

**Supporting Information**

**for**

**Photochemistry with laser radiation in condensed  
phase using miniaturized photoreactors**

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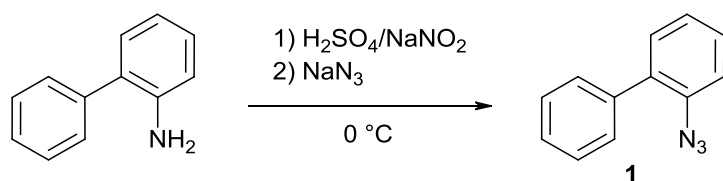
**Description of the flow reactor setup, kinetics, experimental  
procedures and spectroscopic data of all compounds.**

## General

NMR spectra were recorded on a Bruker AM 400, a Bruker Avance 300 or a Bruker DRX 500 spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm,  $\delta$ ) downfield from tetramethylsilane (TMS) and are referenced to residual solvent peaks. All coupling constants ( $J$ ) are absolute values and  $J$  values are expressed in Hertz (Hz). The description of signals include s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The spectra were analyzed according to first order. The signal structure in  $^{13}\text{C}$  NMR was analyzed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal), - = secondary C-atom (negative signal) and  $\text{C}_{\text{quart}}$  = quaternary C-atom (no signal). – EIMS (electron impact mass spectrometry) was performed by using a Finnigan MAT 90 (70 eV). In cases where no MS (EI) spectra could be measured due to the high volatility of the compound, the GC–MS spectra were used for characterization. IR (infrared spectroscopy) was recorded on a FT-IR Bruker alpha. Solvents, reagents and chemicals were purchased from Aldrich, ABCR and Acros. All solvents, reagents and chemicals were used as purchased unless stated otherwise.

## Microreactors used for irradiation

### Synthesis of 2-azidobiphenyl (1) from 2-aminobiphenyl [1,2]



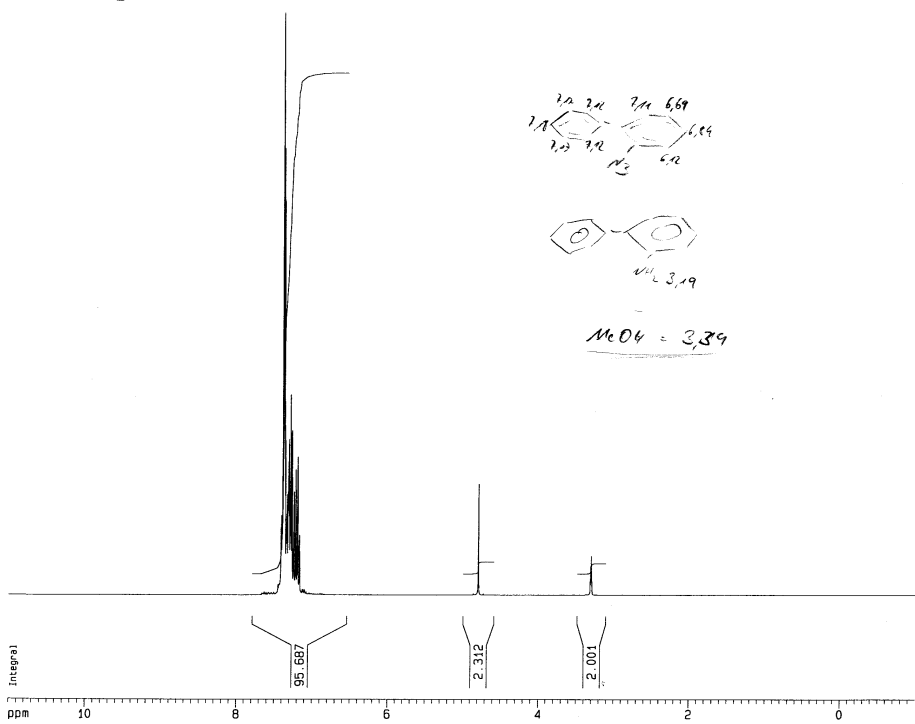
The amine (5.0 g, 30.1 mmol) was treated with 6 mL of H<sub>2</sub>SO<sub>4</sub> (concentrated) in 35 mL of H<sub>2</sub>O. The solution was cooled to 0 °C and 2.48 g of NaNO<sub>2</sub> (36 mmol) in 25 mL H<sub>2</sub>O was added dropwise. The solution became clear and was treated with sodium azide followed by stirring overnight at rt. After filtration and washing (10% Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O) the solid was dried.

Yield: 5.35 g (91%)

Analytical data:

mp:	50 °C (Lit.: 49–50 °C)
GC:	Ret./min: 13.0 (98.6%)
GC–MS:	Ret./min: 13.2
	MS: M <sup>+</sup> 195
HPLC:	Ret./min: 2.7 (0.21%), 3.0 (0.49%), 5.1 (99.3%)

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 Name Avemaria  
 FA-215 *1002*  
 AUTO.N.1H\_STAND MeOD u braese 3



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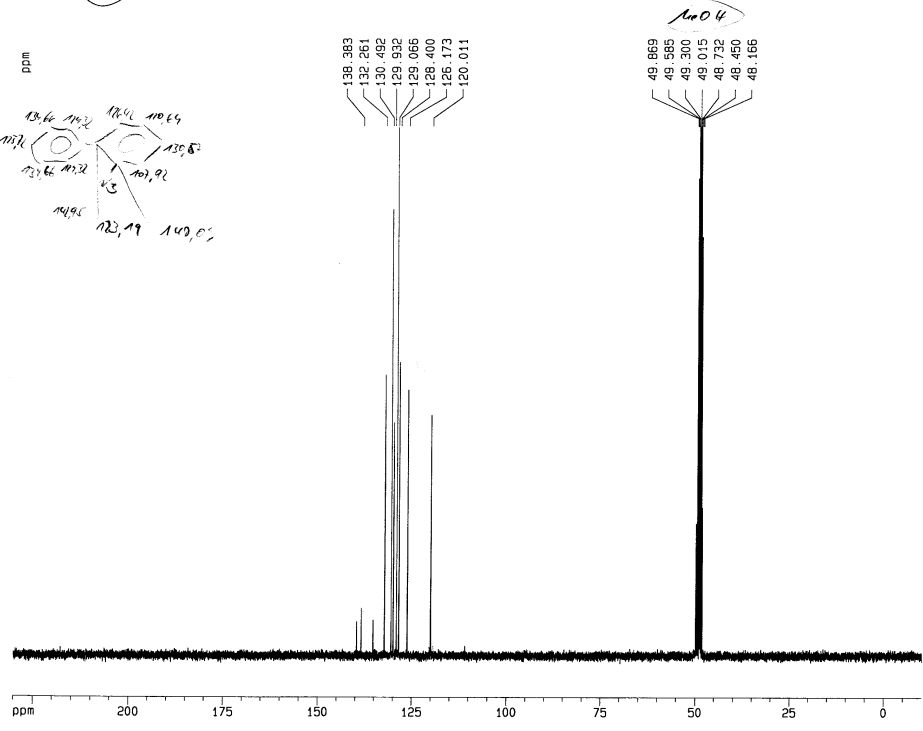
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 HZCM 163.70728 Hz/cm

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 FA-215  
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Current Data Parameters  
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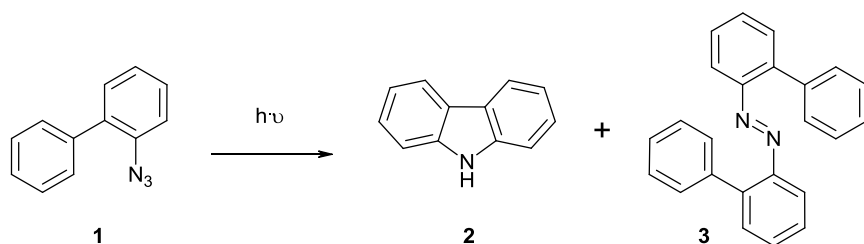
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 HZCM 823.28339 Hz/cm

## Photolysis of 2-azidobiphenyl in benzene [2]



2-Azidobiphenyl (1, 0.502 g, 2.58 mmol) was dissolved in 150 mL of degassed benzene under argon ( $c = 1.73 \times 10^{-2}$  M, Lit:  $2.0 \times 10^{-2}$  M). The reaction solution was heated to 20 °C (cryostat). The photolysis was carried out under stirring and continuous irradiation (xenon lamp, 450 W,  $\lambda > 345$  nm). The pale yellow solution turned reddish–orange in 20 min and a weak gas evolution was observed. The irradiation took place over 24 h. Samples (1 h, 2 h, 18 h, 24 h) were taken and the turnover was determined by GC. The reaction solution was evaporated and dried over magnesium sulfate to give a dark yellow oil.

Analytical data:

Sample after 1 h:

GC: Ret./min: 1.06 (14.81%), 1.14 (4.36%), 12.93 (70.81%), 14.94 (9.63%)  
Ratio starting material:product: 7:1

Sample after 2 h:

GC: Ret./min: 1.07 (29.21%), 1.15 (8.49%), 12.92 (50.77%), 14.93 (10.85%)  
Ratio starting material:product: 5:1

Sample after 18 h:

GC: Ret./min: 1.07 (13.63%), 1.15 (3.96%), 15.0 (39.65%), 15.00 (40.87%)  
Ratio starting material:product: 1:1

Sample after 24 h:

GC: Ret./min: 1.05 (13.95%), 1.12 (4.06%), 12.92 (34.88%), 14.97 (45.33%)  
Ratio starting material:product: 3:4

HPLC: Ret./min:  
0.53 (2.69%), 1.58 (2.86%), 1.95 (1.56%), 2.91 (57.1%), 5.03 (34.2%)  
Ratio starting material:product: 3:5

**Chromatographic separation of photolysis reactions.** Eluent: 10% ether in hexane; Column: 35 mm × 500 mm silica gel 60. 1.8 liters of eluent was used, and the collected fractions (41, each ca. 50 mL) by TLC (eluent: 10% ether in hexane) were evaporated.

Fraction 5–9: yellow oil; 2-azobiphenyl:

GC: Ret./min: 13.25 (98.43%)

HPLC: Ret./min: 5.1 (99%)

Fraction 21–37: white crystals; carbazole):

GC: Ret./min: 1.30 (0.25%), 15.05 (99.75%)

HPLC: Ret./min: 3.00 (97.7%)

Elemental analysis:

Azide 1			Carbazole 2		
Calcd.	C	73.83	Calcd.	C	88.88
	H	4.65		H	2.49
	N	21.52		N	8.64
Found	C	73.62	Found	C	86.28
	H	4.02		H	5.83
	N	21.07		N	8.26

**Photolysis of 2-azidobiphenyl (1) in MeOH**

Procedure, see above.

Analysis:

Starting material, azide

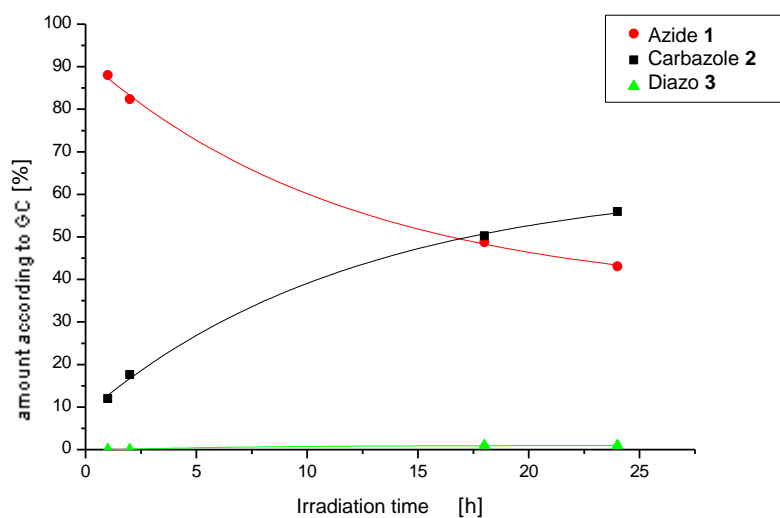
GC: Ret./min: 1.23 (0.2%), 11.39 (0.3%), 13.01 (98.3%), 13.84 (0.5%) 14.94 (0.6%)

Sample after 19 h:

GC: Ret./min: 1.29 (0.5%), 11.39 (0.2%), 12.26 (1.0%), 12.95 (45.5%), 15.00 (50.3%), 24.53 (2.1%)

Ratio starting material:product: 10:9

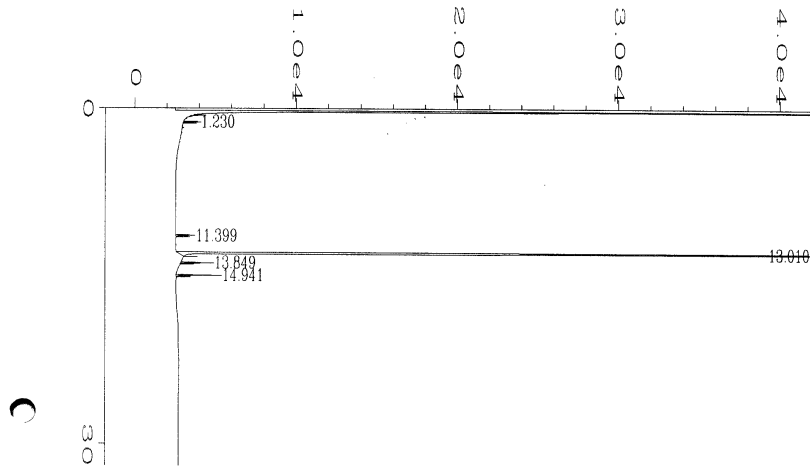
**Graphical representation: conversion of macroscopic experimental procedure of photolysis, a conventional reaction flask, Xe-lamp**



- Products were formed in a first-order kinetic during irradiation
- Plot shows conversion in benzene (GC) was slightly better than in MeOH
- Max. conversion at about 51% after 20 h in methanol with 2.22% side-product (diazobenzene)

**Exemplary GC in MeOH:**

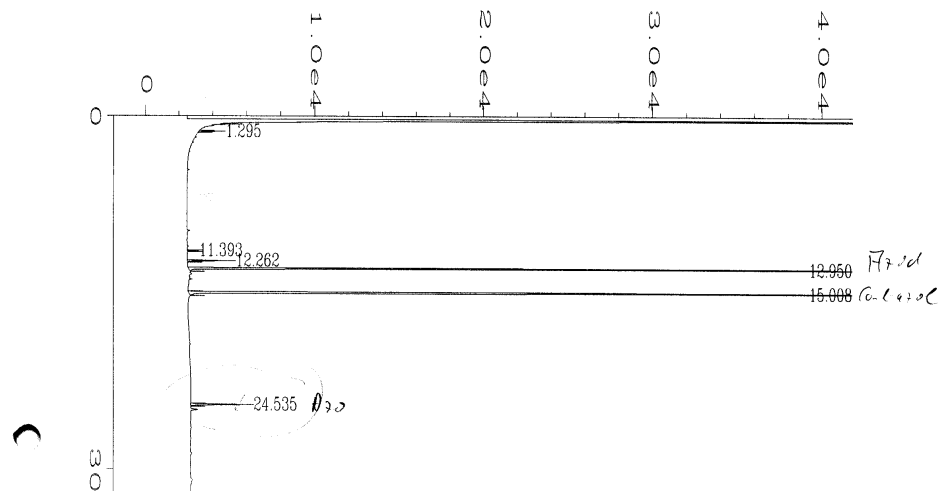
Starting material, azide 1



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Area Percent Report  
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Sample after 19 h



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Area Percent Report  
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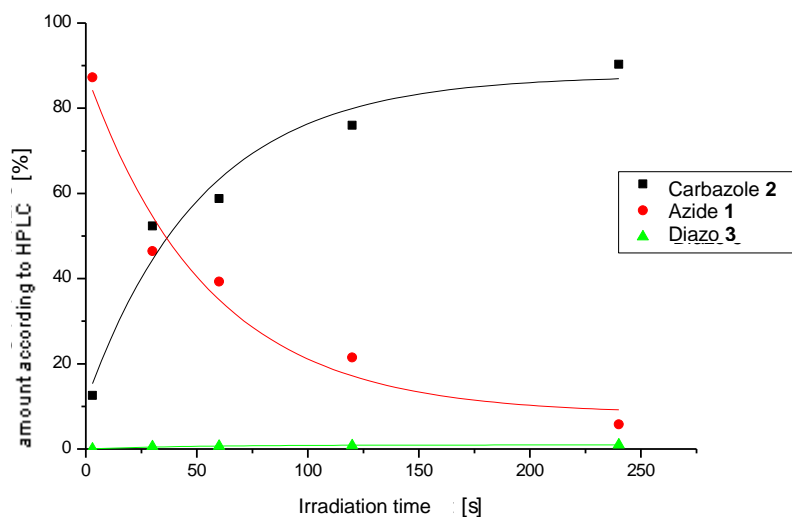
### Photolytic carbazole formation of 2-azobiphenyl using frequency-tripled Nd:YAG laser radiation in a cuvette

In preliminary experiments solutions of 2-azidobiphenyl were irradiated in quartz-glass cuvettes with a laser source. The power and the irradiation time were varied. Laser source: Nd:YAG laser (355 nm) 355-5000, 210S Lightwave Electronics, USA. The pulse frequency of the laser was fixed at 8 kHz (pulse width: 26 ns). The circular beam diameter on the cuvette ( $35 \times 10 \times 10$  mm) is around 8 mm. The penetration depth of the laser in the media (cross-section-considered diffusion cone) is estimated to be about 7 mm. The irradiation time by means of repeated scanning of the specimen varies. It was proceeded at a speed  $v = 10 \text{ mm s}^{-1}$  with a cell length of 30 mm, resulting in an irradiation time per scan of 3 s. The pulse power of the laser was in the range of 0.5 to 3 W corresponding to energy densities of 0.03 to  $0.17 \mu\text{J}/\text{cm}^2$ , and the irradiation time in 2–80 scans (equivalent to 6–240 s / 4 min, see table below).

Power P [Watt]	Time # Scans	Time <i>t</i> [sec]	Carbazole (HPLC, %)	Azide (HPLC, %)	Product/Educt (HPLC)	Conversion in % (HPLC)
0,50	20	60	46,5	52,5	0,89	0,009
1,50	1	3	12,6	87,3	0,14	0,001
1,50	10	30	52,4	46,5	1,13	0,011
1,50	20	60	56,4	42,1	1,34	0,013
1,50	20	60	62,5	35,5	1,76	0,018
1,50	20	60	58,8	39,3	1,50	0,015
1,50	40	120	76,0	21,5	3,53	0,035
1,50	80	240	90,3	5,8	15,70	0,157
3,00	20	60	73,7	23,9	3,08	0,031
3,00	20	60	79,8	17,4	4,58	0,046
3,00	40	120	87,3	9,1	9,60	0,096
3,00	80	240	92,8	1,5	60,23	0,602

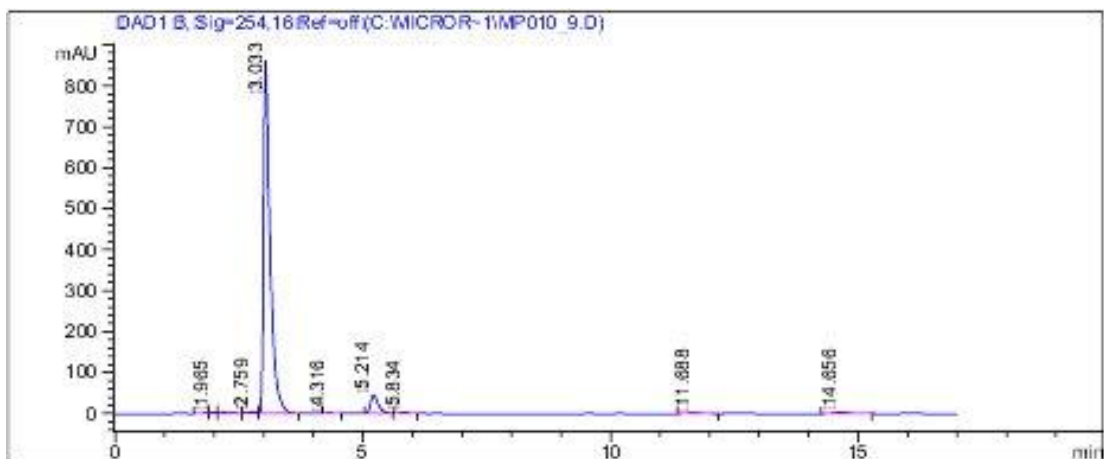


### Graphical representation: Conversion of the photolysis laser radiation (355 nm) in a cuvette



- Products of the exponential growth with time
- Max. turnover at about 90% after 4 min in methanol with 0.95% side-product (diazobenzene)
- Conversion of 52% and 0.57% side product (diazobenzene, after 30 s)

Exemplary HPLC



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-----|-----|-----|-----|-----|-----|-----|-----|
Peak   RetTime Type   Width   Height   Height   Area     Area
-----|-----|-----|-----|-----|-----|-----|-----|
      (min) (min) (min) (mAU)   %         (mAU*s) %
-----|-----|-----|-----|-----|-----|-----|
1      1.832  PV      0.111   2.73949  0.29402  21.3533  0.25
2      1.965  VV      0.129   3.30173  0.35436  29.7444  0.34
3      2.173  VV      0.247   2.90165  0.31142  53.4776  0.62
4      2.759  VV      0.152   5.10301  0.54769  57.0789  0.66
5      3.033  VP      0.128  862.00085  92.51538  798.4937  90.30
6      4.316  FB      0.137   1.49874  0.16085  14.0396  0.16
7      5.214  BB      0.159  45.49478  4.88279  496.2671  5.75
8      5.834  BB      0.196   2.98286  0.32014  40.3533  0.47
9     11.688  PP      0.296   2.27184  0.24383  44.0054  0.51
10    14.656  BB      0.369   3.44291  0.36951  81.6693  0.95
-----|-----|-----|-----|-----|-----|-----|
Totals:                931.73786                8636.4825
  
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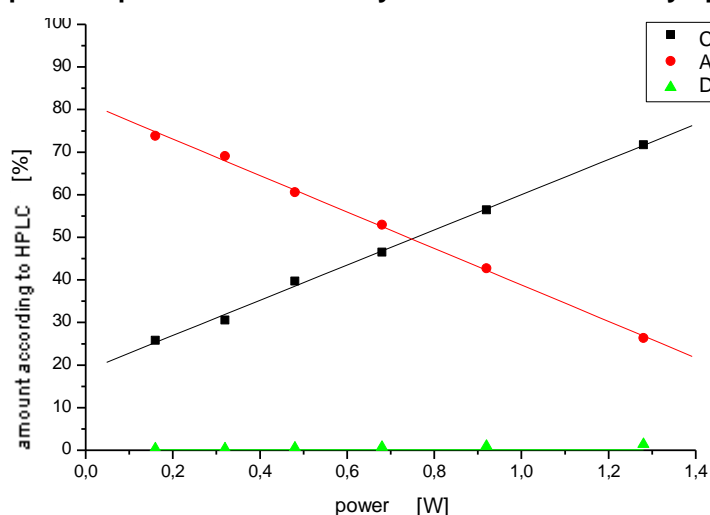
## Photolytic carbazole formation of 2-azobiphenyl using frequency-tripled Nd:YAG laser radiation in a continuously operating microreactor (PTFE)

In miniaturized reactors of type II (see Figure 1, 3 and 4 of the manuscript, dimension of the reactor chamber  $3 \times 5$  mm, 35  $\mu\text{L}$  volume) was added a solution of 2-azidobiphenyl continuously fed with a syringe pump under continuous irradiation with a Nd:YAG laser (355 nm irradiated). At a constant flow of 26 mL/h, the laser pulse power was varied from 0.16 to 1.28 W corresponding to energy densities between 0.02 and 0.17  $\mu\text{J}/\text{cm}^2$ . Furthermore, at a constant power of 0.92 W or 0.12  $\mu\text{J}/\text{cm}^2$ , the flow rate (10 to 100 mL/h) and therefore the dwell time (exposure time) in the reactor were varied. The yield was determined by HPLC.

### HPLC determination of conversion by the photolysis laser radiation (355 nm, constant flow rate 26 mL/h, power variable) in the continuously operated microreactor (PTFE)

Pulse power [W]	Carbazole	Azide
0.16	25.23	73.57
0.32	29.91	68.78
0.48	38.13	60.29
0.68	45.59	52.61
0.92	55.28	42.44
1.28	70.80	26.68

### Graphical representation: Photolysis in the continuously operated microreactor (PTFE)

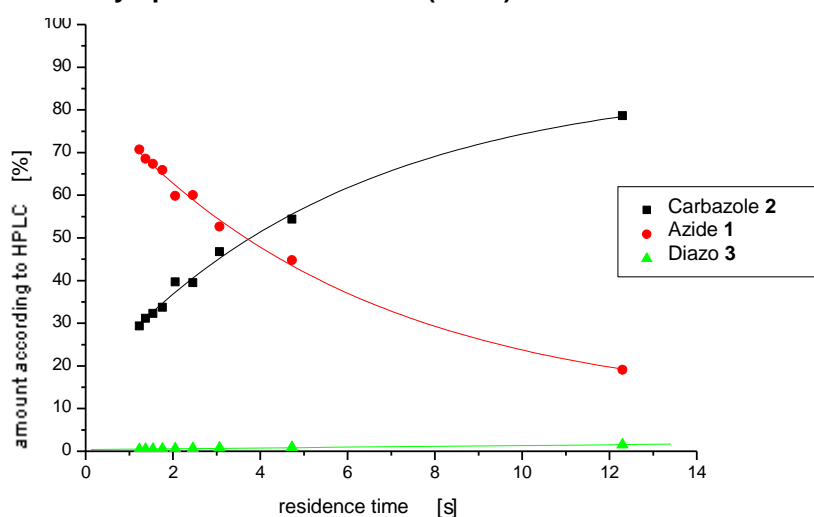


- Products with a linear increase in performance

**HPLC determination of conversion by the photolysis laser radiation (355 nm, 0.92 W constant power, variable flow rate) in the continuously operated microreactor (PTFE)**

Carbazole [% , HPLC]	Azide [% , HPLC]	Time [s]	Flow [mL/h]
77.53	19.32	12.3	10
53.25	44.53	4.73	26
45.86	52.31	3.07	40
38.69	59.70	2.46	50
38.90	59.50	2.05	60
33.00	65.57	1.76	70
31.59	67.02	1.54	80
30.46	68.19	1.37	90
28.73	69.98	1.23	100

**Graphical representation: Conversion of the photolysis laser radiation (355 nm) in the continuously operated microreactor (PTFE)**



- Products with an exponential increase of the time
- Max. conversion at about 79% at a residence in the reaction solution in the miniaturized photoreactor of 12.3 seconds at 1.52% side-product (diazobenzene)

**References:**

1. Smith, Brown; *J. Am. Chem. Soc.* 1951, 73, 2438–2441
2. Swenton, J. S.; Ikeler, T. J.; Williams, B.H. *J. Am. Chem. Soc.* 1970, 92, 3103–3109