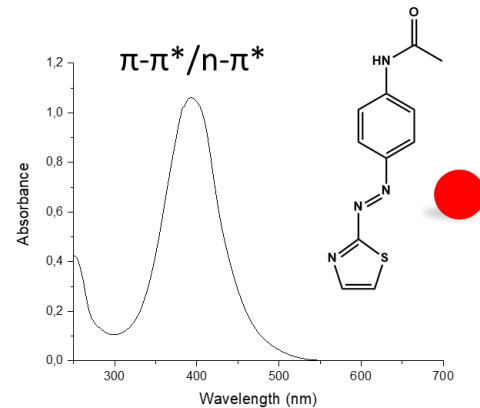


Spectroscopic properties

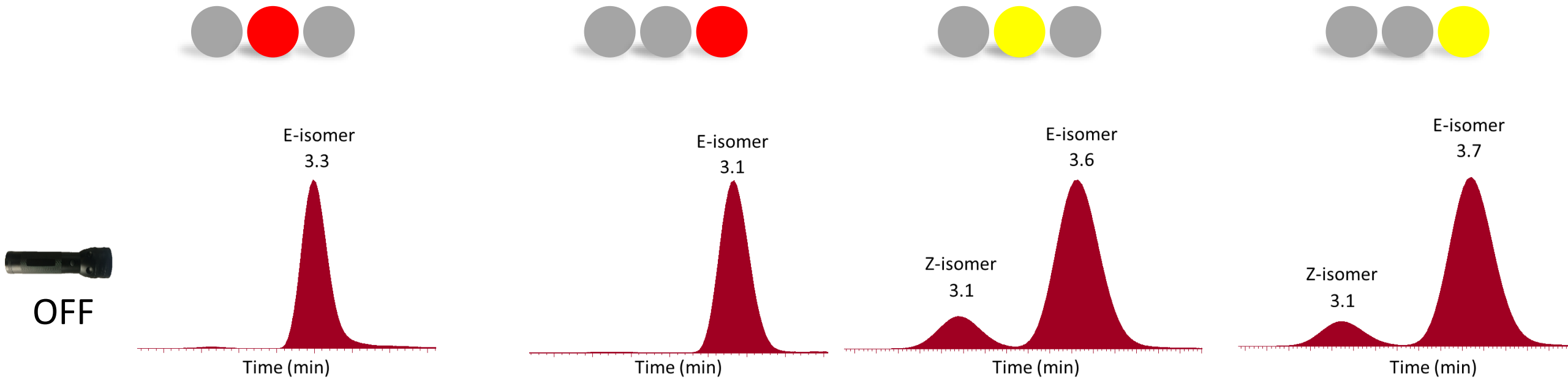


MeOH HPLC, $C \approx 5 \cdot 10^{-5}$ M

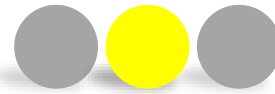
	π - π^* (nm)	n - π^* (nm)
Azo	315	440
Azo- 	394	na
  	370	480
  	370	480
Azo- 	350	430
  	315	410
  	315	410



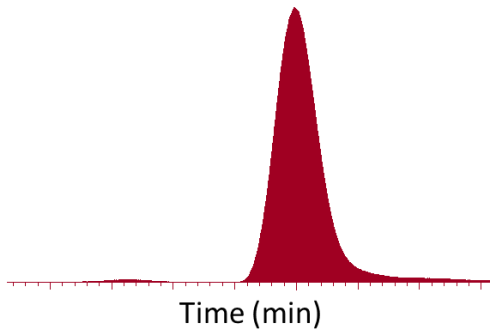
Photoisomerization LC-MS analyses



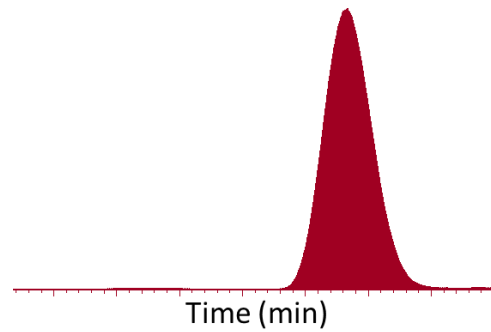
Photoisomerization LC-MS analyses



E-isomer
3.3

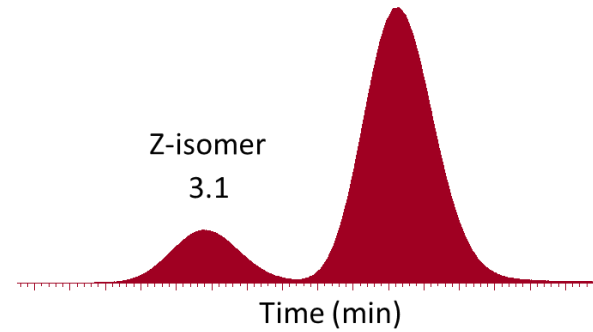


E-isomer
3.1



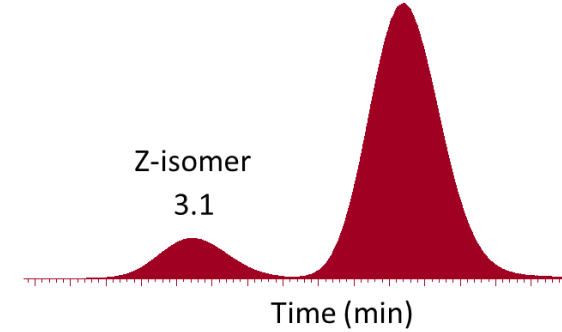
E-isomer
3.6

Z-isomer
3.1

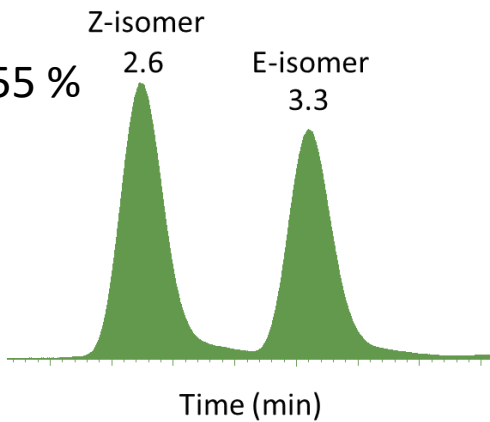


E-isomer
3.7

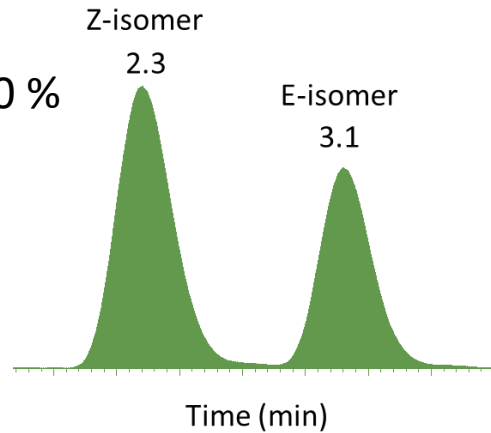
Z-isomer
3.1



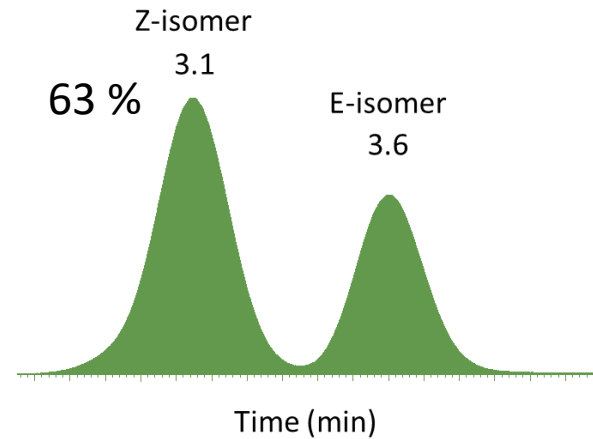
55 %
Z-isomer
2.6
E-isomer
3.3



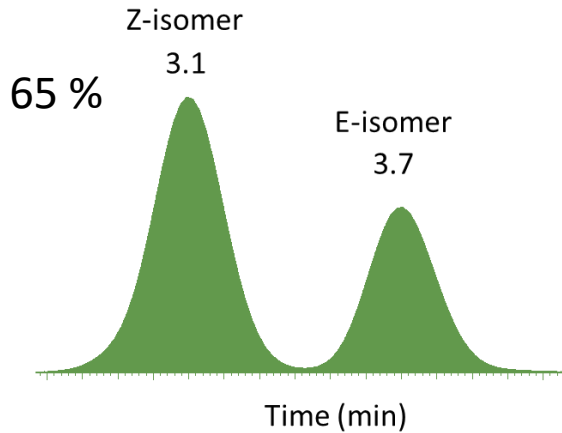
60 %
Z-isomer
2.3
E-isomer
3.1



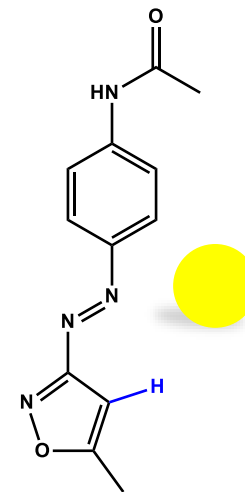
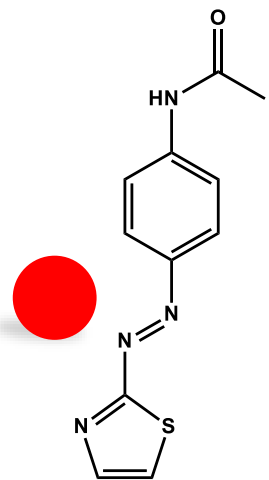
63 %
Z-isomer
3.1
E-isomer
3.6



65 %
Z-isomer
3.1
E-isomer
3.7



Conclusions



Synthesis and
characterization



UV-Visible (π - π^*)

390 nm

370 nm

370 nm

350 nm

315 nm

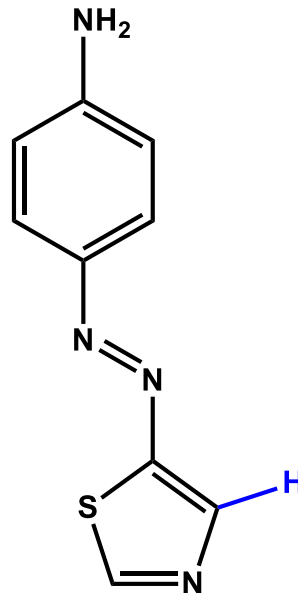
315 nm

Photoisomerization



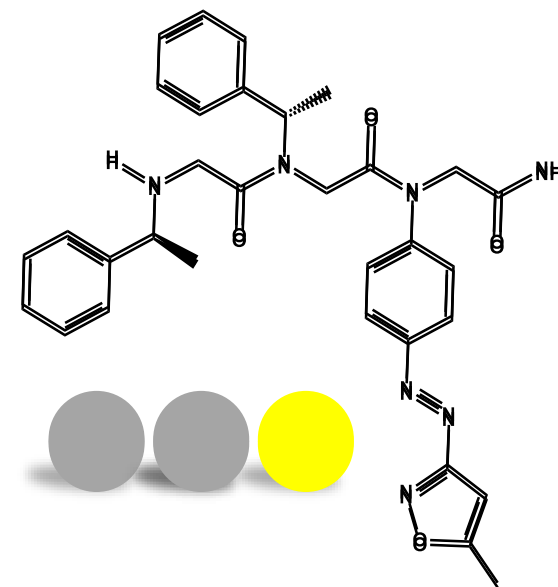
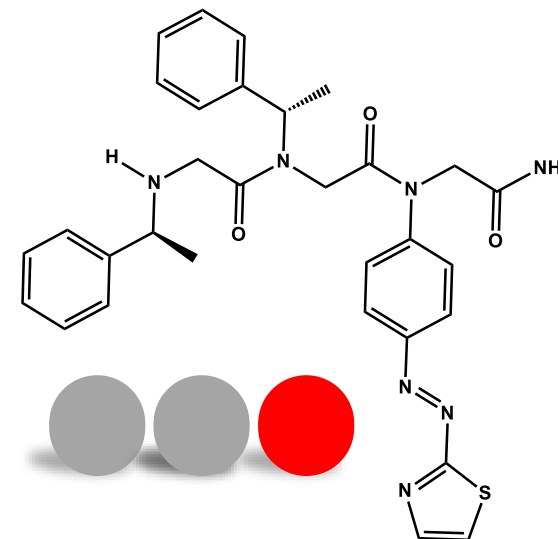
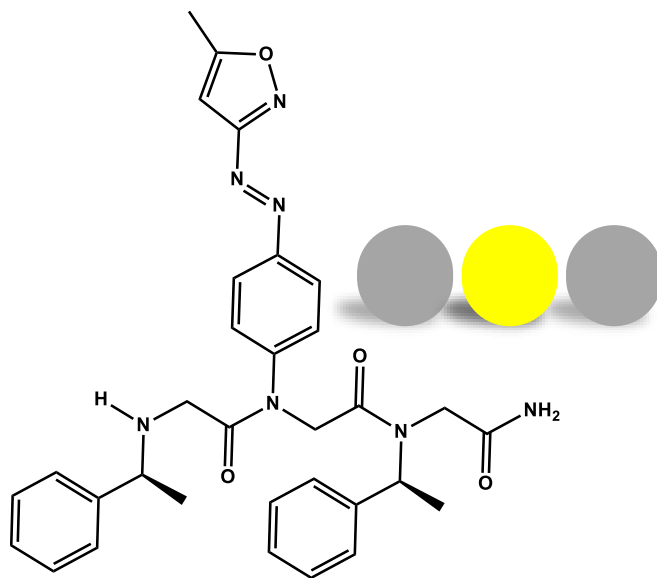
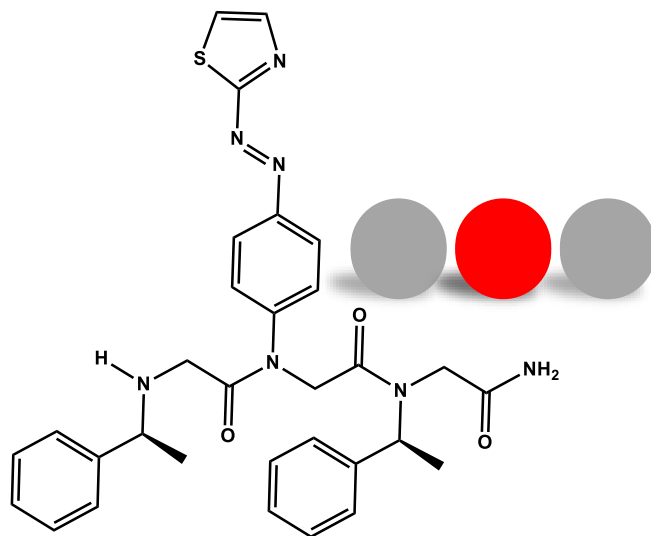
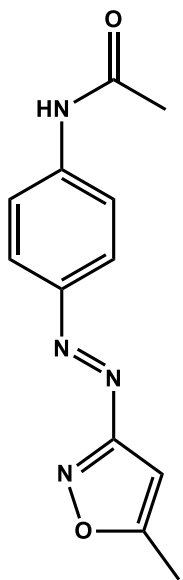
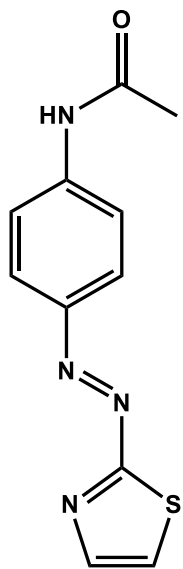
Perspectives

- Understand the stabilization of cis isomer in peptoid by theoretical modelling
- Determination of the other MOST properties : $t_{1/2}$, ΔH , etc.
- Associating both azo-derivatives within a single peptoid
- Synthesize the desired molecule :

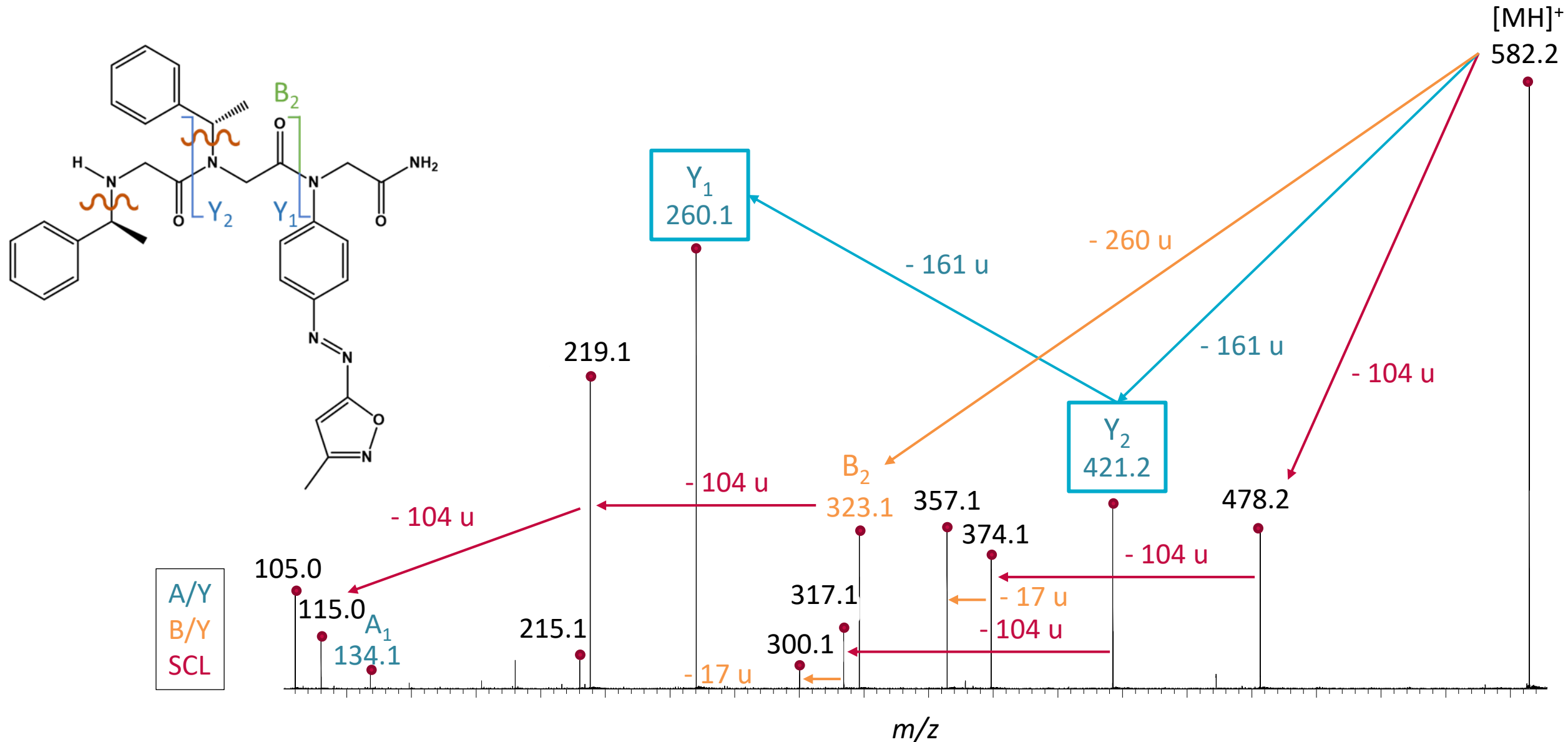


Thank you for your attention

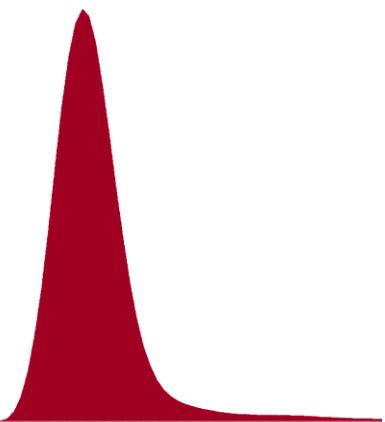
Synthesized Products



Structural Characterization

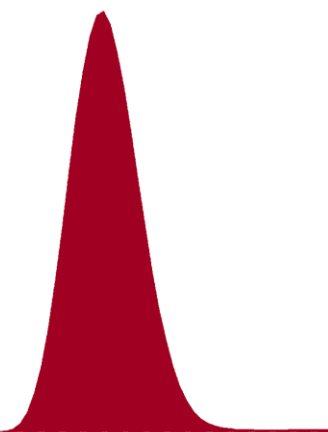


E-isomer
3.3



Time (min)

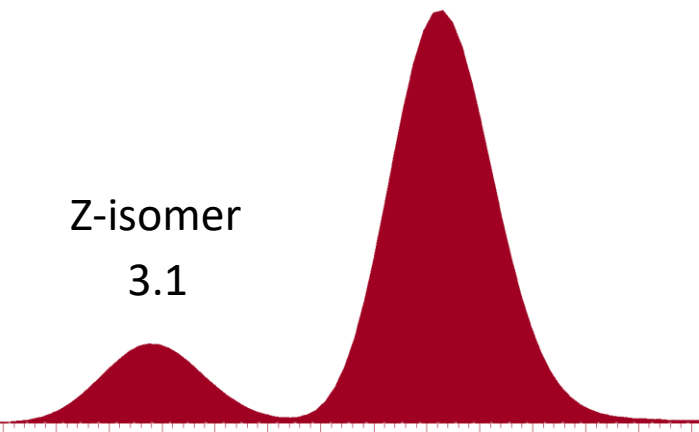
E-isomer
3.1



Time (min)

E-isomer
3.6

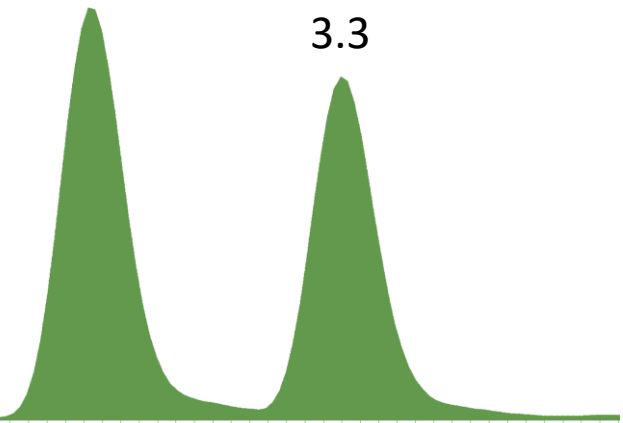
Z-isomer
3.1



Time (min)

Z-isomer
2.6

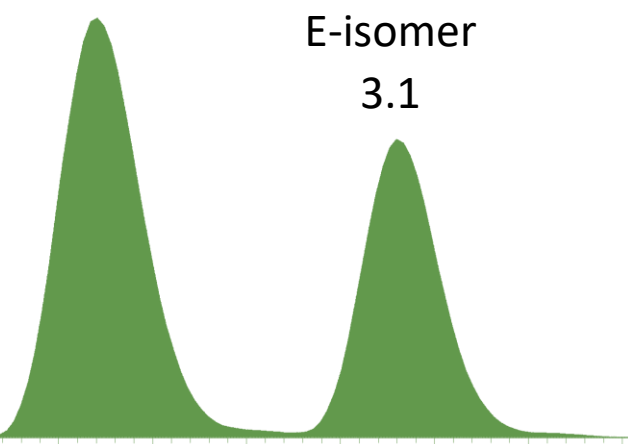
E-isomer
3.3



Time (min)

Z-isomer
2.3

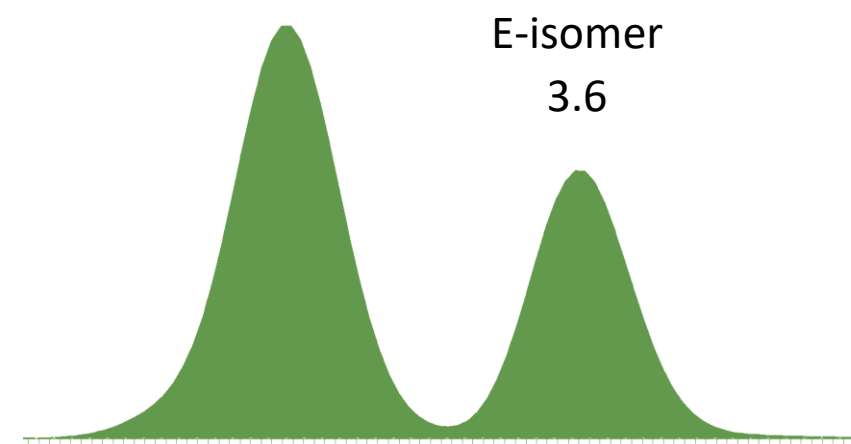
E-isomer
3.1



Time (min)

Z-isomer
3.1

E-isomer
3.6



Time (min)

