Supplementary Information (SI) for Reaction Chemistry & Engineering.

Supporting Information

Process intensification and kinetic investigation of solvent-free photoisomerization of norbornadiene to quadricyclane using photomicroreactors

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1. Materials and Methods

Materials

All starting materials and solvents are used without further purification unless otherwise specified. All the chemicals are commercially available.

Gas chromatography - Flame ionization detector (GC-FID)

The initial temperature of the column oven was 50 °C and kept for 2 minutes. The temperature was then increased to 110 °C at a rate of 20 °C/min and finally to 260 °C at a rate of 30 °C/min.

2. Structure and absorption spectrum of photosensitizers

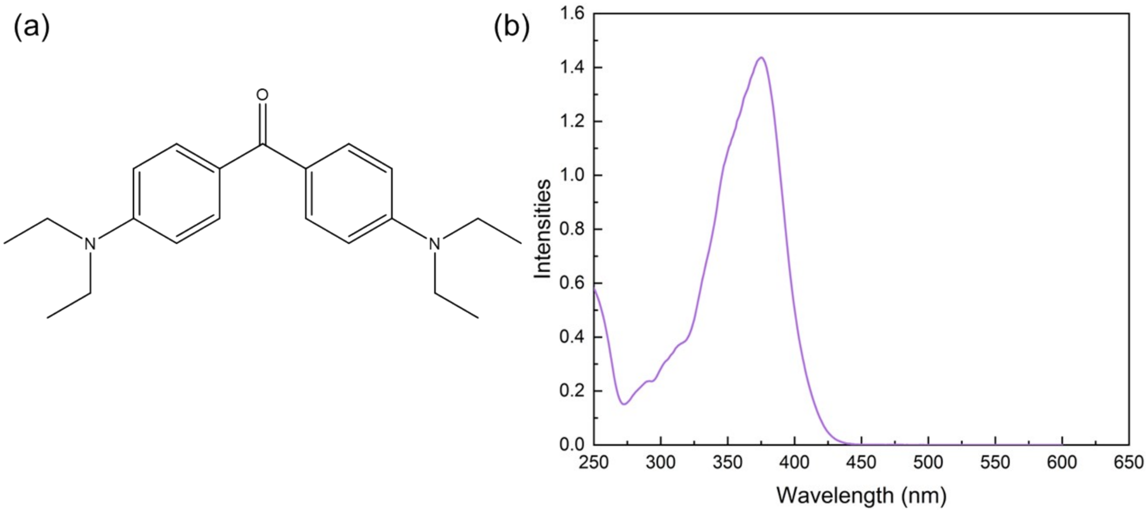


Figure S1. (a) Structure of EMK. (b) UV/Vis absorption spectra of 0.01 mg/ml (3.08×10^{-5} mol/L) EMK in pure NBD with a molar extinction coefficient (ε) of 42861 L/(mol · cm) at 365 nm.

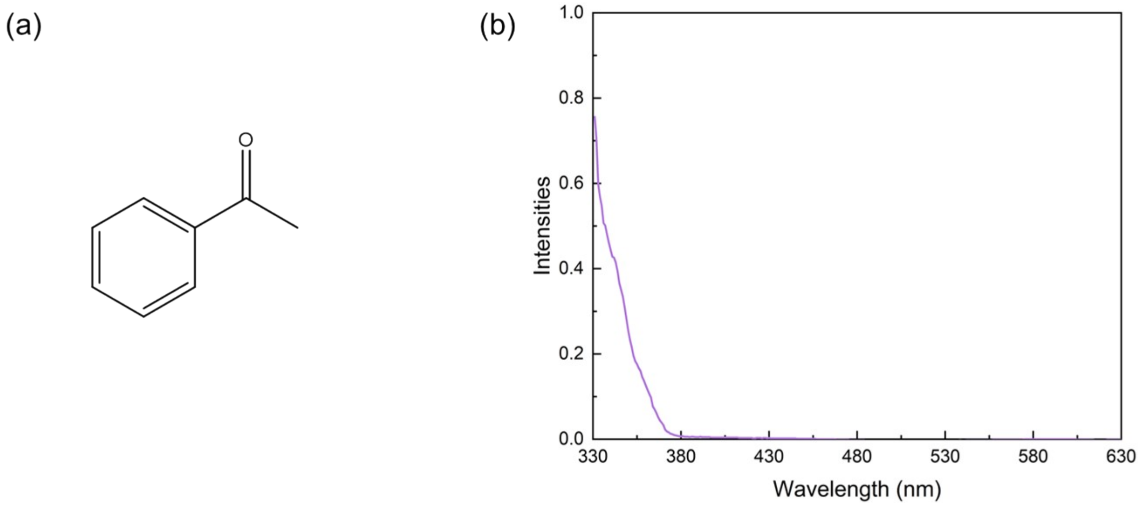


Figure S2. (a) Structure of acetophenone. (b) UV/Vis absorption spectra of 1 mg/ml (8.32×10^{-3} mol/L) acetophenone in pure NBD with a molar extinction coefficient (ε) of 8.41 L/(mol · cm) at 365 nm.

3. Experimental setup

The setup for the experiment is shown in Figure S3. A piston pump was used to deliver the solution, while the solution was controlled to enter the microreactors with different inner diameters through a five-way valve. Subsequently, the reaction solution was irradiated by a UV light source. In this case, the five-way valve and the piston pump were controlled through a Raspberry Pi.

Among them, the connection between the five-way valve and the microreactor is shown in Figure S4. The five-way valve and the stepping motor are firmly connected through the 3D printed parts.

Figure S5 illustrates a comparison of the size of the gears connected to the stepping motor and the five-way valve. The gear structure allows a stepper motor with small torque to push a five-way valve with great resistance.

Figure S6 shows how the microreactors with different inner diameters are arranged inside a box with the light source. The five-way valve has only four outlets, however, five microreactors with different inner diameters were applied in the experiments. Therefore, both 0.5 mm and 0.6 mm microchannels were additionally configured with a two-way to switch the flow path. And Figure S7 shows the structure of plate-type microreactor with 1 mm square channels.

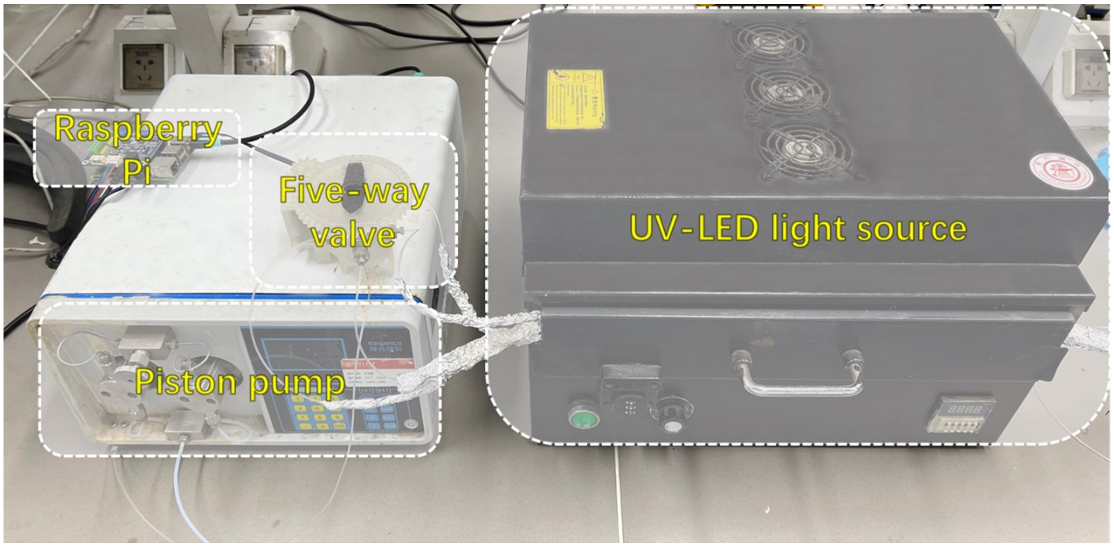


Figure S3. Photo of the photomicroreactor system. Key components are highlighted by text.

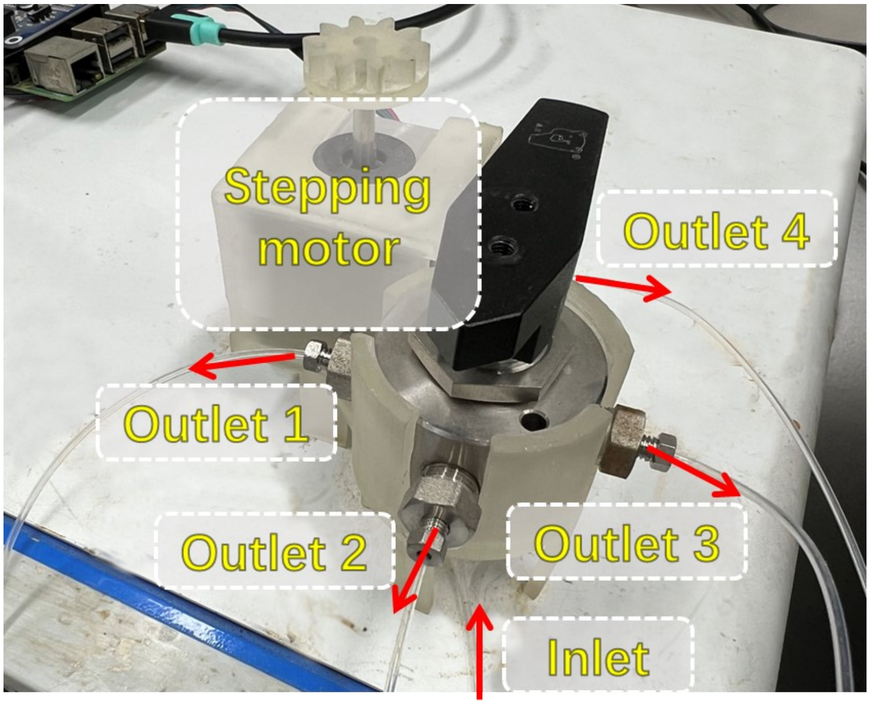


Figure S4. The connection of the five-way valve and the stepping motor.

Figure S5. Comparison of gear sizes for five-way valves and the stepping motor.

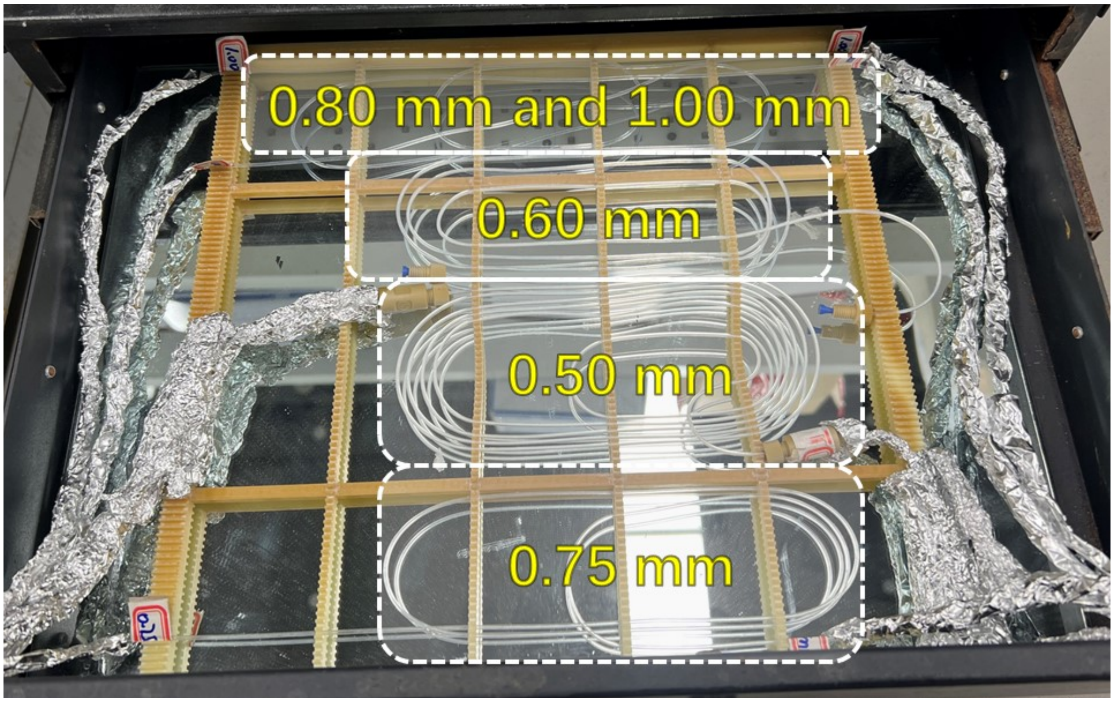


Figure S6. Arrangement of microchannels with different inner diameters within the box with a light source and the placement of reflective mirror for the light source.

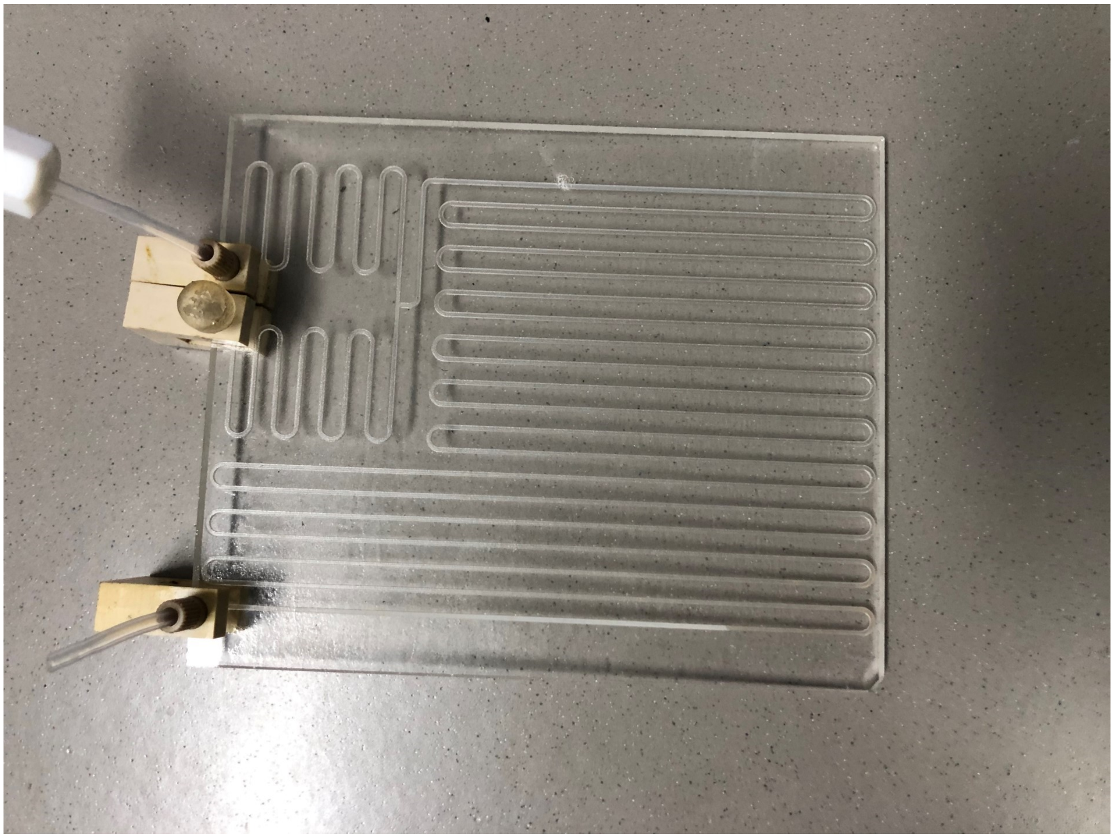


Figure S7. Plate-type microreactor with 1 mm square channels.

4. Emission spectrum and effective photoelectric transformation efficiency of the UV-LED light source

The emission spectrum of the UV-LED light source was measured by a Light UV Spectrometer (HA350UVZ, Hangzhou Benuo Optics Technology Co., Ltd.), and the measurement results are shown in Figure S8. The maximum emission wavelength of the UV-LED light source is 371.0 nm.

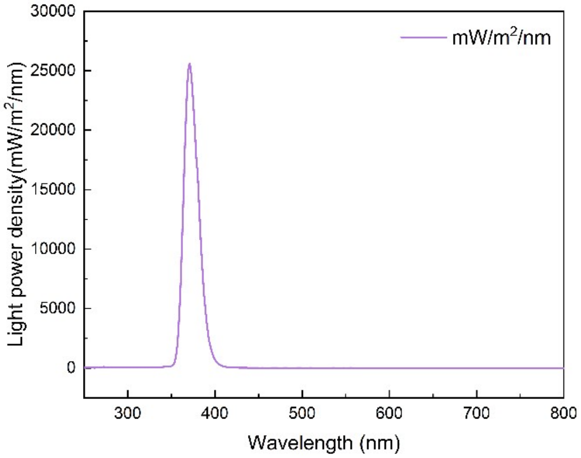


Figure S8. The emission spectrum of the UV-LED light source with the maximum emitting wavelength of 371.0 nm.

The effective photoelectric transformation efficiency of the UV-LED light source was calculated according to the following equation[1]:

$$E = \frac{P_{output}}{P_{input}} = \frac{I \times A}{P_{input}} \qquad \text{* MERGEFORMAT (1)}$$

where P_{output} is the output optical power, P_{input} is the rated electrical power (500 W), I is the light intensity (149.2 mW/cm^2), and A is the effective lighting area (30 cm × 40 cm). Therefore, E was calculated to be 35.81%.

5. Kinetic study

The photochemical isomerization of NBD to QC can be divided into the following intermediate steps:

$$EMK \xrightarrow[hv]{I_0 f} {}^1EMK$$ * MERGEFORMAT (2)

$${}^1EMK \xrightarrow[isc]{k_{2,isc}} {}^3EMK$$ * MERGEFORMAT (3)

$${}^3EMK \xrightarrow[isc]{k_{3,isc}} EMK$$ * MERGEFORMAT (4)

$${}^3EMK + NBD \xrightarrow[TTET]{k_{4,TTET}} EMK + {}^3NBD$$ * MERGEFORMAT (5)

$${}^3EMK + QC \xrightarrow[quench]{k_{5,q}} EMK + QC$$ * MERGEFORMAT (6)

$${}^3NBD \xrightarrow{k_{6,r}} {}^3QC$$ * MERGEFORMAT (7)

$${}^3NBD \xrightarrow[isc]{k_{7,isc}} NBD$$ * MERGEFORMAT (8)

$${}^3QC \xrightarrow[isc]{k_{8,isc}} QC$$ * MERGEFORMAT (9)

Kinetic equations of these reactants and important intermediates in this photoreaction process can be described by Eqs. 10-15, respectively.

$$\frac{dC_{^1EMK}}{dt} = I_0 f - k_{2,isc} C_{^1EMK}$$ * MERGEFORMAT (10)

$$\frac{dC_{^3EMK}}{dt} = k_{2,isc} C_{^1EMK} - k_{3,isc} C_{^3EMK} - k_{4,TTET} C_{^3EMK} C_{NBD} - k_{5,q} C_{^3EMK} C_{QC}$$ *

MERGEFORMAT (11)

$$\frac{dC_{^3NBD}}{dt} = k_{4,TTET} C_{^3EMK} C_{NBD} - k_{6,r} C_{^3NBD} - k_{7,isc} C_{^3NBD}$$ * MERGEFORMAT

(12)

$$\frac{dC_{^3QC}}{dt} = k_{6,r}C_{^3NBD} - k_{8,isc}C_{^3QC}$$ * MERGEFORMAT (13)

$$\frac{dC_{NBD}}{dt} = k_{7,isc}C_{^3NBD} - k_{4,TTET}C_{^3EMK}C_{NBD}$$ * MERGEFORMAT (14)

$$\frac{dC_{QC}}{dt} = k_{8,isc}C_{^3QC}$$ * MERGEFORMAT (15)

By making the assumption that during the photochemical transformation the dynamic equilibrium of ^{1}EMK, ^{3}EMK, ^{3}NBD, and ^{3}QC can be achieved and the reaction rates of these intermediates are zero. The concentrations of ^{3}EMK, ^{3}NBD and ^{3}QC can be described by Eq. 16-18.

$$C_{^3EMK} = \frac{I_0}{k_{3,isc} + k_{4,TTET}C_{NBD} + k_{5,q}C_{QC}}$$ * MERGEFORMAT (16)

$$C_{^3NBD} = \frac{k_{4,TTET}C_{^3EMK}C_{NBD}}{k_{6,r} + k_{7,isc}}$$ * MERGEFORMAT (17)

$$C_{^3QC} = \frac{k_{4,TTET}k_{6,r}C_{^3EMK}C_{NBD}}{(k_{6,r} + k_{7,isc})k_{8,isc}}$$ * MERGEFORMAT (18)

And the photoisomerization rate can be obtained:

$$\begin{aligned} \frac{dC_{QC}}{dt} &= -\frac{dC_{NBD}}{dt} \\ &= I_0 \frac{k_{4,TTET}k_{6,r}C_{NBD}}{k_{8,isc}(k_{6,r} + k_{7,isc})(k_{3,isc} + k_{4,TTET}C_{NBD} + k_{5,q}C_{QC})} \\ &= I_0 \frac{k_{6,r}}{k_{8,isc}(k_{6,r} + k_{7,isc})} \frac{C_{NBD}}{\frac{k_{3,isc}}{k_{4,TTET}} + C_{NBD} + \frac{k_{5,q}}{k_{4,TTET}}C_{QC}} \end{aligned}$$ * MERGEFORMAT

(19)

As:

$$C_0 = C_{NBD} + C_{QC}$$ * MERGEFORMAT (20)

where C_0 is the initial concentration of NBD. Then:

$$\begin{aligned}\frac{dC_{QC}}{dt} &= -\frac{dC_{NBD}}{dt} \\ &= I_0 \frac{k_{6,r}}{k_{8,isc}(k_{6,r}+k_{7,isc})} \frac{C_{NBD}}{\frac{k_{3,isc}}{k_{4,TTET}} + C_{NBD} + \frac{k_{5,q}}{k_{4,TTET}}(C_0 - C_{NBD})} \\ &= I_0 \frac{k_{6,r}}{k_{8,isc}(k_{6,r}+k_{7,isc})} \frac{C_{NBD}}{\frac{k_{3,isc}}{k_{4,TTET}} + (1-\frac{k_{5,q}}{k_{4,TTET}})C_{NBD} + \frac{k_{5,q}}{k_{4,TTET}}C_0}\end{aligned}$$ *

MERGEFORMAT (21)

Let:

$$K_3 = \frac{k_{5,q}}{k_{4,TTET}}$$ * MERGEFORMAT (22)

Then:

$$\begin{aligned}\frac{dC_{QC}}{dt} &= -\frac{dC_{NBD}}{dt} \\ &= I_0 \frac{k_{6,r}}{k_{8,isc}(k_{6,r}+k_{7,isc})} \frac{C_{NBD}}{\frac{k_{3,isc}}{k_{4,TTET}} + (1-\frac{k_{5,q}}{k_{4,TTET}})C_{NBD} + \frac{k_{5,q}}{k_{4,TTET}}C_0} \\ &= I_0 \frac{k_{6,r}}{k_{8,isc}(k_{6,r}+k_{7,isc})(1-K_3)} \frac{C_{NBD}}{\frac{k_{3,isc}}{k_{4,TTET}-k_{5,q}} + C_{NBD} + \frac{K_3}{1-K_3}C_0}\end{aligned}$$ *

MERGEFORMAT (23)

Let:

$$K_1 = \frac{k_{6,r}}{k_{8,isc}(k_{6,r}+k_{7,isc})(1-K_3)}$$ * MERGEFORMAT (24)

$$K_2 = \frac{K_3}{1 - K_3}$$ * MERGEFORMAT (25)

$$K_4 = \frac{k_{3,isc}}{k_{4,TTET} - k_{5,q}}$$ * MERGEFORMAT (26)

Then:

$$\begin{aligned}
\frac{dC_{QC}}{dt} &= -\frac{dC_{NBD}}{dt} \\
&= I_0 \frac{k_{6,r}}{k_{8,isc}(k_{6,r} + k_{7,isc})(1 - K_3)} \frac{C_{NBD}}{\frac{k_{3,isc}}{k_{4,TTET} - k_{5,q}} + C_{NBD} + \frac{K_3}{1 - K_3} C_0} \\
&= I_0 \frac{K_1 C_{NBD}}{K_4 + K_2 C_0 + C_{NBD}} \\
&= I_0 \frac{K_1}{\frac{K_4}{C_{NBD}} + K_2 \frac{C_0}{C_{NBD}} + 1}
\end{aligned}$$

*

MERGEFORMAT (27)

Since $C_{NBD}/C_0 = 1-x$ (x is the conversion of NBD), the photoisomerization rate can be obtained as:

$$\frac{dC_{QC}}{dt} = -\frac{dC_{NBD}}{dt} = I_0 \frac{K_1 C_{NBD}}{K_4 + K_2 C_0 + C_{NBD}} = I_0 \frac{K_1}{\frac{K_4}{C_{NBD}} + K_2 \frac{1}{1-x} + 1}$$ *

MERGEFORMAT (28)

6. Mass transport limitation

The assumption of plug-flow behavior was made to put the residence time distribution model aside, the criteria of which is based on Bodenstein number (*Bo*) [2]:

$$Bo = \frac{\bar{u}L}{D_T} \qquad \text{* MERGEFORMAT (29)}$$

$$D_T = D + \frac{\bar{u}^2 d^2}{4\beta D} \qquad \text{* MERGEFORMAT (30)}$$

where $\bar{u}$ is the average flow velocity, L is the length of the microchannel, d is the inner diameter, D_T is the Taylor dispersion coefficient, D is the mass diffusion coefficient, and β is the geometrical constant (48 for circular capillaries). *Bo* represents the ratio of convection to diffusion. When *Bo* is greater than 100, the flow system can be approximated as a plug flow with small deviations.

Herein, mass diffusion coefficient was calculated by Wilkinson-Chan equation[3]:

$$D_{AB} = 7.4 \times 10^{-8} \frac{T\sqrt{\varphi_B M_B}}{\mu_B {V_A}^{0.6}} \qquad \text{* MERGEFORMAT (31)}$$

where φ_B is the association parameter of solvent (QC), and its value is 1.0, M_B is molecular weight of solvent, and its value is 92.14, T is the absolute temperature, 313 K (due to the heat generated by LEDs), V_A is the molar volume of solute (NBD) at its normal boiling point with a value of 91.7 cm^3/mol, and μ_B is the viscosity of solvent (1 cp). And the calculated D_{AB} is $1.5 * 10^{-9}$ m^2/s.

The calculated *Bo* results for microreactors with different inner diameters at different residence times are shown in Table S1.

In addition, considering that the transverse secondary flow provided by the coiled capillary microreactor can reduces the dispersion effect, the calculated *Bo* value will be smaller than the authentic one.[4] Therefore, it can be reasonably inferred that the plug-flow behavior can be achieved in this study.

Three dimensionless numbers, Da_I, Da_{II}, and *Fo*, are commonly used to determine whether mass transfer limitations have been eliminated in a chemical reaction. Tristan et al.[5] suggested that the concentration distribution across the cross-section of the photomicroreactor would be uniform if $Da_{II} < 1$ and $1/Fo < 1$. Since the reaction is a zero-order reaction, the three dimensionless numbers are given by:

$$Da_I = \frac{kt}{C_0} \qquad \text{* MERGEFORMAT (32)}$$

$$Da_{II} = \frac{kd^2}{D_{AB}C_0} \qquad \text{* MERGEFORMAT (33)}$$

$$Fo = \frac{D_{AB}t}{d^2} \qquad \text{* MERGEFORMAT (34)}$$

The calculated Da_{II} and $1/Fo$ results for microreactors with different inner diameters at different residence times are shown in Table S2. From the results of the calculations, it can be seen that the requirements can be met under almost all conditions, except for a few conditions where the residence time is very short and the reaction is only just getting started. However, as the concentration of the substrate is extremely high at the beginning of the reaction, the heterogeneous concentration due to the velocity field will not affect the performance of reaction order.

Table S1. Bo results for microreactors with different inner diameters at different residence times.

	0.50 mm i.d. L=2.04 m		0.60 mm i.d. L=1.41 m		0.75 mm i.d. L=0.91 m		0.80 mm i.d. L=0.80 m		1.00 mm i.d. L=0.51 m	
	t/min	Bo	t/min	Bo	t/min	Bo	t/min	Bo	t/min	Bo
without mirror	3	207	2.5	120	3	92	3	81	5	86
	6	415	5	240	6	184	6	162	10	173
	9	622	7.5	360	9	276	9	243	15	259
	12	829	10	480	12	368	12	324	20	345
	15	1036	12.5	600	15	460	15	405	25	430
with mirror	3	207	2.5	120	3	92	3	81	4	69
	6	415	5	240	6	184	6	162	8	138
	9	622	7.5	360	9	276	9	243	12	207
	12	829	10	480	12	368	12	324	16	276
	15	1036	12.5	600	15	460	15	405	20	345

Table S2. Da_{II} and $1/Fo$ results for microreactors with different inner diameters at different residence times.

Without reflective mirror						
L=2.04 m i.d.=0.50 mm K=0.0122	t/min	3	6	9	12	15
	DaII	0.23	0.23	0.23	0.23	0.23
	1/Fo	0.93	0.46	0.31	0.23	0.19
L=1.41 m i.d.=0.60 mm K=0.0107	t/min	2.5	5	7.5	10	12.5
	DaII	0.28	0.28	0.28	0.28	0.28
	1/Fo	1.60	0.80	0.53	0.40	0.32
L=0.91 m i.d.=0.75 mm K=0.0089	t/min	3	6	9	12	15
	DaII	0.37	0.37	0.37	0.37	0.37
	1/Fo	2.08	1.04	0.69	0.52	0.42
L=0.80 m i.d.=0.80 mm K=0.0080	t/min	3	6	9	12	15
	DaII	0.38	0.38	0.38	0.38	0.38
	1/Fo	2.37	1.19	0.79	0.59	0.47
L=0.51 m i.d.=1.00 mm K=0.0054	t/min	5	10	15	20	25
	DaII	0.40	0.40	0.40	0.40	0.40
	1/Fo	2.22	1.11	0.74	0.56	0.44
With reflective mirror						
L=2.04 m i.d.=0.50 mm K=0.0174	t/min	3	6	9	12	15
	DaII	0.32	0.32	0.32	0.32	0.32
	1/Fo	0.93	0.46	0.31	0.23	0.19
L=1.41 m i.d.=0.60 mm K=0.0154	t/min	2.5	5	7.5	10	12.5
	DaII	0.41	0.41	0.41	0.41	0.41
	1/Fo	1.60	0.80	0.53	0.40	0.32
L=0.91 m i.d.=0.75 mm K=0.0127	t/min	3	6	9	12	15
	DaII	0.53	0.53	0.53	0.53	0.53
	1/Fo	2.08	1.04	0.69	0.52	0.42
L=0.80 m i.d.=0.80 mm K=0.0113	t/min	3	6	9	12	15
	DaII	0.54	0.54	0.54	0.54	0.54
	1/Fo	2.37	1.19	0.79	0.59	0.47
L=0.51 m i.d.=1.00 mm K=0.0080	t/min	4	8	12	16	20
	DaII	0.59	0.59	0.59	0.59	0.59
	1/Fo	2.78	1.39	0.93	0.69	0.56

7. Calculation of dimensionless time

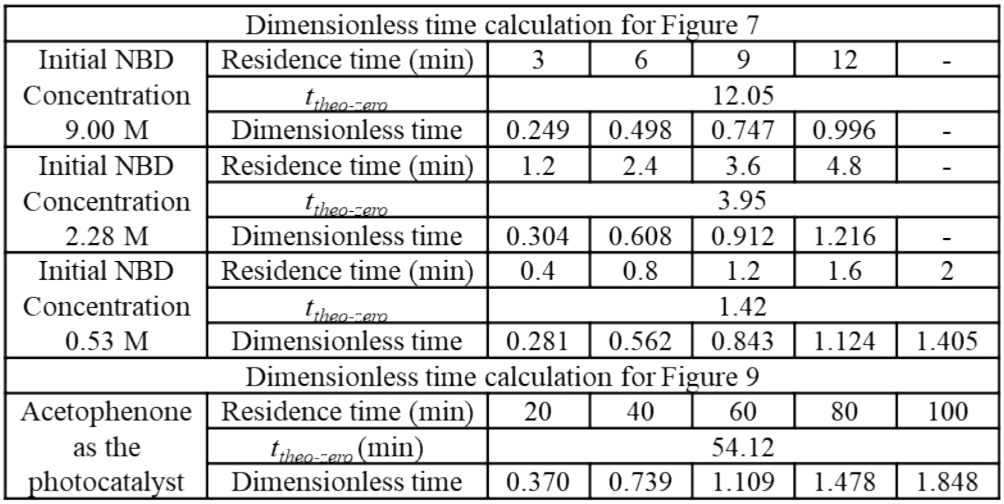
The dimensionless time is calculated according to the following formula:

$$DimensionlessTime = \frac{t}{t_{theo-zero}} = \frac{t}{C_0 / k_{liner}} \text{\\* MERGEFORMAT (35)}$$

where t is the real residence time, and $t_{\text{theo-zero}}$ is the time required for the complete conversion of norbornadiene assuming a zero-order reaction. C_0 is the initial concentration of NBD, and k_{liner} is the reaction rate in the initial stage of the reaction (the linear part when the reaction kinetics does not deviate from the zero-order).

Accordingly, the calculation results of the dimensionless time in Figures 7 and 9 are shown in Table S3.

TABLE S3. The calculation results of the dimensionless time in Figures 7 and 9.



Dimensionless time calculation for Figure 7						
Initial NBD Concentration 9.00 M	Residence time (min)	3	6	9	12	-
	$t_{theo-zero}$	12.05				
	Dimensionless time	0.249	0.498	0.747	0.996	-
Initial NBD Concentration 2.28 M	Residence time (min)	1.2	2.4	3.6	4.8	-
	$t_{theo-zero}$	3.95				
	Dimensionless time	0.304	0.608	0.912	1.216	-
Initial NBD Concentration 0.53 M	Residence time (min)	0.4	0.8	1.2	1.6	2
	$t_{theo-zero}$	1.42				
	Dimensionless time	0.281	0.562	0.843	1.124	1.405
Dimensionless time calculation for Figure 9						
Acetophenone as the photocatalyst	Residence time (min)	20	40	60	80	100
	$t_{theo-zero}$ (min)	54.12				
	Dimensionless time	0.370	0.739	1.109	1.478	1.848

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8. Utilization of the irradiation

The apparent quantum yield (AQY) of the photocatalytic system can be calculated according to the following equation:

$$AQY = \frac{N_r}{N_{photon}} = \frac{n(QC)N_A hc}{PSt\lambda} = \frac{1.2\times10^8 n(QC)}{PSt\lambda}$$ * MERGEFORMAT

(36)

Here, N_A is Avogadro constant (6.02×10^{23}); h is Planck constant (6.63×10^{-34} J s); c is the lightspeed (3×10^8 m s^{-1}); P is the incident light power density (0.1492 W cm^{-2}); S is the area of the incident light cross section (32.4 cm^2); t is the reaction time; λ is the incident light wavelength (371 nm). Therefore, the AQY for the capillary with 0.5 mm i.d. was calculated to be 30.07%.

In addition, the energy utilization efficiency can be evaluated by the photonic efficiency ξ[1]:

$$\xi = \frac{r_a}{q}$$ * MERGEFORMAT (37)

where r_a is the average reaction rate and q is the photon flux emitted by the UV-LED. These two parameters r_a and q can be calculated as follows:

$$r_a = YC_0Q_L$$ * MERGEFORMAT (38)

$$q = \frac{P_{output}\times\lambda}{h\times c\times N_A}$$ * MERGEFORMAT (39)

where C_0 is the initial concentration of NBD, Q_L is the volumetric flow rate of the liquid phase, Y is the yield of QC. For the capillary with 0.5 mm i.d., the flow rate was 1.66 ml/h without reflective mirror and 2.32 ml/min with reflective mirror, and the yield of QC could both reach 99.5%. Accordingly, the photonic efficiency in the photomicroreactor reached 1.47%. When a reflective mirror was used, the photonic efficiency was further increased to 2.12%. The low photonic efficiency was mainly caused by the fact that most of the light irradiation area was not utilized when only a microreactor with an inner diameter of 0.5 mm was used (see Figure S6).

9. COMSOL simulation

The light distribution in photo microreactors was simulated using COMSOL Multiphysics 6.2. In the simulation process, the intensity of light was tracked using the ‘Geometrical Optics’ module in ‘Ray Optics’, where the wavefronts are treated as rays that can propagate through optically large geometries and reflect or refract at boundaries.

The simulation was performed from the 2D domain for five microreactors with inner diameter of 0.5 mm, 0.60 mm, 0.75 mm, 0.80 mm and 1.00 mm. A fine mesh was used for the entire cross-section of the microchannel and the edges of the microchannel were set as boundary layers for denser mesh (see Figure S9).

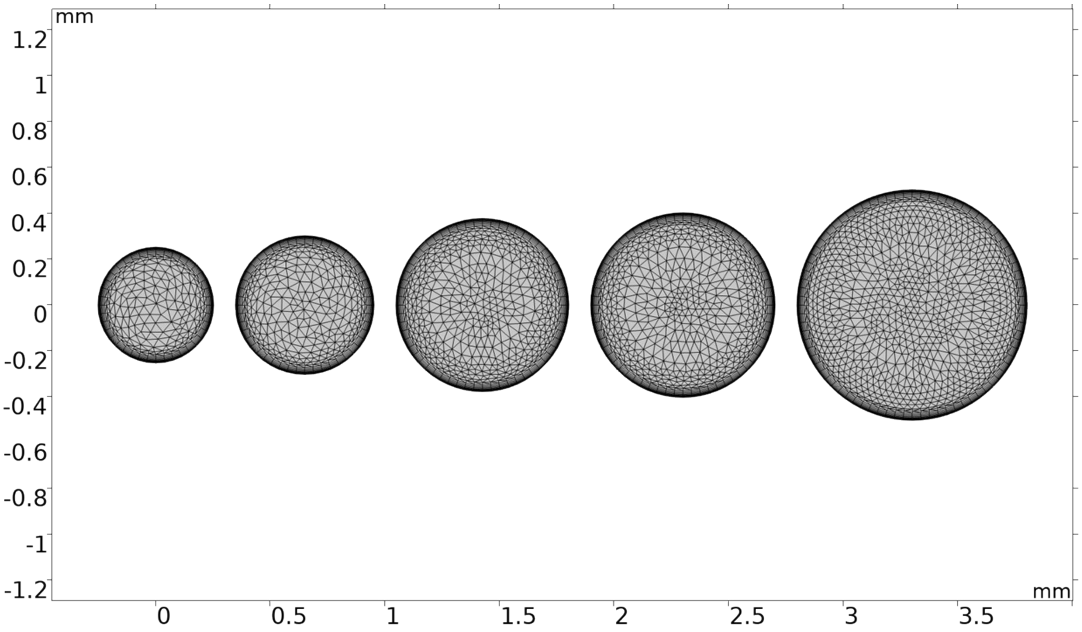

Figure S9. Modeling and internal meshing of five microchannels with different inner diameters.

The calculation equation for ray tracing in COMSOL is:

$$\frac{d\mathbf{q}}{dt}=\frac{\partial\omega}{\partial\mathbf{k}}$$ * MERGEFORMAT (40)

$$\frac{d\mathbf{k}}{dt}=-\frac{\partial\omega}{\partial\mathbf{q}}$$ * MERGEFORMAT (41)

A ‘scattering domain’ was used to model the molar extinction coefficient, and the scattering model of ‘Deterministic’ was selected. The ray intensity and power will continuously decrease as rays propagate through the capillary profile and the total number or rays will remain the same. As the number density and size of the scattering particles are spatially uniform, the intensity and power will decay exponentially, just as Bouguer–Lambert–Beer Law. The ‘Specify cross section’ was selected for ‘Cross section calculation’, so the final calculation equations are:

$$\sigma_{ext}=\sigma_{abs}+\sigma_{sca}$$ * MERGEFORMAT (42)

$$\frac{dI}{ds}=-\gamma_{ext}I$$ * MERGEFORMAT (43)

$$\frac{dQ}{ds}=-\gamma_{ext}Q$$ * MERGEFORMAT (44)

$$\gamma_{ext}=\pi NR^{2}Q_{ext}$$ * MERGEFORMAT (45)

$$x_{sc}=\frac{2\pi R}{\lambda},\lambda=\frac{\lambda_{0}}{n_{amb}}$$ * MERGEFORMAT (46)

The light intensity distribution in five microreactors with the inner diameters of 0.5 mm, 0.60 mm, 0.75 mm, 0.80 mm and 1.00 mm is shown in Figure 12 in the Manuscript.

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10. Influence of microchannel wall thickness and material

The transmittance of the PFA film with 0.6 mm thickness at 368 nm is 80%[6]. Since UV-Vis spectrophotometer is used for measurement, the transmittance value has superimposed two reflections, that is, from air to PFA material and from PFA material to air. Reflection takes place in the interface of two media with different refractive indexes. Given that incident light has two different polarizations physically, which are s-polarized and p-polarized, reflection coefficients can be calculated by the following Fresnel equation:

$$R_s = \left(\frac{n_1 \cos\theta_1 - n_2 \cos\theta_2}{n_1 \cos\theta_1 + n_2 \cos\theta_2} \right)^2 \qquad \text{* MERGEFORMAT (47)}$$

$$R_p = \left(\frac{n_1 \cos\theta_2 - n_2 \cos\theta_1}{n_1 \cos\theta_2 + n_2 \cos\theta_1} \right)^2 \qquad \text{* MERGEFORMAT (48)}$$

where R_s and R_p are the reflection coefficients of s-polarized and p-polarized photons, respectively, and are defined as the ratio of the intensity of the reflected light to the incident light regarding two different polarizations. n_1 and n_2 are the refractive indices of two media, and θ_1 and θ_2 are the incident and refracted angles of the light, respectively. By hypothesizing that the amounts of each kind of polarized photons are the same, the average reflection coefficient R_{ave} can be simplified as the following:

$$R_{ave} = \frac{R_s + R_p}{2} \qquad \text{* MERGEFORMAT (49)}$$

When light is irradiated vertically from the air (n=1) into the PFA material (n=1.34) or from the FPA material into the air, the average reflection coefficient is calculated to be

2.11%. After deducting these two light reflections, the net transmittance of PFA material is 83.5%. Using a form similar to the Lambert-Bouguer-Beer law, the transmittance of PFA can be expressed as:

$$\lg(\frac{I_0}{I}) = \lg(0.835) = \varepsilon l = \varepsilon \times 0.6(mm)$$ * MERGEFORMAT (50)

where I_0 is the initial light intensity, I is the transmitted light intensity, ε is the transmission coefficient of the PFA material, and l is the thickness of the PFA material. Accordingly, the transmission coefficient of PFA is 0.130 mm^{-1}.

For glass materials ($n \approx 1.5$), although glass has a high transmittance in visible light (generally greater than 90%), its transmittance in ultraviolet light is low. When the wavelength is 380 nm, the transmittance of glass is about 85%, which is equivalent to the PFA material.

Therefore, the transmittance under different tube wall thickness and different materials can be calculated according to the following formula:

$$\frac{I'}{I_0'} = (1 - R_{a-c})T_p(1 - R_{c-NBD})$$ * MERGEFORMAT (51)

where I' is the light intensity irradiating into the reaction mixture, I_0' is the incident light intensity, and T_p is the transmittance of the capillary microreactor, which can be calculated by Eq. 45. $R_\mathrm{a–c}$ is the average reflection coefficient between air and capillary, $R_\mathrm{c–NBD}$ is the average reflection coefficient between the capillary microreactor and the reaction mixture

(NBD without solvent, n=1.47), and both of them can be calculated by the following equation:

$$R=\frac{\int_0^{\theta\max}\left(\frac{n_1\cos\theta_1-n_2\cos\theta_2}{n_1\cos\theta_1+n_2\cos\theta_2}\right)^2\cos\theta_1 d\theta_1+\int_0^{\theta\max}\left(\frac{n_1\cos\theta_2-n_2\cos\theta_1}{n_1\cos\theta_2+n_2\cos\theta_1}\right)^2\cos\theta_1 d\theta_1}{2\times\int_0^{\theta\max}\cos\theta d\theta}$$ * MERGEFORMAT (52)

where $\theta_{\max}$ is the angle between the light and the outer diameter when the parallel light just hits the edge of the inner diameter of the microchannel. Beyond this angle, the light cannot irradiate into the reaction liquid and can only pass through the gap between the outer diameter and the inner diameter. In the formula, cosθ is multiplied before integrating the Fresnel equation and averaging it, because the number of photons of parallel light is proportional to the irradiated area, and dθ at a larger angle corresponds to a smaller irradiated area.

The results of the light intensity irradiating into the reaction mixture of microchannels with different capillary diameters, materials, wall thicknesses are shown in Table S4.

TABLE S4 The light intensity irradiating into the reaction mixture of microchannels with different capillary diameters, materials, wall thicknesses

Material	o.d./mm	i.d./mm	Wall thickness/mm	T_p	$R_{a\text{-}c}$	$R_{c\text{-}NBD}$	I'/I_0'
PFA	1.5875	0.5	0.5438	0.8492	0.0212	0.0462	0.7929
PFA	1.5875	0.6	0.4938	0.8621	0.0212	0.0462	0.8049
PFA	1.5875	0.75	0.4188	0.8817	0.0213	0.0462	0.8231
PFA	1.5875	0.8	0.3938	0.8884	0.0213	0.0462	0.8293
PFA	1.5875	1	0.2938	0.9155	0.0217	0.0462	0.8543
Glass	-	-	0.5	0.8500	0.0400	0.0001	0.8159

As can be seen from Table S4, different materials and wall thicknesses have little effects on the light intensity irradiating into the reaction mixture, and I'/I_0' is basically between 80% and 85%. Therefore, under the current experimental conditions, it can be considered that the effects of microchannel materials, diameters, and wall thicknesses on reaction kinetics can be ignored.

11. Boundary and maximum relative error for zero-order kinetics

The maximum relative error of using zero-order reaction kinetics was characterized by performing nonlinear regression and zero-order reaction kinetics regression on the reaction results.

Integrating Eq. 28 in Supporting Information Section 5, the concentration of NBD with the residence time can be obtained as the following equation:

$$(K_4 + K_2 C_0)\ln(C_0 / C_{NBD}) + (C_0 - C_{NBD}) = K_1 t \backslash * \text{ MERGEFORMAT}$$

(53)

The above equations and zero-order reaction kinetics were separately used to regress the experimental results in FIGURE 6, and the results are shown in FIGURE S10.

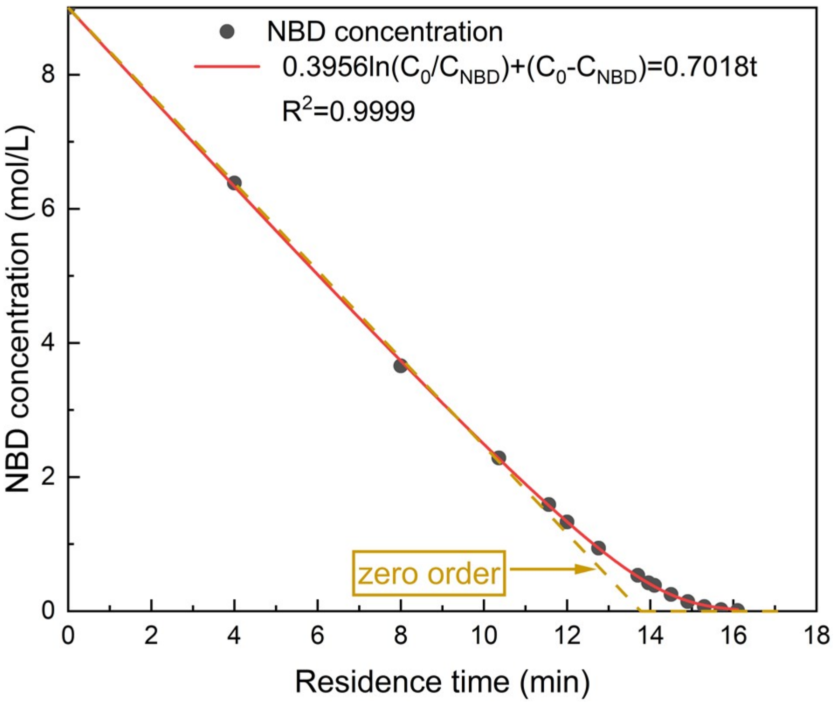

FIGURE S10. Plot of regression results using zero-order reaction kinetics and a nonlinear equation.

As can be seen from Figure S10, the maximum relative error of the two regression methods occurs when the conversion rate just reaches 100%. At this time, the result of nonlinear regression is that the concentration of NBD is 0.4863M. That is, the NBD conversion is 94.6%. Accordingly, the maximum relative error between nonlinear regression and zero-order reaction kinetics regression is 5.7%.

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12. The scope of application of the apparent kinetic equation

According to the apparent rate constant obtained in Eq. 20 in the Manuscript and Section 6 in Supporting Information, the applicable capillary diameter range for zero-order kinetics can be calculated.

When using circular microchannels, Equation 20 in the Manuscript can be transformed into:

$$\frac{dC_{QC}}{dt} = -\frac{dC_{NBD}}{dt} = 1.83\times10^{-3}\frac{4}{\pi d}\times I_e \text{ \\* MERGEFORMAT (54)}$$

where the parameter I_e refers to the effective light intensity, mW/cm^2. Parameter d refers to the diameter of the capillary, mm.

The residence time for full conversion of norbornadiene (t_f) under solvent free conditions can be calculated by:

$$t_f = \frac{C_0}{1.83\times10^{-3}}\times\frac{\pi d}{4}\times\frac{1}{I_e} = \frac{9.87}{1.83\times10^{-3}}\times\frac{\pi d}{4}\times\frac{1}{I_e} \text{ \\* MERGEFORMAT}$$

(55)

According to Supporting Information Section 6, to ensure the concentration distribution across the cross-section of the photomicroreactor to be uniform, Da$_{II}$ < 1 and 1/Fo < 1 should be guaranteed, that is:

$$Da_{II} = \frac{kd^2}{D_{AB}C_0} = \frac{1.83\times10^{-3}\frac{4}{\pi d}\times I_e(mol/L/\min)\times d^2(mm^2)}{1.5\times10^{-9}(m^2/s)\times9.87(mol/L)} < 1\text{\\*}$$

MERGEFORMAT (56)

$$Fo = \frac{D_{AB}t}{d^2} = \frac{1.5\times10^{-9}(m^2/s)\times\frac{9.87}{1.83\times10^{-3}}\times\frac{\pi d}{4}\times\frac{1}{I_e}(\min)}{d^2(mm^2)} > 1$$*

MERGEFORMAT (57)

And it can be further deduced that:

$$d < \frac{381.24}{I_e}$$ * MERGEFORMAT (58)

It should be noted that the two constrains of $Da_{II} < 1$ and $1/Fo < 1$ are defined based on the assumption of monodirectional light direction[5]. Therefore, when using a reflector to achieve double-sided irradiation, the above constraints do not have to be strictly followed. In this case, the microchannel is equivalent to two semicircular microchannels with half the thickness placed in parallel. Therefore, it is reasonable to relax the above restriction by two times, that is:

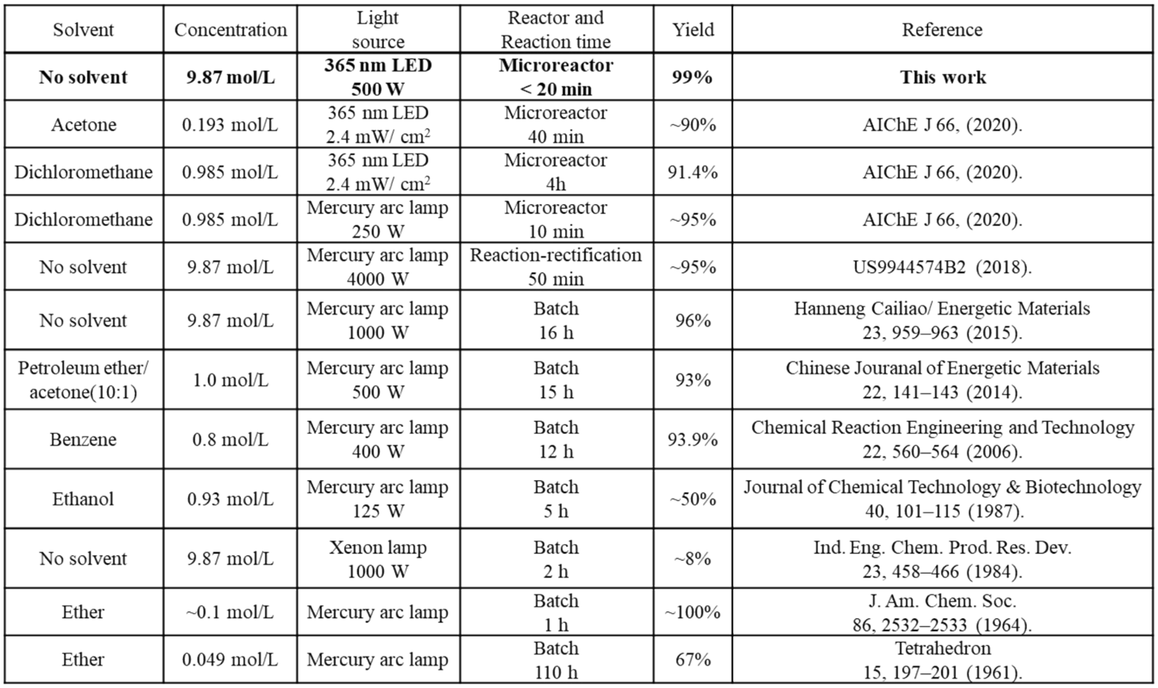
$$\frac{d}{2} < \frac{381.24}{I_e} \rightarrow d < \frac{762.48}{I_e}$$ * MERGEFORMAT (59)

Therefore, when the light intensity is 149.2 mW/cm^2, the inner diameter needs to be less than 5.1 mm. When the light intensity reaches 330 mW/cm^2, the inner diameter needs to be less than 2.3 mm.

13. Comparison of the reported quadricyclane synthesis systems with our system

The comparison of the reported quadricyclane synthesis systems with our system is shown in Table S5. Compared with Figure 16 (c), the table adds the synthesis results under solvent conditions.

Table S5. Comparison of the reported quadricyclane synthesis systems with our system[6–14].



Solvent	Concentration	Light source	Reactor and Reaction time	Yield	Reference
No solvent	**9.87 mol/L**	**365 nm LED 500 W**	**Microreactor < 20 min**	**99%**	**This work**
Acetone	0.193 mol/L	365 nm LED 2.4 mW/ cm^2	Microreactor 40 min	~90%	AIChE J 66, (2020).
Dichloromethane	0.985 mol/L	365 nm LED 2.4 mW/ cm^2	Microreactor 4h	91.4%	AIChE J 66, (2020).
Dichloromethane	0.985 mol/L	Mercury arc lamp 250 W	Microreactor 10 min	~95%	AIChE J 66, (2020).
No solvent	9.87 mol/L	Mercury arc lamp 4000 W	Reaction-rectification 50 min	~95%	US9944574B2 (2018).
No solvent	9.87 mol/L	Mercury arc lamp 1000 W	Batch 16 h	96%	Hanneng Cailiao/ Energetic Materials 23, 959–963 (2015).
Petroleum ether/ acetone(10:1)	1.0 mol/L	Mercury arc lamp 500 W	Batch 15 h	93%	Chinese Jouranal of Energetic Materials 22, 141–143 (2014).
Benzene	0.8 mol/L	Mercury arc lamp 400 W	Batch 12 h	93.9%	Chemical Reaction Engineering and Technology 22, 560–564 (2006).
Ethanol	0.93 mol/L	Mercury arc lamp 125 W	Batch 5 h	~50%	Journal of Chemical Technology & Biotechnology 40, 101–115 (1987).
No solvent	9.87 mol/L	Xenon lamp 1000 W	Batch 2 h	~8%	Ind. Eng. Chem. Prod. Res. Dev. 23, 458–466 (1984).
Ether	~0.1 mol/L	Mercury arc lamp	Batch 1 h	~100%	J. Am. Chem. Soc. 86, 2532–2533 (1964).
Ether	0.049 mol/L	Mercury arc lamp	Batch 110 h	67%	Tetrahedron 15, 197–201 (1961).

14. NMR spectra

Below is the most typical set of experimental data for a full set of zero-order reaction kinetics, i.e., no reflective mirror, 0.5 mm inner diameter of the capillary, and light intensity of 149.2 mW/cm^2.

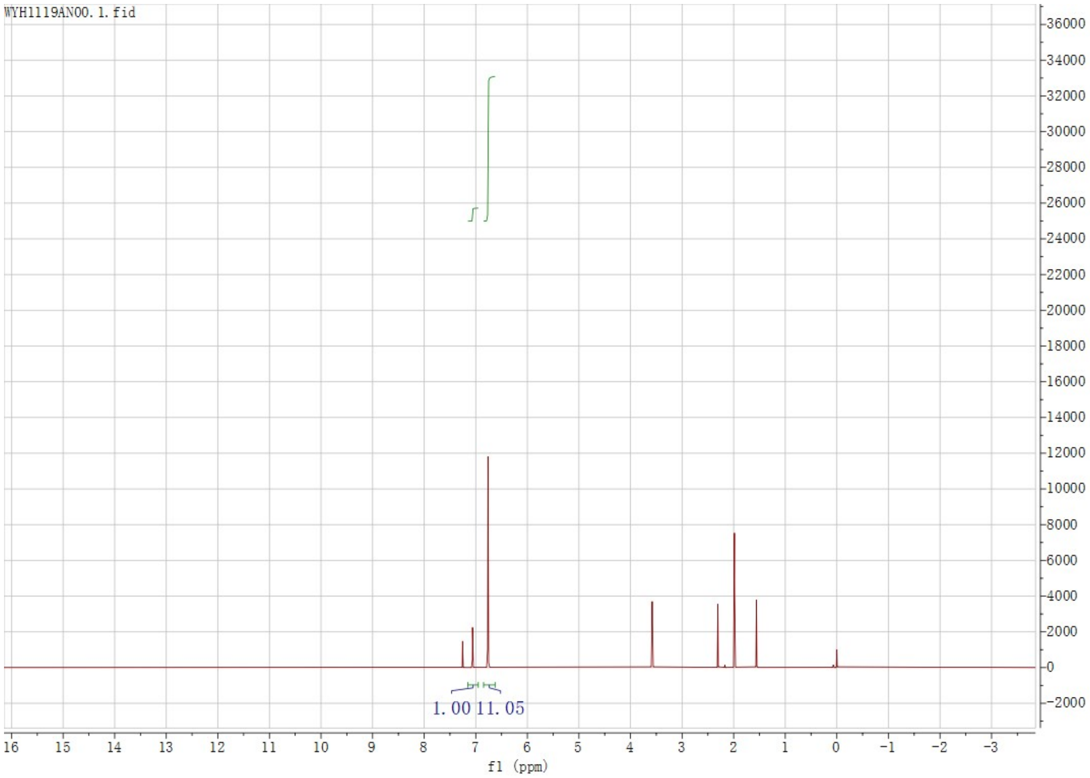


Figure S11. NMR spectrum of the reaction solution prior to the reaction. The initial NBD concentration is 9 M with 10 wt. % paraxylene as the internal standard and 0.55 wt. % EMK as the photosensitizer, and the inner diameter of the capillary is 0.50 mm.

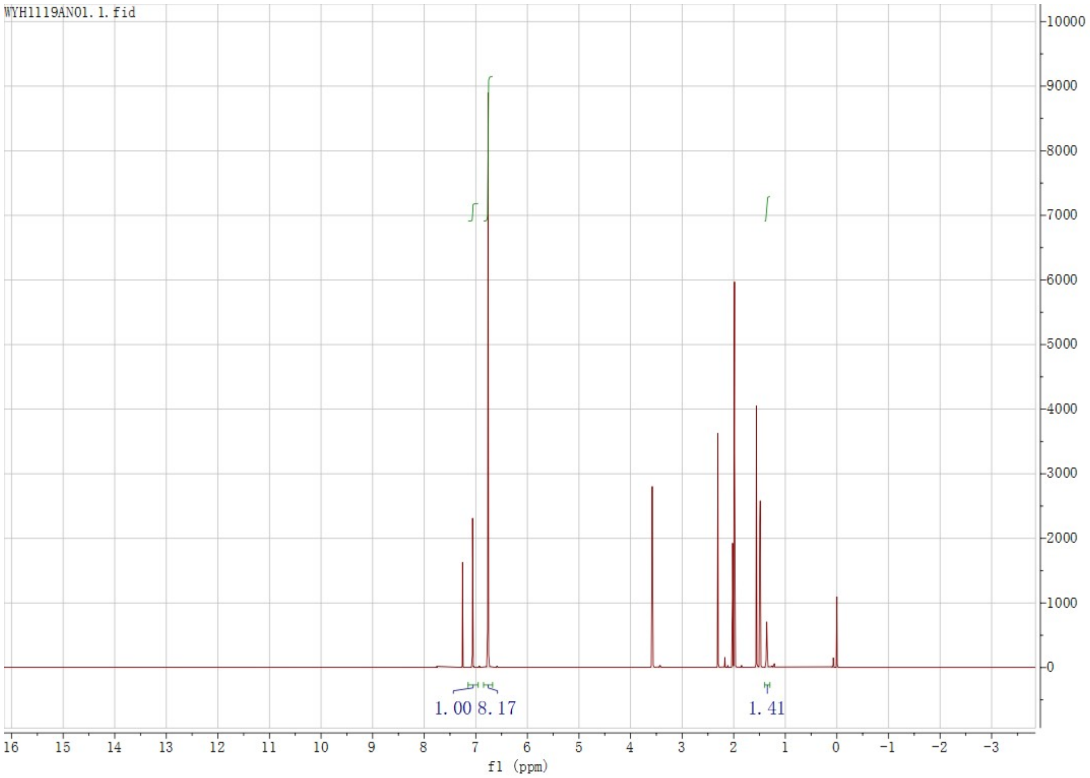


Figure S12. NMR spectrum of the reaction solution at a residence time of 3 min. The initial NBD concentration is 9 M with 10 wt. % paraxylene as the internal standard and 0.55 wt. % EMK as the photosensitizer, and the inner diameter of the capillary is 0.50 mm.

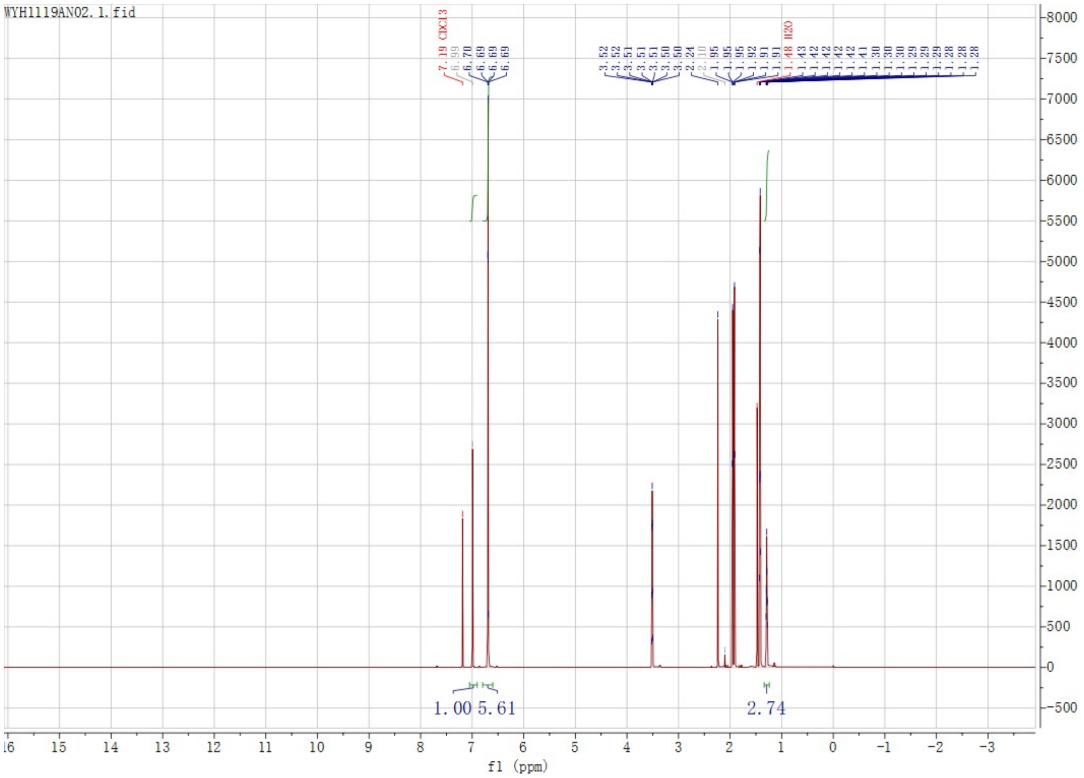


Figure S13. NMR spectrum of the reaction solution at a residence time of 6 min. The initial NBD concentration is 9 M with 10 wt. % paraxylene as the internal standard and 0.55 wt. % EMK as the photosensitizer, and the inner diameter of the capillary is 0.50 mm.

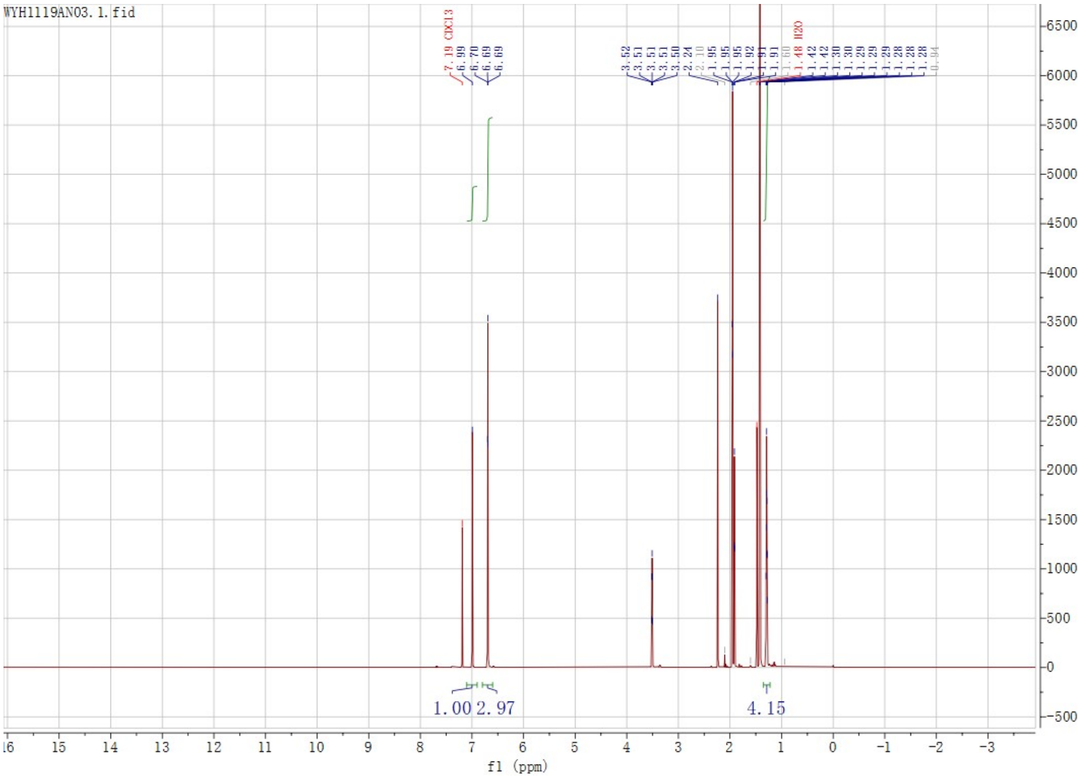


Figure S14. NMR spectrum of the reaction solution at a residence time of 9 min. The initial NBD concentration is 9 M with 10 wt. % paraxylene as the internal standard and 0.55 wt. % EMK as the photosensitizer, and the inner diameter of the capillary is 0.50 mm.

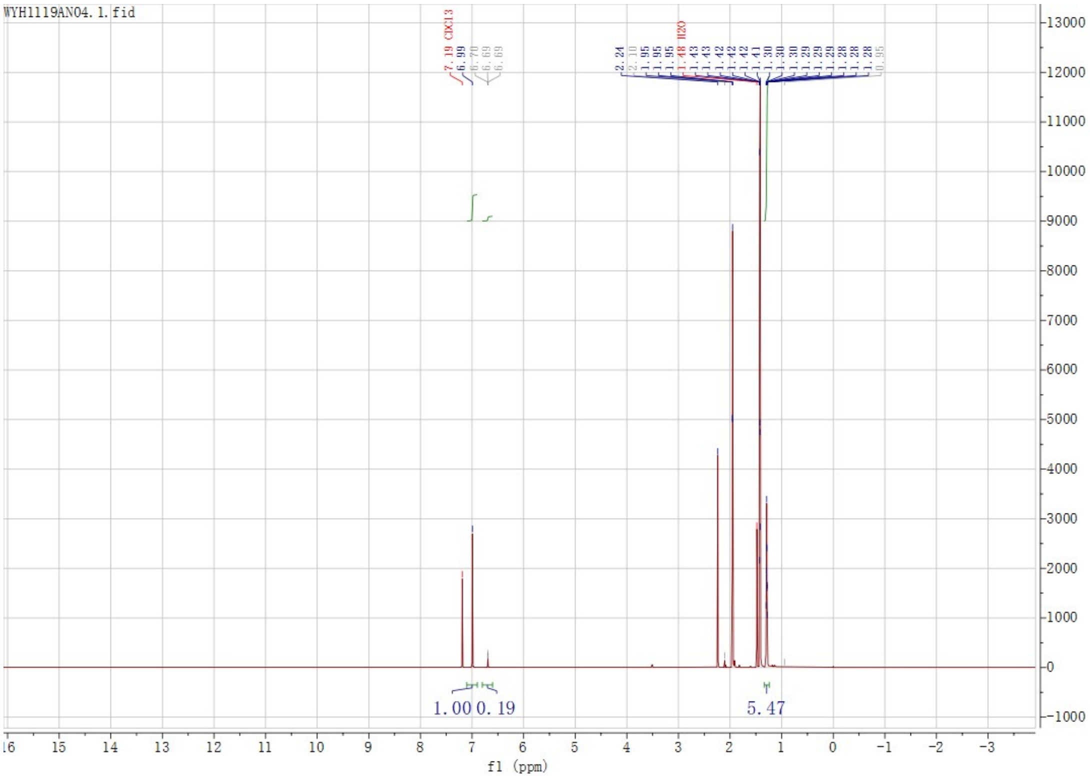


Figure S15. NMR spectrum of the reaction solution at a residence time of 12 min. The initial NBD concentration is 9 M with 10 wt. % paraxylene as the internal standard and 0.55 wt. % EMK as the photosensitizer, and the inner diameter of the capillary is 0.50 mm.

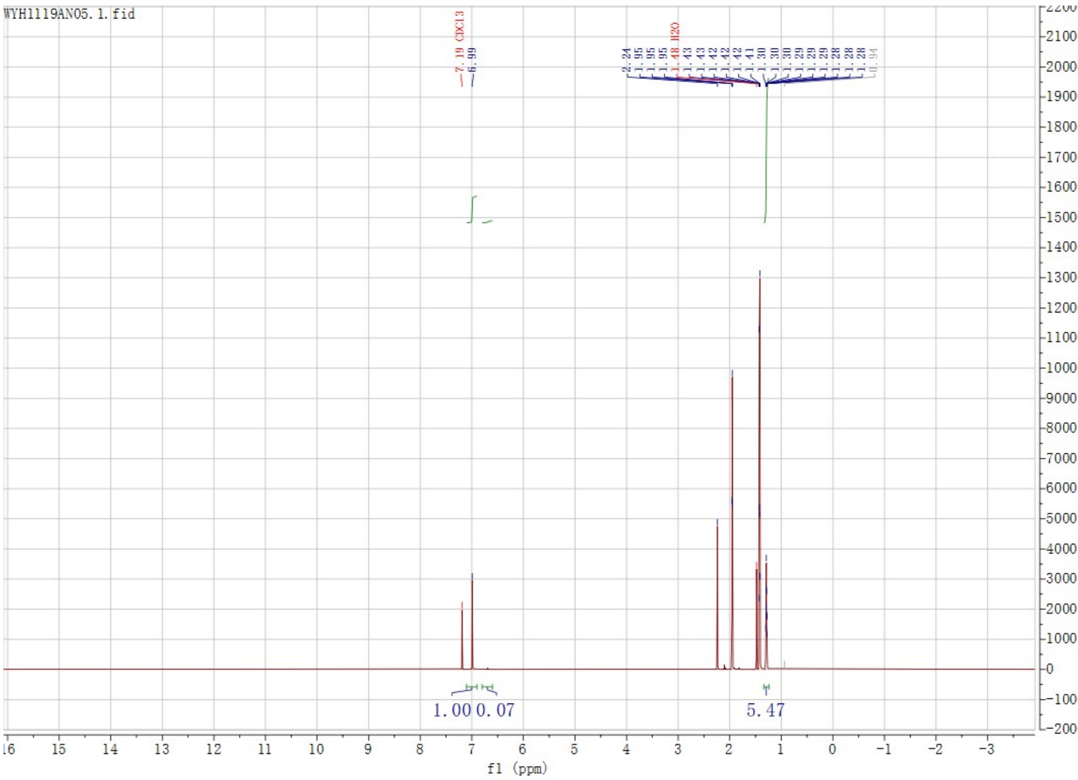


Figure S16. NMR spectrum of the reaction solution at a residence time of 15 min. The initial NBD concentration is 9 M with 10 wt. % paraxylene as the internal standard and 0.55 wt. % EMK as the photosensitizer, and the inner diameter of the capillary is 0.50 mm.

15. GC results

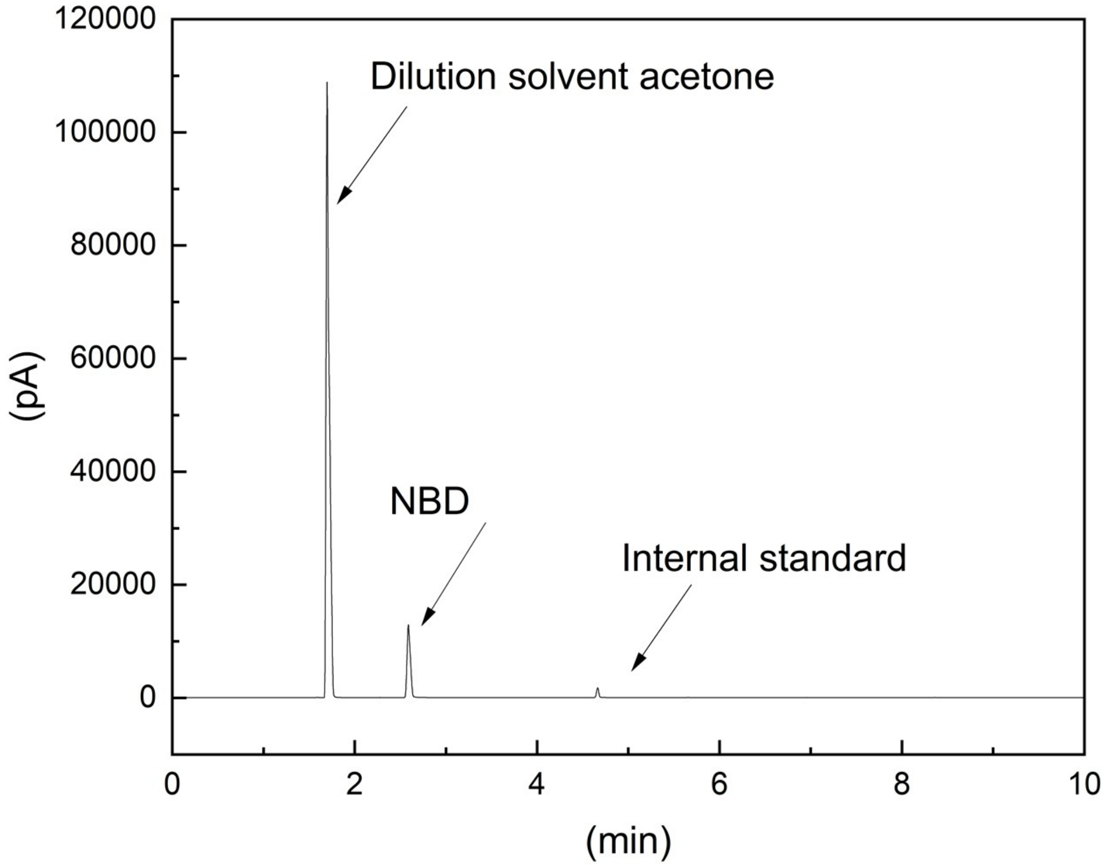


Figure S17. GC spectrum of the reaction solution prior to the reaction.

	Retention time [min]	Area
NBD	2.588	32798.3
QC	-	-
Internal standard	4.666	3135.3

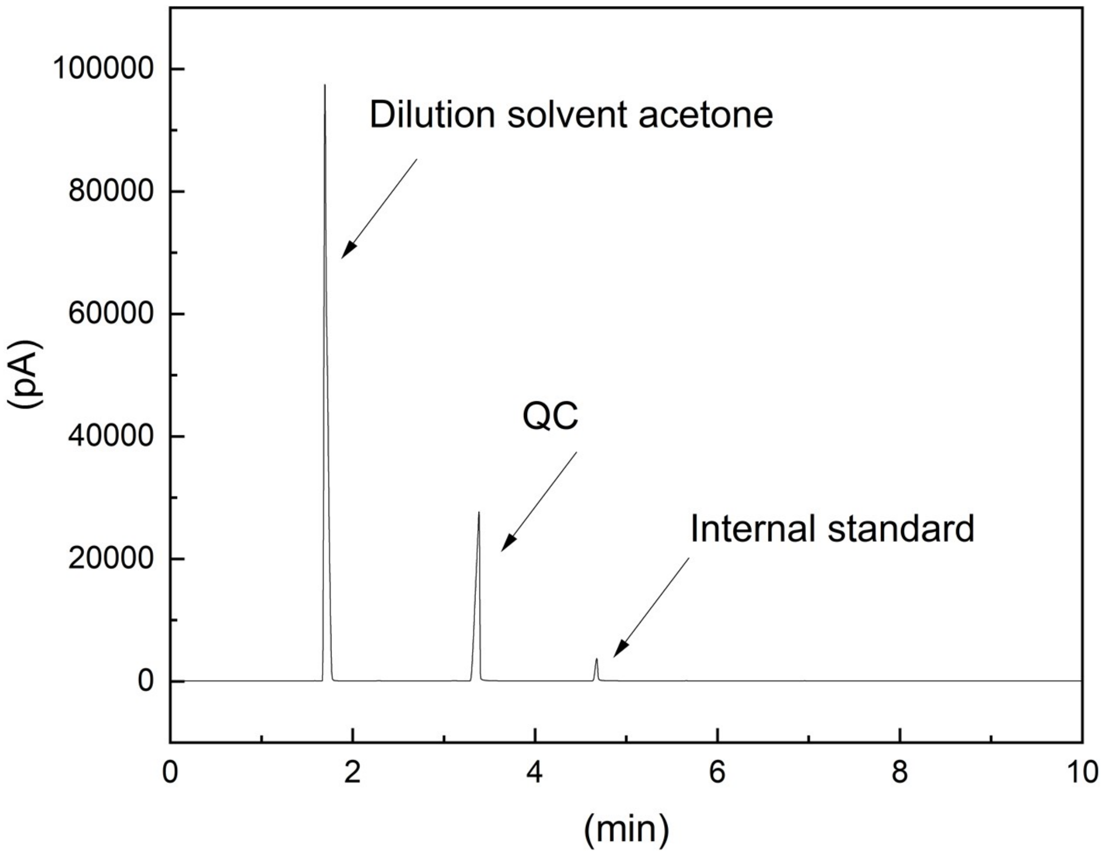


Figure S18. GC spectrum of the reaction solution with full conversion of NBD.

	Retention time [min]	Area
NBD	2.581	24.7
QC	3.383	86609.7
Internal standard	4.676	7709.5

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