Heterogeneous Acid Catalysis Using a Perfluorosulfonic Acid Monolayer-Functionalized Microreactor

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The inner walls of a glass microreactor were functionalized in a one-step procedure with a single layer of a strong perfluoroalkylsulfonic acid. The applicability of the catalytic device was demonstrated in the successful hydrolysis of benzaldehyde dimethyl acetal in acetonitrile, achieving quantitative conversion within a residence time of only 60 s. Furthermore, the catalytic system showed high conversion for the Friedlander quinoline synthesis between 2-aminobenzophenone and ethyl acetoacetate. The cyclization of pseudoionone in methylcyclohexane proved the wide applicability of the acid-functionalized microreactor also for reactions carried out in apolar media. The platform showed activity for 6 h to 2 days, depending on the solvent, and was reactivated by simple treatment with the catalyst precursor.

Keywords: microreactor, heterogeneous acid catalysis, catalytic monolayer, Friedlander synthesis, deacetalization

1. Introduction

Heterogeneous catalysis using microreactors has obtained a great deal of attention in recent years with numerous examples of the anchoring of organic, metal, and enzymatic catalysts inside a microstructured system [1]. Several advantages derive from this strategy, including continuous product formation, simple catalyst separation and its re-use, and less waste. Microreactors exhibit large surface-to-volume ratios which, along with an improved heat and mass transfer, offer a huge surface available for functionalization, a key feature in the heterogenization of a chemical process [2–4]. As pointed out by Kirschning et al. [5] already some years ago, organic chemistry is moving towards a new dawn characterized by the use of enabling techniques and the quest for new synthetic technology platforms. Thereby, a particular focus is put on the combination of immobilized catalysts and continuous-flow processes [6].

In recent years, several examples of flow-through syntheses have been reported utilizing immobilized catalysts. The most used approach is by filling the microstructured reactor with packed columns, usually constituting of a functionalized solid support [7–10], or by using flow-through materials, especially monoliths [11–14]. Although these strategies offer advantages such as increased active surface and wide choice of supports and catalysts, the randomly packed catalytic beds may lead to uncontrolled fluid dynamics, broad residence time distributions, and low selectivity. However, microstructured reactors with a wall catalyst rather than conventional reactors with catalyst pellets offer good control over the reaction conditions [15]. In fact, wall-coated systems have gained increasing attention, with several examples ranging from Au-films [16], enzymes [17], to polymer brushes [18–21]. Another approach involves the use of a nanoparticle-containing catalytic membrane at the laminar flow interface of a microflow reactor [22].

Acid-catalyzed reactions are of great interest in organic synthesis, with widespread application in industry. These reactions are mostly performed using strong mineral acids, such as sulfuric acid or hydrogen fluoride, which are deployed in a homogeneous fashion and hence as single use reagents. However, the increasing concerns of environment protection and safety issues have stimulated the development of stable, reusable, and highly active solid acid catalysts [23, 24]. Therefore, efforts have been made to transform a successful homogeneous catalyst into a heterogeneous catalytic system, i.e., an acid catalyst immobilized on some form of support, especially by functionalization of ordered mesostructured silica [25, 26] or polymer-based materials [27, 28]. Although characterized by high acid loadings and activity, these procedures mostly suffer from a tedious multi-step preparation process and incomplete functionalization. In contrast, Alvaro et al. [29, 30] reported a single step anchoring of a perfluoroalkanesulfonic acid group onto mesoporous crystalline material-41 = Mobil crystalline material-41 (MCM-41) and Santa Barbara amorphous-15 (SBA-15). The resulting material showed a significant enhancement in catalytic activity for the esterification of carboxylic acids and Friedel–Crafts acylations. The same strategy was followed by Hicks et al. [31], who tethered the fluorinated sultone precursor to SBA-15. The hybrid organic–inorganic material was used as co-catalyst/support for the activation of various zirconocenes for the production of polyethylene. The group of Fierro used amorphous silica gel as support for the covalent anchoring of β-sultone to the hydroxylic groups on the silica surface. The hybrid organic–inorganic system was tested in the esterification reaction of acetic acid with methanol [32]. So far, these procedures have not been implemented in microfluidic devices, in which acid catalysts have been introduced mostly through packed-bed supports [11, 33].

Herein, we report the functionalization of a glass microreactor by single-step anchoring of a perfluoroalkylsulfonic acid, from a precursor β-sultone to the inner walls. This simple procedure allows the formation of a single layer of a strong organic acid catalyst, in contrast to other studies where films or brushes, containing multiple catalytic sites, are required to give a reasonable catalytic activity (vide supra). A large advantage of this process is that it obviates an activation step as the acid is formed by the surface coupling reaction. Its high activity and versatility is demonstrated in the hydrolysis of benzaldehyde dimethyl acetal, the Friedlander annulation to give quinolones, and the cyclization of pseudoionone. These examples confirmed the enhancing effect of the microstructured system on these reactions as compared to lab scale conditions.

2. Results and Discussion

2.1. Catalytic Monolayer Preparation. The construction of a catalytic acid layer was first performed on an activated flat silicon dioxide surface in order to be able to characterize the immobilized catalyst. The anchoring was carried out by single-step

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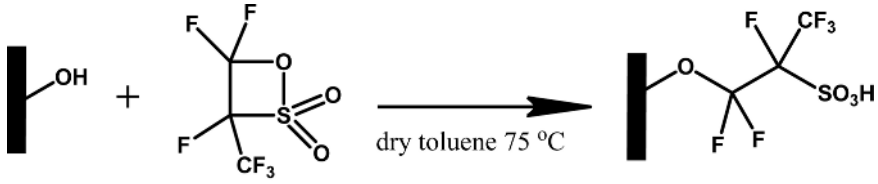
Scheme 1. Functionalization of flat silicon dioxide surface and glass microreactor by β-sultone (**1**)



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ring opening via reaction of 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid β-sultone (hereafter β-sultone, **1**) with the surface OH groups of the silicon oxide surface (Scheme 1), in an analogous procedure as reported in literature [29].

The introduction of the sultone moiety on the silica surface was proven by X-ray photoelectron spectroscopy (XPS), clearly showing the presence of the terminal sulfur and the fluorine atoms. Yet, it also revealed the presence of a 1.4-nm thick carbonaceous layer on top of the β-sultone layer, probably from contamination from the air. The observed F/C ratio (2.4), when taking into account only the carbon fraction bound to F atoms, is close to the theoretical value of 2, while the S/C ratio was 0.14 (expected 0.3). These values are in agreement with those observed by Hicks et al. [31], where the β-sultone moiety was used for the functionalization of amorphous silica gel.

With Fourier transform infrared spectroscopy (FT-IR) analysis, the single layer of organic acid was not detectable. The thickness of the flat surface was measured by ellipsometry to give an average value of 2.3 nm. The result is in agreement with the expected thickness of a single layer of β-sultone together with the deposited carbon layer. Additionally, an XPS simulation of the attenuated carbon signal indicated a 0.8-nm β-sultone layer underneath the adventitious carbon.

The same procedure was applied for the functionalization of a glass microreactor. A solution of β-sultone (**1**) in dry toluene was flowed through the microstructured reactor and let to react for 4 h at 75 °C. This simple procedure allowed the functionalization of the inner surface of the microreactor by a single layer of perfluorinated sulfonic acid. The unreacted reagent was washed away by extensive rinsing with toluene. The microreactor used consisted of a 2 inlets Y-shaped mixing portion and an outlet for the collection of the sample. Two reactors were used, differing in the internal volume (13 μL and 0.3 μL, Figure 1). The thus obtained platform was applied in different continuous-flow acid-catalyzed reactions.

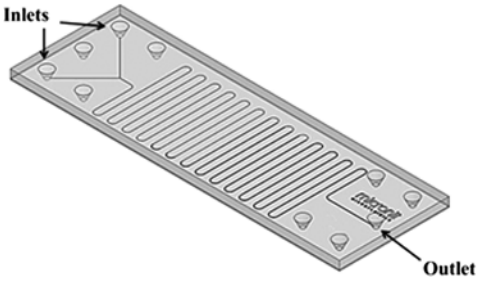
2.2. Sulfonic Acid-Catalyzed Reactions. The sulfonic acid-functionalized microreactor was tested in the deprotection reaction of benzaldehyde dimethyl acetal (BDMA **2**, Scheme 2) [34]. BDMA and water were dissolved in acetonitrile and flowed through the 0.3-μL device at room temperature. This microreactor gives rise to short residence times (4–72 s) using flow rates ranging from 4 to 0.250 μL/min. The conversion of the reaction at different residence times was followed by gas chromatography (GC), checking the formation of benzaldehyde **3**, which was the only product formed.

The conversion profile for the formation of benzaldehyde (**3**) is shown in Figure 2. The system turned out to be highly active in the deprotection reaction, reaching already full conversion in about 60 s of residence time. Assuming a full coverage of the inner surface of the microreactor by β-sultone, a catalyst loading of 0.01 *w*/*w*% was calculated. A first order fitting of the experimental data gave a rate constant of $(6.3 \pm 0.7) \times 10^{-2}$ s^{-1}. Gill et al. [35] investigated the use of four different sulfonic acid-functionalized silica nanoparticles in the hydrolysis of BDMA. Best results were obtained when a perfluorosulfonic acid catalyst was employed, reaching full conversion within 5 min. Our results demonstrate the enhanced activity provided by the use of a sulfonic acid monolayer-functionalized microfluidic platform.

When a bare microreactor was used without functionalization, a negligible conversion (<5%) was detected using the same reaction conditions, confirming that the perfluorosulfonic acid groups are responsible for the catalytic activity.

Furthermore, the Friedlander annulation of 2-aminobenzophenone (**4**) and ethyl acetoacetate (**5**) to give quinoline derivative **6** was tested under continuous-flow conditions using the acid-functionalized microreactor (Scheme 3) [36].

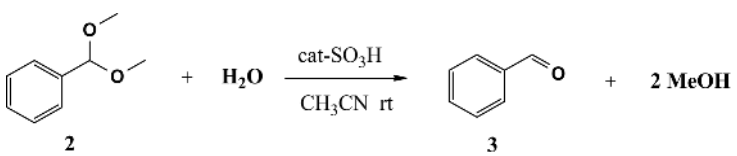
2-Aminobenzophenone (**4**) was flowed through the 13-μL microreactor with a twofold excess of ethyl acetoacetate (**5**) in acetonitrile at 70 °C, in order to have residence times of 2–13 min (flow rates in the range of 1–5 μL/min). The course of the reaction



13 μL	Int. Volume (μL)	0.3 μL
150	Width (μm)	150
150	Depth (μm)	20

Figure 1. Schematic representation of the glass microreactors used

Scheme 2. Deprotection of benzaldehyde dimethyl acetal (**2**)



2 **3**

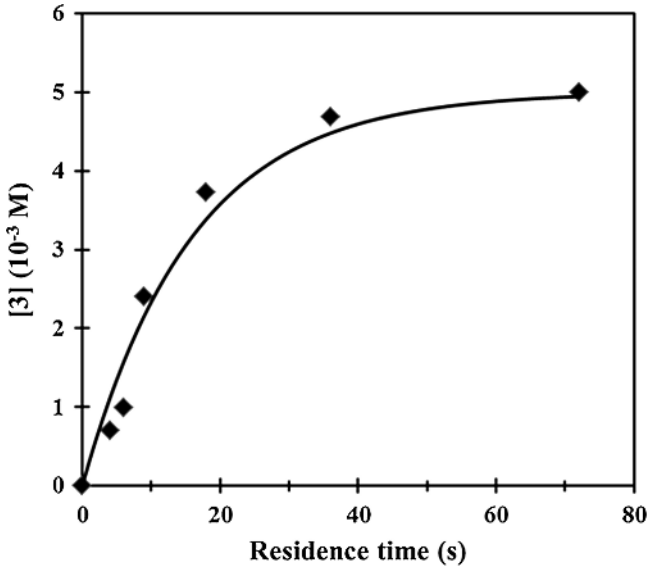
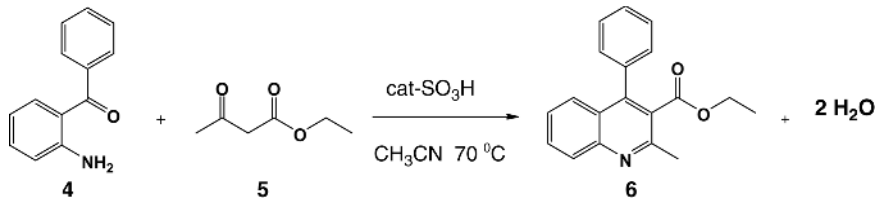


Figure 2. Formation of benzaldehyde (**3**) by hydrolysis of BDMA (**2**, 5×10^{-3} M) in a β-sultone-functionalized microreactor at different residence times at room temperature

Scheme 3. Friedlander synthesis between 2-aminobenzophenone (**4**) and ethyl acetoacetate (**5**)



was monitored by on-line ultraviolet (UV) following the disappearing of the absorbance of compound **4** at a wavelength of 374 nm (Figure 3). The formation of quinoline derivative **6** was unequivocally proven using GC analysis excluding the possibility that the UV disappearance originates from an acid–base reaction.

Assuming a full coverage of the inner surface of the microreactor with the β-sultone moiety, a loading of 15 *w*/*w*% of catalyst was calculated.

Many literature examples of the acid-catalyzed Friedlander synthesis using 2-aminobenzophenone (**4**) and ethyl acetoacetate (**5**) give yields up to 90% for longer reaction times (13 min vs 2.5 h), using about 100-fold higher concentrations, mostly at higher temperatures, and at a comparable amount of catalyst employed [37]. No conversion was detected when a bare microreactor was used, thus again confirming the catalytic role of the perfluorinated sulfonic acid moiety.

In order to prove the wider applicability of our catalytic platform, the sulfonic acid-functionalized microreactor was tested in the acid-catalyzed cyclization of pseudoionone (**7**) in the apolar methylcyclohexane to give α- (**8**) and β-ionone (**9**; Scheme 4).

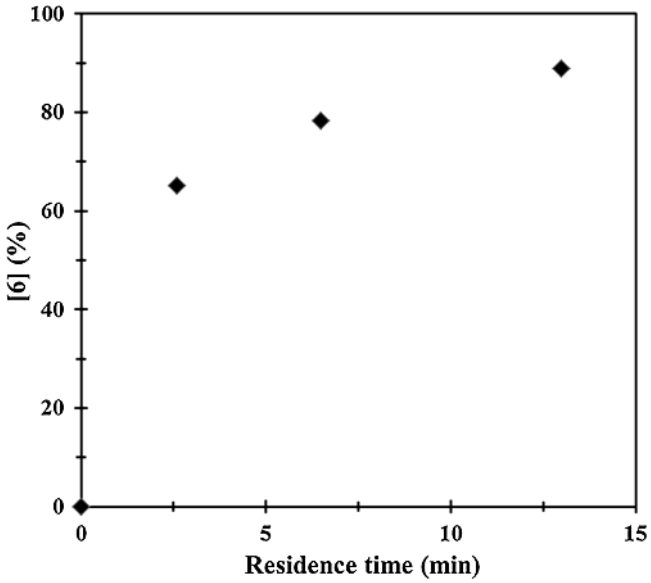
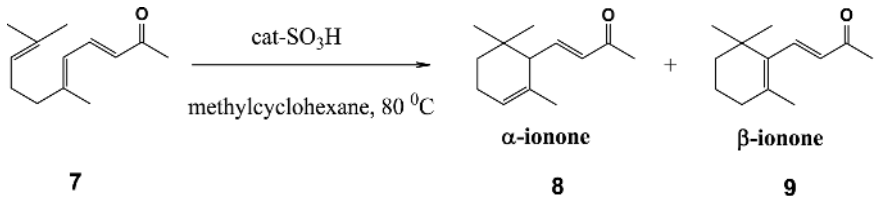


Figure 3. Conversion of 2-aminobenzophenone (**4**; 3×10^{-5} M) in a β-sultone-functionalized microreactor at different residence times (T = 70 °C)

Scheme 4. Cyclization of pseudoionone (**7**)



α-Ionone is widely used in the synthesis of perfumes and cosmetics, whereas β-ionone is a precursor in the synthesis of vitamin A and β-carotene [38].

A solution of the starting reagent **7** in methylcyclohexane was introduced in the 13-μL microreactor and let to react at different reaction times (flow rates between 1 and 15 μL/min) at 80 °C. The reaction was followed by on-line UV detection by monitoring the disappearing of the reagent absorbance at λ=282 nm. As confirmed in a separate lab scale experiment, the α-isomer (rac-**8**) is the main reaction product while the β-isomer (**9**) is formed in < 2% [39]. The conversion profile of pseudoionone (**7**) in the acid-functionalized device is shown in Figure 4.

The experimental data gave rise to a first order rate constant of $(3.5 \pm 1.0) \times 10^{-1}$ min^{-1} showing a conversion of pseudoionone (**7**) up to 60% in less than 15 min residence time (catalyst loading of 40 *w*/*w*%). The use of a macroreticular sulfonic-perfluorinated polystyrene ion-exchange resin by Lin et al. [40] displayed a conversion of 70% in a reaction time of 30 min using 0.2 M pseudoionone (**7**). Therefore, the β-sultone-functionalized device again confirmed its excellent properties under the reaction conditions used. No conversion was observed when the reaction was carried out in a bare microreactor under the same conditions.

The microfluidic catalytic platform could be used continuously for several runs maintaining its activity. However, in the deprotection of BDMA (Scheme 2), a decrease in activity after 6–7 h of continuous utilization was observed. This gradual deactivation over time may be due to the possible hydrolysis of the Si–O–C bond under the conditions used [29]. Gill et al. [35] claim that the presence of water may be responsible for this hydrolysis, while some of the activity could be due to the formed free sulfonic acid. Preliminary experiments to block the possible residual free silanol groups by reaction with *n*-dodecyldimethylmethoxy silane or the introduction of an extra C-3 spacer between the surface and the sulfonic acid did not affect the stability of the layer. Despite the decrease in activity over time, simple treatment of the microreactor with a fresh solution of β-sultone (**1**) ensured the recovery of the initial activity and its use for several consecutive runs.

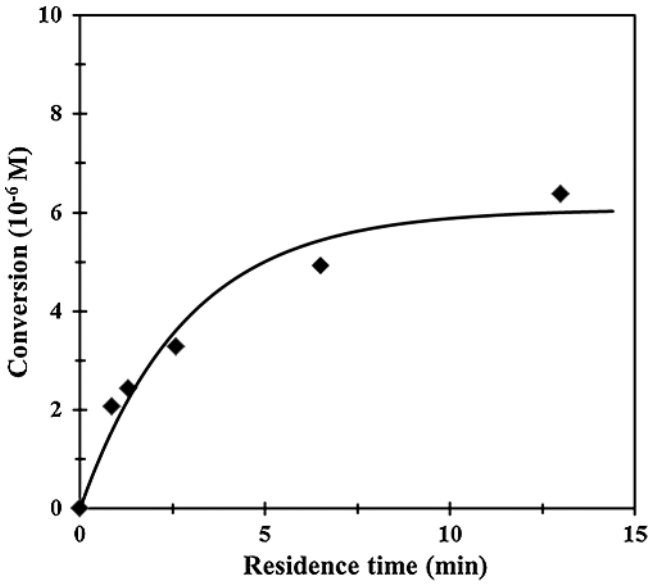


Figure 4. Conversion of pseudoionone (**7**; 10^{-5} M) in a β-sultone-functionalized microreactor at different residence times (T = 80 °C)

The use of apolar media, as in the cyclization of pseudoionone (Scheme 4), showed a markedly slow decrease in activity, and the reaction could be run for at least two consecutive days without loss of activity.

3. Conclusions

We have presented a simple procedure to functionalize the inner walls of a glass microreactor with strong perfluorosulfonic acid groups via single-step anchoring of β-sultone (**1**). Although there is only a catalytic monolayer present, the system turned out to be highly active in different acid-catalyzed reactions. In other examples [18–21], the inner walls had to be coated, via a rather laborious procedure, with polymer brushes containing many catalytic sites to induce a reasonable catalytic activity. The combination of heterogeneous acid catalysis to continuous-flow syntheses follows the lines of the growing environmental protection and green chemistry issues. The easy introduction of a catalytic monolayer on the inner wall microreactor is very promising for other types of catalysts to study a variety of reactions in a simple way.

4. Experimental

4.1. Materials and Equipment. The chemicals and solvents were purchased from Sigma-Aldrich unless otherwise stated and were used without purification unless specified. 1,2,2-Trifluoro-2-hydroxy-1-trifluoromethylethanesulphonic acid sultone (95%) (**1**) was purchased from ABCR chemicals. Water was purified with the Milli-Q pulse (Millipore, R = 18.2 MΩ cm) ultra pure water system. Acetonitrile and toluene were purified through a solvent purification system dispensing ultra dry solvents (MBraun, MB-SPS-800). GC experiments were performed with an Agilent DB-5MS UI column (30 m × 0.32 mm i.d., 25-μm film thickness) with a constant pressure of 11.9 psi. On-line UV experiments were carried out using a micro high-performance liquid chromatography (HPLC) flow-through cell (ZEUTEC Opto-Eletronik, Germany), with a spectral ultraviolet–visible–near-infrared (UV–Vis–NIR) range of 250–2500 nm, an optical path length of 10 mm, and an internal volume of 2 μL. The flow cell is connected, via 2 optical fibers (SR 600 nm, Ocean Optics Inc., The Netherlands), to a miniature deuterium halogen light source (DT-Mini-2-GS, Mikropack GmbH, Germany) and to a high-resolution miniature fiber optic spectrometer (HR4000, Ocean Optics Inc., The Netherlands). Ellipsometry measurements were performed with a plasmon ellipsometer (λ = 632.8 nm), assuming a refractive index of 1.5 for the organic compound. For XPS, a Quantera Scanning X-ray Multiprobe instrument was used, equipped with a monochromatic Al Kα X-ray source producing approximately 25 W of X-ray power. XPS data were collected from a surface area of 1000 × 300 μm with a pass energy of 224 eV and a step energy of 0.8 eV for survey scan and 0.4 for high-resolution scans. For quantitative analysis, high-resolution scans were used. FT-IR

analysis was performed using a Nicolet 6700 instrument (Thermo Scientific) in transmission mode.

4.2. Flow Apparatus. In all microreactor experiments, the sample solutions were mobilized by means of a PHD 22/2000 series syringe pump (Harvard Apparatus, United Kingdom) equipped with 500-μL flat tip syringes (Hamilton). Syringes were connected to fused silica capillaries (100 μm i.d., 362 μm o.d., Polymicro Technologies) by means of Upchurch Nanoport™ assembly parts (i.e., Nano-Tight™ unions and fittings, Upchurch Scientific Inc. USA). During the experiments, the microreactor was placed in a home-built chip holder designed for fitting fused silica fibers into the inlet/outlet chip reservoirs by means of commercially available Upchurch Nanoport™ assembly parts. The temperature in the microreactor was controlled by interfacing a thermoelectric module with a heat sink to the microreactor. The temperature variation on the glass surface of the microreactor measured with a thermocouple was $< \pm 0.1$ °C. A glass microreactor with a residual volume of 13 μL (dimensions: 150 μm width and 150 μm depth) and one with a residual volume of 0.3 μL (dimensions: 150 μm width and 20 μm depth) were purchased from Micronit Microfluidics.

4.3. Functionalization of Flat Silicon Dioxide Surface and Microreactor. 1,2,2-Trifluoro-2-hydroxy-1-trifluoromethylethanesulphonic acid sultone (β-sultone; **1**) was grafted on a flat silicon dioxide surface and within a glass microreactor in an analogous procedure as reported in literature [29]. Both the silicon surface and the microreactor were cleaned with a piranha solution (H_2SO_4:H_2O_2 3:1) and then copiously rinsed with water and dried with a stream of nitrogen (caution: piranha solution is a very strong oxidant and reacts violently with many organic materials). The cleaned silicon wafers were soaked in a 0.1-M solution of β-sultone (**1**) in dry toluene and kept for 4 h at 75 °C. For functionalization in the device, the same solution was flowed for 4 h at a flow rate of 0.05 μL/min at 75 °C. Silicon wafers and microchannels were rinsed with dry toluene to remove the unreacted reagent and dried with a stream of nitrogen.

4.4. Catalytic Studies Inside the Microreactor. Benzaldehyde dimethyl acetal (**2**; BDMA, 5 mM) and water (10 mM) were dissolved in dry acetonitrile and passed through a 0.3-μL internal volume microreactor kept at room temperature at flow rates from 4 μL/min to 0.250 μL/min. The reaction products were collected and analyzed off-line by GC.

2-Aminobenzophenone (**4**; 30 μM) and ethyl acetoacetate (**5**; 60 μM) in dry acetonitrile were passed through a 13-μL internal volume microreactor kept at 70 °C at flow rates varying from 15 μL/min to 1 μL/min. The reaction was monitored by on-line UV, with the outlet of the device connected to the UV flow cell through a back pressure regulator. The conversion curve was obtained by monitoring the disappearing of the 2-aminobenzophenone **4** absorption at a wavelength of 374 nm. The consumption of the reagent corresponds to the formation of quinoline (**6**), with no side products being formed.

A 15-μM solution of pseudoionone (**7**) in methylcyclohexane was passed through a 13-μL internal volume reactor at 80 °C at flow rates varying from 15 μL/min to 1 μL/min. The reaction profile was monitored by on-line UV connecting the outlet of the device to a UV flow cell through a back pressure regulator. The conversion profile was determined by disappearance of the reagent absorption at 282 nm.

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