Synthesis, Photoisomerisation and Characterisation of a *Z*-olefin

Light2X Project: A first step towards artificial photosynthesis

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Introduction

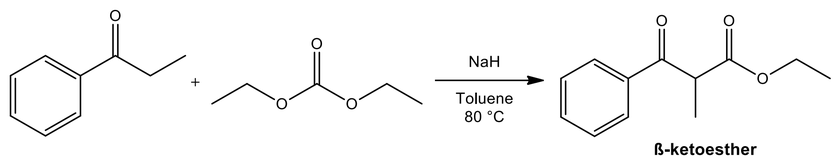
Renewable energy systems show an inconsistent output and mismatches with energy demand of the market, what causes some energy surpluses and shortages throughout the year. The Light2X Project aims to store energy in a chemical bond by a photochemical route that connects hydrogen (H_2) to the ultimate waste product CO_2, in order to produce so-called solar fuels and C1-chemicals/products.

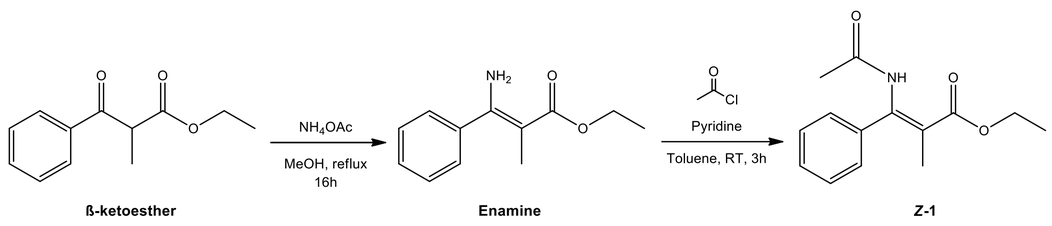
As the above mentioned reaction is difficult to work on, the first step in the execution of the project is the photoisomerization and hydrogenation of a double bond of an industrially interesting compound. The reaction is being planned as an one-pot reaction to be ran in a reactor developed by the other part of the team.

Materials & Method

SYNTHESIS

Z-ethyl-3-acetamido-2-methyl-3-phenylacrylate





The final product was purified by automated column chromatography (n-heptane-EtOAc 5:1)

PHOTOISOMERISATION

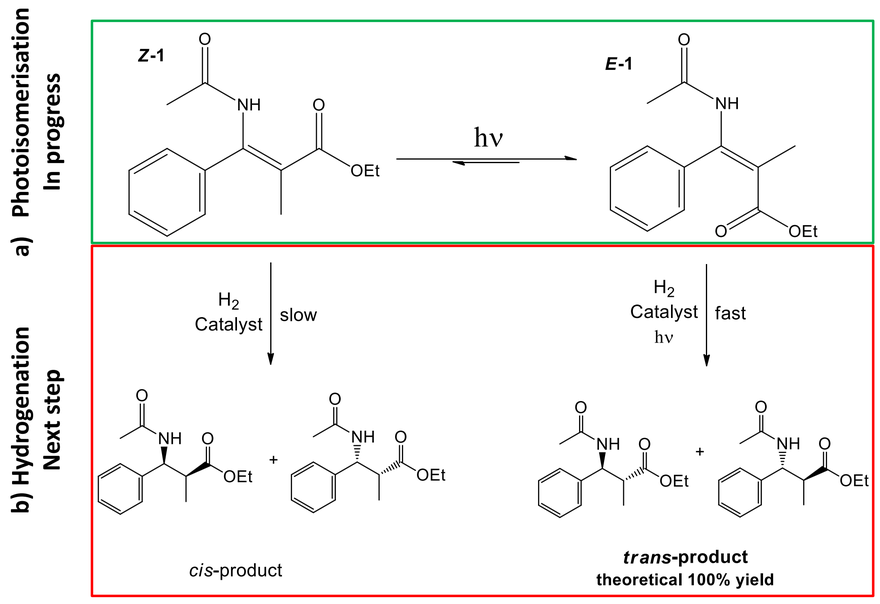


Figure 1. Scheme for a) *Z*/*E* photoisomerisation followed by b) asymmetric hydrogenation yielding mainly the *trans*-product from *E*-1 hydrogenation.

Z-1 was dissolved in THF and placed between UV-lights over 24 hours. Photoisomerisation progress was monitored by Thin Layer Chromatography – TLC (Figure 2).

After 24 hours: ^{1}H NMR sample was collected.

Results & Discussion

PHOTOISOMERISATION

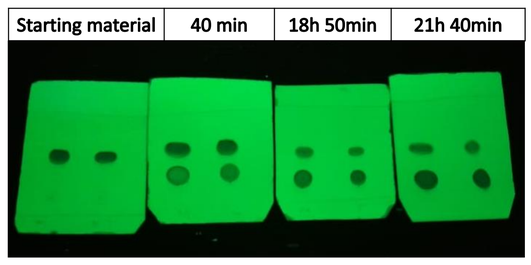


Figure 2. TLC showing the photoisomerization progress.

^{1}H NMR shows all peaks for *Z*-1 and *E*-1. Conversion was calculated based on the *Z*-1 remaining peaks in comparison with the same hydrogen peaks for *E*-1.

The resulting percentage of *E*-1 in the mixture was approximately 80%.

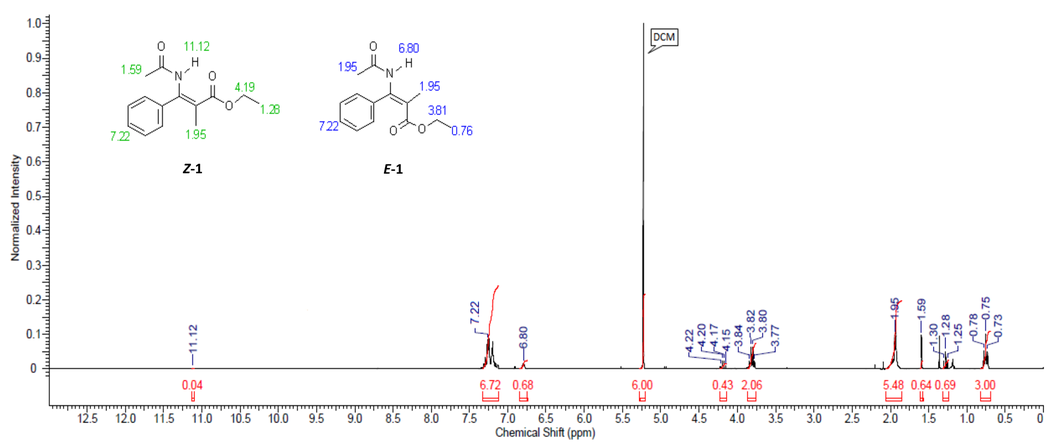


Figure 3. ^{1}H NMR spectrum on $CDCl_3$ [300 MHz]

Both results are consistent because even though TLC is not a quantitative technique, it is possible to see from the intensity of the dots that the *E*-1 formation increases with the time while *Z*-1 quantity decreases.

Conclusion

- *Z*-1 was synthesized properly;
- Automated column chromatography is an efficient method to separate *Z*-1 of undesired products obtained together in the synthesis;
- THF is a suitable solvent for isomerization over 24 hours. With 24 hours it showed a satisfactory conversion and no side-products;

Next Steps

- Find the setup to purify *E*-1 using the automated column chromatography;
- Research a proper asymmetric catalyst that is not affected by UV-light;
- Run hydrogenation and photoisomerization followed by hydrogenation tests in THF (Figure 1b);
- Test the reactor.

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