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# **Electronic Supplementary Information**

# Device for Automated Screening of Irradiation Wavelength and Intensity – Wavelength Dependence of Photoreactions with an Arylazo Sulfone in Continuous Flow

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# 1) Materials

4'-Methoxyacetanilide was received from abcr GmbH (Karlsruhe, Germany) in a purity of 98%. Sodium nitrite (NaNO<sub>2</sub>) was received from Carl Roth (Karlsruhe, Germany) in a purity of ≥98%. Sodium methanesulfinate was received from TCI Deutschland GmbH (Eschborn, Germany) in a purity of >90%. Acetonitrile (HiPerSolv CHROMANORM for HPLC) was purchased from VWR Chemicals (Darmstadt, Germany). Water was obtained from a Milli–Q gradient purification system (Millipore, Bedford, MA). All other chemicals were received from Sigma–Aldrich (St. Louis, MO) in a purity of at least 98%. All chemicals were used without further purification.

# 2) Photoreactor design

The design of the custom-built photoreactor has been described previously.<sup>1</sup> The LED arrays are also custom-built and were matched to the geometry of the photoreactor. Figure S1 repeats Figure 2 for easy reference of the description below.



Figure S1. Modular design of the custom-built photo-flow reactor (left side) and the LED arrays (right).

The reactor plate (f) is made of stainless steel to provide chemical resistance and to dissipate reaction heat. A heat sink ( $0.5 \text{ K W}^{-1}$ , ABL Components, Birmingham, UK, g) and a heat-conducting foil (SFT80-0.15,  $0.2 \text{ K W}^{-1}$ , AMEC Thermasol, Norfolk, UK) are attached on the rear side of the reactor. The heat-conducting foil provides good heat transfer between the reactor plate and the heat sink. The 48 mm cooling fins ensure that reactions take place under isothermal conditions. The inlet (h) and outlet (i) for the reaction solution are also placed on the rear side of the reactor to allow connection to the HPLC system. A chemically resistant FEP polymer foil (fluorinated ethylene propylene, 1.3 mm, e) is placed on top of the reactor plate, and a PMMA plate (poly(methyl methacrylate)), 2.0 mm, d) is placed over the FEP foil to provide mechanical stability. Via the reactor window (c) above the PMMA plate, the reactor is fixed with twelve screws. In the center of the reactor window, a cross bar with another five screws is attached to prevent spilling between parallel segments of the reactor channel. In addition, the reactor window defines the area that is irradiated by the LED

arrays. A reactor bracket (b) connects the reactor to the automation system. The LED array is positioned as close as possible to the reactor to minimize irradiation losses. Each LED array holds twelve identical LEDs (k) mounted on an aluminium housing with a heat sink (I) on the rear side. Power for the LEDs is supplied through the power supply connectors (m) on the rear side of the housing. A ventilation slit (j) assists in cooling the LEDs. Two radial fans placed next to the LED array in operation prevent overheating (Figure S2): one radial fan blows over the LEDs, the other over the heat sink fins.



Figure S2. Photograph of an LED array with radial fan.

The reactor plate (Figure S3) contains a 1.5 mm wide and 0.5 mm deep channel for the reaction solution. The shallow channel depth minimizes the penetration depth of the LEDs. (A shallower channel could not be milled into the plate for technical reasons.) The reaction channel is flanked by a deeper channel lined with fluoroelastomer FPM (inner sealing) to prevent spilling between parallel sections of the channel. As an additional safety feature, a deep surrounding channel lined with fluoroelastomer FPM (outer sealing) ensures that spilled reaction solution cannot leave the reactor plate.



Figure S3. Technical drawing of the reactor plate.

The reactor volume determines the reaction time at different flow rates. All irradiated volumes of the different geometrical elements contribute to the reactor volume of 0.845 mL. A photograph of the reactor plate with coloring as in Figure S3 is shown in Figure S4 besides a top view onto the closed reactor.



Figure S4. Top: Reactor plate with colored channels. Bottom: Top view onto the closed reactor.

### 3) LED arrays characterization

Table S1 lists the details of the LEDs used for the custom-built LED arrays. Each array contains twelve identical LEDs, six of them connected in series. Power was supplied through an adjustable power supply with two channels (30 V, 3 A, PEAKTECH 6180, Ahrensburg, Germany).

λ (nm)	Power <sup>a</sup> (W)	Product name	Vendor	Costs <sup>b</sup> (€)
373	5.00	Roschwege Star-UV365-05-00-00	Conrad <sup>c</sup>	104.00
375	3.00	3 W High Power LED 370nm–380nm	Avonec <sup>d</sup>	6.05
383	3.00	3 W High Power LED 380nm–390nm	Avonec	4.65
403	3.00	Roschwege Star-UV405-03-00-00	Conrad	18.73
416	3.00	3 W High Power LED 410nm–420nm	Avonec	2.40
430	3.00	3 W High Power LED 430nm–435nm	Avonec	1.85
442	2.17	ILH-OW01-DEBL-SC211-WIR200	RS Components <sup>e</sup>	7.45
464	2.17	ILH-OW01-BLUE-SC211-WIR200	RS Components	6.47
495	3.00	3 W High Power LED 490nm–495nm	Avonec	2.33
504	2.24	ILH-GD01-VEGR-SC201	RS Components	7.01
518	3.00	3 W High Power LED 515nm–525nm	Avonec	1.44
522	2.17	ILH-OW01-TRGR-SC211	RS Components	7.81

Table S1. LEDs used for the LED arrays.

a: Maximum applicable electrical power as specified by the vendor. b: Costs per LED. c: Conrad Electronic SE (Hirschau, Germany). d: Avonec (Essen, Germany). e: RS Components (Corby, UK).

A calibrated spectroradiometer PS–200 (Apogee Instruments, Logan, UT) was used to determine the current sensitivity of the irradiance for all LED arrays (Figures S5– S16). The irradiance was quantified as the power spectral density (PSD, in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), which gives the amount of photons that hit the detector per unit area and time integrated over all emitted wavelengths. The template and holder to fix the detector positions were made with a 3D printer (Ultimaker 2+). The PSD values were determined for currents between 100 and 700 mA (maximum applicable current) or until the detector limit of the spectroradiometer was reached (saturation). With the low currents used for the wavelength screenings in continuous flow, detector saturation did not occur, so that deviations of >3% from the reference PSD can be excluded. With the high currents required to achieve 900% of the reference PSD for the wavelength screening in batch, detector saturation was inevitable. The PSD values for higher currents were extrapolated from the PSD values measured at currents below the detector saturation level. The accompanying uncertainty in the extrapolated PSD values of the LED arrays was acceptable, because the batch screening served only to find appropriate conditions for selective synthesis of the intermediate.



**Figure S5.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 373 nm.



**Figure S6.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 375 nm.



**Figure S7.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 383 nm.



**Figure S8.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 403 nm.



Figure S9. Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 416 nm.



Figure S10. Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 430 nm.



**Figure S11.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 442 nm.



**Figure S12.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 464 nm.



Figure S13. Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 495 nm.



**Figure S14.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 504 nm.



**Figure S15.** Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 518 nm.



Figure S16. Emission spectrum and current sensitivity curve of the LED array with  $\lambda_{max}$  at 522 nm.

## 4) LED-array automation setup

For a fully automated setup, a linear actuator (ISELGermanyAG, Eichenzell, Germany) was bought and complemented by a custom-built carriage that can accommodate up to ten LED arrays simultaneously (Figure S17).



Figure S17. Technical drawing of the linear actuator (b) with ten LED arrays on the carriage (a).

The photoreactor is mounted above the middle of the linear actuator. Changes of the irradiation wavelength are effected by a movement of the linear actuator that places the selected LED array below the photoreactor (Figure S18).



**Figure S18.** Top: Technical drawing of the linear actuator with photo–flow reactor (a) and the radial fans (b) for active cooling of the LED array in operation. Bottom: Photograph of the complete automation setup.

The linear actuator and the LED arrays are connected to a custom-built electrical control device (Figure S19).



**Figure S19.** Interior of the electrical control unit that applies the appropriate voltage and current to the LED arrays.

In-house written software is used to determine which LED array on the carriage is put into operation below the photoreactor (setting the irradiation wavelength) as well as the current applied to the operative array and the operation time (setting the irradiation intensity and time). The software was written with Free Pascal in the Lazarus development environment (www.lazarus-ide-org). Through creation of timetables a sequence of events can be programmed so that the software enables fully automated screening of the irradiation wavelength and intensity (Figure S20).

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3840277322-08092021-1542.dbf						
	PROGNR	MODULPLAT	LEDNR	INTENS	ZEIT_S	*
	a) 10	b) 1	C) 1	d) 100	e) 2700	
	20	2	2	100	2700	
	30	3	3	100	2700	
	40	4	4	100	2700	
	50	5	5	100	2700	
	60	6	6	100	2700	
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Figure S20. Screenshot of the software program for creating schedules for the automation system.

The first column (a) determines the order in which the timetable entries are processed. The second column (b) indicates the slot position on the carriage tray, the third column (c) designates the LED array (LED 1, 373 nm; LED 2, 375 nm, etc.). The separation of slot position and LED array identity by the software allows high flexibility and the exchange of LED arrays on the carriage. The current sensitivity curves of all LED arrays (Figures S5–S16) are imported into the software. This enables translation of a chosen irradiation intensity (third column, d) into the respective current that needs to be applied to a given LED array. In Figure S20, the intensity is set to 100, which corresponds to the PSD of the weakest LED array at the maximum applicable current (reference PSD value). Please note that intensities above 100% are possible for any but the weakest array. The last column (e) specifies the irradiation time in seconds. The software verifies that data entries are reasonable and prevents the start of the program in case of obvious errors.

### 5) Two-dimensional reaction-analysis setup

The two-dimensional flow platform for parallel reaction and analysis (Figure S21) was described in detail previously.<sup>1</sup> The centerpiece of the first dimension is formed by a quaternary pump and a binary pump. The quaternary pump was used for screenings with atmospheric oxygen, the binary pump was used for screenings under inert gas conditions. The quaternary pump has four independent channels for precise control of the flow rate and the concentration of each reactant. A substrate solution (1 or 7, 12.5 mmol/L) and a dioxaborolane solution (2, 50 mmol/L) in acetonitrile/water 9/1 (v/v) as well as the neat binary solvent mixture were connected to the quaternary pump. The neat solvent mixture is used to dilute the substrate solution and determine suitable reactant concentrations for the screening. The binary pump is easier to connect to the inert gas flasks. A stainless-steel capillary tube was attached directly to the pump heads of the binary pump, which was connected to inert gas flasks containing the reactant solutions through a septum. The flasks remained connected to an inert gas line during the entire screening process to prevent a pressure drop due to withdrawal of solution. A backpressure regulator set to 50 bar was placed between the pumps and the photoreactor to ensure smooth operation of the HPLC pumps. Without backpressure regulator, only about 2–3 bar backpressure would be applied, for which the HPLC pumps are not actually designed. No backpressure was applied to the photoreactor.

The second dimension consists of a standard HPLC system for chromatographic separations. A 2-position/6-port valve with an injection loop of  $1.3 \,\mu$ L volume mounted behind the reactor connects the first dimension with the second dimension. An inline diode array detector (DAD) is used to monitor the total UV absorbance of the reaction solution; constant UV absorbance indicates that the system operates in steady state. The flow path of the setup is shown in Figure S21.



Figure S21. Flow path for automated wavelength screening with up to ten LED arrays.

A photograph of the platform is shown in Figure S22. The individual parts of the HPLC system were received from Agilent Technologies (Waldbronn, Germany).



**Figure S22.** The first dimension for reaction control is shown on the left side, the second dimension for chromatographic analysis is shown on the right side. After leaving the photoreactor (g) the reaction solution is transferred via the 2-position/6-port valve (k) to the second dimension. Reaction control: a) reactant solutions; b) quaternary pump (Agilent 1260 Infinity Series, G1311B); c) thermostatted HPLC column compartment (Agilent 1290 Infinity Series, G1316C); d) binary pump (Agilent 1290 Infinity Series, G4220A); e) Jet Weaver V35 Mixer; f) back-pressure regulator; g) photoreactor; h) LED-array rack; i) linear actuator; j) electrical control device for LED automation; k) 2-position/6-port valve (Agilent 1290 Series, G1170A); l) inline DAD (Agilent 1200 Series, G4220A); o) thermostatted HPLC column compartment (Agilent 1290 Infinity Series, G1316C). Chromatographic analysis: m) eluents; n) binary pump (Agilent 1290 Infinity Series, G4220A); o) thermostatted HPLC column compartment (Agilent 1290 Infinity Series, G1316C) with separation column (Chromolith HighResolution RP-18 endcapped, 100 x 4.6 mm, Merck KGaA, Darmstadt); p) DAD (Agilent 1290 Infinity Series, G4212A).

The separation conditions for chromatographic analysis by the online-coupled HPLC system were tuned to achieve baseline separation of all reactants, products and side products in the shortest possible analysis time (Figure S23). The separation was performed at 25°C in reversed-phase mode on an endcapped  $C_{18}$  column through gradient elution with a water–acetonitrile mobile phase at a flow rate of 1 mL min<sup>-1</sup>.

Time (min) <sup>a</sup>	Water (vol %)	Acetonitrile (vol %)
0.00	77	23
3.19	72	28
3.20	52	48
6.19	52	48
6.20	0	100
8.19	0	100
8.20	77	23
10.18	77	23

**Table S2.** Gradient used for chromatographic analysis of thereaction without additive.

a: Injection at 0.08 min.

**Table S3.** Gradient used for chromatographic analysis of thereaction with additive.

Time (min) <sup>a</sup>	Water (vol %)	Acetonitrile (vol %)
0.00	77	23
2.19	72	28
2.20	42	58
5.69	42	58
5.70	22	78
7.39	0	100
8.99	0	100
9.00	77	23
11.00	77	23

a: Injection at 0.08 min.



**Figure S23.** Chromatogram from the wavelength screening of the reaction with additive. The additive **2** itself does not absorb in the wavelength range of the DAD.

For external quantification of the separated compounds from their chromatographic peaks, calibration curves were acquired (Figures S24–S32). The quarternary pump was programmed to dilute the stock solution of a compound in acetonitrile/water 9/1 (v/v) by mixing it with the neat binary solvent mixture at various volumetric ratios to produce ten different concentrations. These solutions were sequentially fed to the chromatographic analysis system via the 2-position/6-port valve. Data points for the calibration curves were received from the area of a chromatographic peak at a specific detection wavelength and feed concentration. The determination was repeated under the gradient elution conditions of Tables S2 and S3. Compounds 1, 3, 4 and 5 showed linear behavior over the calibrated range under the gradient elution conditions of Tables S2 (Figures S24–S27).



**Figure S24.** Calibration curve of the substrate 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene (1) at a detection wavelength of 261 nm.



Figure S25. Calibration curve of methoxybenzene (3) at a detection wavelength of 271 nm.



Figure S26. Calibration curve of 4-methoxyphenol (4) at a detection wavelength of 261 nm.



Figure S27. Calibration curve of 4-methoxyacetanilide (5) at a detection wavelength of 271 nm.

Compounds **1**, **3**, **5** and **6** showed linear behavior over the calibrated range under the gradient elution conditions of Table S3 (Figures S28–S31).



**Figure S28.** Calibration curve of the substrate 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene (1) at a detection wavelength of 261 nm.



Figure S29. Calibration curve of methoxybenzene (3) at a detection wavelength of 280 nm.



Figure S30. Calibration curve of 4-methoxyacetanilide (5) at a detection wavelength of 280 nm.



Figure S31. Calibration curve of the dioxaborolane 6 at a detection wavelength of 261 nm.



Figure S32. Calibration curve of the intermediate 7 at a detection wavelength of 261 nm.

A calibration curve that passes through the origin could not be obtained for the intermediate, despite evaluating several detection wavelengths. The calibration curve of **7** is therefore only valid for concentrations between 1.25 and 12.5 mmol/L (Figure S32).

Overall, the adherence to linearity observed in the calibration curves of the compounds confirms the precision and high reproducibility of data generation with our set-up.

### 6) Synthesis

#### 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene (1)



The arylazo sulfone **1** was prepared according to the literature from 4methoxybenzenediazoniumtetrafluoroborate (**8**), prepared as described below.<sup>3,4</sup> The diazonium salt **8** (1.275 g, 5.74 mmol) was dissolved in dichloromethane (29 mL) and the solution cooled to 0 °C. After addition of sodium methanesulfinate (0.645 g, 6.31 mmol) the suspension was stirred

at 0 °C for 30 minutes and then overnight at room temperature. The precipitate was filtered off and washed with dichloromethane. The filtrate was concentrated under reduced pressure. Recrystallization in *n*-hexane yielded **1** as yellow needles (1.03 g, 4.78 mmol, 83%). The NMR spectroscopic data were in accordance with those reported in the literature.<sup>4</sup>

<sup>1</sup>**H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.00–7.90 (m, 2 H), 7.09–6.99 (m, 2 H), 3.94 (s, 3 H), 3.19 (s, 3 H). — <sup>13</sup>**C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.9, 143.4, 127.5, 115.1, 56.1, 35.0.

#### 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)

<sup>OMe</sup> The dioxaborolane **6** was generated in the photo–flow reactor. A quaternary pump was used to supply the photoreactor with an arylazo sulfone solution (**1**, 12.5 mmol/L, 100 mL) and an 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2dioxaborolane) solution (**2**, 50 mmol/L, 100 mL) in acetonitrile/water 9/1 (v/v) at a flow rate of 0.2 mL/min. The photoreactor was irradiated with the 416 nm LED array (at an applied current of 700 mA) and the reaction solution collected from the outlet for 16.7 hours. The solution was then concentrated under reduced pressure. Purification by column chromatography on silica gel with *n*-pentane/ethyl acetate 10/1 (v/v) yielded **6** as white solid (14 mg, 59.8 µmol, 2.4%). The NMR spectroscopic data were in accordance with those reported in the literature.<sup>5</sup>

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.83–7.74 (m, 2 H), 6.96–6.90 (m, 2 H), 3.86 (s, 3 H), 1.37 (s, 12 H). — <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.3, 136.7, 113.5, 83.7, 55.2, 25.0.

#### 4-Methoxybenzenediazonium methanesulfonate (7)



OMe

The arylazo sulfone 1 (70.0 mg, 327  $\mu$ mol) was dissolved in a mixture of water (2.5 mL) and acetonitrile (22.5 mL). The solution was irradiated with the 504 nm LED array (at an applied current of 700 mA) in the presence of atmospheric oxygen for 3 h. The solution was then concentrated under reduced pressure and dried under vacuum to

yield **7** (68.0 mg, 296 µmol, 91%) as a brown solid.

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 8.69–8.57 (m, 2 H, H2), 7.55–7.42 (m, 2 H, H3), 4.04 (s, 3 H, OMe), 2.32 (s, 3 H, SMe). — <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 168.8 (C4), 136.1 (C2), 117.2 (C3), 103.4 (C1), 57.5 (OMe), 39.7 (SMe). — ESI (HR-MS) calcd. for C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>O<sup>+</sup>: 135.0553; found 135.0552, calcd. for CH<sub>3</sub>O<sub>3</sub>S<sup>-</sup>: 94.9808; found 94.9808.

#### 4-Methoxybenzenediazoniumtetrafluoroborate (8)

The diazonium salt **8** was prepared according to the literature.<sup>2</sup> 4-Methoxyaniline (12.3 g, 100 mmol) was dissolved in water (35 mL) and an aqueous HBF<sub>4</sub> solution (48%, 35 mL). The mixture was cooled in an ice–salt bath to –5 °C before a pre-cooled solution of NaNO<sub>2</sub> (7.25 g,

105 mmol) in water (15 mL) was added dropwise. The drop frequency was kept so that the temperature of the reaction mixture stayed below 5 °C to prevent product loss. After complete addition of the NaNO<sub>2</sub> solution, the mixture was stirred for 30 minutes at -5 °C. Afterwards, the diazonium salt was collected by filtration and washed with cold water and diethylether. Drying in vacuo yielded **8** as a purple solid (20.805 g, 93.7 mmol, 94%). The NMR spectroscopic data were in accordance with those reported in the literature.<sup>6</sup>

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 9.02–8.88 (m, 2 H), 7.96–7.85 (m, 2 H), 4.62 (s, 3 H). — <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 168.9, 136.2, 117.4, 103.3, 57.5.

# 7) NMR spectra

<sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded at ambient temperature on a Bruker Avance 300 NMR spectrometer. The chemical shifts are reported in parts per million (ppm) relative to the signal of the solvents DMSO-d<sub>6</sub> (<sup>1</sup>H NMR 2.50 ppm; <sup>13</sup>C NMR 39.52 ppm) and CDCl<sub>3</sub> (<sup>1</sup>H NMR 7.26 ppm; <sup>13</sup>C NMR 77.16 ppm). Multiplicities are reported using the following abbreviations: s (singlet), m (multiplet).



### 1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene (1)

<sup>13</sup>C NMR: (75 MHz, CDCl<sub>3</sub>).

### 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



S32

### 4-Methoxybenzenediazonium methanesulfonate (7)



<sup>13</sup>C NMR: (75 MHz, DMSO-d<sub>6</sub>).



HMBC of 7.

## 4-Methoxybenzenediazoniumtetrafluoroborate (8)



<sup>13</sup>C NMR: (75 MHz, DMSO-d<sub>6</sub>).

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