流动化学在光催化领域的应用

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2023年5月13日

提纲

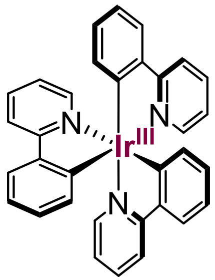
一 可见光催化的重要性和局限性

二 流动化学的基础知识

三 常见的泵和连续流光反应器

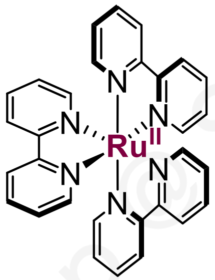
四 连续流条件下铈-光催化反应的放大应用研究

2.1 研究背景：光催化反应的重要性



Ir^{III}(ppy)$_3$

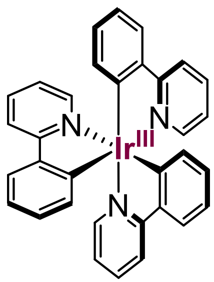
- Chemically stable
- Visible light absorption
- Long-lived MLCT excited state
- Effiective oxidant and reductant



Ru^{II}(bpy)$_3$$^{2+}$

D. W. C. MacMillan, et al. *J. Org. Chem.* **2016**, *81*, 6898–6926.
T. Noël, et al. *Chem. Rev.* **2022**, *122*, 2752–2906.

1.1 光催化反应的重要性



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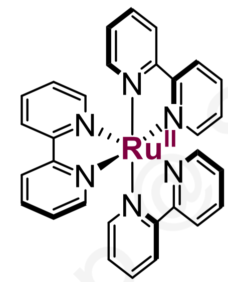
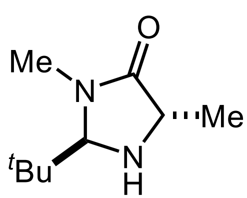


$Ru^{II}(bpy)_3^{2+}$

Transition-metal catalysis



Enantioselective catalysis

Electrocatalysis

Biocatalysis

D. W. C. MacMillan, et al. *J. Org. Chem.* **2016**, *81*, 6898–6926.
T. Noël, et al. *Chem. Rev.* **2022**, *122*, 2752–2906.

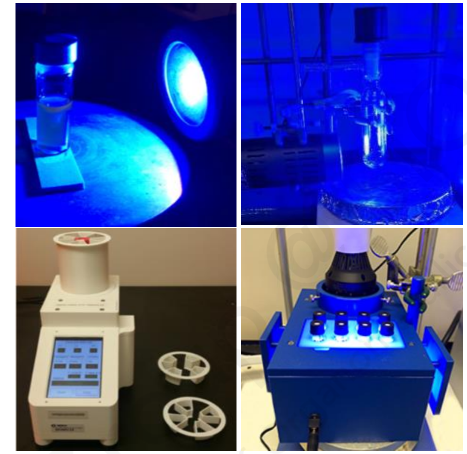
2.1 研究背景：光催化反应的局限性

Traditional UV Photoreaction

- Low selectivity
- High cost light sources
- Scale-up issues

Visible-Light Photocatalysis

- Highly selective and powerful
- Energy efficient and durable LED



Scale-up issues

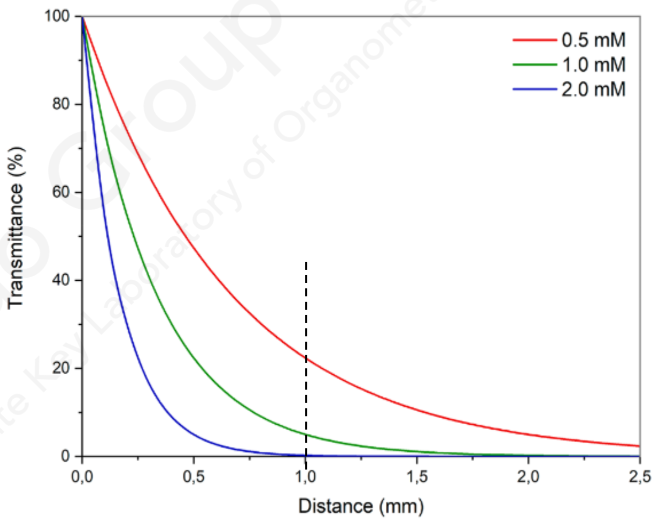
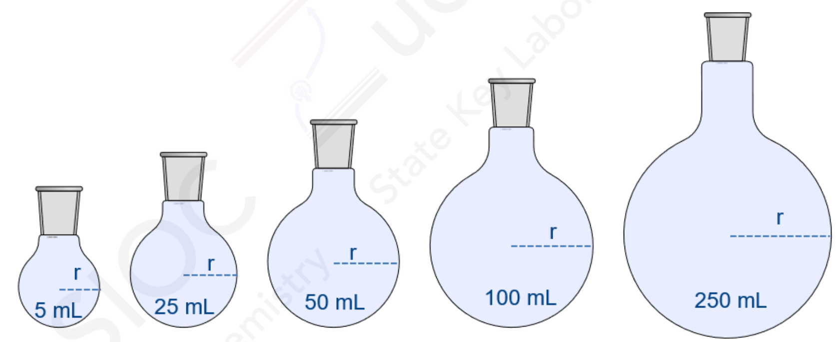


Figure 4. Attenuation of light as a function of distance in a photocatalytic reaction using $Ru(bpy)_3Cl_2$ (c = 0.5, 1, and 2 mM, ε = 13 000 $cm^{-1}\cdot M^{-1}$) utilizing the Bouguer−Lambert−Beer correlation



Radius (m)	0.014	0.021	0.025	0.033	0.043
Interfacial area (m^2m^{-3})	107	70	60	46	35

R. Baxendale, et al. *Org. Process Res. Dev.* **2016**, *20*, 327–360.
T. Noël, et al. *Chem. Rev*. **2022**, *122*, 2752–2906.

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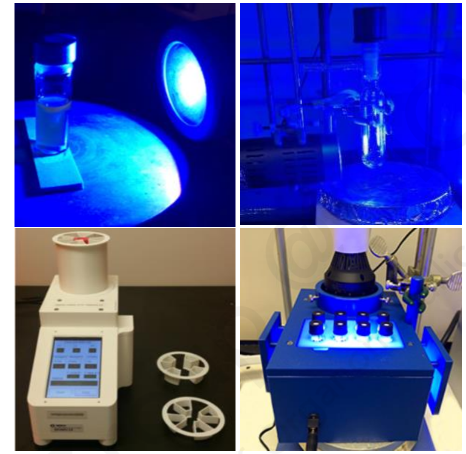
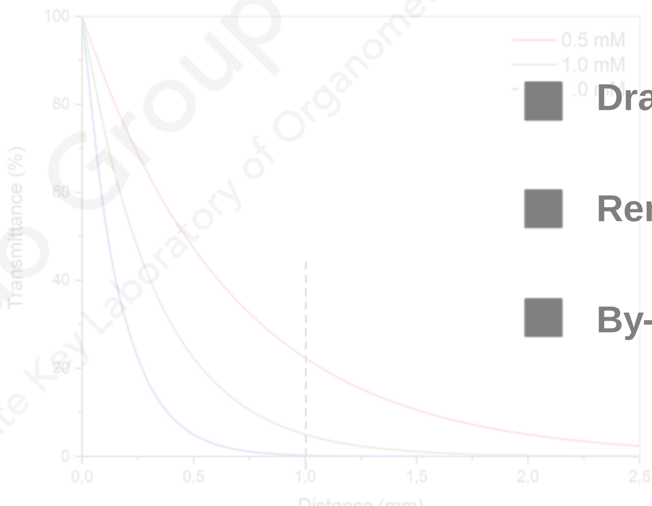


- Low selectivity
- High cost light sources
- Scale-up issues
- Highly selective and powerful
- Energy efficient and durable LED

Scale-up issues



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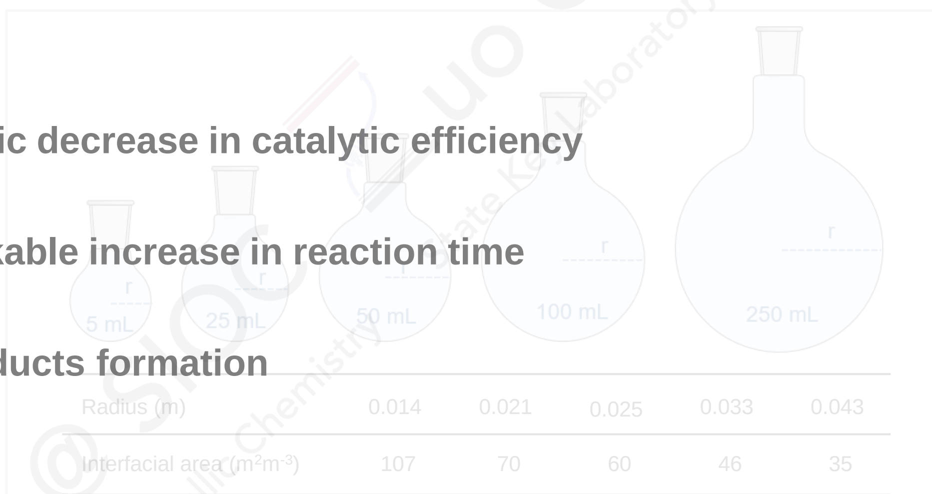
- Dramatic decrease in catalytic efficiency
- Remarkable increase in reaction time
- By-products formation



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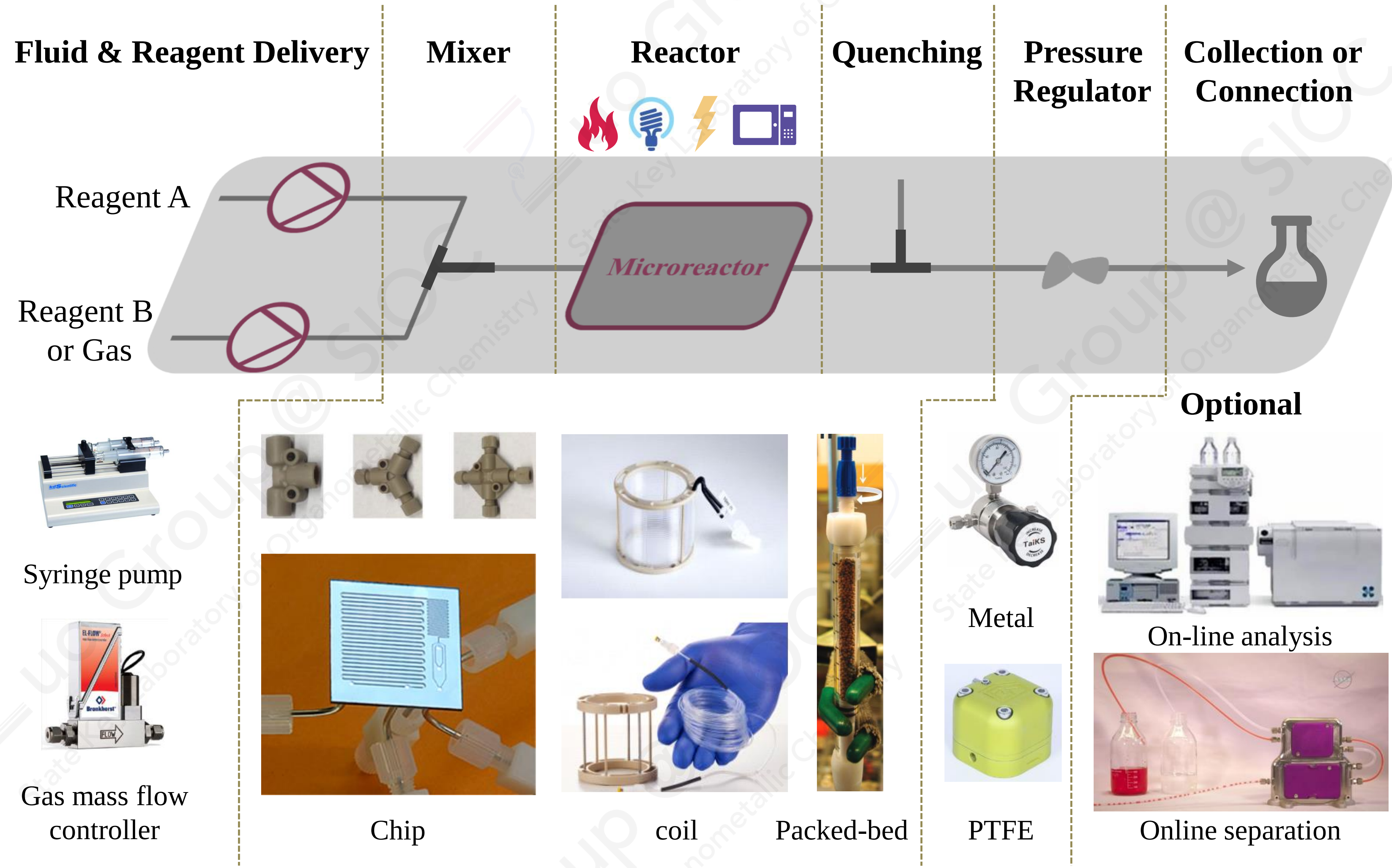
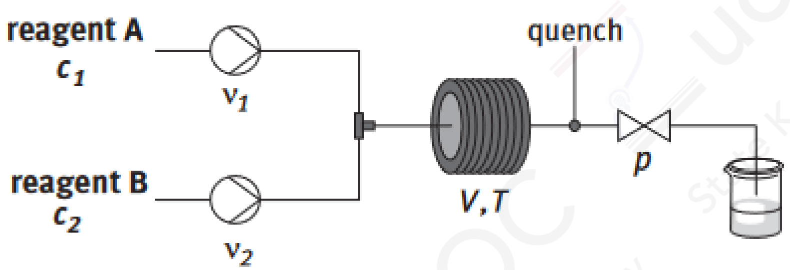
2.1 流动化学装置



K. Gilmore, et al. *Chem. Soc. Rev.* **2020**, *49*, 8910–8932.

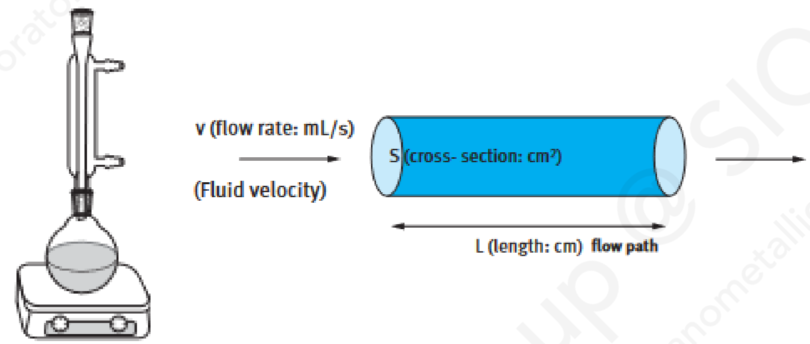
2.2 流动反应与间歇式反应的区别

Stoichiometry



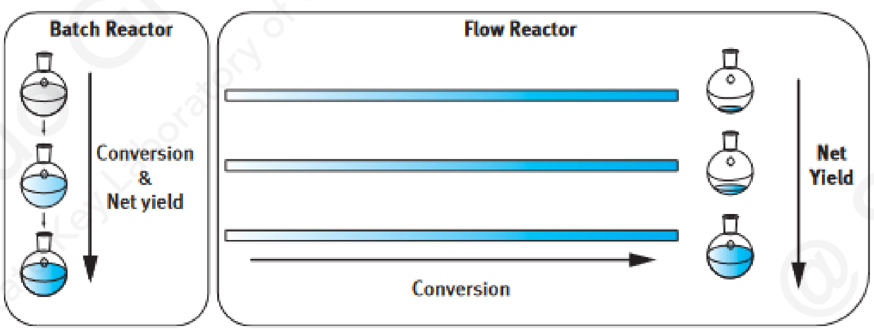
Batch: c, η **Flow:** c, η, $\boldsymbol{v}$

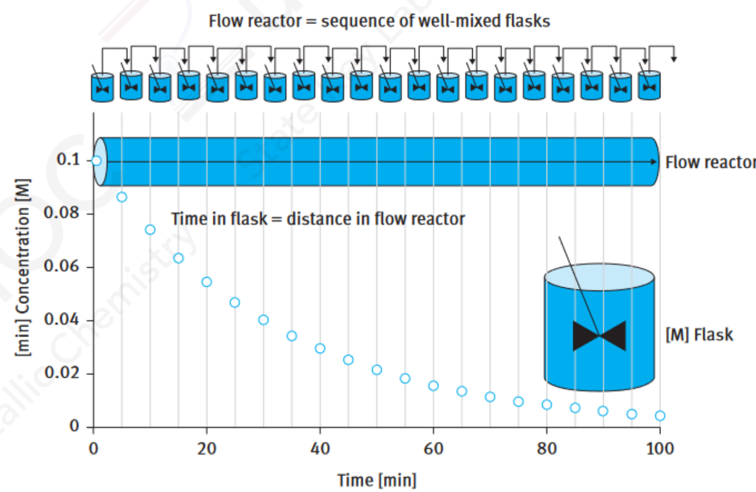
Reaction time & Residence time



Batch: t **Flow:** $t_R = \dfrac{V}{v_1 + v_2}$ $t_R = \dfrac{V}{v_L + v_G/P}$

Reaction progress & Steady-state characteristics

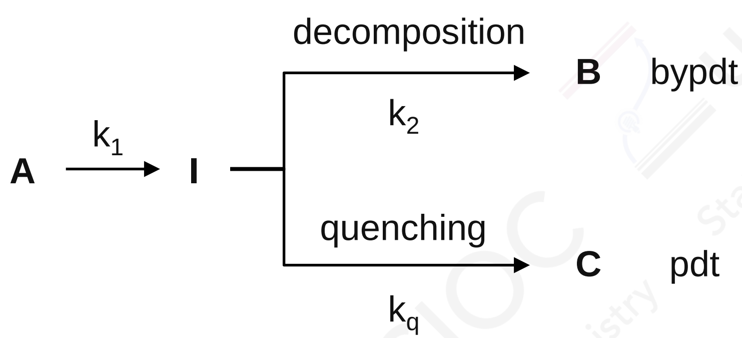




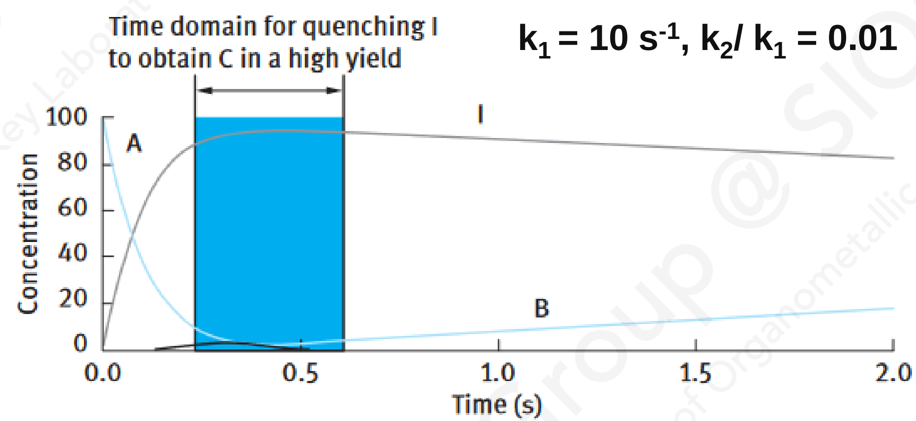
F. Darvas, G. Dormán, V. Hessel, S. V. Ley, Eds. , *Flow Chemistry – Fundamentals*, De Gruyter, **2021**.

2.3 流动化学的特征和优势

Continuous-flow characteristics



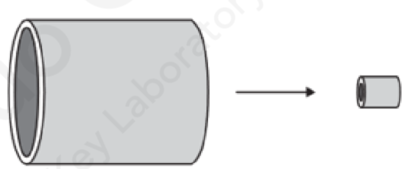
$k_q > k_1 > k_2$



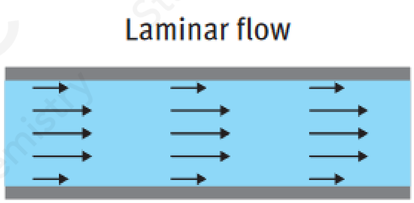
$k_1 = 10\ s^{-1}$, $k_2/k_1 = 0.01$

Precise residence time control

Large specific surface area (d < 1 mm, large S)



Size	1/100
Surface area	1/10000
Volume	1/1000000
Surface / Volume	100



Diffusion time

$$t_d = \frac{d^2}{D}$$

Uniform mixing: flow (*ms* to *s*) *vs.* batch (*s* to *h*)

F. Darvas, G. Dormán, V. Hessel, S. V. Ley, Eds. , *Flow Chemistry – Fundamentals*, De Gruyter, **2021**.

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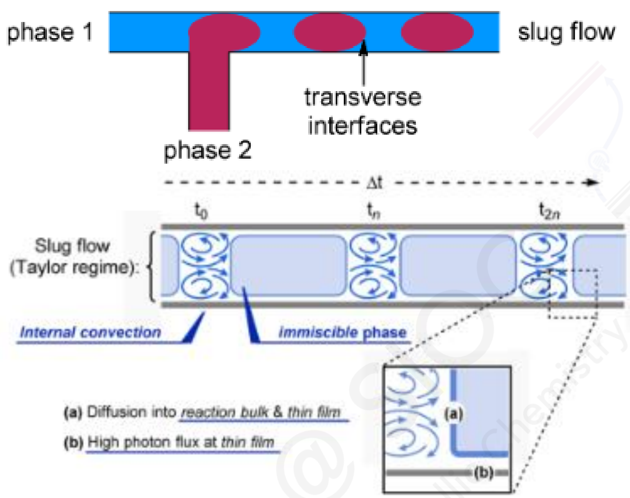
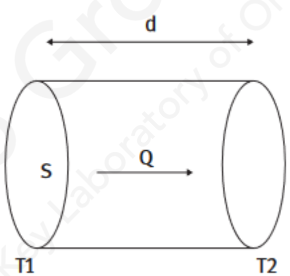


Table 1. Interfacial Surface Areas for Various Reactors[a]

type of reactor	interfacial area (m^2 m^{-3})
5 mL round-bottom flask (rbf)[b]	141
50 mL rbf[b]	66
250 mL rbf[b]	38
tube reactors, horizontal and coiled	50–700
tube reactors, vertical	100–2000
gas–liquid microchannel	3400–18000

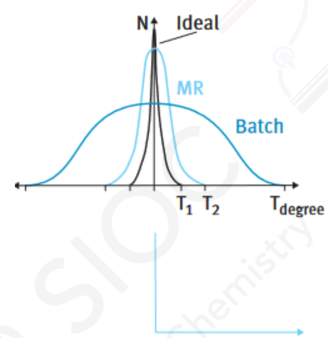
[a]Reproduced from Mallia et al.[59] [b]Calculated for half-filled round-bottom flasks when the liquid is static using, $\frac{a}{v_{1/2}} = \frac{150}{\sqrt[3]{3v/4\pi}}$.

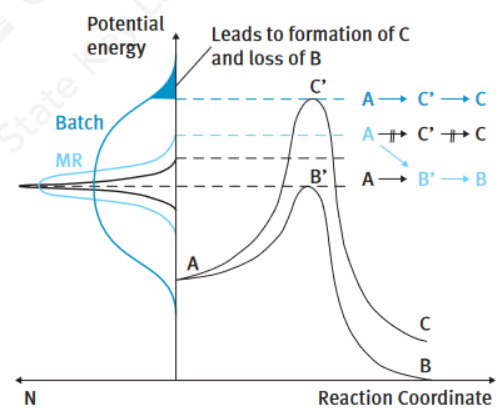
Fast mass transfer: flow (*ms* to *s*) *vs.* batch (*min* to *h*)



Heat transfer

$$\boxed{\frac{Q}{t} = kS\frac{\Delta T}{d}}$$



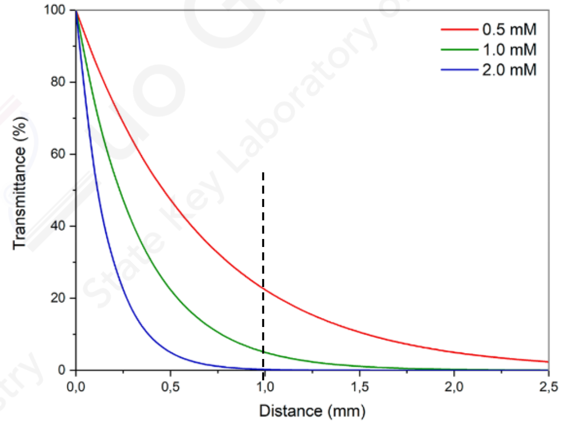


Fast heat exchange: flow (*ms* to *s*) *vs.* batch (*min* to *h*)

F. Darvas, G. Dormán, V. Hessel, S. V. Ley, Eds. , *Flow Chemistry – Fundamentals*, De Gruyter, **2021**.

2.3 流动化学的特征和优势

- **Large specific surface area (d < 1 mm, large S)**



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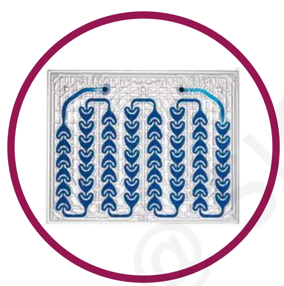
- **Sufficient and uniform light**



- **Precise residence time control**
- **Efficient mixing**
- **Fast mass and heat exchange**
- **Improved irradiation**
- **Improved selectivity and reproducibility**
- **Reliable scale-up**

T. Noël, et al. *Chem. Rev*. **2022**, *122*, 2752–2906.

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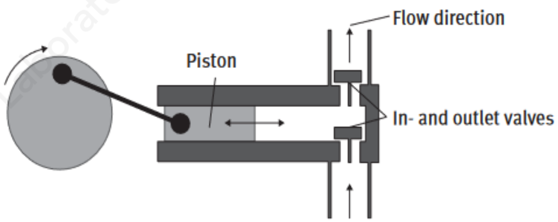
3.1 常见的流动化学泵

■ syringe pump

■ Precisely deliver constant & pulsation-free fluids, ranging from μL/min to mL/min

■ Constrained capacity and inability to mix

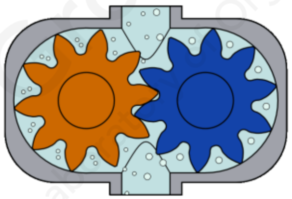
■ Piston pump



■ Most commonly used pumps in flow

■ Unsuitable for extremely low flow rates or gas-liquid & liquid-solid mixtures

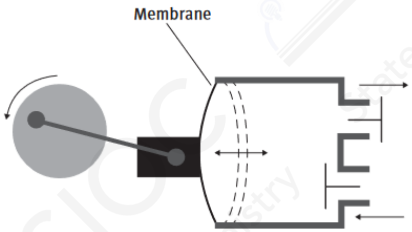
■ Gear pump

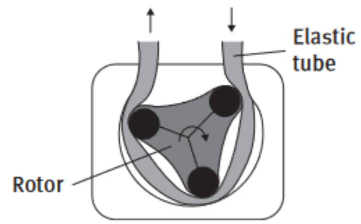


■ Working under up to 200 bar, suitable for high-viscosity fluids

■ Considerable noise and exhibit significant flow pulsation

■ diaphragm pump & Peristaltic pump





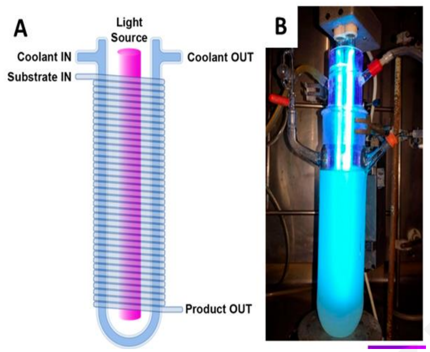
■ Suitable for corrosive liquids & liquid-solid mixtures

■ Substantial flow pulsation and operate at relatively low pressures (<10 bar)

F. Darvas, G. Dormán, V. Hessel, S. V. Ley, Eds. , *Flow Chemistry – Fundamentals*, De Gruyter, **2021**.

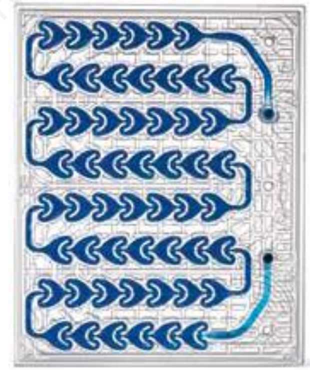
2.2 常见的连续流光反应器

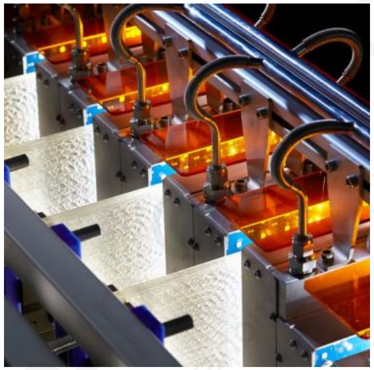
Capillary microreactors



Flexible & Cheap　Non-durable

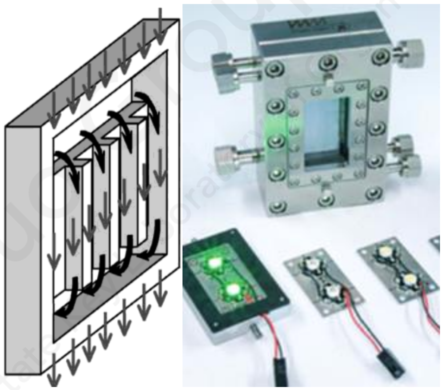
Glass microreactors

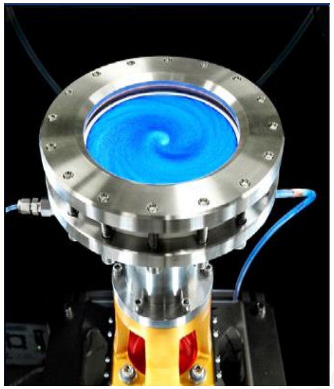




Very large S/V ratio　high cost

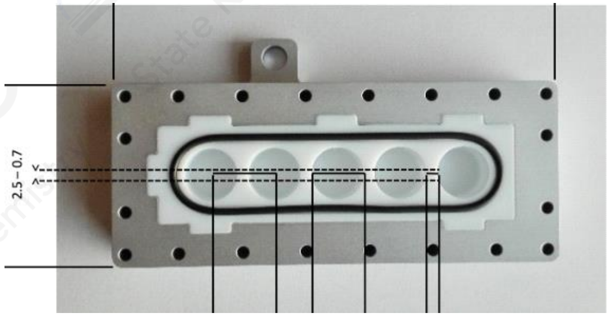
FFMR and RS-SDR eactor





Very large S/V ratio　Slow flow rate

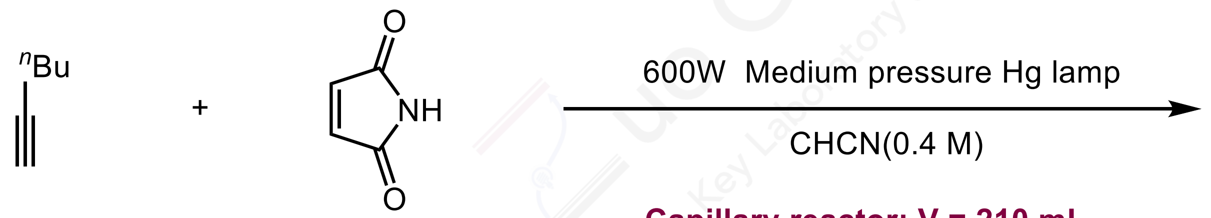
Packed-bed and CSTR eactor



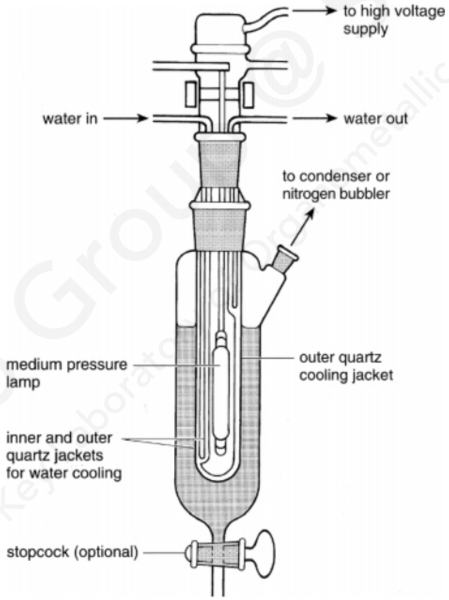
Solid operation　Catalyst leaching

Noël, T. et al. *Chem. Rev.* ***2016***, *116*, 10276–10341.

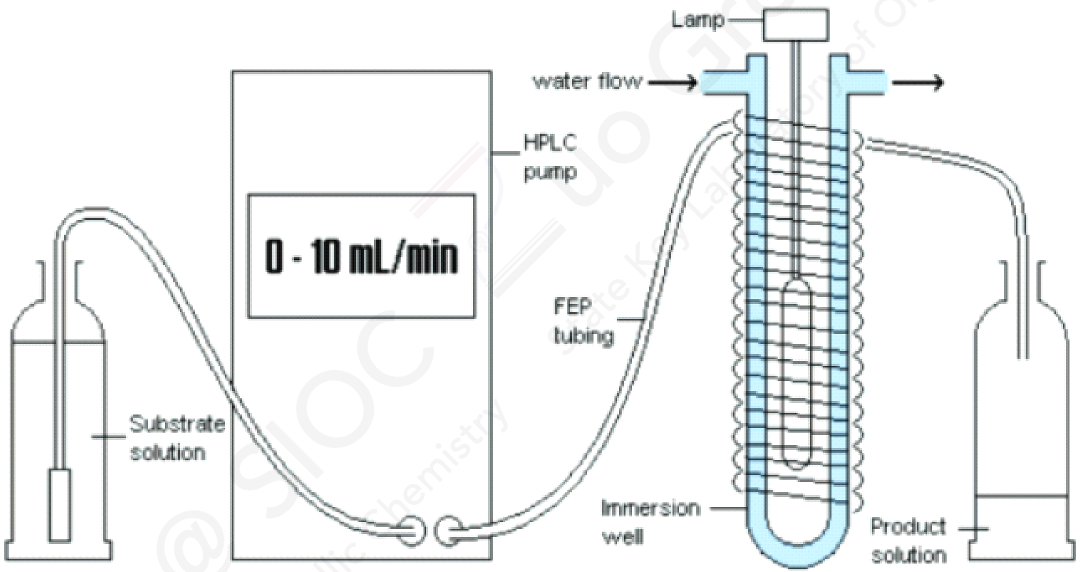
3.3 盘管反应器



Capillary reactor: V = 210 mL
t_R= 26 min, 83% yield, 685 g/d



batch photochemical reactor



FEP Capillary reactor

M. B. Berry, K. I. Booker-Milburn, et al. *J. Org. Chem*. **2005**, *70,* 7558–7564.

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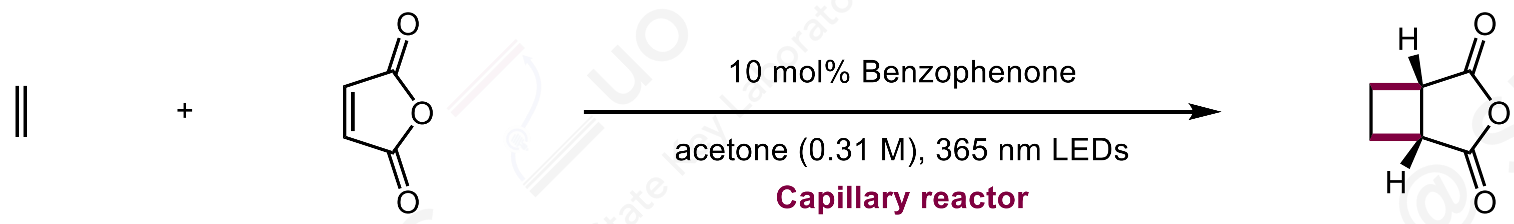
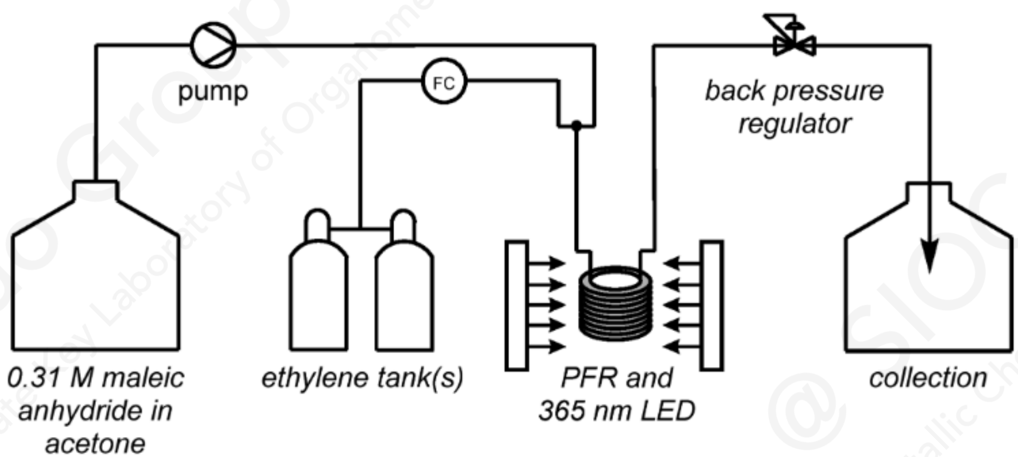


V = 0.25 L, 96% yield, 14 g/d

V = 1.6 L (32 m), t_R= 2 h, 91% yield, 646 g/d

V = 21 L (400 m), t_R= 2 h, 61% yield, 51.8 kg/7d (7.4 kg/d)



M. G. Beaver, E. Zhang, et al. *Org. Process Res. Dev.* **2020**, *24*, 2139–2146.

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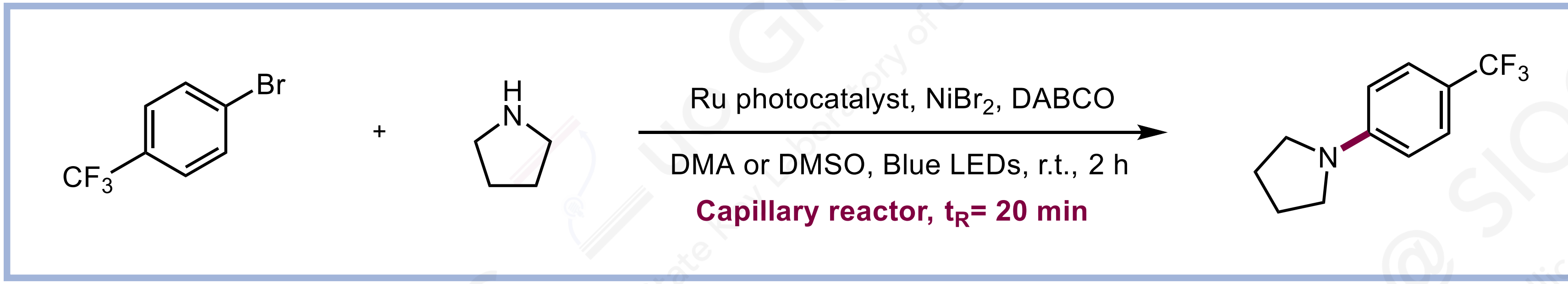
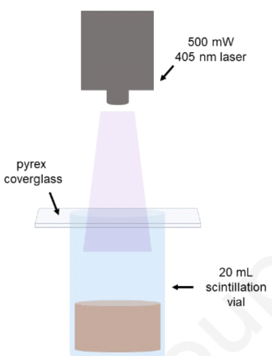
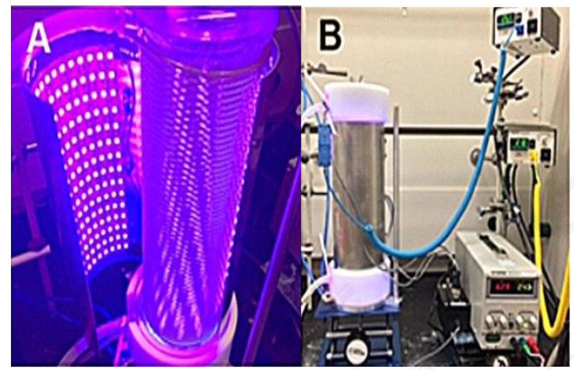




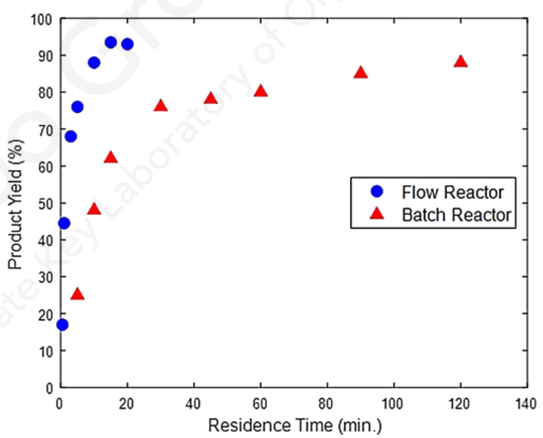


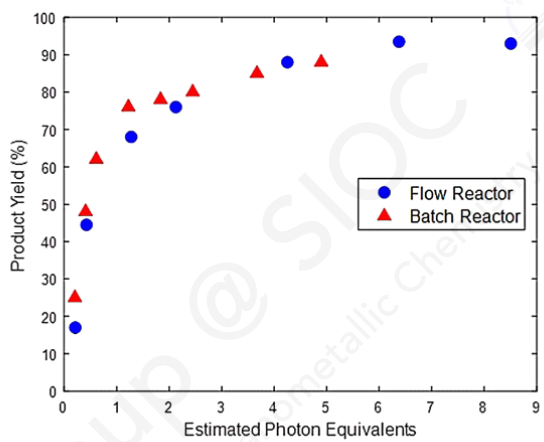
Batch: 88%, 2.8 g/d

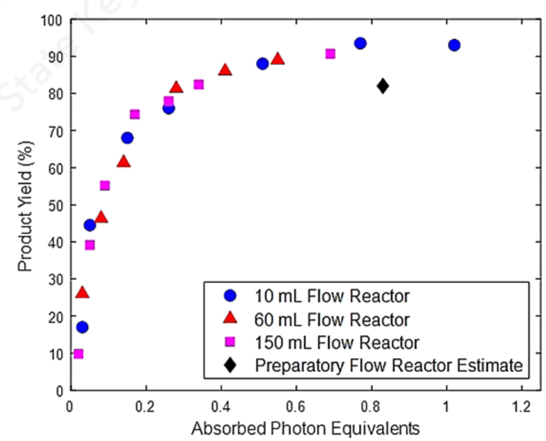
10 mL: 87%, 34 g/d

60 mL: 89%, 207 g/d

150 mL: 82%, 476 g/d







E. B. Corcoran, J. P. McMullen, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 11964–11968.

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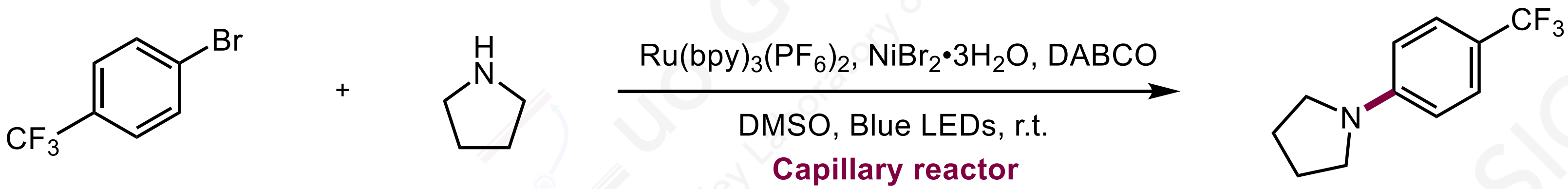
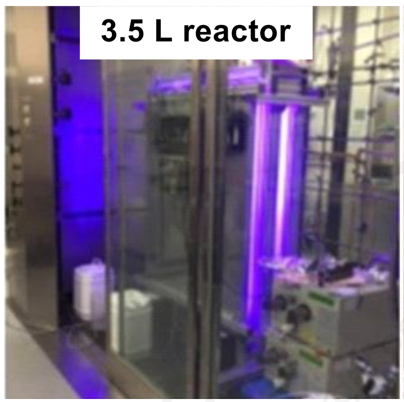
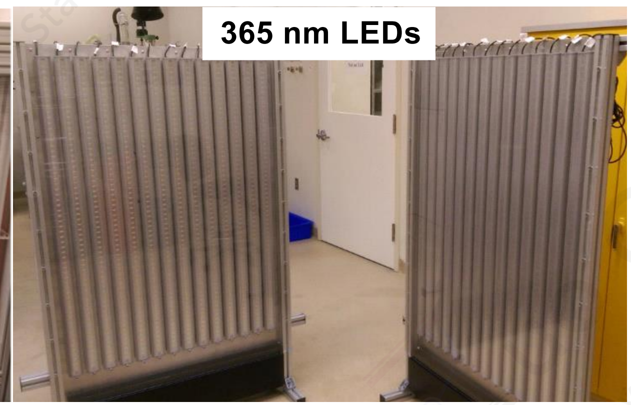
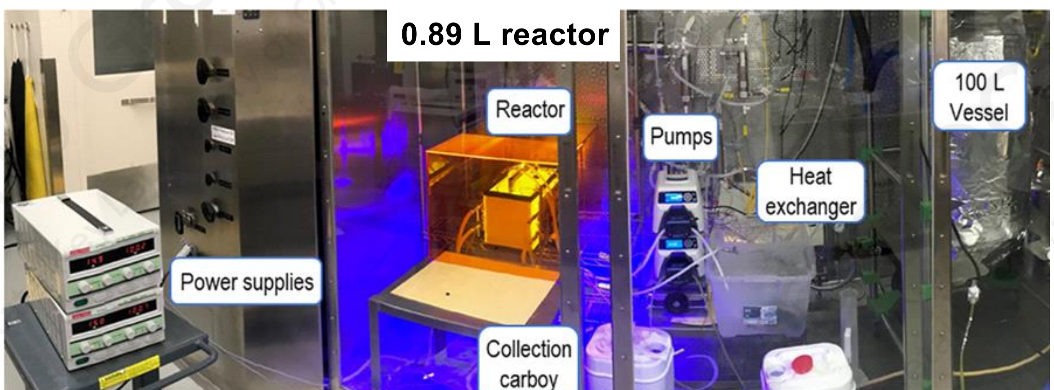


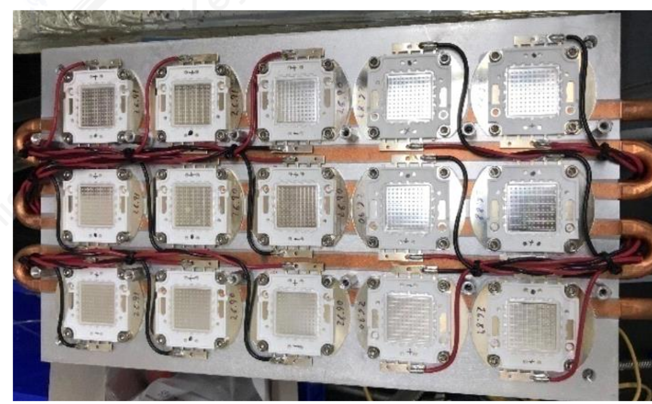




3.5 L Capillary reactor:
t_R= 20 min, 82%, 10 kg/d
(90% predicted)

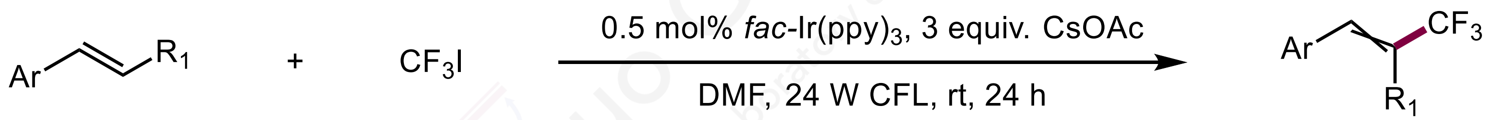
0.89 L Capillary reactor:
t_R= 8.5 min, 90%, 12 kg/d



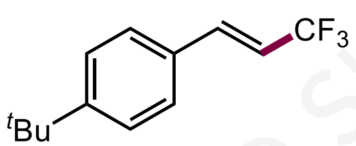


E. B. Corcoran, J. P. McMullen, et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 11964–11968.
F. Lévesque, M. J. Di Maso, et al. *Org. Process Res. Dev*. **2020**, *24*, 2935–2940.

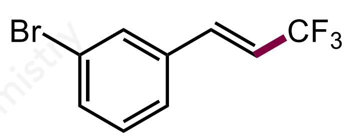
3.3 盘管反应器



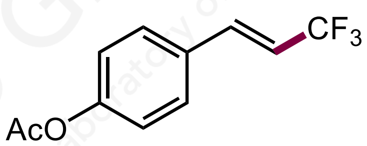
Capillary reactor: 25 mL



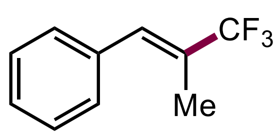
Batch: 92% (45:55 E/Z)
Flow: 97% (94:6 E/Z), t_R=30 min



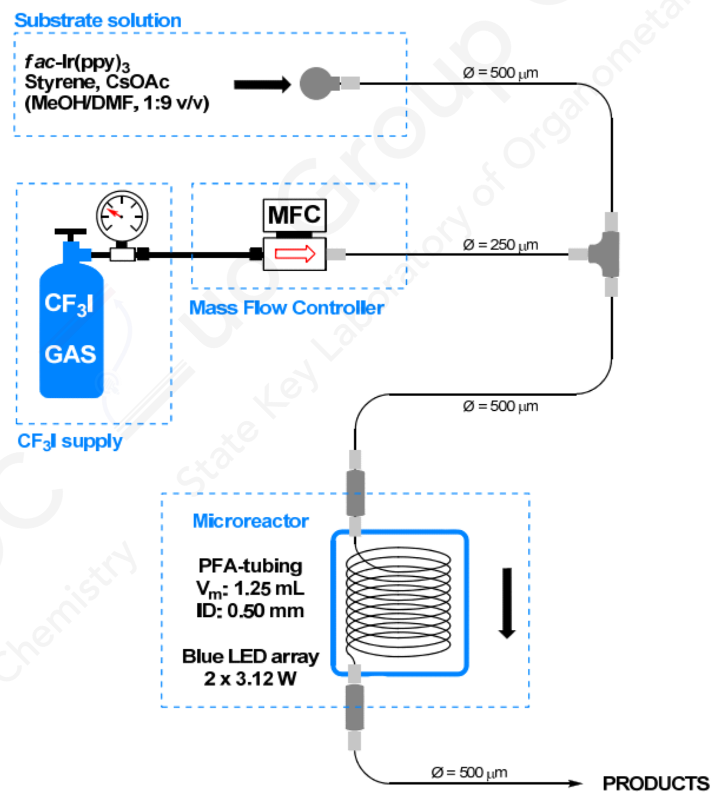
Batch: 81% (46:54 E/Z)
Flow: 80% (97:3 E/Z), t_R=90 min



Batch: 91% (19:81 E/Z)
Flow: 98% (98:2 E/Z), t_R=90 min

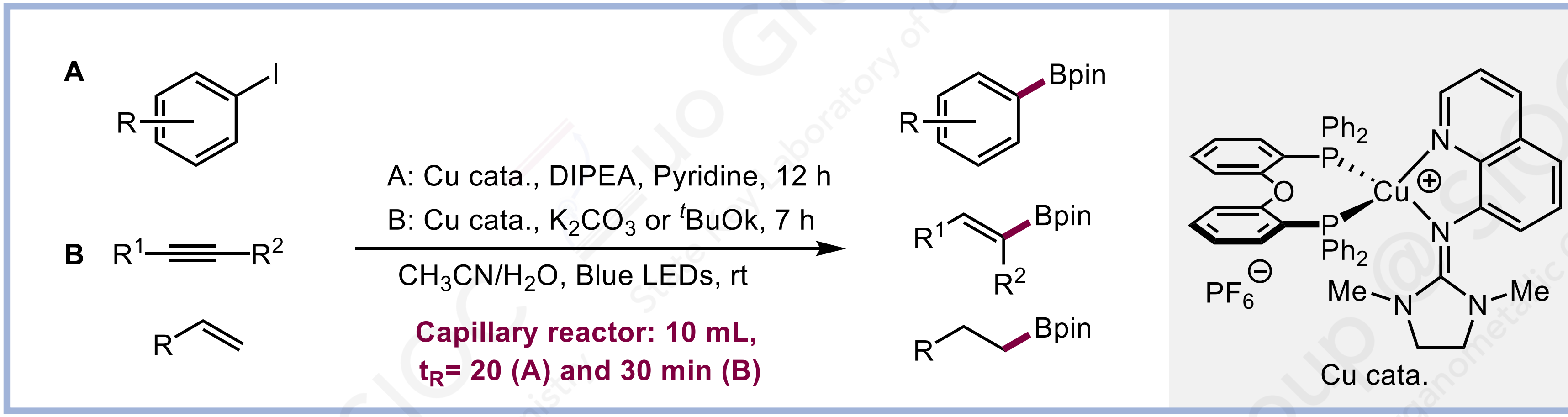


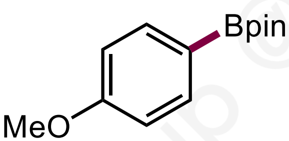
Batch: 75% (69:31 E/Z)
Flow: 76% (E only), t_R=80 min



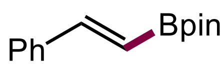
T. Noël, et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 15549–15553.

3.3 盘管反应器

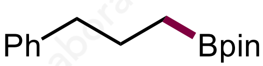




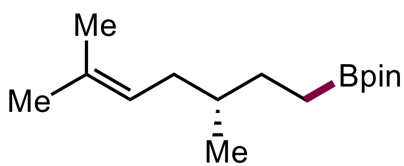
A: batch: 79%, 0.01 mmol/h
flow: 73% yield, 2.2 mmol/h



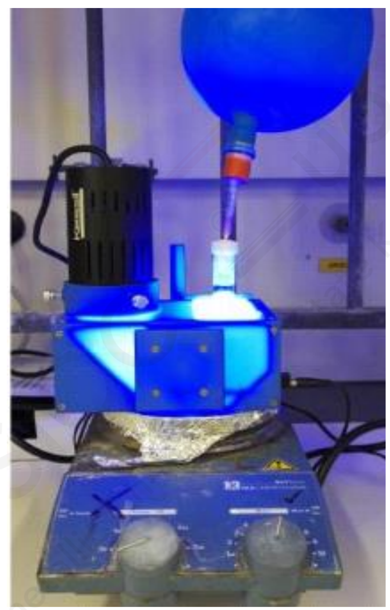
B: batch: 87%, 0.02 mmol/h
flow: 91%, 1.8 mmol/h

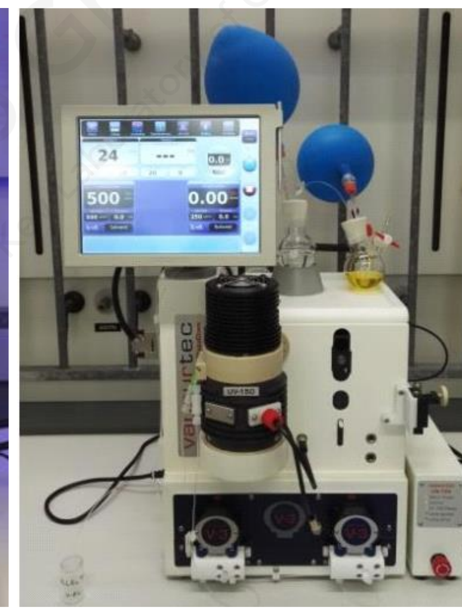


B: batch: 87%, 0.02 mmol/h
flow: 91%, 1.8 mmol/h



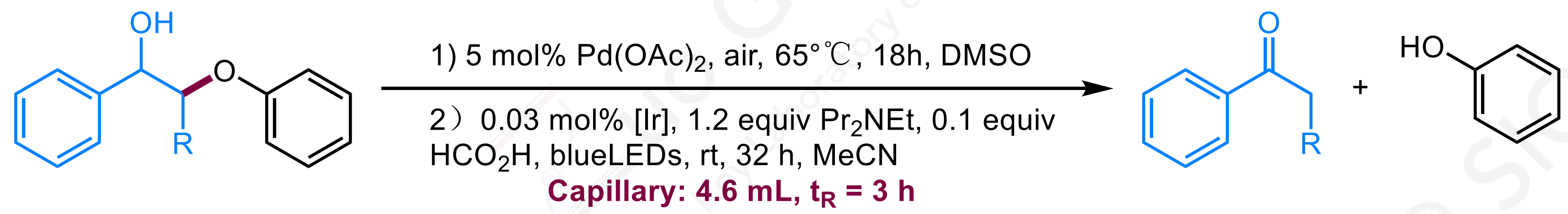
B: batch: 79%, 0.02 mmol/h
flow: 85%, 1.7 mmol/h

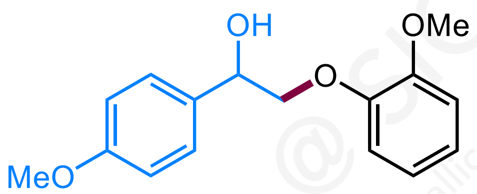




T. Poisson, et al. *Chem. Eur. J.* **2019**, *25*, 3262–3266.
T. Poisson, et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 14498–14503.

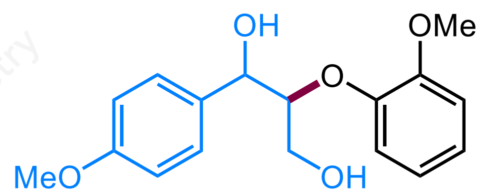
3.3 盘管反应器





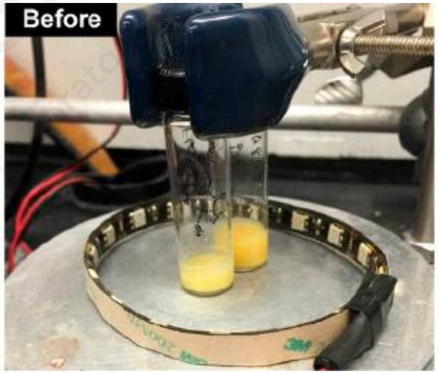
batch: 94%, 92%, **0.013 mmol/h**

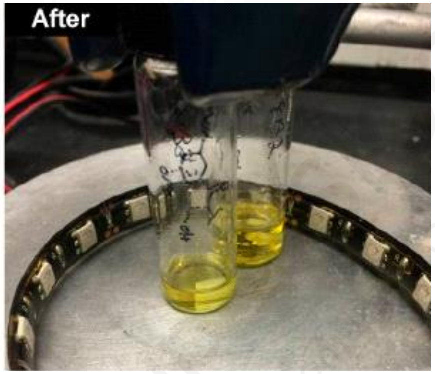
flow: 79%, 66%, 0.4 mmol/h

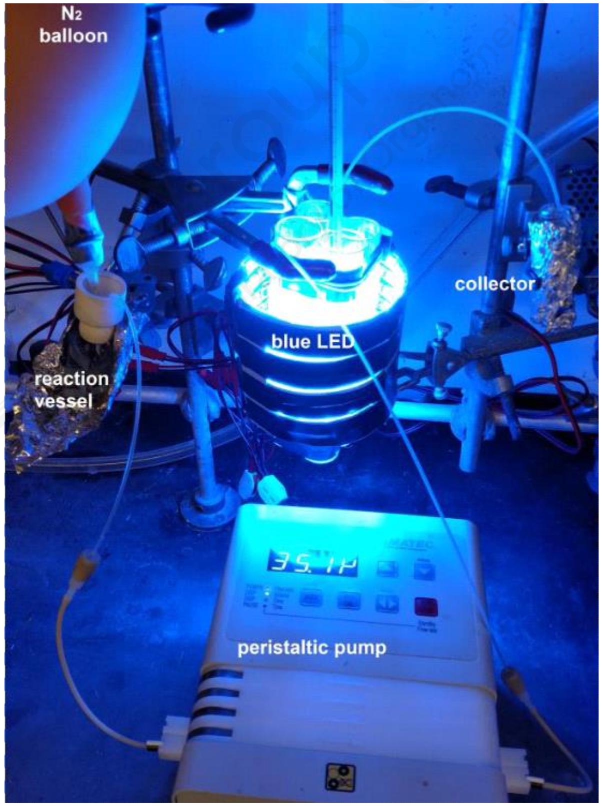


batch: 87%, 83%, **0.013 mmol/h**

flow: 77%, 63%, 0.4 mmol/h

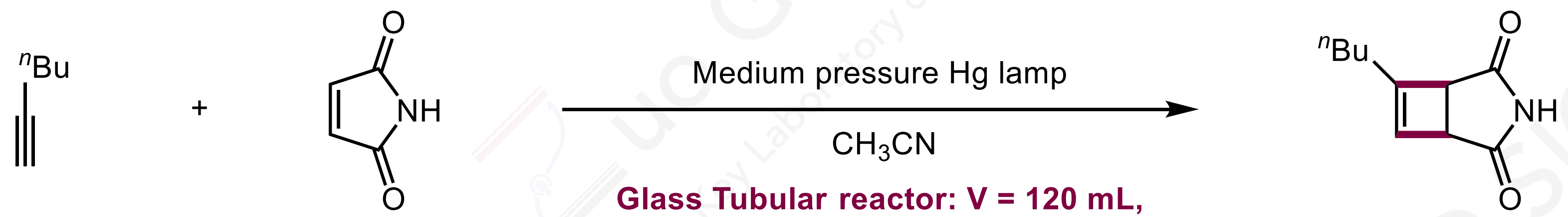




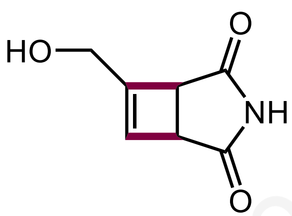


C. R. J. Stephenson, et al. *ACS Catal.* **2019**, *9*, 2252–2260.

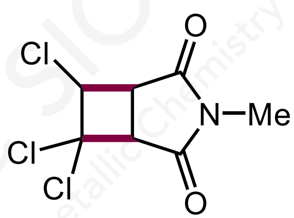
3.4 平行管反应器



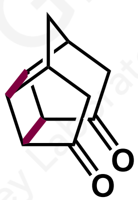
Glass Tubular reactor: V = 120 mL,
t_R = 3.3 min, 65% yield, 0.6 kg/d



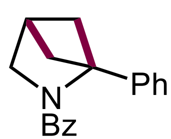
t_R = 3.3 min
64%, 0.51 kg·d^{-1}



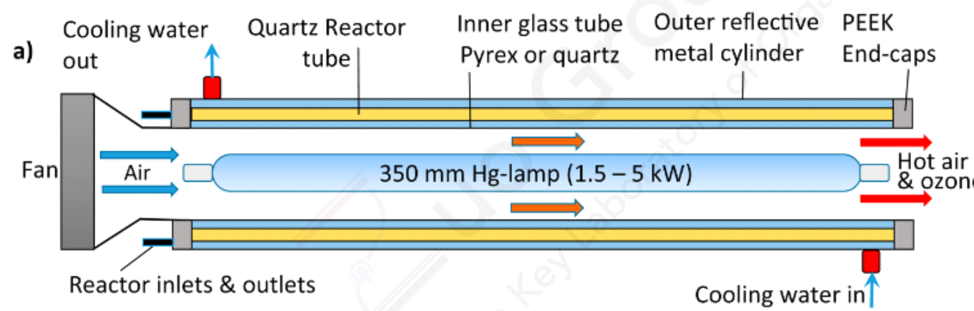
t_R = 8 min
64%, 0.69 kg·d^{-1}

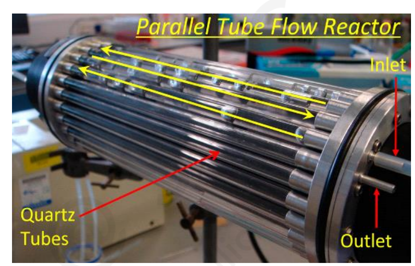


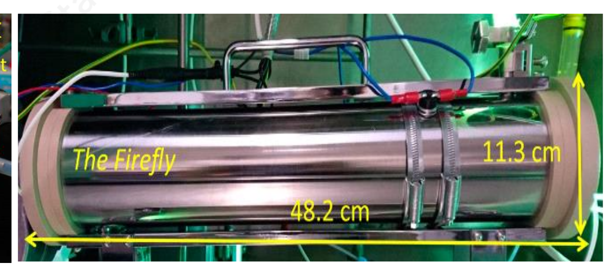
t_R = 3.3 min
89%, 8.1 kg·d^{-1}



t_R = 13 min
86%, 1.2 kg·d^{-1}

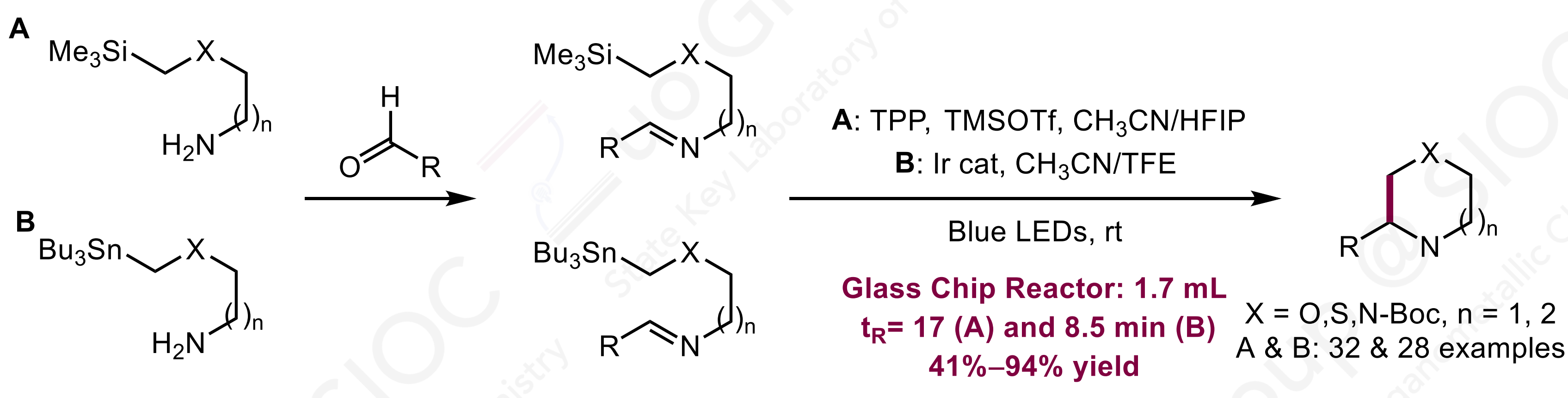


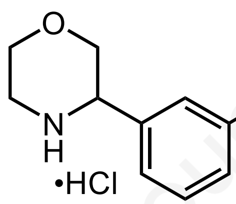




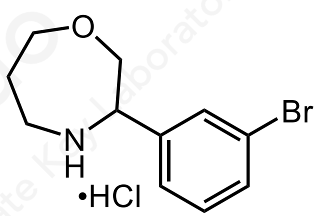
L. D. Elliott, K. I. Booker-Milburn, et al. *Org. Process Res. Dev.* **2016**, *20*, 1806–1811.

3.5 芯片反应器

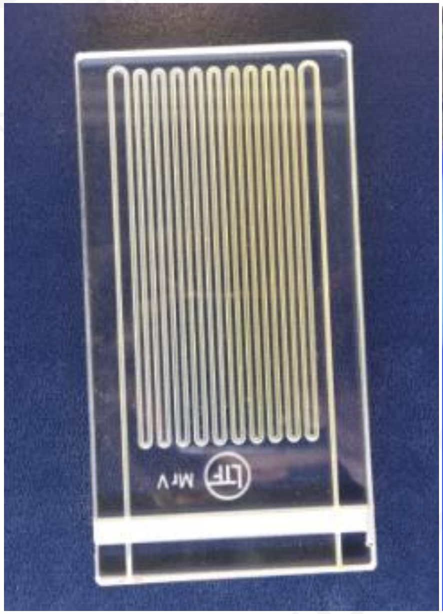




A: 67% yield, 2.8 g/d

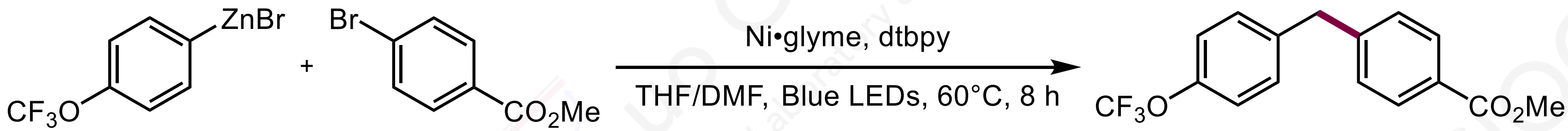


B: 41% yield, 1.7 g/d



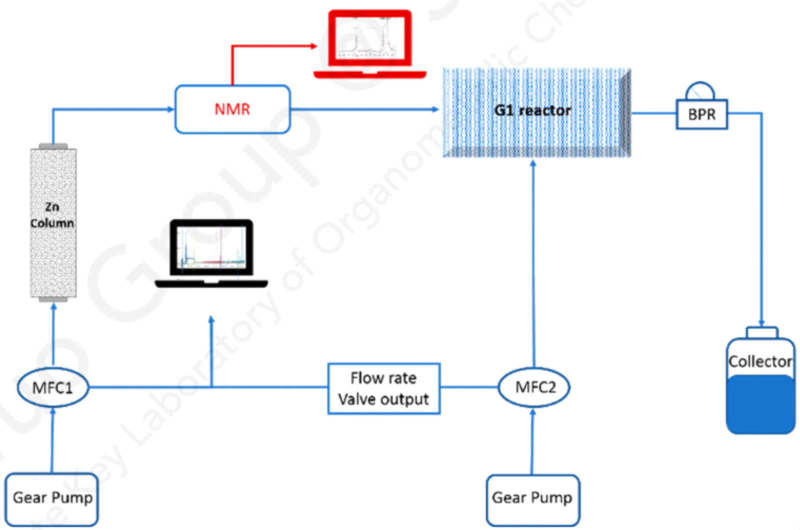
J. W. Bode, et al. *Org. Lett.* **2017**, *19*, 4696–4699.
J. W. Bode, et al. *Org. Lett.* **2018**, *20*, 2071–2075.

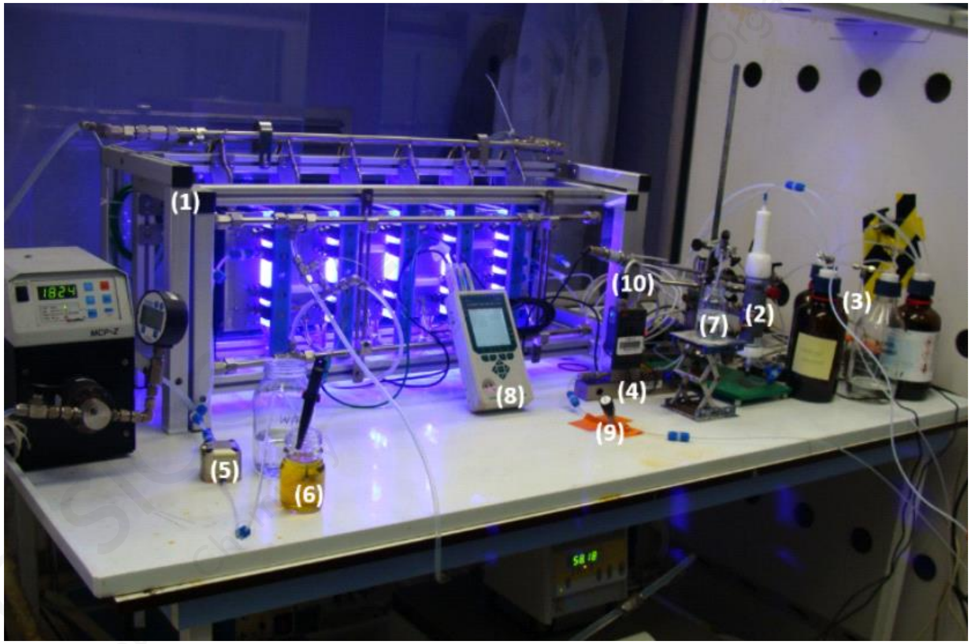
3.5 芯片反应器



Batch: 39%

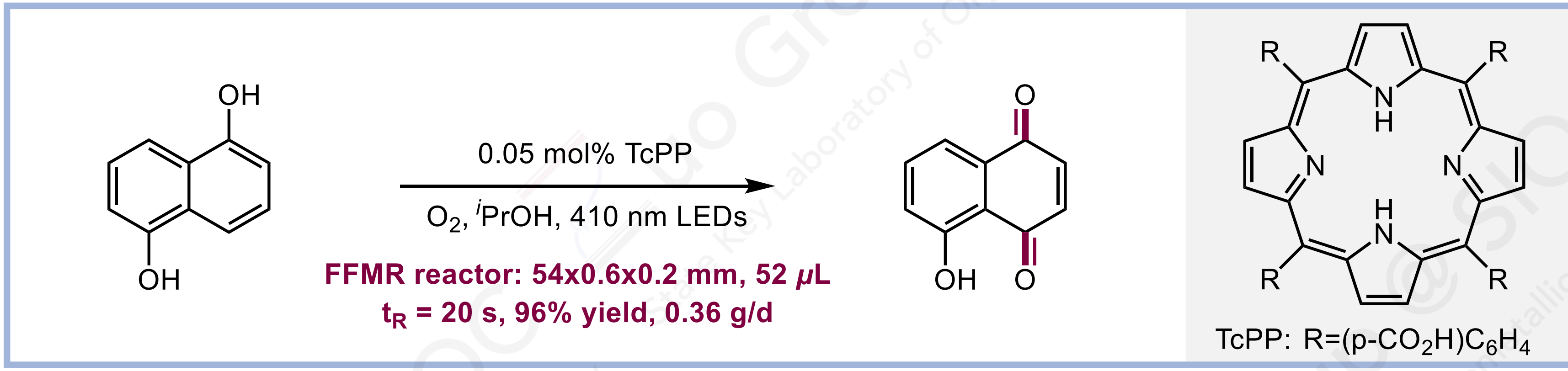
1. Capillary reactor: 10 mL, t_R= 20 min — Flow 1: 93%, 0.8 g/h
2. Glass reactor: 40 mL, t_R= 15 min — Flow 2: 93%, 5.6 g/h

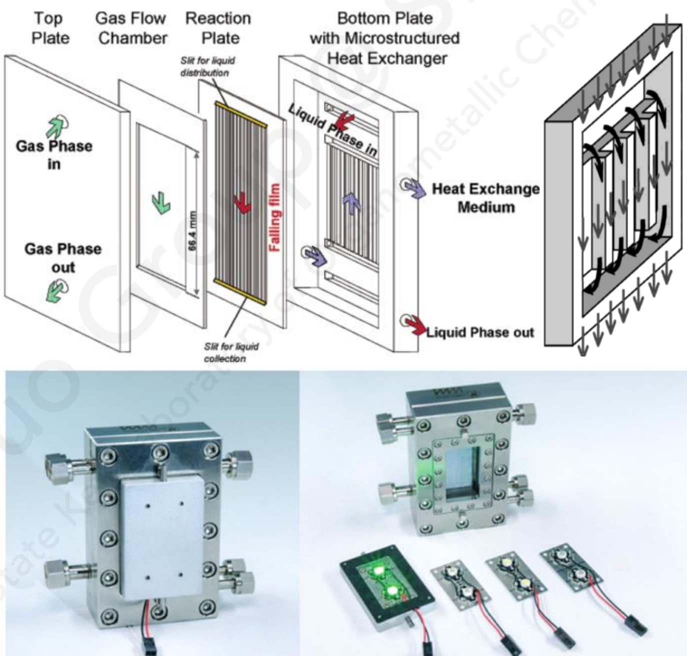




J. Alcázar, et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 8473–8477.
J. Alcazar, et al. *J. Org. Chem.* **2019**, *84*, 4748–4753.

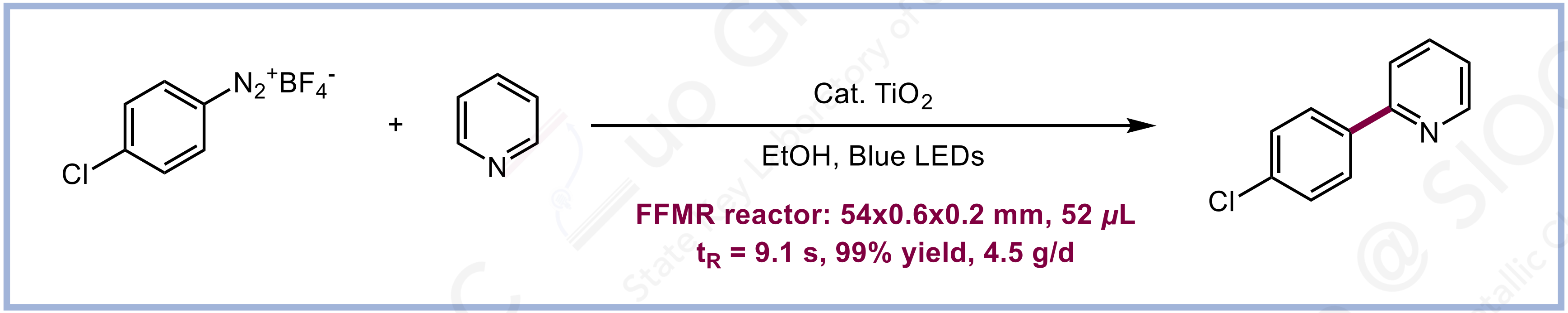
3.6 降膜反应器

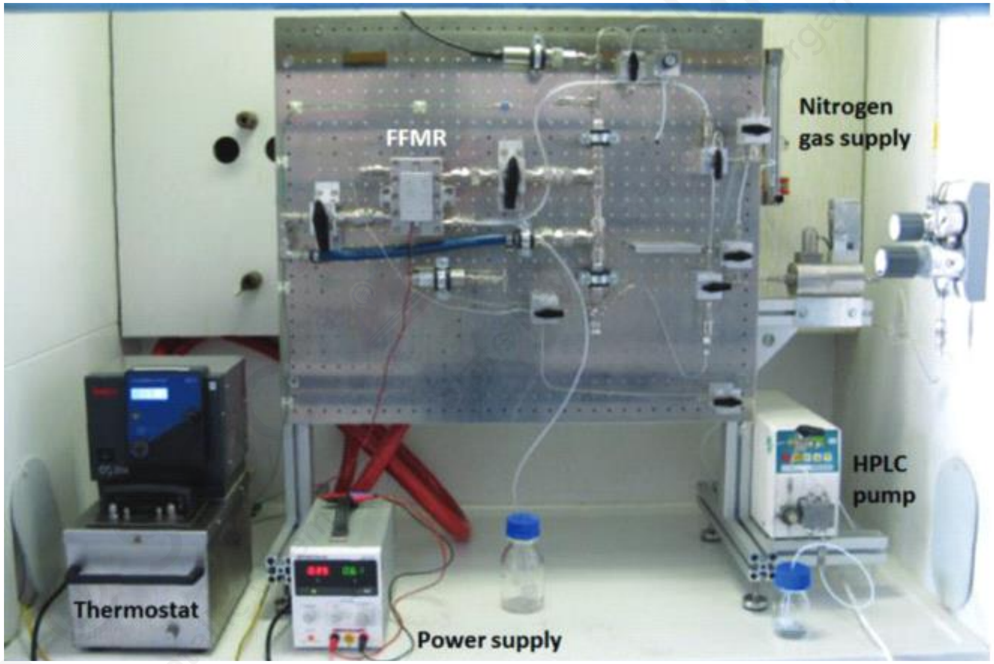




T. H. Rehm, et al. *React. Chem. Eng.* **2016**, *1*, 636–648.

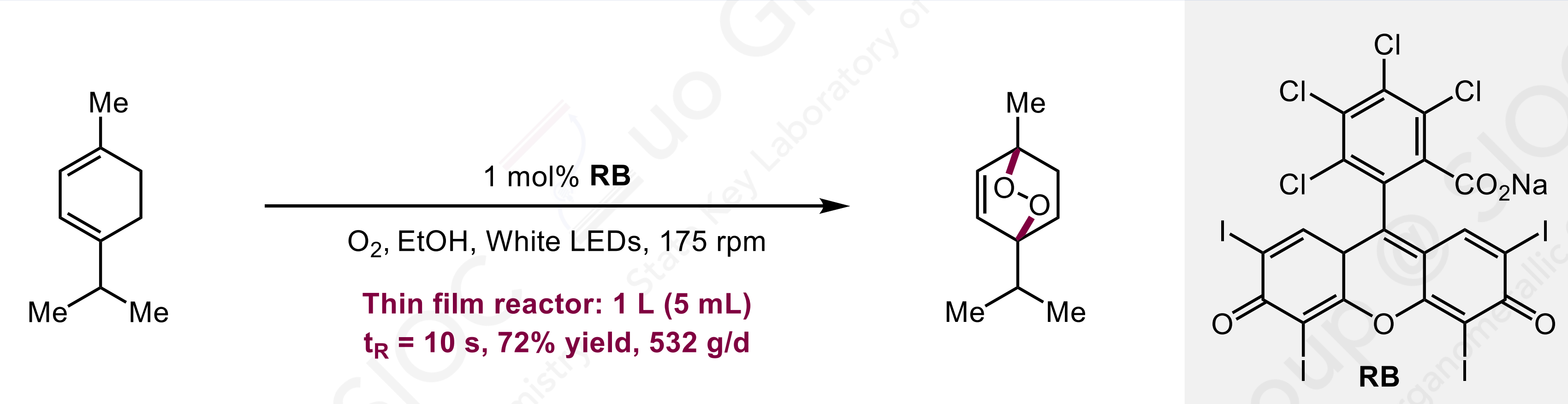
3.6 连续流光反应器：降膜反应器

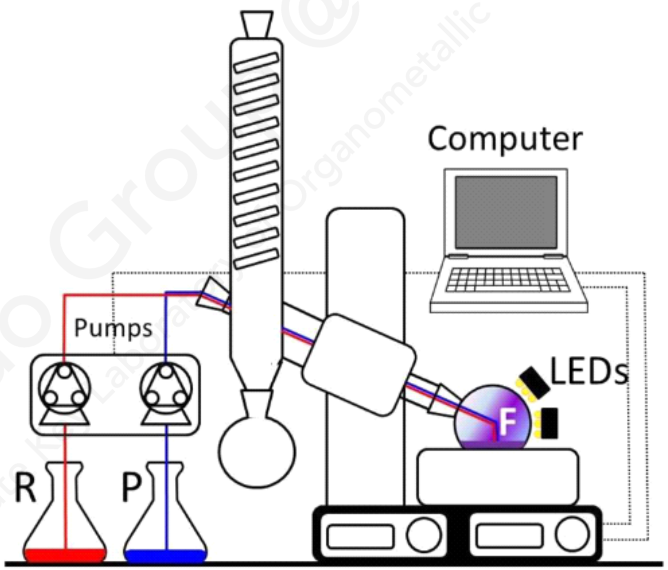


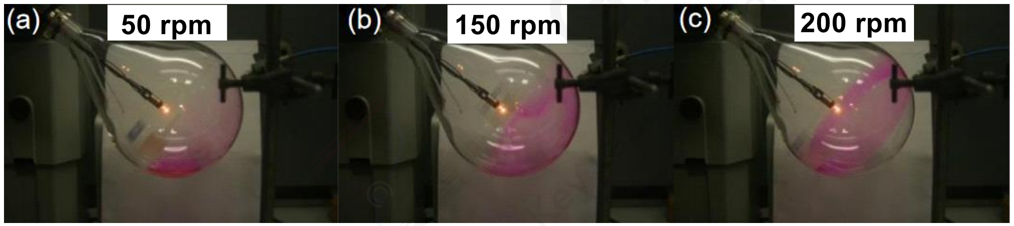


M. Rueping, T. H. Rehm,et al. *Green Chem.* **2017**, *19*, 1911–1918.

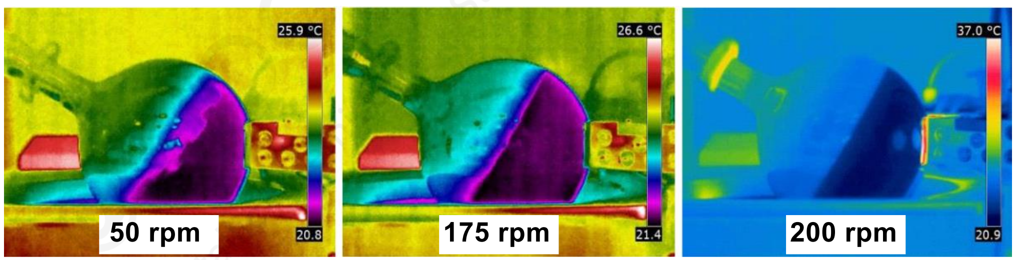
3.7 基于旋蒸的膜反应器







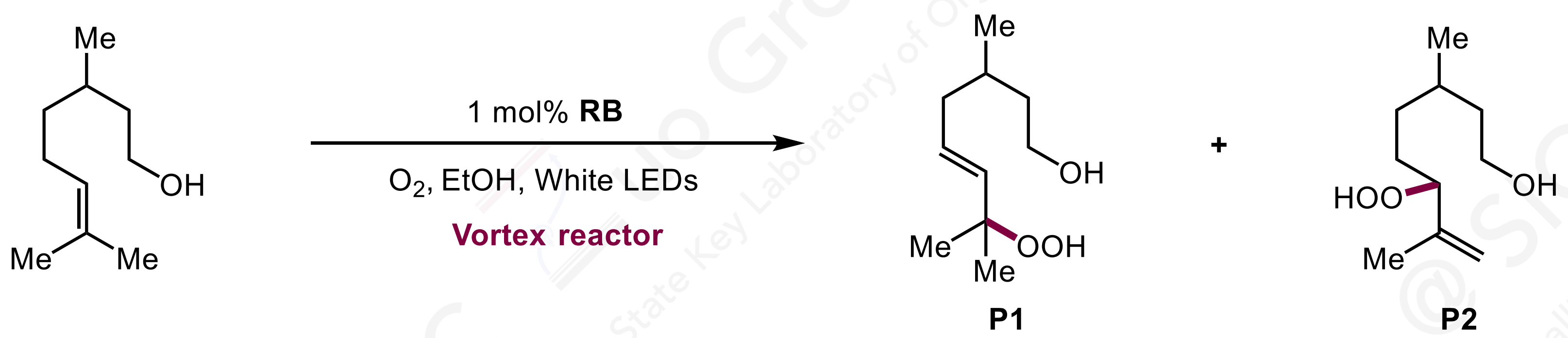
film thickness measurements showing the three types of fluid behaviour

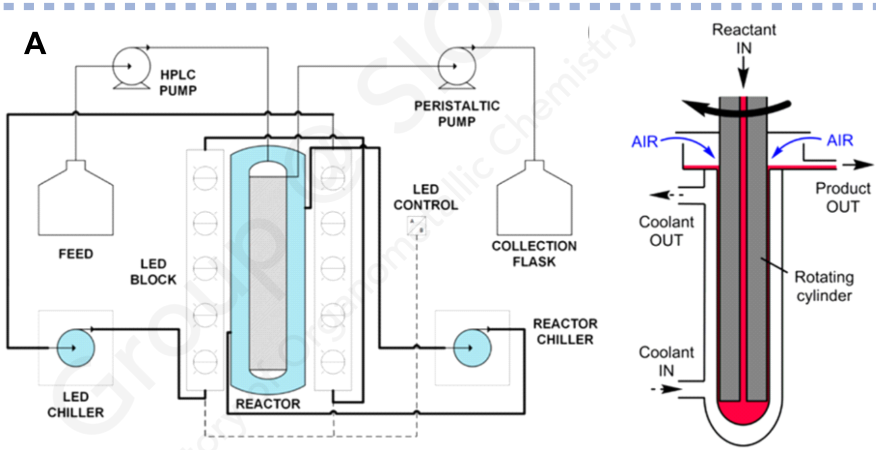


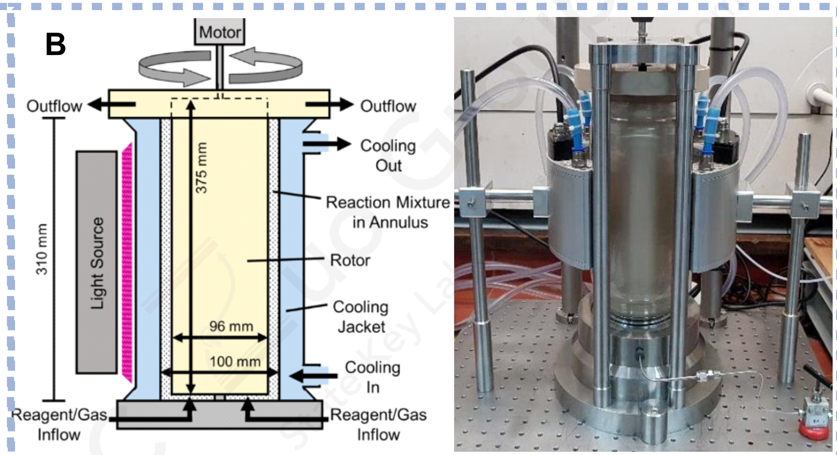
Thermal imaging photographs of a 1 L RB flask in a water bath at r.t..

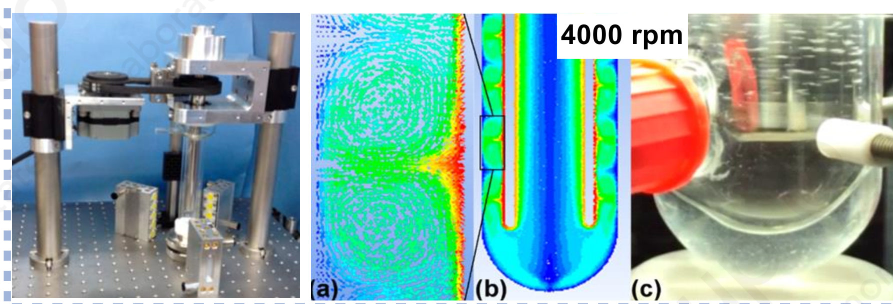
M. Poliakoff, M. W. George, et al. *Org. Process Res. Dev.* **2016**, *20*, 1792–1798.

3.8 涡流反应器







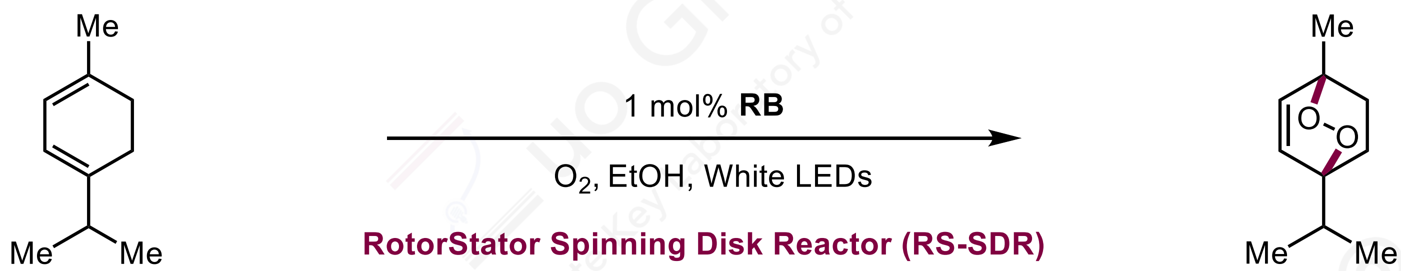


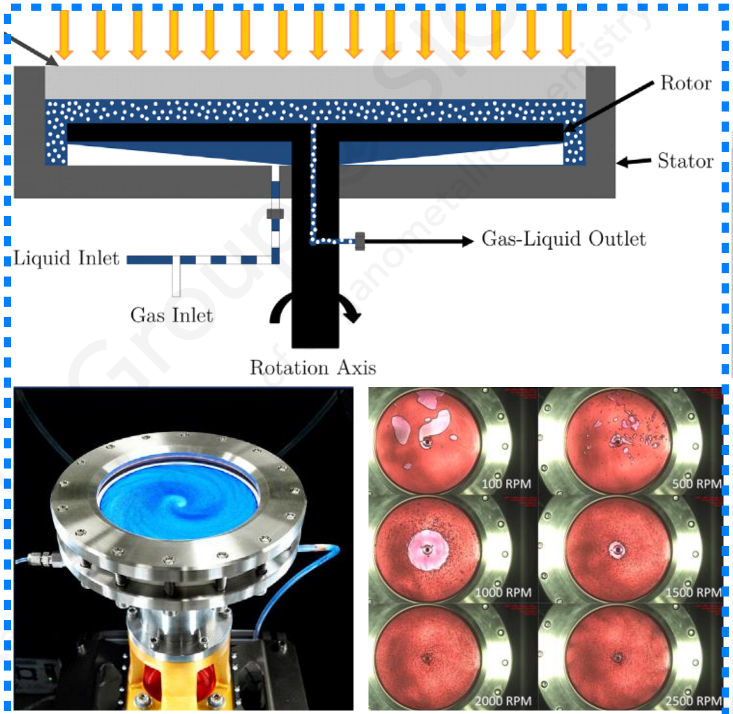
Vortex reactor A: ID = 1 mm, V = 8 mL, rpm = 4000, t_R = 32 min, 95% yield, 6.4 g/d.

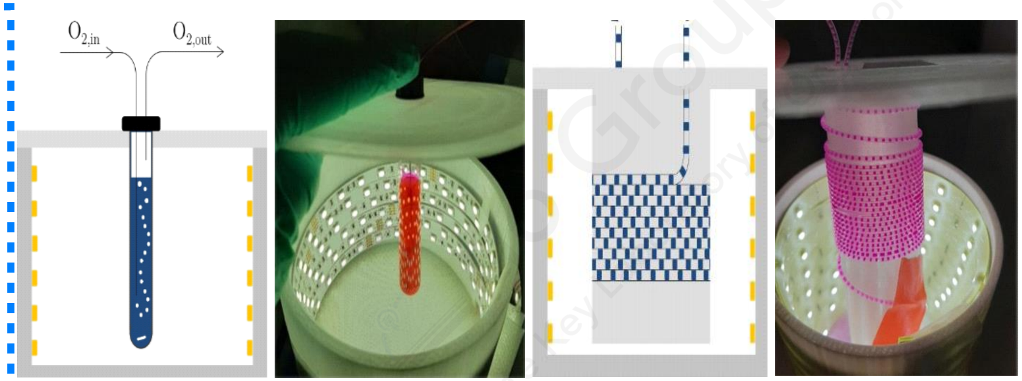
Vortex reactor B: ID = 2 mm, V = 280 mL, rpm = 660, t_R = 7 min, 92% yield, 2.0 kg/d.

M. Poliakoff, M. W. George, et al. *Org. Process Res. Dev.* **2017**, *21*, 1042–1050.
M. Poliakoff, M. W. George, et al. *Org. Process Res. Dev.* **2020**, *24*, 201–206.

3.9 转子-定子圆盘反应器







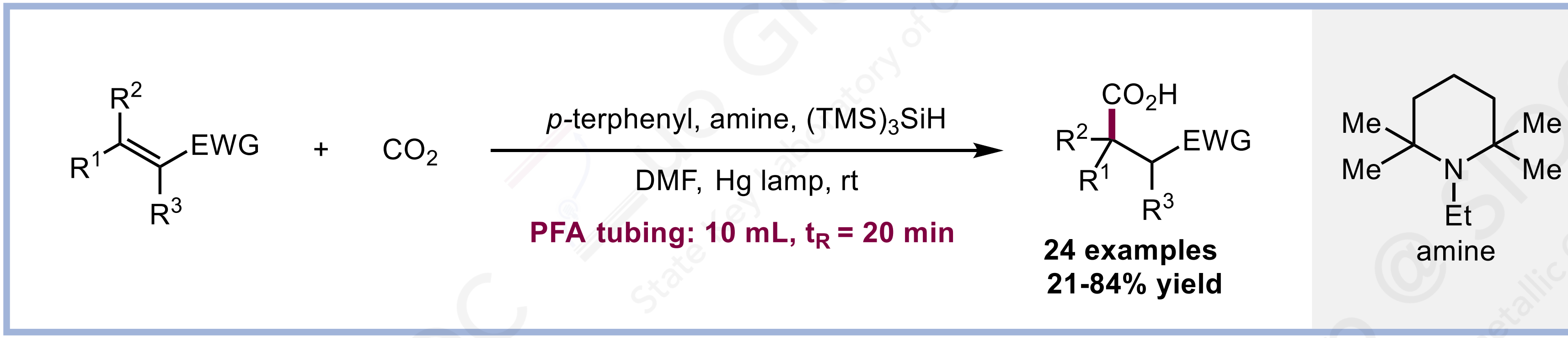
RS-SDR reactor: V = 64 (27) mL, rpm = 2000, t_R = 27 s, 67% yield, 1.1 kg/d, 2.8 M/s Productivity /Volume

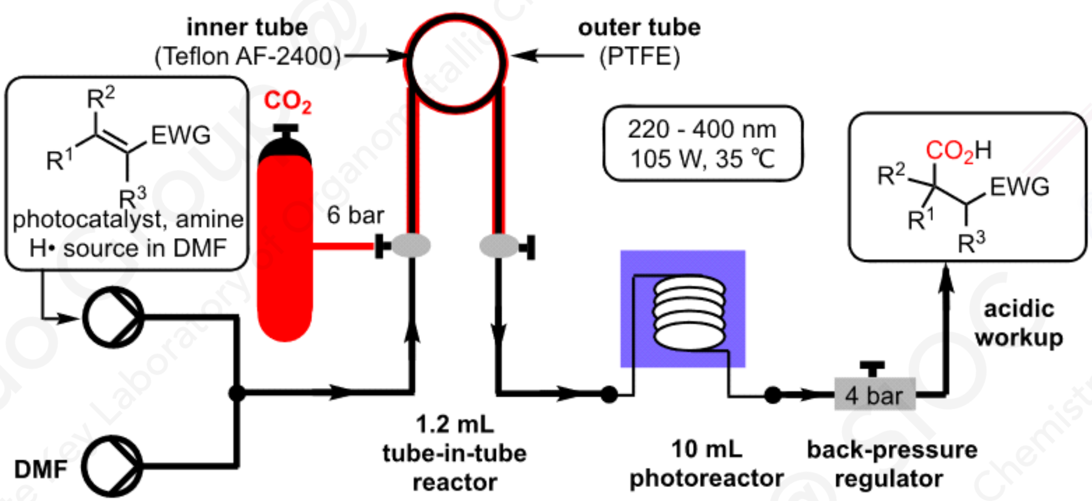
Batch reactor: 0.021 M/s Productivity /Volume

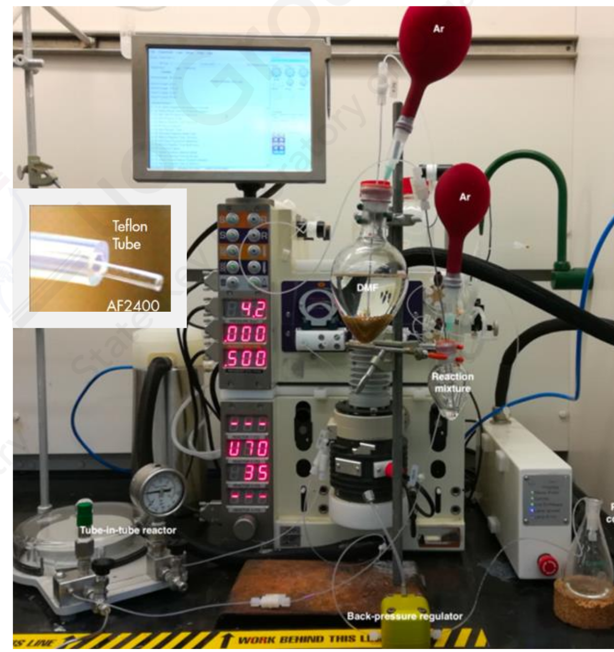
Capillary reactor: 1.2 M/s Productivity /Volume

T. Noël, J. van der Schaaf, et al. *Chem. Eng. J.* **2020**, *400*, 125875.

3.10 管中管反应器

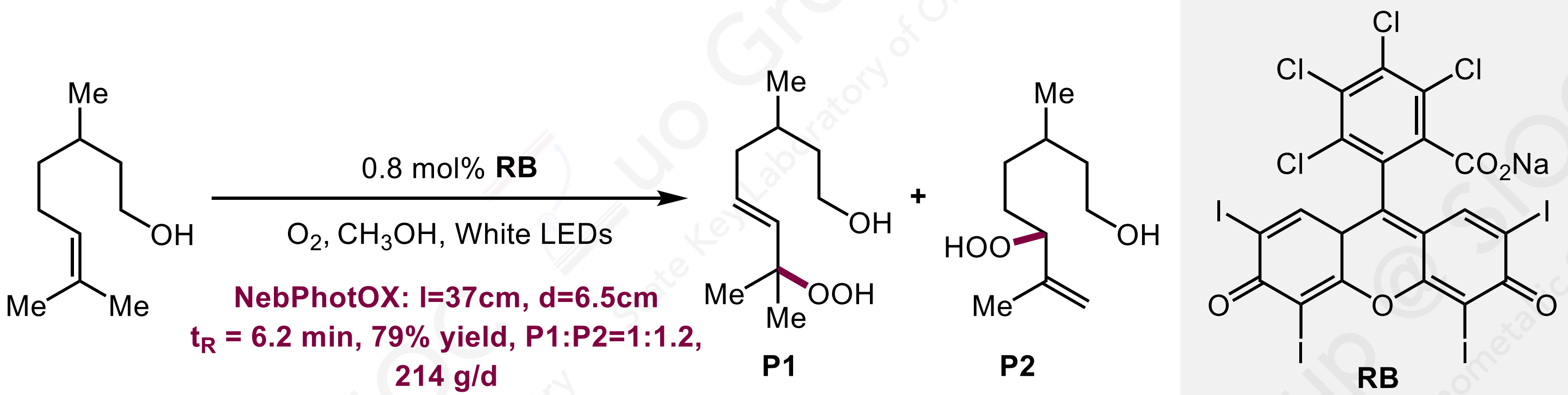


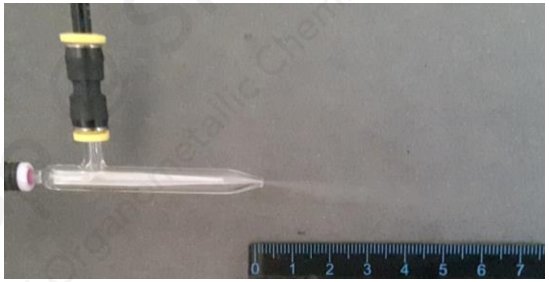


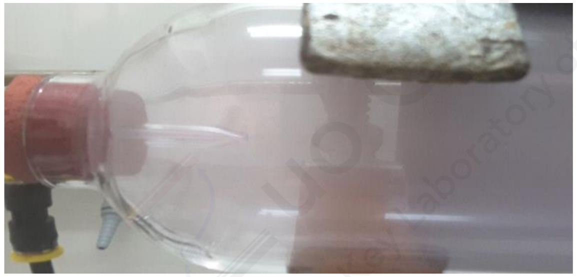


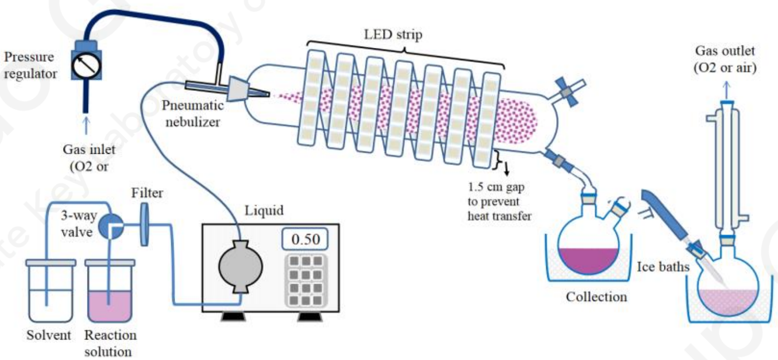
D. Romo, et al. *ACS Catal.* **2021**, *11*, 1309–1315.

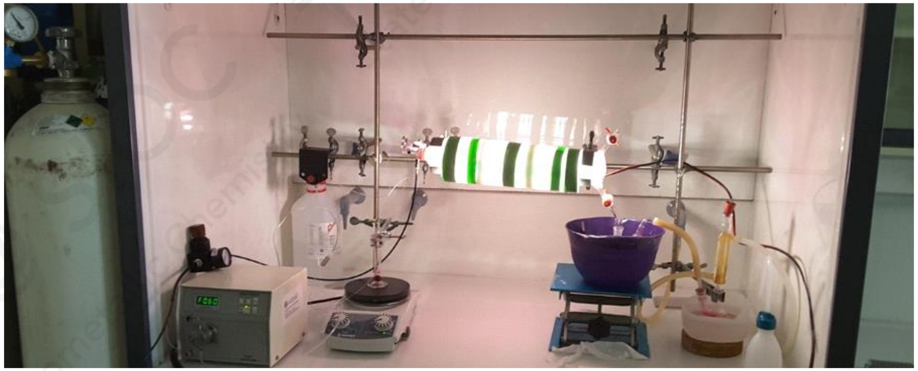
3.11 气动雾化反应器





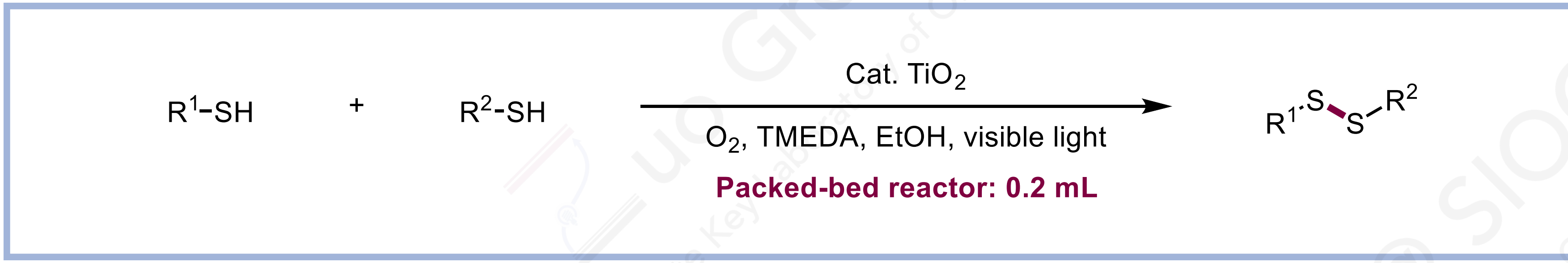


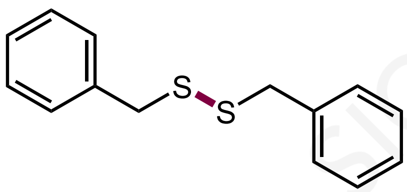




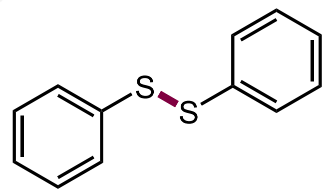
G. Vassilikogiannakis, et al. *ChemPhotoChem* **2017**, *1*, 173–177.

3.12 填充床反应器

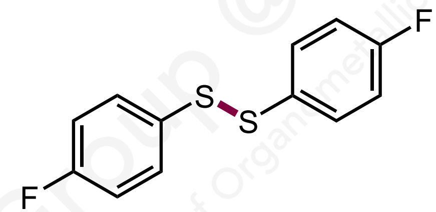




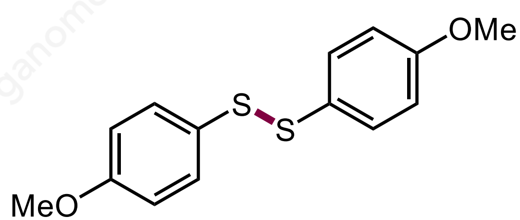
batch: 8 h, 75%
flow: 5 min, 60%



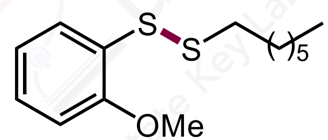
batch: 2 h, 95%
flow: 3 min, 99%



batch: 3 h, 96%
flow: 3 min, 93%



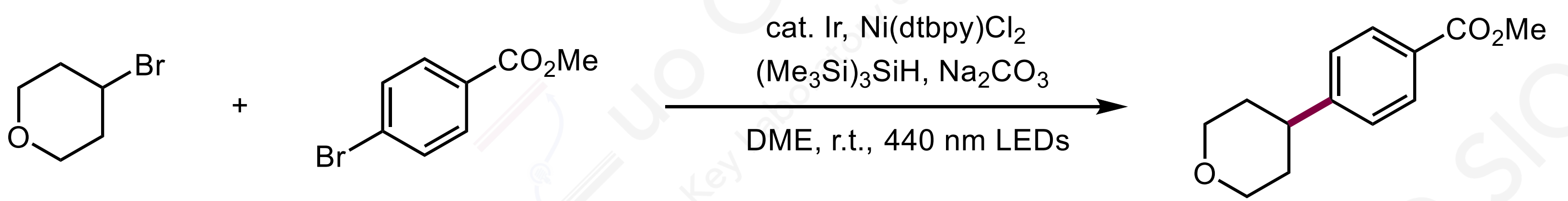
batch: 5 h, 91%
flow: 3 min, 78%



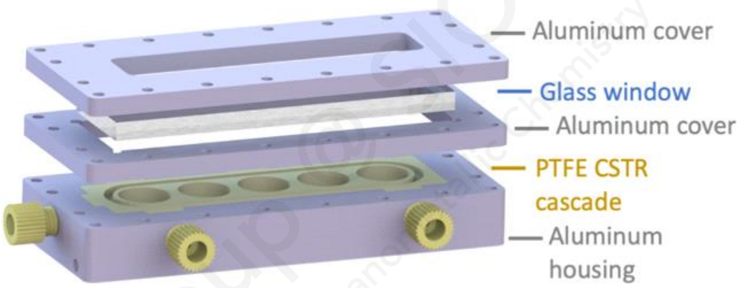
flow: 3 min, 86%

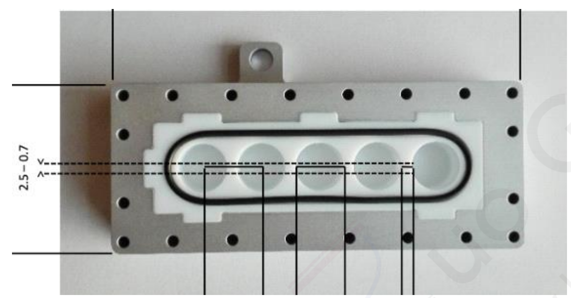
T. Noël, et al. *ChemSusChem* **2016**, *9*, 1781–1785.

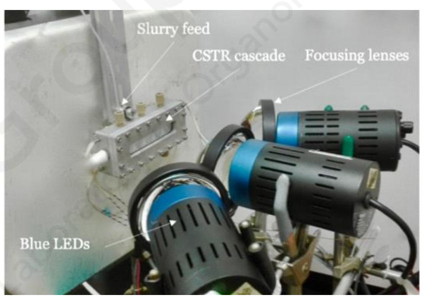
3.13 连续搅拌罐级联反应器

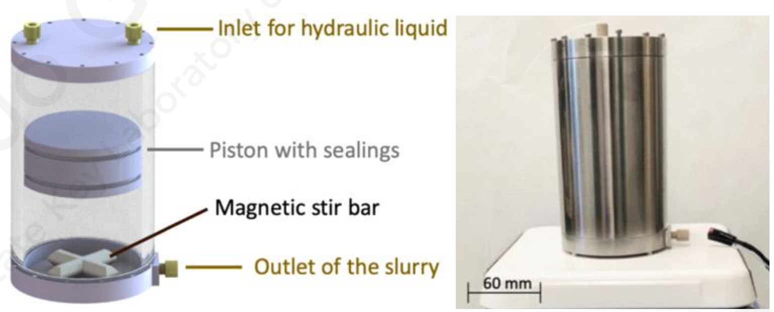


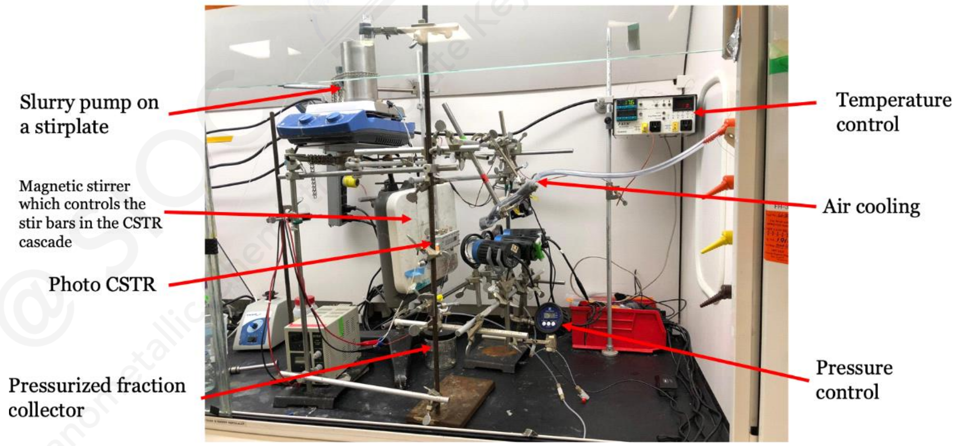
Continuous Stirred-Tank Reactor (CSTR) Cascade:
5.3 mL, t_R= 30 min , 77% yield (batch: 80%), 77 mg/h





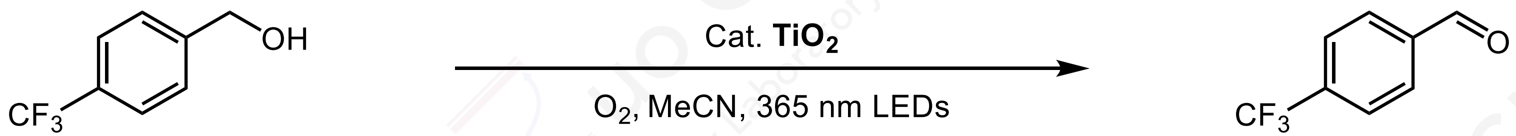




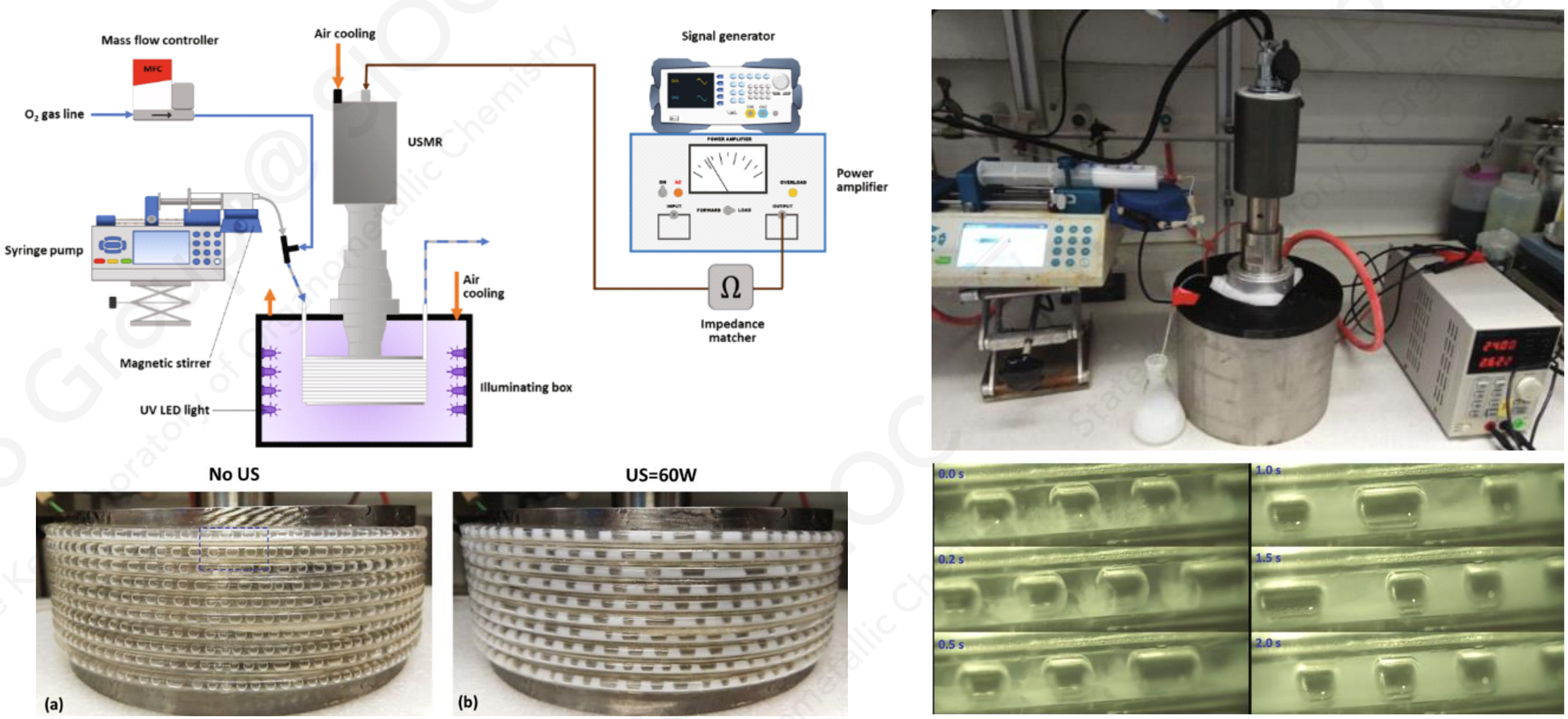


E. I. Altinoglu, K. F. Jensen, et al. *Org. Process Res. Dev.* **2019,** *23,* 2699–2706.

3.14 超声辅助盘管反应器



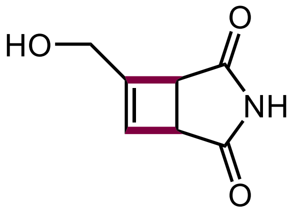
Ultrasonic Glass Capillary Reactor:
V = 12.9 mL, t_R = 28 min, 86% yield, 3.6 time higher



T. Noël, et al. *Chem. Eng. J.* **2022**, *428*, 130968.

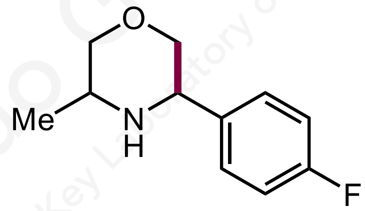
3.15 连续流反应器在光催化领域的应用概览

Photocycloadditions



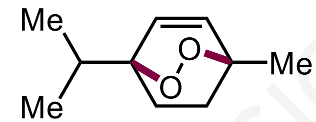
flow: 64%, 3.3 min, 0.5 kg/d
batch: 79%, 1 h

Photocyclization



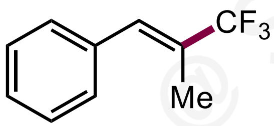
flow: 57%, 8.5 min
batch: 59%, 16 h

Photocatalytic Oxidations



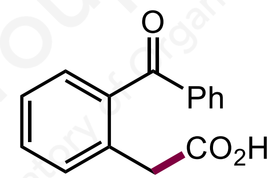
flow: 270 mmol/h
batch: 0.4 mmol/h

Photocatalytic Halogenation



flow: 76%, 1.3 h, *E* only
batch: 73%, 24 h, 69:31 *E/Z*

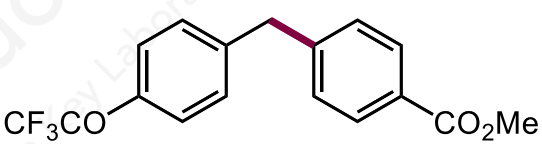
Photocatalytic Carboxylation



flow: 98%, 1.3 h
batch: 75%, 24 h

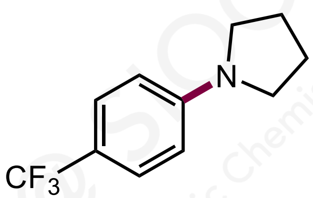
Photocatalytic Cross-Coupling Reactions

C–C Formation



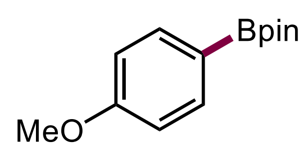
flow: 93%, 15 min, 5.6 g/h
batch: 39%, 8 h, 7.7 mg/h

C–N Formation



flow: 90%, 8.5 min, 12kg/d
batch: 96%, 19 h

C–B Formation



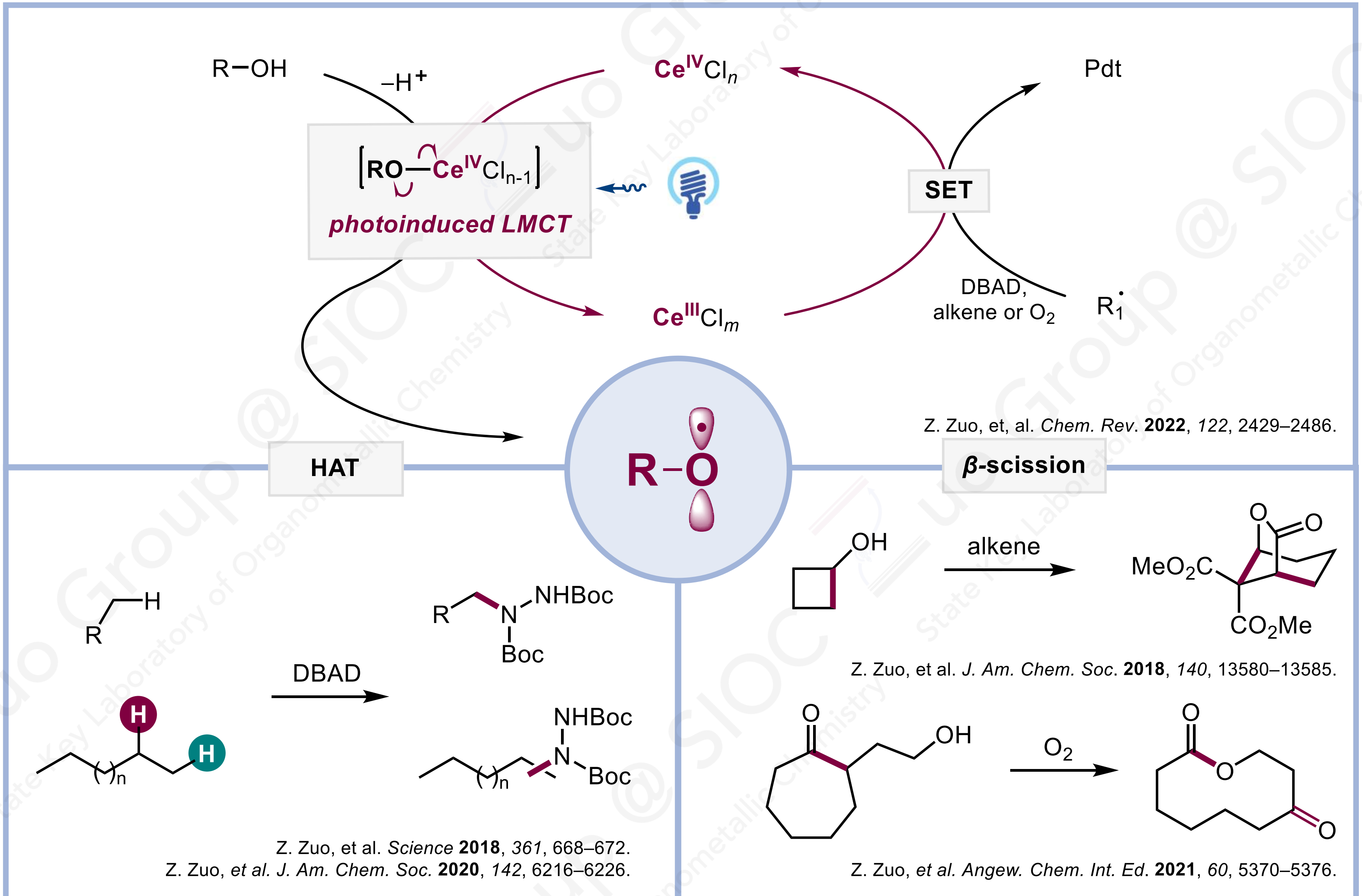
flow: 81%, 20 min
batch: 79%, 12 h

T. Noël. et al. *Chem. Rev.* **2016**, *116*, 10276–10341.

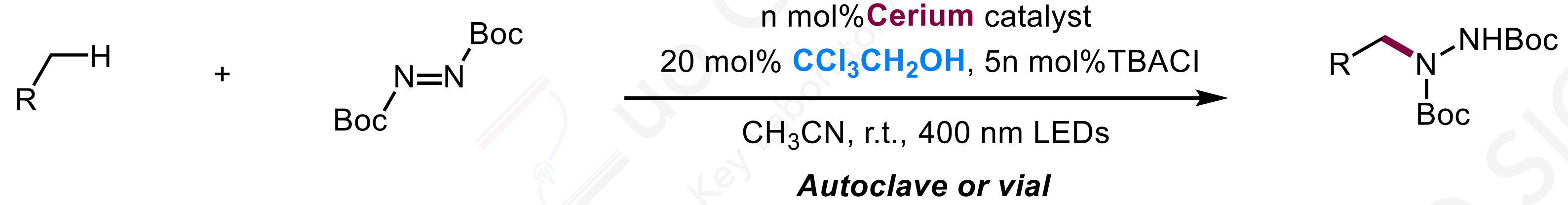
T. Noël, et al. *Chem. Rev.* **2022**, *122*, 2752–2906.

提纲

3.1 氧自由基介导的转换



3.2 铈-光催化的轻质烷烃胺化反应



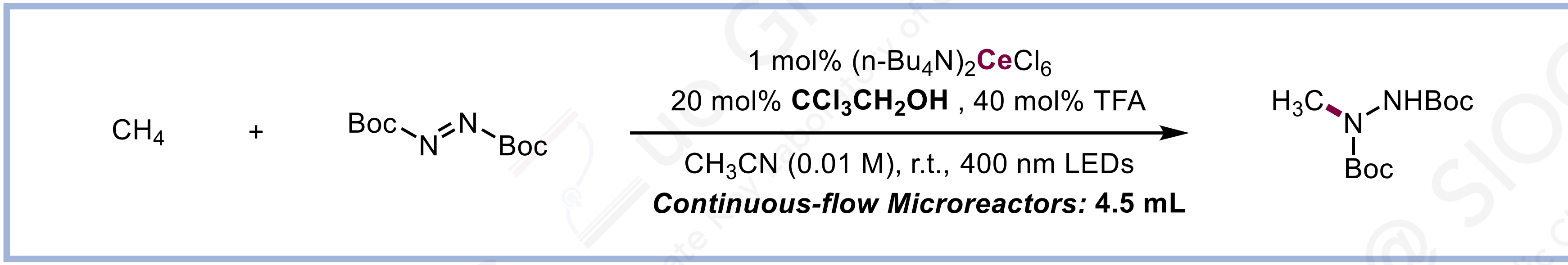
Entry	Alkane	Cerium catalyst	Loading (mol%)	time (h)	Yield (%)	TON
1[a]	Methane (50 bar)	$(n\text{-}Bu_4N)_2CeCl_6$	0.5	2	41	82
2[b]	Ethane (10 bar)	$CeCl_3$	0.01	4	97	2900
3[c]	Propane (1bar)	$CeCl_3$	0.5	9	70	140
4[d]	Butane (1 bar)	$CeCl_3$	0.5	6	76	152
5	R = *c*-C_6H_{11}	$CeCl_3$	0.5	16	81	162

[a] no TBACl, with 40 mol% TFA. [b]DIAD instead of DBAD. [c]2°:1°=1:1. [d]2°:1°=1.7:1.

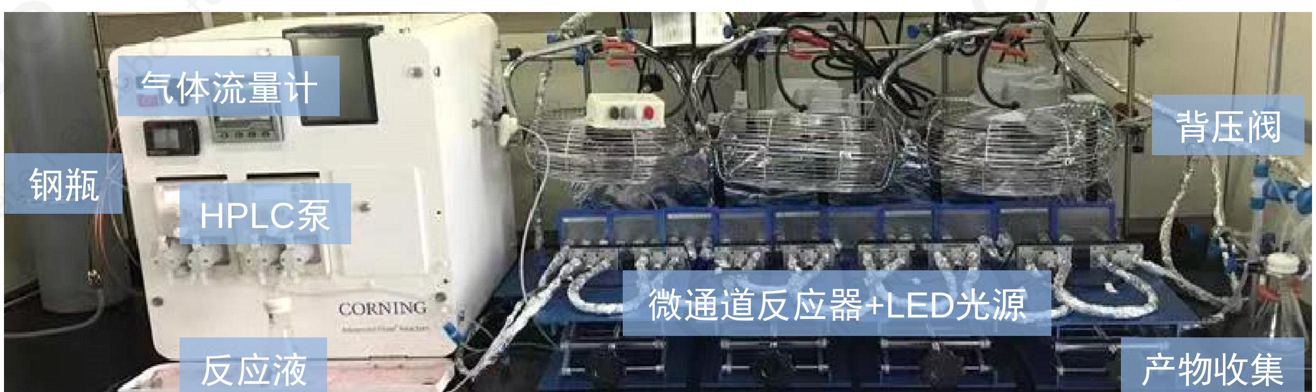
Datas from A. Hu,. and J.-J. Guo

Z. Zuo, et al. *Science* **2018**, *361*, 668–672.

3.2 铈-光催化的轻质烷烃胺化反应

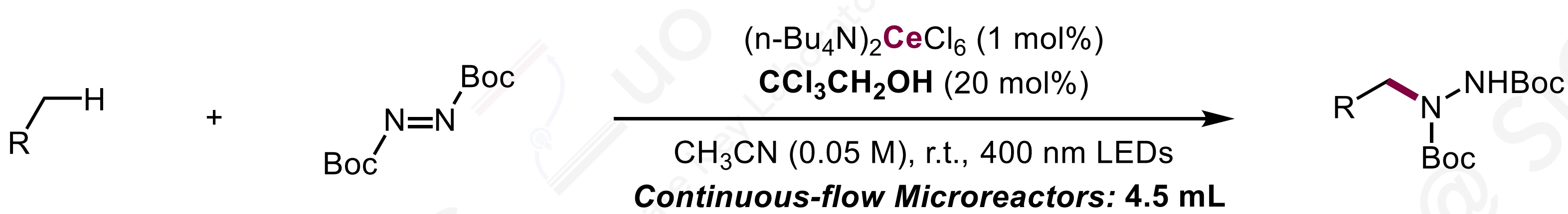


Entry[a]	P_{CH4}	V_G (mL/min)	V_L (mL/min)	t_R (min)	Yield (%)	Productivity (mmol/d)
1	13 bar	10.0	0.75	6	9	1.0
2		2.0	0.30	15	12	0.52
3		1.5	0.15	30	14	0.30
4	18 bar	1.5	0.15	30	15	0.32
5		6.0	0.30	15	15	0.60



$$t_R = \frac{V}{V_G/P + V_L}$$

3.2 铈-光催化的轻质烷烃胺化反应

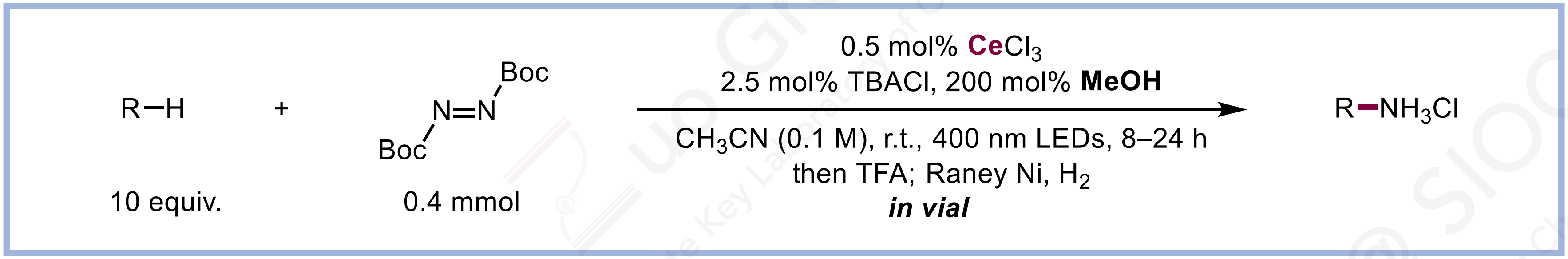


Entry	Alkane	V_G (mL/min)	V_L (mL/min)	t_R (min)	Yield (%)	Production (mmol/d)	Production in batch (mmol/d)
1[a]	Ethane (15 bar)	24	0.75	6	90	**48**	**0.59**
2[b]	Propane (8 bar)	24	0.75	6	76	**41**	**0.74**
3[c]	Butane (4 bar)	30	0.75	6	56	**31**	**1.2**
4[d]	cyclohexane (22 mL)	—	0.5	9	70	**100**	**0.48**

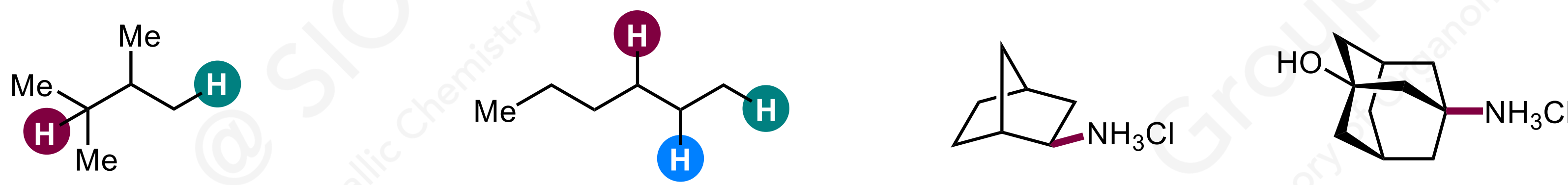
[a] DIAD instead of DBAD. [b] 2° : 1° = 1 : 1. [c] 2° : 1° = 1.8 : 1. [d] In liquid mode at 0.2 M.

Z. Zuo, et al. *Science* **2018**, *361*, 668–672.

3.3 铈-光催化的烷烃选择性胺化反应



Substrate scope

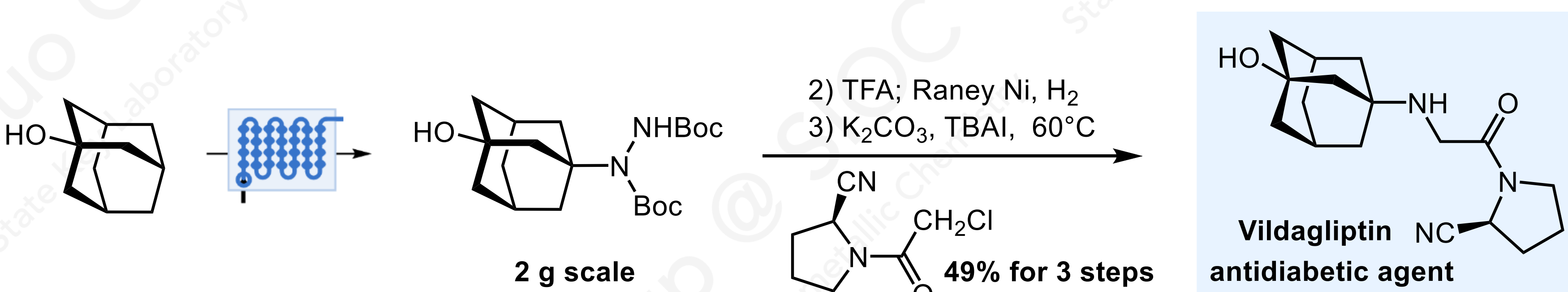


MeOH: 81%, 97 : 3
^{t}BuOH: 49%, 64 : 36
CCl_3CH_2OH: 83%, 44 : 56

MeOH: 82%, 47 : 48 : 3
CCl_3CH_2OH: 85%, 39 : 39 : 22

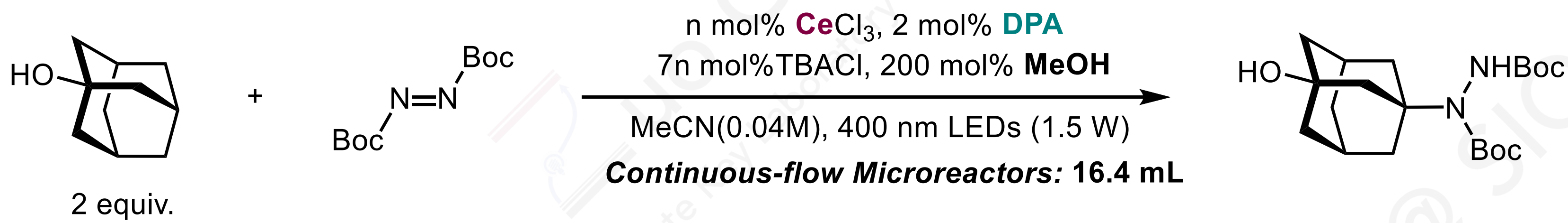
72% yield

79% yield, 9 h



Z. Zuo, et al. *J. Am. Chem. Soc.* **2020**, *142*, 6216–6226.

3.3 铈-光催化的烷烃选择性胺化反应

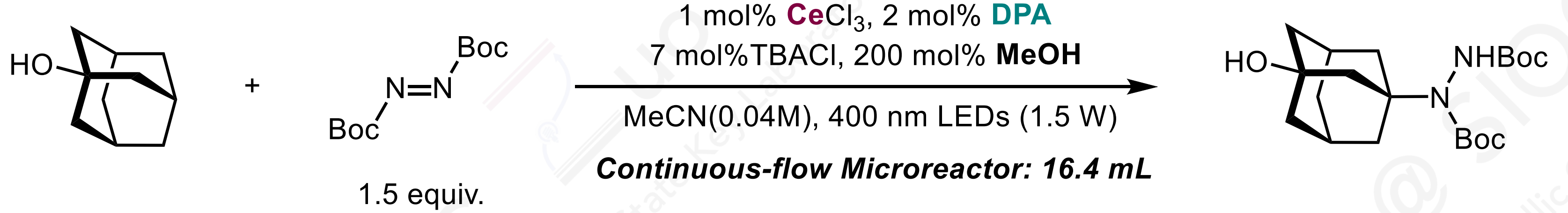


Entry	V_L (mL/min)	t_R (min)	DPA	$CeCl_3$	MeOH	Yield (%)	Productivity (mmol/d)
1	2.0	8.2	—	n = 1	200 mol%	14%	16
2			**2 mol%**	**n = 1**	**200 mol%**	**40%**	**46**
3			2 mol%	n = 1	400 mol%	42%	48
4			2 mol%	n = 5	200 mol%	44%	50
5[a]	1.0	16	**2 mol%**	n = 1	**200 mol%**	**56%**	**34**
6[b]			2 mol%	n = 1	200 mol%	57%	34
7			5 mol%	n = 1	200 mol%	58%	34

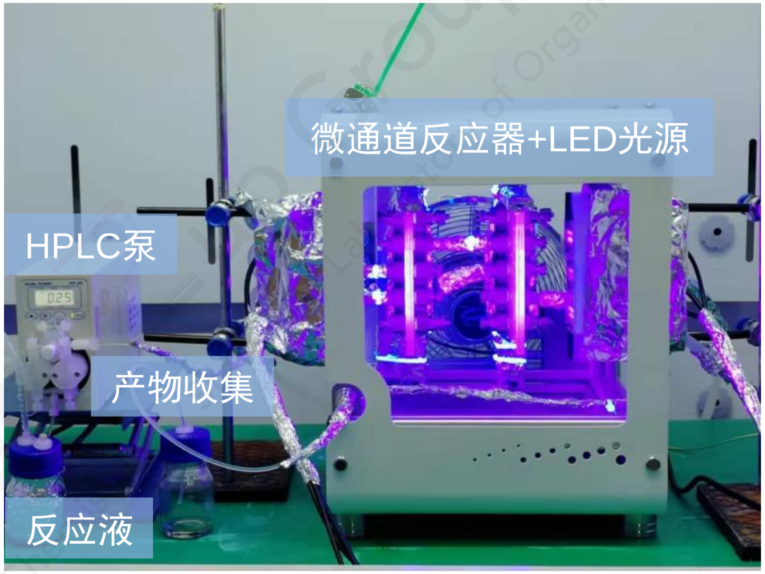
[a] 4% DBAD remained. [b] 400 nm LEDs (2.0 W)

Z. Zuo, *et al. J. Am. Chem. Soc.* **2020**, *142*, 6216–6226.

3.3 铈-光催化的烷烃选择性胺化反应

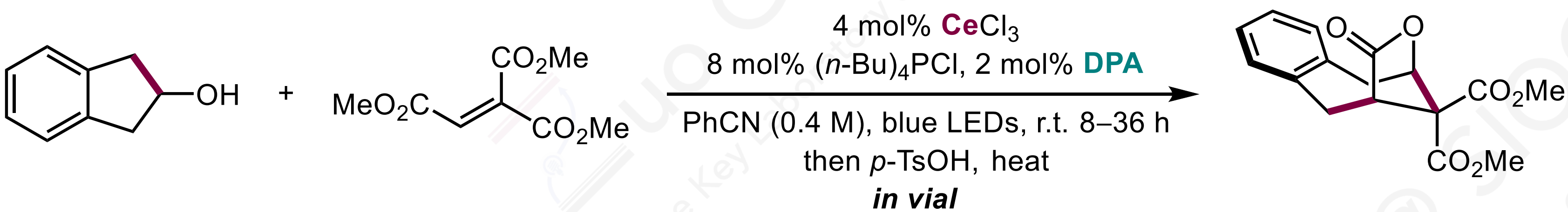


Entry	V_L (mL/min)	t_R (min)	DBAD (%)	Yield (%)	Productivity (mmol/d)
1	1.0	16	38%	**50%**	**29**
2	0.5	33	20%	**59%**	**17**
3	**0.25**	**66**	**2%**	**66%**	**9.4**

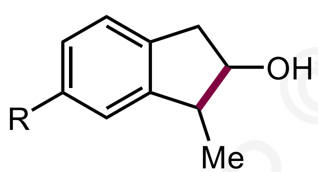


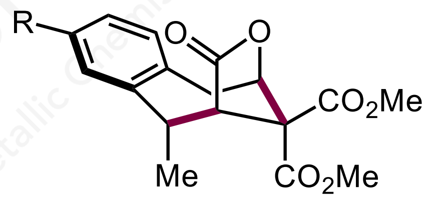
Z. Zuo, et al. *J. Am. Chem. Soc.* **2020**, *142*, 6216–6226.

3.4 铈-光催化的环醇和烯烃形式环加成反应

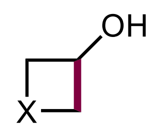


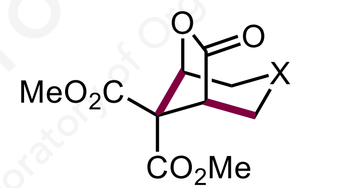
Substrate scope



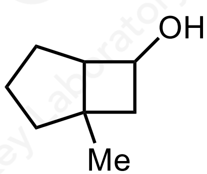


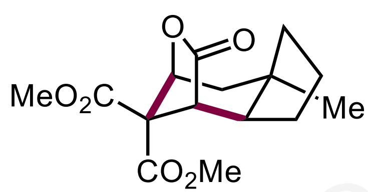
R = OMe, 54% yield, d.r. = 1.3:1
R = Br, 72% yield, d.r. = 2:1



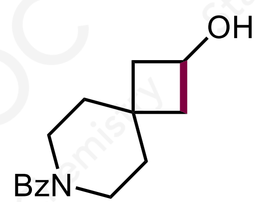


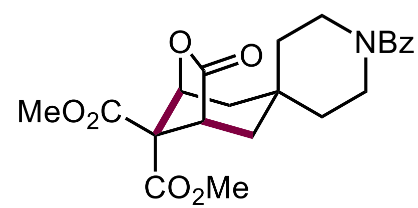
X = C, 93% yield, 8 h
X = NCbz, 75% yield





65%, d.r. = 1.2:1

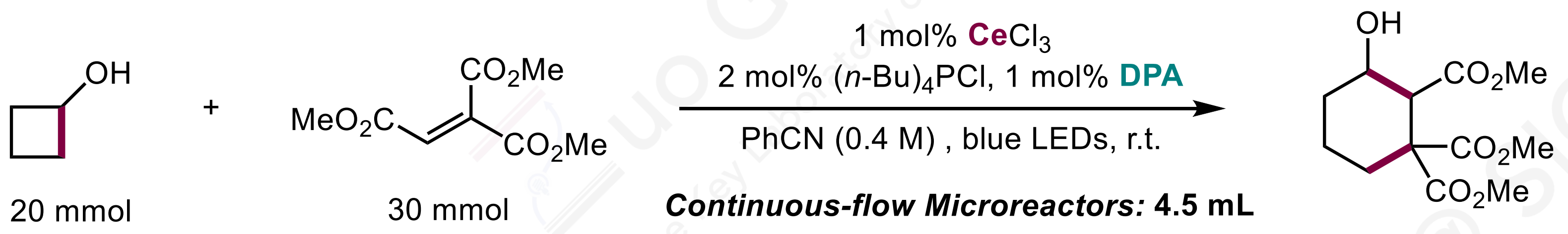




64% yield

Z. Zuo, et al. *J. Am. Chem. Soc.* **2018**, *140*, 13580–13585.

3.4 铈-光催化的环醇和烯烃形式环加成反应

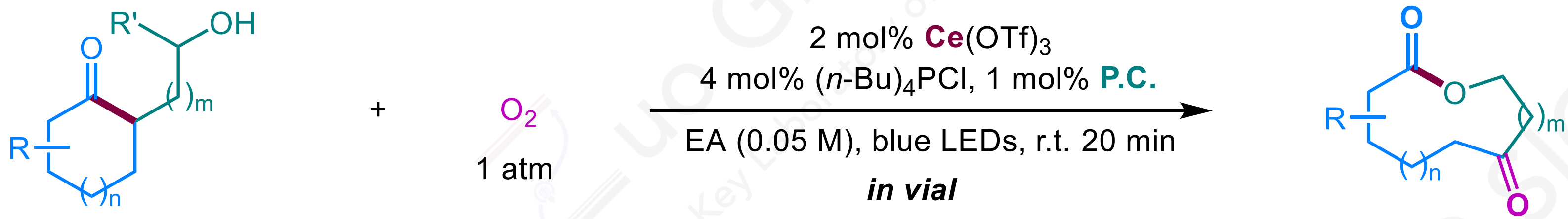


Entry	Mode	V_L (mL/min)	t_R (h)	Yield (%)	Productivity (mmol/d)
1	single-pass	0.15	0.5	11%	9.6
2[a]	recirculated	1.5	—	80%	**10.6** (batch: 0.57)

[a] Reaction time: 36 h.

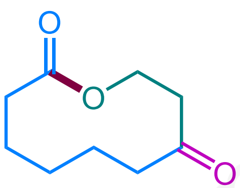
Z. Zuo, et al. *J. Am. Chem. Soc.* **2018**, *140*, 13580–13585.

3.5 铈-光催化的环酮氧化扩环反应

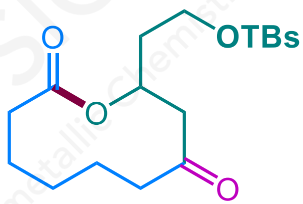


> 100 examples

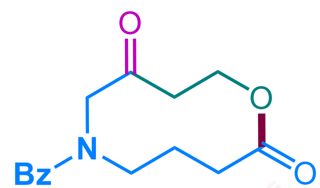
Substrate scope



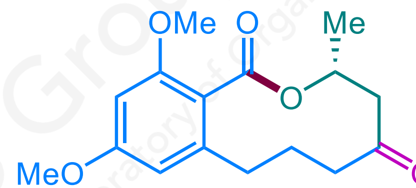
n = 1, 60% yield
n = 5, 60% yield
n = 9, 72% yield



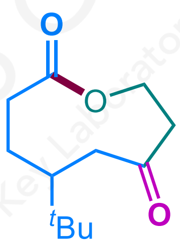
74% yield



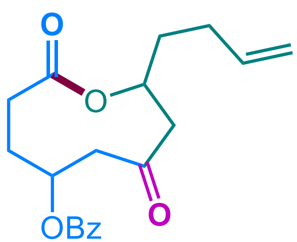
68% yield



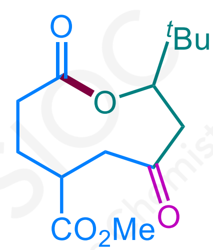
77% yield



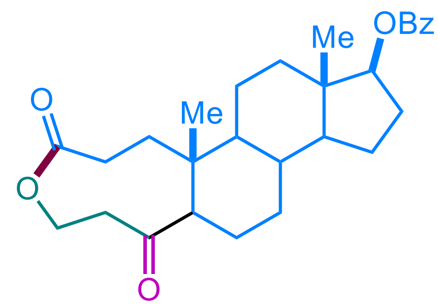
66% yield



54% yield, 1.5:1 d.r.



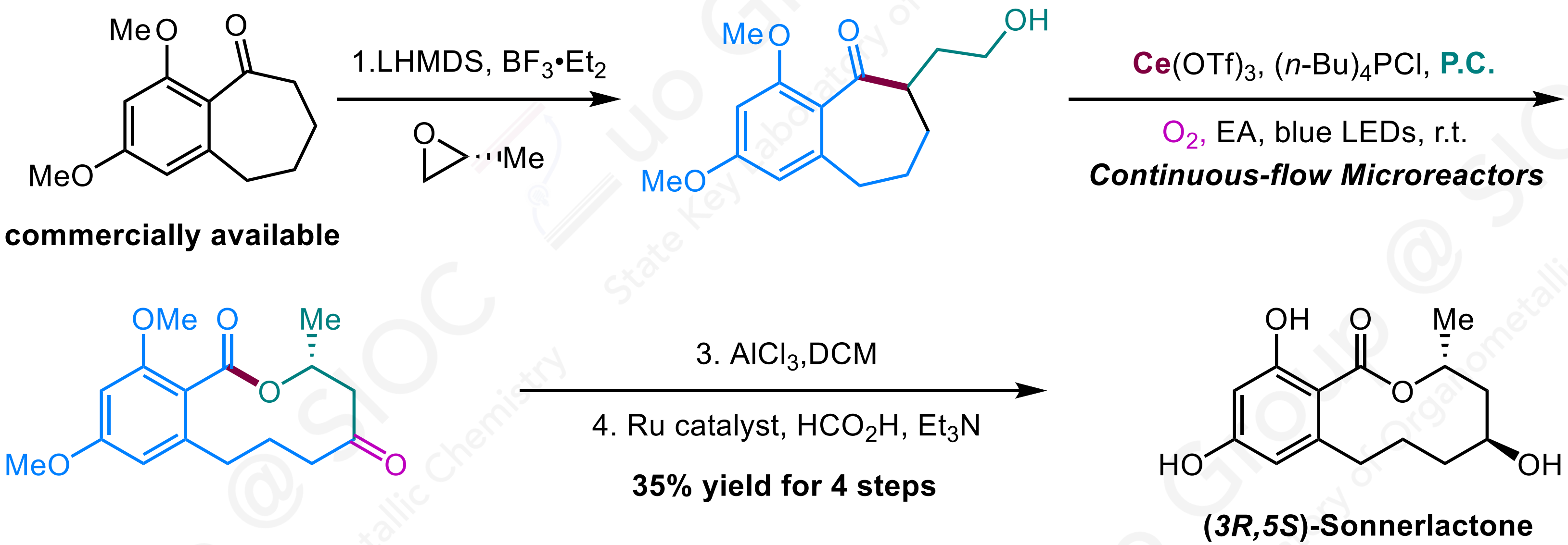
65% yield, 1.8:1 d.r.



73% yield

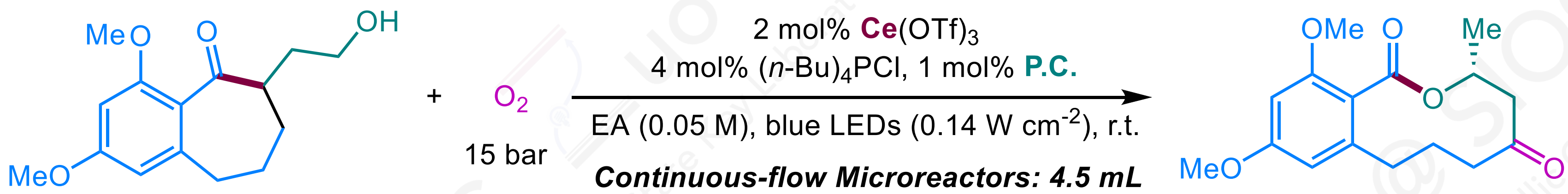
Z. Zuo, *et al. Angew. Chem. Int. Ed.* **2021**, *60*, 5370–5376.

3.5 铈-光催化的环酮扩环反应



Z. Zuo, et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 5370–5376.

3.5 铈-光催化的环酮扩环反应



Entry[a]	V_L (mL/min)	V_g (mL/min)	t_R (min)	Yield (%)	Productivity (mmol/d)
1	0.40	1.0	10	**55%**	**17.8**
2	0.30	1.0	12	**65%**	**17.5**
3[a]	**0.15**	**1.0**	**20**	**78%**	**15.3** (batch: 5.5)

[a] isolated yield.

Z. Zuo, et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 5370–5376.