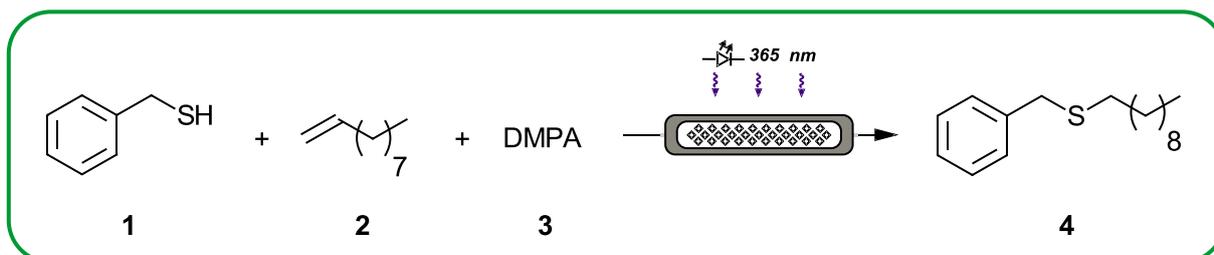


## Application Note 2

### Photoinitiated thiol-ene coupling in flow

Data courtesy of EcoSynth, authored by dr. ir. Wouter Debrouwer

#### 1. ABSTRACT



Scheme 1. Thiol-ene reaction between benzyl mercaptan and 1-decene

The photoinitiated thiol-ene reaction between benzyl mercaptan and 1-decene yields 46 kg sulfide per day when performed in the HANU-reactor.

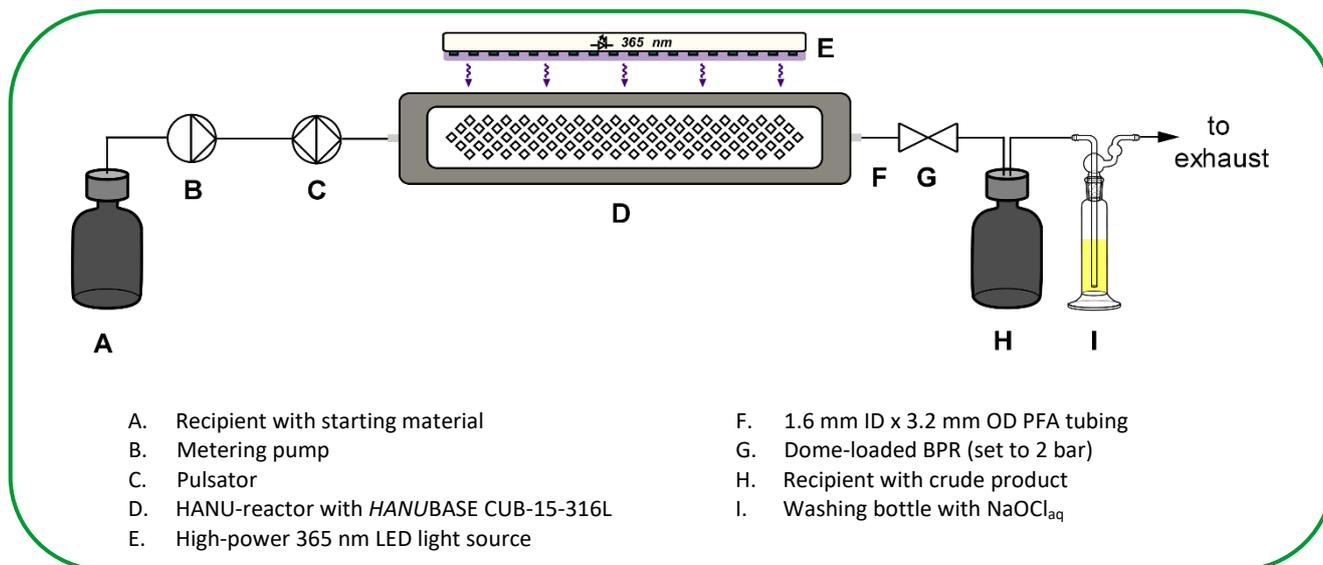
#### 2. BACKGROUND

The addition of a thiol to an alkene, commonly known as thiol-ene coupling, has been recognized to meet the requirements of a “click reaction” (Bowman, *Angew. Chem. Int. Ed.*, **2010**, 49, 1540-1573). A light-induced thiol-ene coupling provides a high degree of control over process initiation. In this example an industrially relevant photoinitiator was used to join two non-activated starting materials under irradiation with high-power 365 nm LEDs. A more elaborate study was published by Huvaere *et al.* (*ChemPhotoChem*, **2018**, 2, 884-889).

#### 3. EXPERIMENT

##### 3.1 Setup

The setup with the HANU-reactor is depicted in Scheme 2. The reactor base has cubic static mixing elements, an irradiated volume of 14 mL and is made of stainless steel 316L (Model: HANUBASE CUB-15-316L). Recipient **A** was sealed with a septum equipped with a N<sub>2</sub>-balloon. The outlet of recipient **H** was connected to a gas washing bottle filled with 3.4 wt% aqueous NaOCl-solution to eliminate sulfide odor. In addition, all chemical manipulations were performed in a well-ventilated fume hood due to benzyl mercaptan’s odor. The recipients and transparent tubing were shielded from light by means of aluminum foil. The photon flux entering the reactor amounted to 2.7 x 10<sup>-4</sup> einstein/s as determined by ferrioxalate actinometry.



**Scheme 2. Setup of the experiment**

### 3.2 Procedure

Benzyl mercaptan (350 g, 2.82 mol, 1 equiv) was mixed with 1-decene (474.30 g, 3.38 mol, 1.2 equiv) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, Irgacure 651, 14.44 g, 0.06 mol, 0.02 equiv). The system was filled with the starting mixture and any residual air pockets were removed. Subsequently, the BPR was pressurized to 2 barg and the flow rate was set to 50 mL/min to obtain an irradiation time of 17 seconds. The pulsation frequency was 3 Hz and center-to-peak amplitude in the reactor was 2.1 mm. Finally, the LEDs were placed on top of the reactor lid and they were switched on. The reaction was performed at ambient temperature. After 51 seconds (3x residence time), collection was started.

### 3.3 Results

GC-FID analysis of the crude showed that > 93% conversion of benzyl mercaptan **1** had taken place with 86% yield of sulfide. This corresponds to a productivity of 1.94 kg/h or 46.7 kg/d, resulting in a space-time-yield of 139 kg/L/h. The sulfide could be purified by means of two-stage distillation.

## 4. CONCLUSION

In summary, the 14 mL lab-scale HANU-reactor was employed to perform a photoinitiated thiol-ene reaction. The coupling of benzyl mercaptan and 1-decene resulted in 46 kg/d of sulfide, showcasing the potential of the HANU-reactor to produce significant amounts of product.

**For more detailed information about this application note or the HANU-reactor in general, please contact Creaflow at [info@creaflow.be](mailto:info@creaflow.be).**