Electronic Supporting Information for

Pressure-tolerant polymer microfluidic device fabricated by simultaneous solidification-bonding method and flash chemistry application

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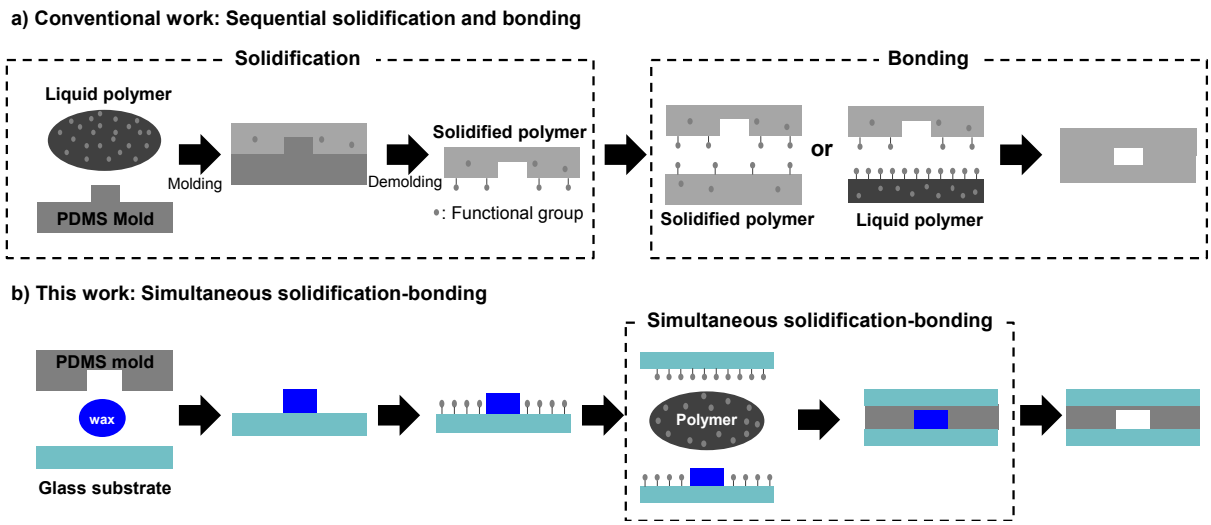
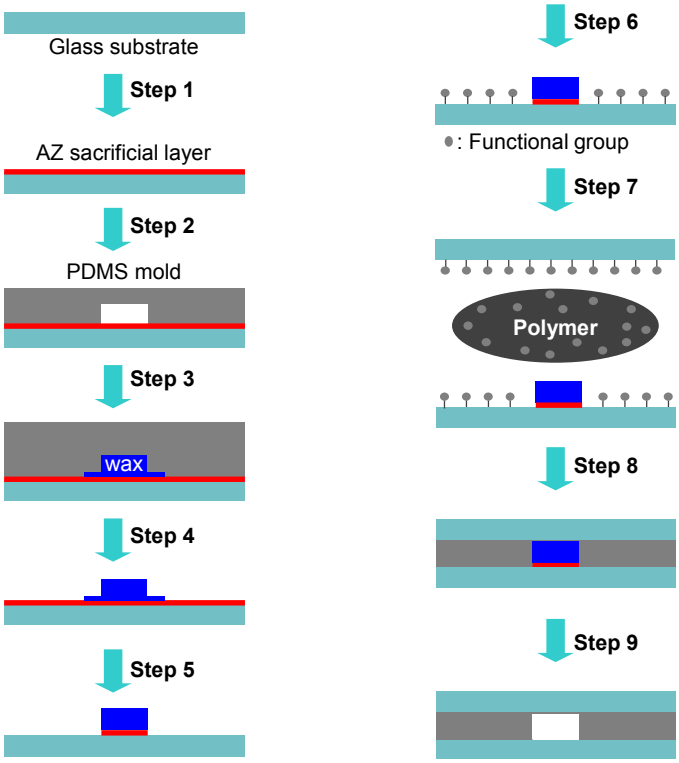
Wurong Ren worked at Professor Kim's lab under a co-advisor program.

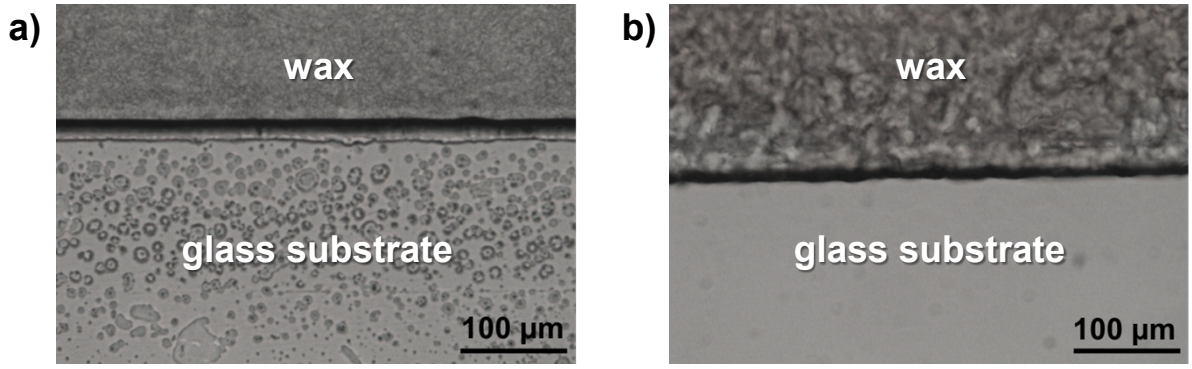
Wurong Ren and Heejin Kim contributed equally to this work.



Scheme S1 Schematic illustration for the difference between conventional sequential solidification and bonding method and simultaneous solidification-bonding method developed in this work. a) Sequential solidification and bonding method as conventional. b) Simultaneous solidification-bonding (SSB) method.



Scheme S2 Full detailed process including the wax-patterning on glass substrate using sacrificial layer for the fabrication of polymer-glass microreactor. Step 1: coating of AZ sacrificial layer on glass substrate. Step 2: reversible bonding of plasma treated PDMS mold and AZ coated glass substrate. Step 3: infiltrating liquid wax into PDMS mold in oven at 80 ºC. Step 4: removing PDMS mold after wax solidification. Step 5: lifting-off AZ sacrificial layer by acetone. Step 6: chemical functionalization of glass surface. Step 7: casting the matrix polymer on glass substrate. Step 8: simultaneous solidification-bonding between the matrix polymer and the glass substrates. Step 9: removal of wax template.



without AZ sacrificial layer

with AZ sacrificial layer

Fig. S1 Effect of AZ sacrificial layer on the wax pattern on glass substrate. a) Wax pattern with spilled thin wax layer on glass substrate upon no use of AZ sacrificial layer, the spilled wax (< 1 μm thick) prevents the direct bonding between glass and polymer matrix. b) Definite wax pattern on glass substrate by removal of the spilled wax layer when lift-off the AZ sacrificial layer by developing process.

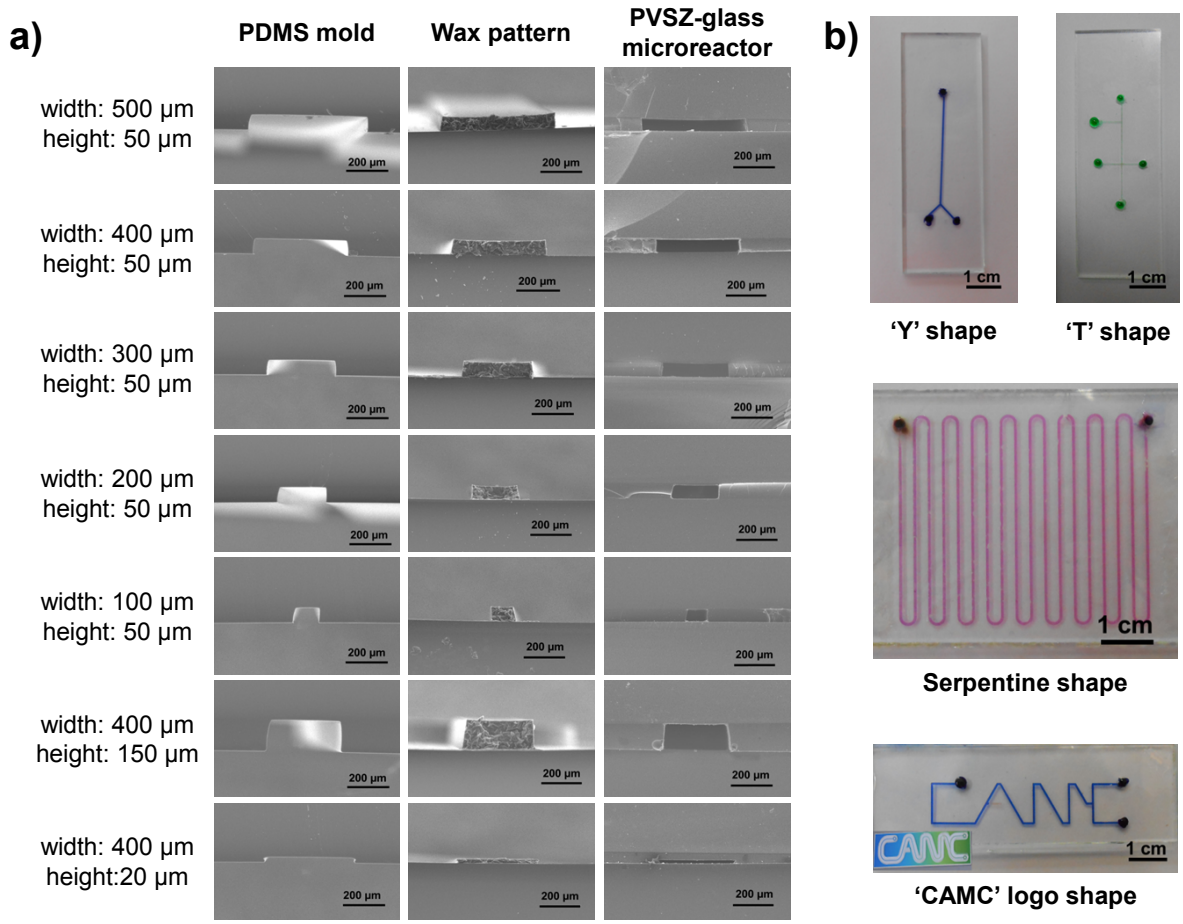


Fig. S2 Fabrication of various PVSZ-glass microreactors with different microchannel dimensions. a) Cross-sectional SEM images of PDMS mold, patterned wax on glass substrate and derived PVSZ-glass microreactor with various channel widths ranging from 100 to 500 μm and channel heights ranging from 20 to 150 μm, and the apparent concave of wax and channel is mainly because of the sink of PDMS with low modulus. b) Optical images of PVSZ-glass microreactors (color-ink filled) with various channel design including 'Y' shape, 'T' shape, serpentine shape and 'CAMC' logo shape.

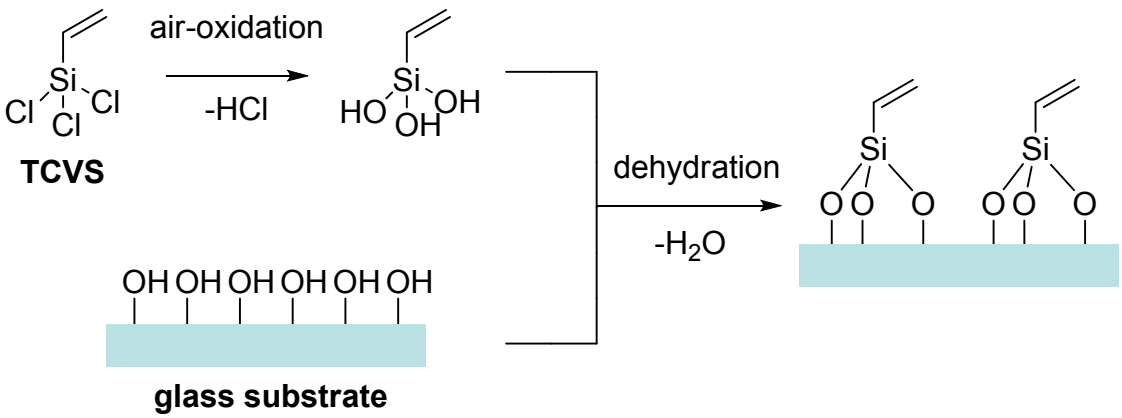


Fig. S3 Vinyl functionalization chemistry of the glass surface using trichlorovinylsilane (TCVS). Si-Cl bond in TCVS was hydrolyzed into Si-OH bond and formed Si-O-Si bond with Si-OH on glass surface.

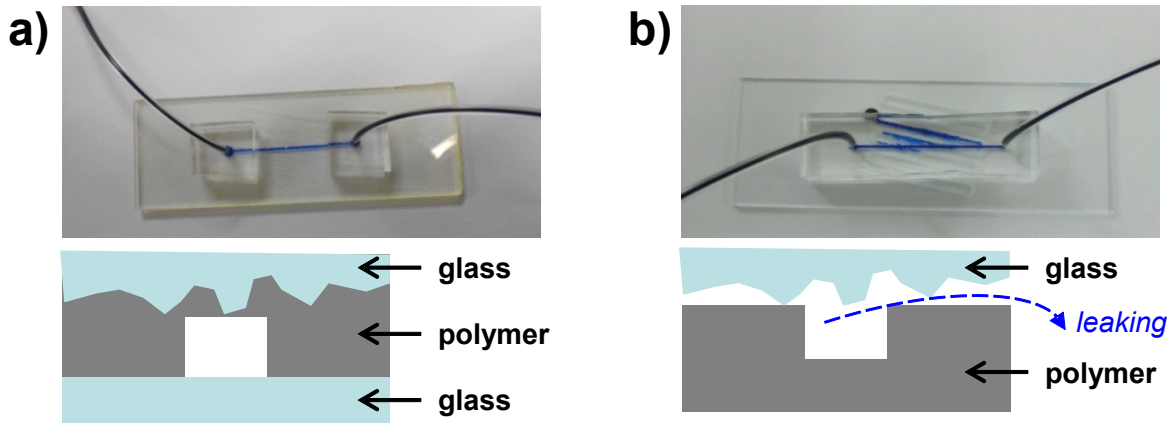
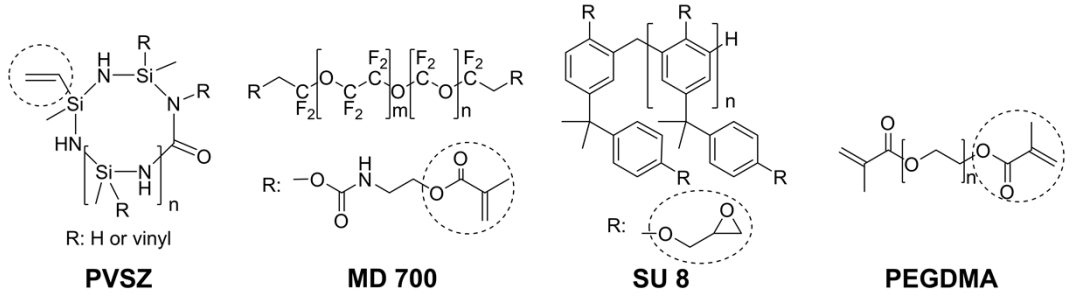


Fig. S4 Comparative leaking behavior of the microchannels by bonding between the polymer matrix and the uneven rough glass cover fabricated by SSB method and conventional sequential method. a) No leaking channel fabricated by SSB method. b) Leaking channel fabricated by conventional method. The uneven rough glass cover was obtained by HF etching with the maximum etching depth of 100 μm.

Fig. S5 PVSZ-glass microreactor with built-in mixer and the mixing performance. a) Fabrication scheme of the microreactor with built-in mixer (500 μm x 100 μm x 30 mm) from the corresponding PDMS mold. b) Optical microscopic images of the initial part (0 to 2.5 mm, left image), the middle part (13.7 to 16.2 mm, center image) and the end part (27.5 to 30 mm, right image) with total flow of 5 μL/min of each solution. e) Color intensity profiles at different positions across the microchannel width (500 μm), measured by Image J Software.

a)



PVSZ **MD 700** **SU 8** **PEGDMA**

NOA 81: adhesive containing thiol groups **Duralco 4525**: resin containing epoxy groups

b)

Polymer matrix	Functional group in polymer matrix	Reagent for substrate treatment	Functional group on substrate
PVSZ	vinyl	TCVS[a] or TEVS[b]	vinyl
MD 700	methacrylate	MPTMS[c]	methacrylate
SU 8	epoxy	GPTMS[d]	epoxy
PEGDMA	methacrylate	MPTMS	methacrylate
NOA 81	thiol	TCVS[a]	vinyl
Duralco 4525	epoxy	GPTMS[d]	epoxy

[a] Trichlorovinylsilane. [b] Triethoxyvinylsilane. [c] 3-Mercaptopropyltrimethoxysilane [d] (3-Glycidoxy-propyl)methyldiethoxysilane.

Fig. S6 Detailed chemistry of the used polymers and the functionalized glass surface for polymer-glass microreactors. a) Chemical structure of various matrix polymers with functional groups (in the circle). b) Summarized chemistry of polymer matrix and glass surface.

Fig. S7 PVSZ-glass microreactor system for synthesis of tryptanthrin by flash chemistry. a) Whole set-up for the synthesis of tryptanthrin under high flow rate conditions. b-e) Real-time optical images observed at the end position of reaction part R1 as a function of reaction time; b) 14 ms at flow rate A of 6 mL/min, c) 22 ms at flow rate A of 4 mL/min, d) 43 ms at flow rate A of 2 mL/min, e) 86 ms at flow rate A of 1 mL/min.

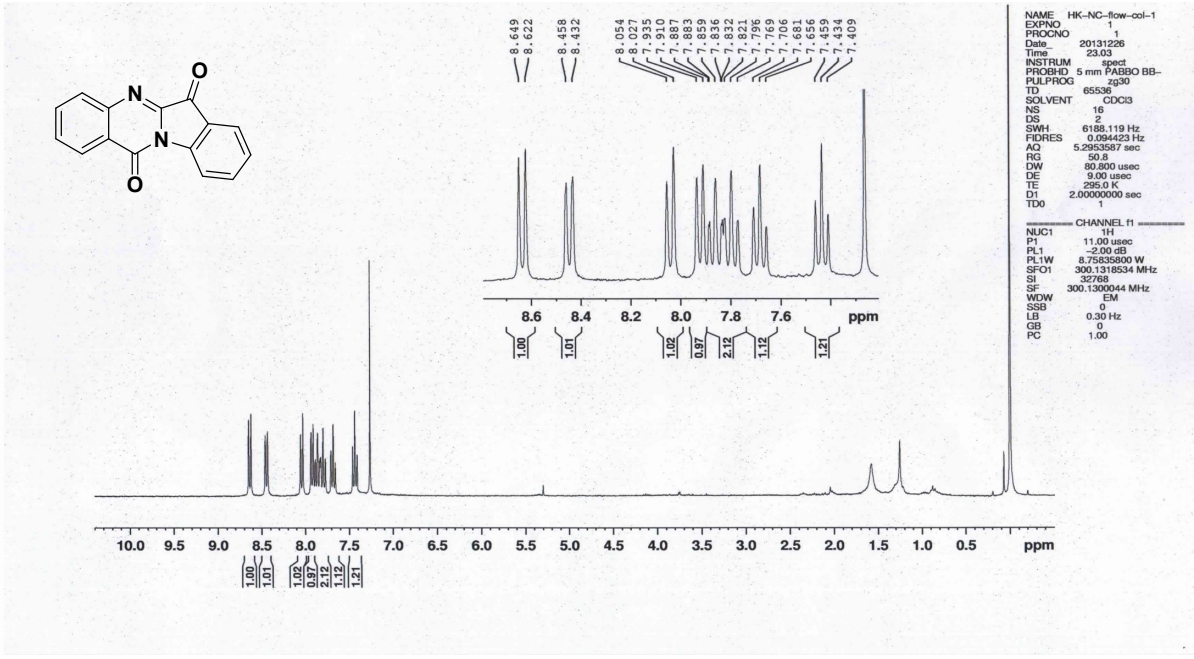


Fig. S8 ^{1}H NMR spectrum of tryptanthrin in $CDCl_3$

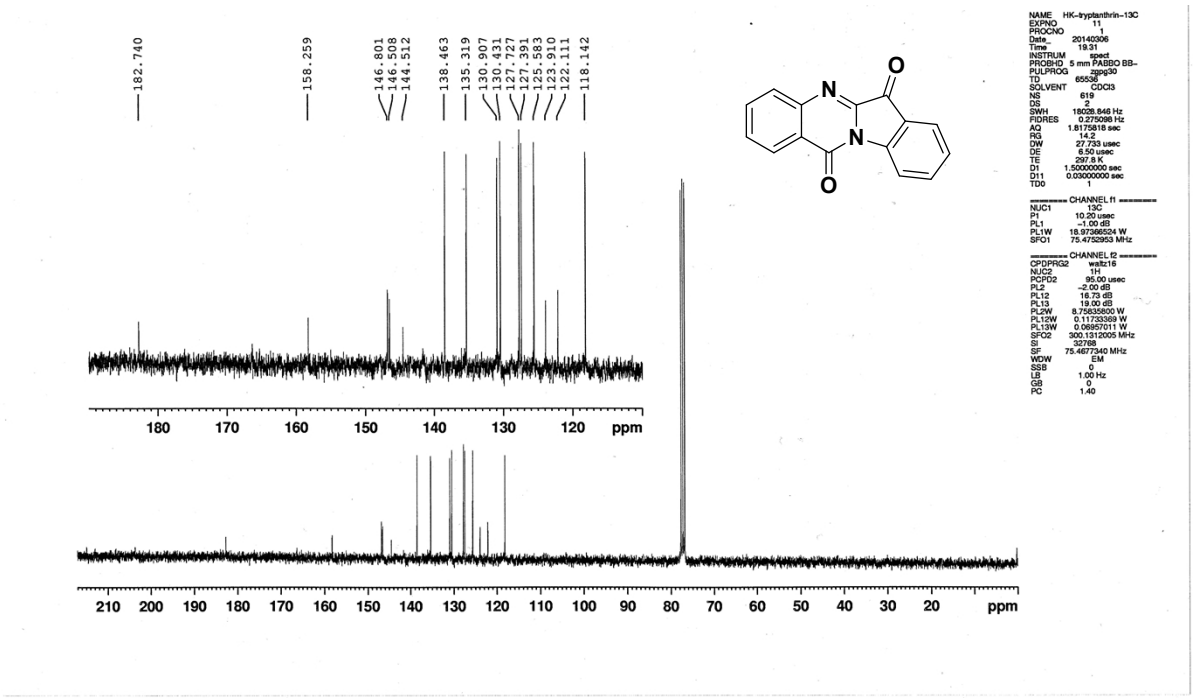


Fig. S9 ^{13}C NMR spectrum of tryptanthrin in $CDCl_3$

Tab. S1 A list of the reported burst pressures in various microreactors.

Sample	Channel fabrication	Bonding method	Bonding condition	Burst pressure	Reference
PDMS/glass substrate	Soft lithography	iCVD	200 °C, iCVD system	11700 kPa (1700 psi)	*Lab Chip* **2013**, *13*, 1266
polyimide/PI	Laser ablation	Fusion bonding	300 °C, 10 kPa	70 bar (1000 psi)	*Angew. Chem. Int. Ed.* **2010**, *49*, 7063
PU/PU	Soft lithography	PU bonding (dry and wet)	R.T.	326 kPa (47 psi)	*Lab Chip* **2012**, *12*, 960
PDMS/PET	Soft lighoraphy	PDMS-assisted interfacial bonding	Oxygen plasma	400 kPa (58 psi)	*Adv. Mater.* **2011**, *23*, 5551
PC/PC	Milling machine	Surface swelling induced welding	125-135 °C, 50-400 kPa	550 kPa (80 psi)	*Lab Chip* **2010**, *10*, 1324
PFPE/PFPE	Soft lithography	Partial curing	68 °C; 0.5 kPa	2.5 bar (36 psi)	*Lab Chip* **2011**, *11*, 2035
PFA/PFA	Laser ablation	Fusion bonding	260 °C, pressure	245 kPa (35 psi)	*Lab Chip* **2012**, *12*, 4236

Tab. S2 The relationship between flow rate, pressure and the yield of the product on the flow synthesis of tryptanthrin in a PVSZ-glass microreactor (**R1**: 300 μm x 150 μm x 40 mm, **R2**: 300 μm x 150 μm x 5 mm)

Entry	Flow rate A (mL/min)	Total flow rate (mL/min)	Pressure (psi)	Reaction time in R1 (ms)	Yield (%)
1	1	1.75	0	86	58[a]
2	2	3.5	5	43	59[a]
3	4	7.5	76	22	74[b]
4	6	10.5	239	14	90[b]

[a] The yield of tryptanthrin was obtained by ^{1}H NMR with an internal standard, 4-iodoanisole.
[b] Isolated yield by column chromatography.