

# ***Chemical Recycling of Polystyrene***

**2022.4.16 Literature Seminar**

**M2 Wataru Shigematsu**

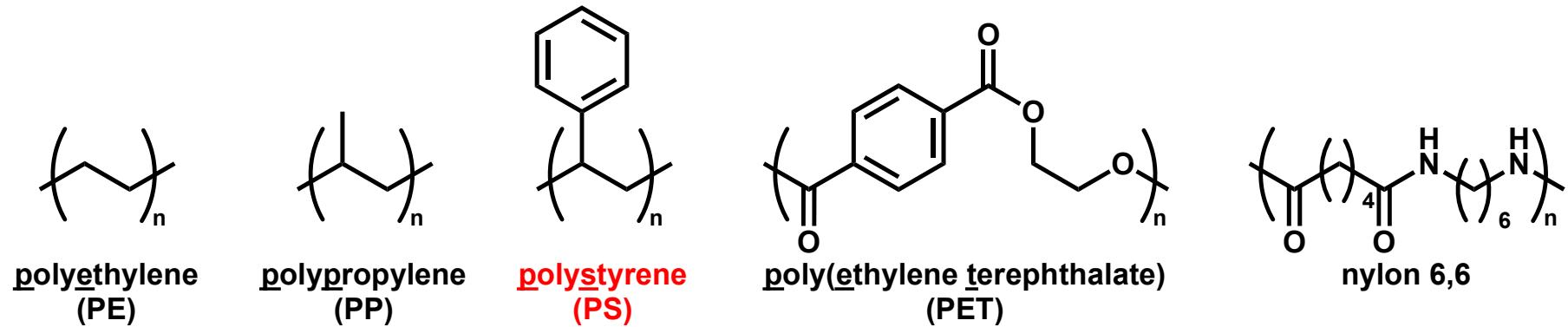
# **Contents**

- 1. Introduction of Synthetic Plastics**
- 2. Previous Method of Chemical Recycling of Synthetic Plastics**
- 3. Chemical Recycling of Polystyrene via Acid-Catalyzed Aerobic Oxidation**
- 4. Summary**

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# Synthetic Plastics



General Purpose PS  
(GPPS)

- Hard but brittle
- Colorless and transparent



High Impact PS  
(HIPS)

- Copolymer
- High impact resistance
- Milky white

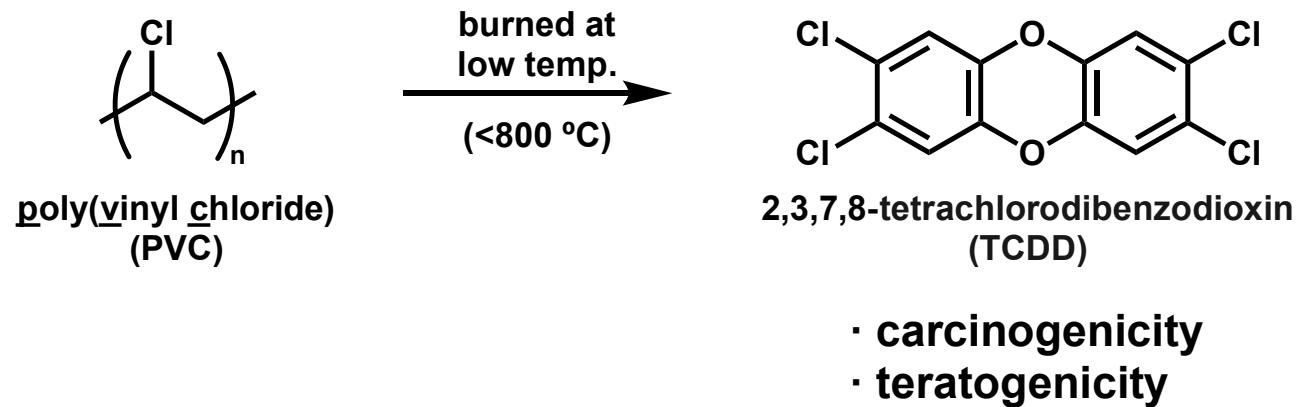


Expanded PS  
(EPS)

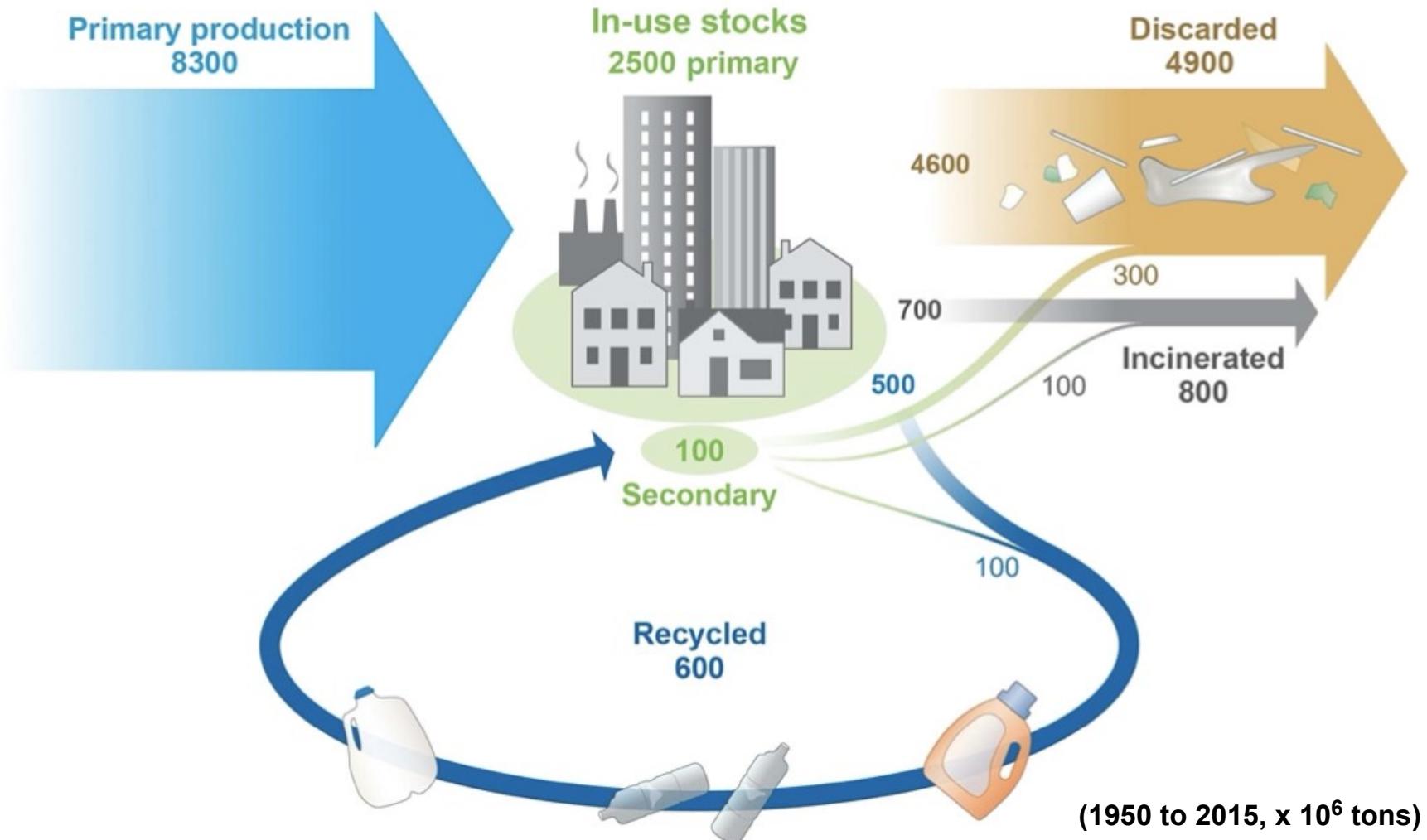
- High impact resistance
- High thermal Insulation Performance



# Problems of Synthetic Plastics (1)



# Problems of Synthetic Plastics (2)

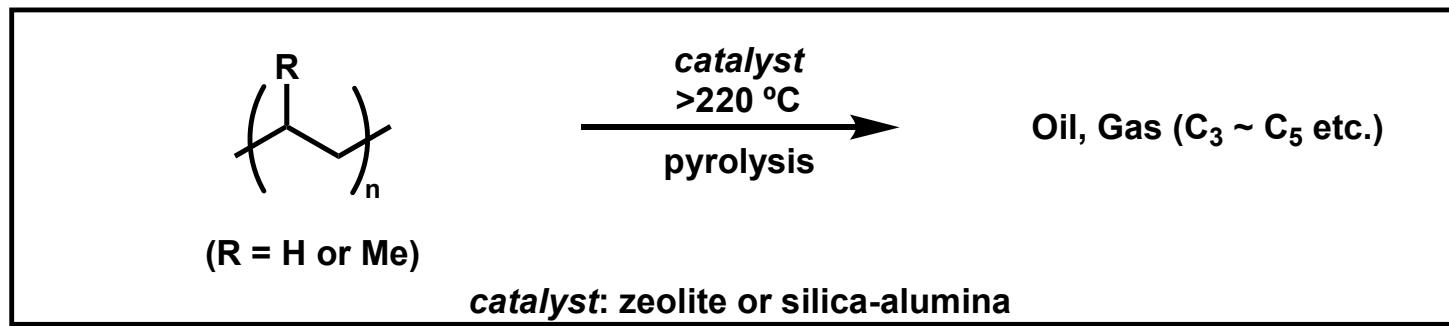


1) Geyer, R.; Jambeck, J. R.; Law, K. L. *Sci. Adv.* **2017**, 3, e1700782.

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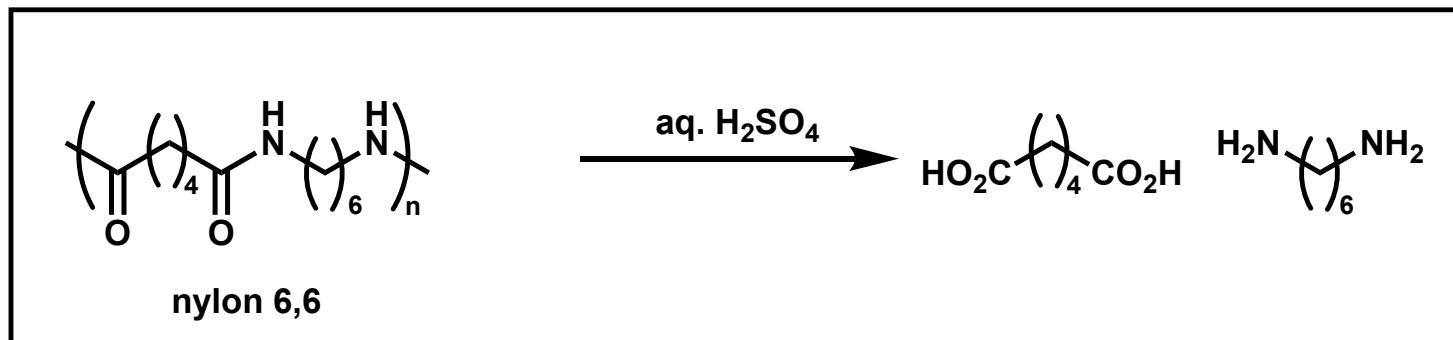
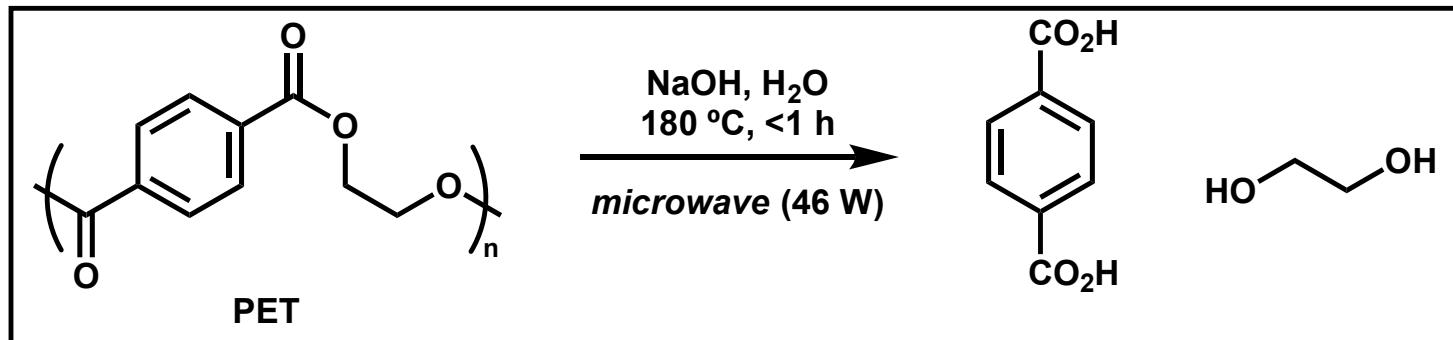
# Pyrolysis of Polyethylene and Polypropylene



- High temperature and high cost

1) Miao, Y.; von Jouanne, A.; Yokochi, A. *Polymers*, **2021**, *13*, 449.

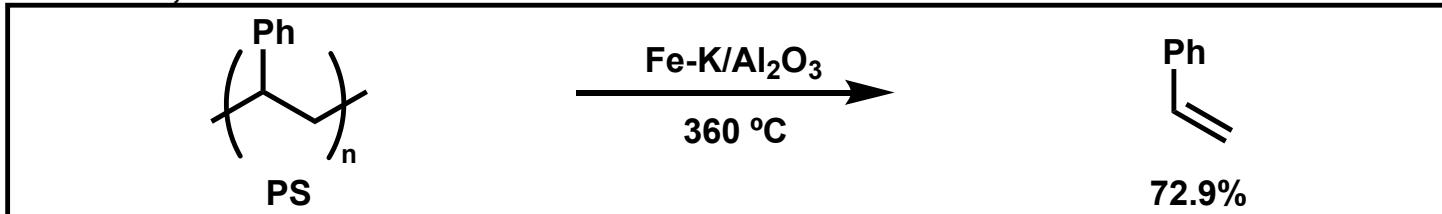
# Hydrolysis of PET and Nylon 6,6



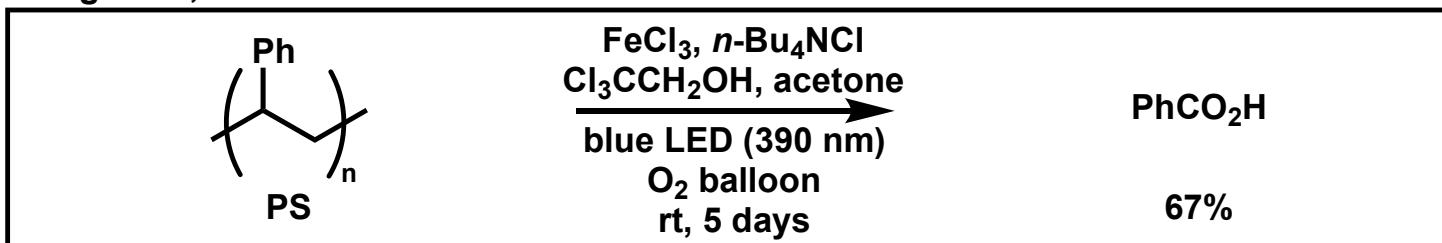
- 
- 1) Siddiqui, M. N.; Achilias, D. S.; Redhwi, H. H.; Bikaris, D. N.; Katsogiannis, K.-A. G.; Karayannidis, G. P. *Macromol. Mater. Eng.* **2010**, 295, 575.  
2) Dimitris, S.; Achilias, L. *Material Recycling - Trends and Perspectives* **2012**, 3, 64.

# Previous Chemical Recycling of PS

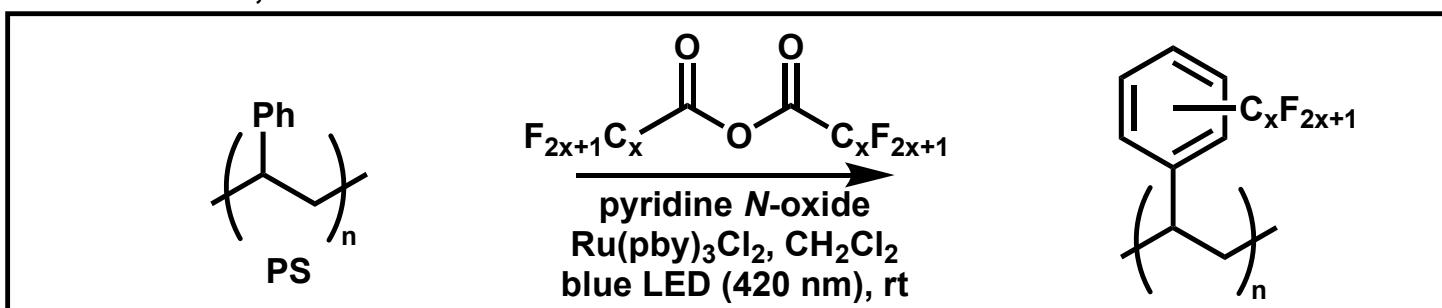
Kim et al., 2003



Zeng et al., 2021



Leibfarth et al., 2019



- 1) Kim, J.-S.; Lee, W.-Y.; Lee, S.-B.; Kim, S.-B.; Choi, M.-J. *Catal. Today* **2003**, *87*, 59.
- 2) Zhang, G.; Zhang, Z.; Zeng, R. *Chin. J. Chem.* **2021**, *39*, 3225.
- 3) Lewis, S. E.; Wilhelmy, B. E.; Leibfarth, F. A. **2019**, *10*, 6270.

# **Contents**

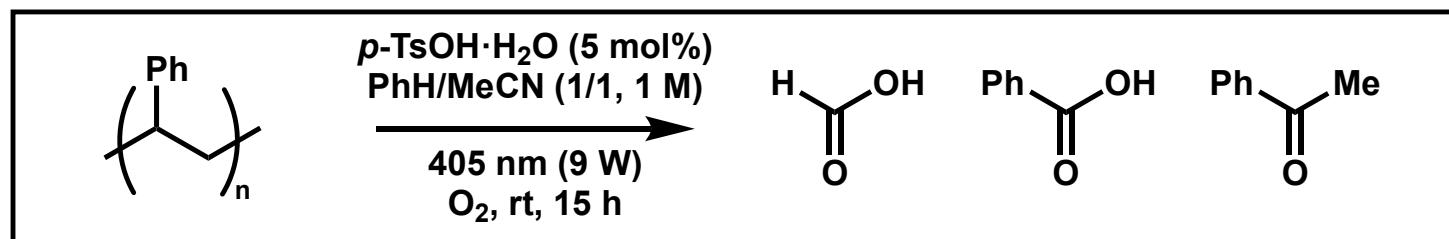
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# **Prof. Xiao**



- 1982 B.S. @ the Northwest University**
- ~1992 Ph.D @ the University of Alberta**
- 1992 Postdoctoral Fellow**  
**(Prof. Richard J. Puddephatt)**
- 1994 Joined the ERATO Molecular Catalyst Project (Prof. Noyori)**
- 1996 Principal Scientist**  
**@ the University of Liverpool**
- 2005 Professor @ the University of Liverpool**

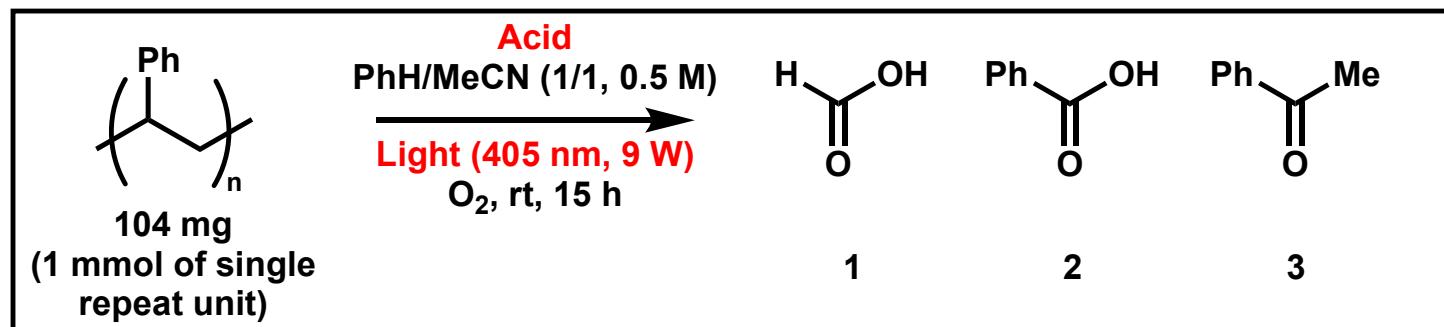
# Chemical Recycling of Polystyrene by Xiao's Group



- Low cost · Mild reaction conditions
- Green chemistry · High selectivity
- Commodity chemicals were obtained.

1) Huang, Z.; Shanmugam, M.; Liu, Z.; Brookfield, A.; Bennett, E. L.; Guan, R.; Herrera, D. E. V.; Lopez-Sanchez, J. A.; Slater, A. G.; McInnes, E. J. L.; Qi, X.; Xiao, J. *J. Am. Chem. Soc.* **2022**, DOI: 10.1021/jacs.2c01410. 12

# Necessity of Acid-catalyst and Light



Entry	Acid (mol%) <sup>b</sup>	Solvent	Yield [%] <sup>b,c</sup>		
			1	2	3
1	HOTf (5)	benzene/CH <sub>3</sub> CN (1/1)	72	40	2
2	-	benzene/CH <sub>3</sub> CN (1/1)	0	0	0
3 <sup>d</sup>	HOTf (5)	benzene/CH <sub>3</sub> CN (1/1)	0	0	0
4 <sup>e</sup>	HOTf (5)	benzene/CH <sub>3</sub> CN (1/1)	70	40	2
5 <sup>f</sup>	HOTf (5)	benzene/CH <sub>3</sub> CN (1/1)	7	2	<1

<sup>b</sup>) based on the single repeat unit (1 mmol) of PS

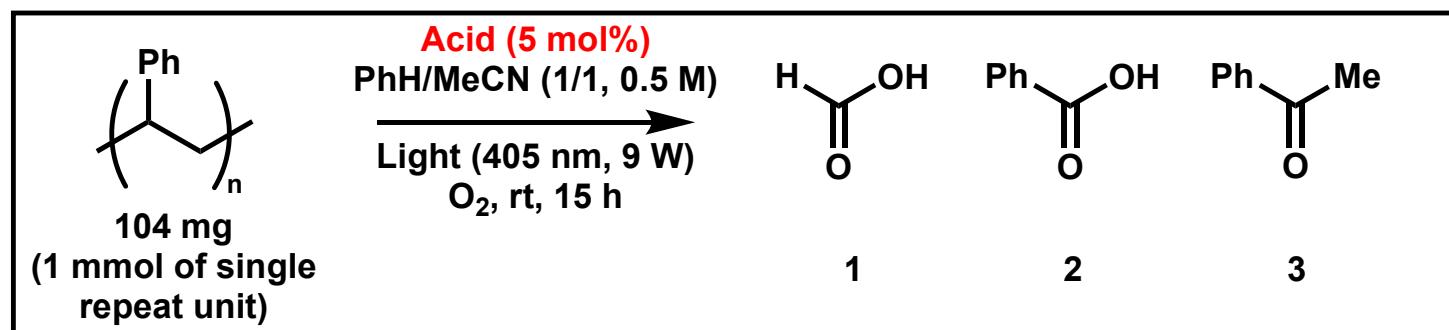
<sup>c</sup>) NMR yield (internal standard: 1,3,5-trimethoxybenzene)

<sup>d</sup>) without light

<sup>e</sup>) The light (365 nm) was used.

<sup>f</sup>) The light (475 nm) was used.

# Optimization of Acid-catalyst

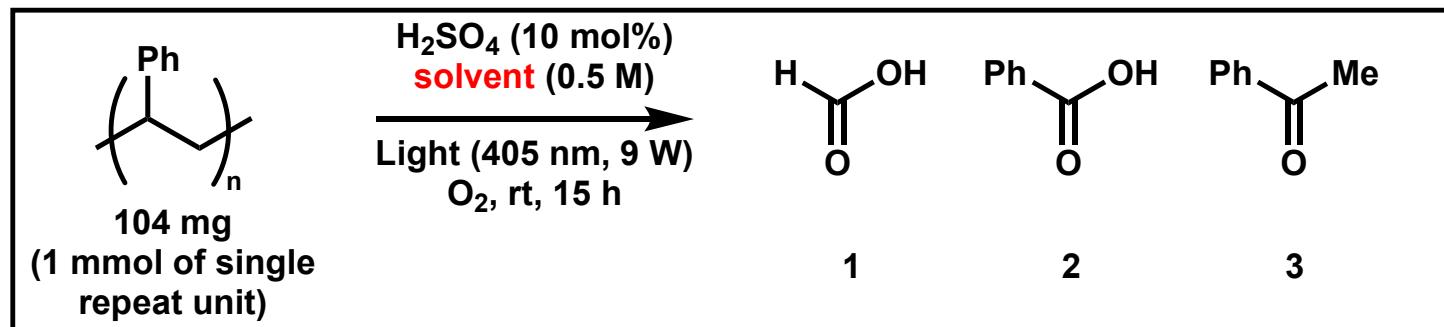


Entry	Acid (mol%) <sup>b</sup>	Solvent	Yield [%] <sup>b,c</sup>		
			1	2	3
6	CF <sub>3</sub> COOH (5)	benzene/CH <sub>3</sub> CN (1/1)	0	0	0
7	CH <sub>3</sub> SO <sub>3</sub> H (5)	benzene/CH <sub>3</sub> CN (1/1)	78	35	2
8	HNO <sub>3</sub> (5)	benzene/CH <sub>3</sub> CN (1/1)	3	2	<1
9	H <sub>2</sub> SO <sub>4</sub> (5)	benzene/CH <sub>3</sub> CN (1/1)	69	40	2
17	pTsOH • H <sub>2</sub> O (5)	benzene/CH <sub>3</sub> CN (1/1)	74	43	2
27 <sup>i</sup>	Sc(OTf) <sub>3</sub> (5)	benzene/CH <sub>3</sub> CN (1/1)	38	18	2
28 <sup>i</sup>	La(OTf) <sub>3</sub> (5)	benzene/CH <sub>3</sub> CN (1/1)	24	24	2
29 <sup>i</sup>	Zn(OTf) <sub>2</sub> (5)	benzene/CH <sub>3</sub> CN (1/1)	0	0	0
30 <sup>i</sup>	CeCl <sub>3</sub> (5)	benzene/CH <sub>3</sub> CN (1/1)	0	0	0

<sup>b)</sup> based on the single repeat unit (1 mmol) of PS

<sup>c)</sup> NMR yield (internal standard: 1,3,5-trimethoxybenzene)    <sup>i)</sup> PhH/MeCN (1/1, 1 M)

# Solvent Effect

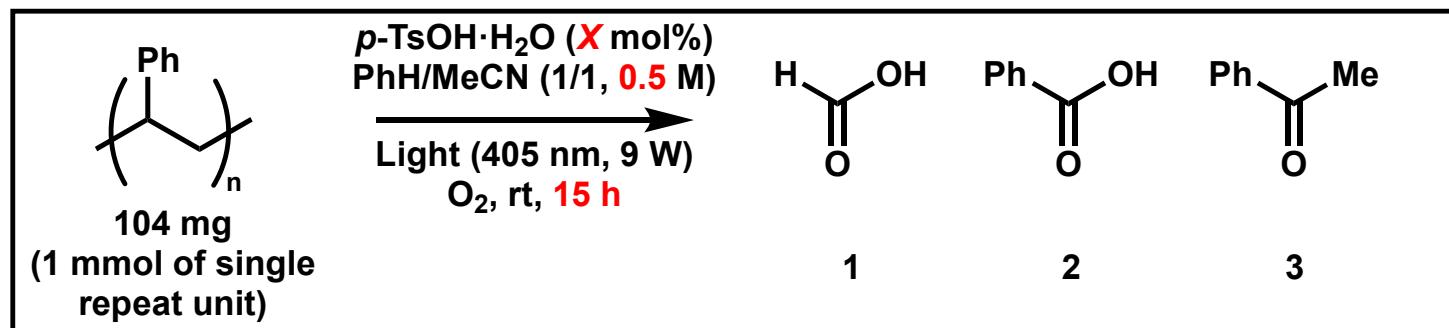


Entry	Acid (mol%) <sup>b</sup>	Solvent	Yield [%] <sup>b,c</sup>		
			1	2	3
10	H <sub>2</sub> SO <sub>4</sub> (10)	benzene/CH <sub>3</sub> CN (1/1)	72	44 (43)	2
12	H <sub>2</sub> SO <sub>4</sub> (10)	benzene	0	0	0
13	H <sub>2</sub> SO <sub>4</sub> (10)	CH <sub>3</sub> CN	0	0	0
14	H <sub>2</sub> SO <sub>4</sub> (10)	acetone	0	0	0
15	H <sub>2</sub> SO <sub>4</sub> (10)	EtOAc	4	2	<1
16	H <sub>2</sub> SO <sub>4</sub> (10)	DCE	53	27	1

b) based on the single repeat unit (1 mmol) of PS

c) NMR yield (internal standard: 1,3,5-trimethoxybenzene)  
isolated yield in parentheses

# Optimization of the details



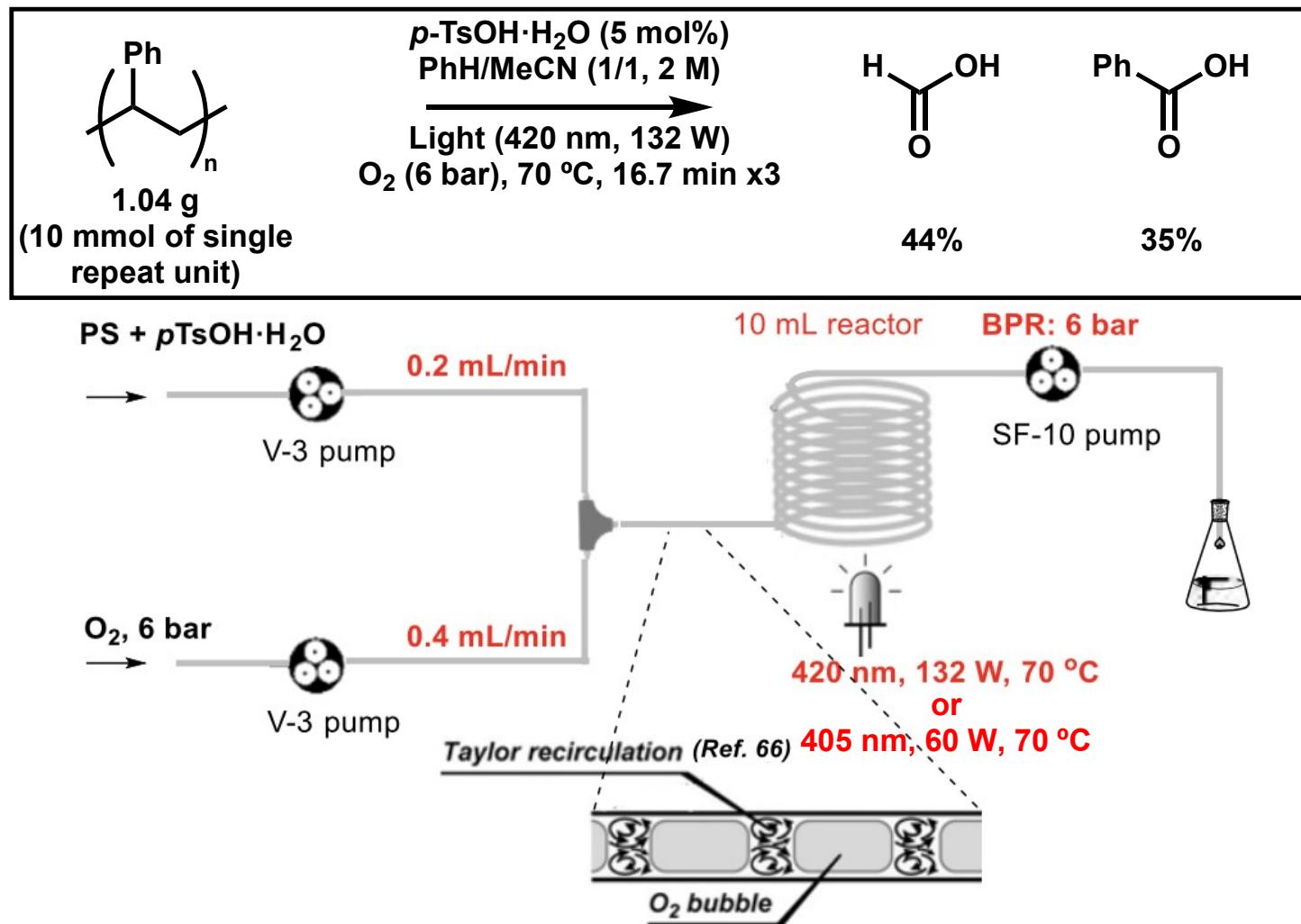
Entry	Acid (mol%) <sup>b</sup>	Solvent	Yield [%] <sup>b,c</sup>		
			1	2	3
17	<i>p</i> TsOH • H <sub>2</sub> O (5)	benzene/CH <sub>3</sub> CN (1/1)	74	43	2
18	<i>p</i> TsOH • H <sub>2</sub> O (7)	benzene/CH <sub>3</sub> CN (1/1)	63	50	2
19	<i>p</i> TsOH • H <sub>2</sub> O (10)	benzene/CH <sub>3</sub> CN (1/1)	65	52	1
20	<i>p</i> TsOH • H <sub>2</sub> O (20)	benzene/CH <sub>3</sub> CN (1/1)	51	53	1
21 <sup>g</sup>	<i>p</i> TsOH • H <sub>2</sub> O (10)	benzene/CH <sub>3</sub> CN (1/1)	58	47	1
22 <sup>h</sup>	<i>p</i> TsOH • H <sub>2</sub> O (10)	benzene/CH <sub>3</sub> CN (1/1)	49	50	1
23 <sup>i</sup>	<i>p</i> TsOH • H <sub>2</sub> O (5)	benzene/CH <sub>3</sub> CN (1/1)	67	50 (51)	2

<sup>b</sup> based on the single repeat unit (1 mmol) of PS

<sup>c</sup> NMR yield (internal standard: 1,3,5-trimethoxybenzene), isolated yield in parentheses

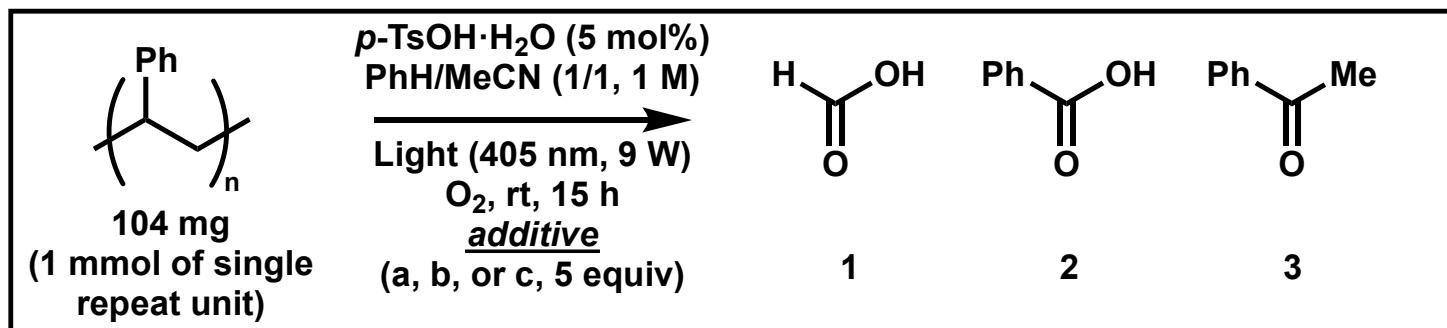
<sup>g</sup> 10 h <sup>h</sup> 24 h <sup>i</sup> PhH/MeCN (1/1, 1 M)

# Application to Flow Reaction

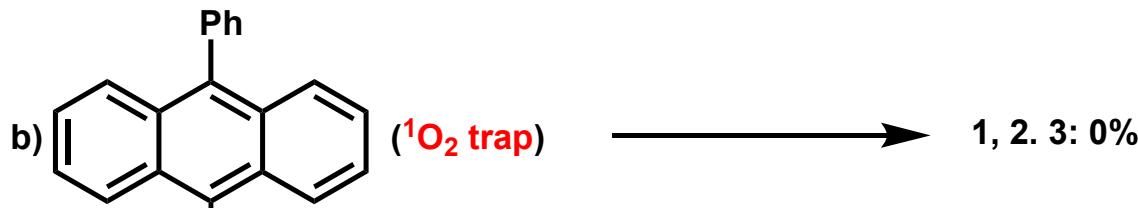


- 1) Huang, Z.; Shanmugam, M.; Liu, Z.; Brookfield, A.; Bennett, E. L.; Guan, R.; Herrera, D. E. V.; Lopez-Sanchez, J. A.; Slater, A. G.; McInnes, E. J. L.; Qi, X.; Xiao, J. *J. Am. Chem. Soc.* **2022**, DOI: 10.1021/jacs.2c01410. 17

# Analysis of the Reaction Mechanism (1)



additive: a)NaN<sub>3</sub> (<sup>1</sup>O<sub>2</sub> scavenger)



c)TEMPO (radical scavenger)

**•<sup>1</sup>O<sub>2</sub> is involved in the reaction.  
•The reaction occur via radical pathway.**



How to generate <sup>1</sup>O<sub>2</sub>?

# How to Generate $^1\text{O}_2$ ?

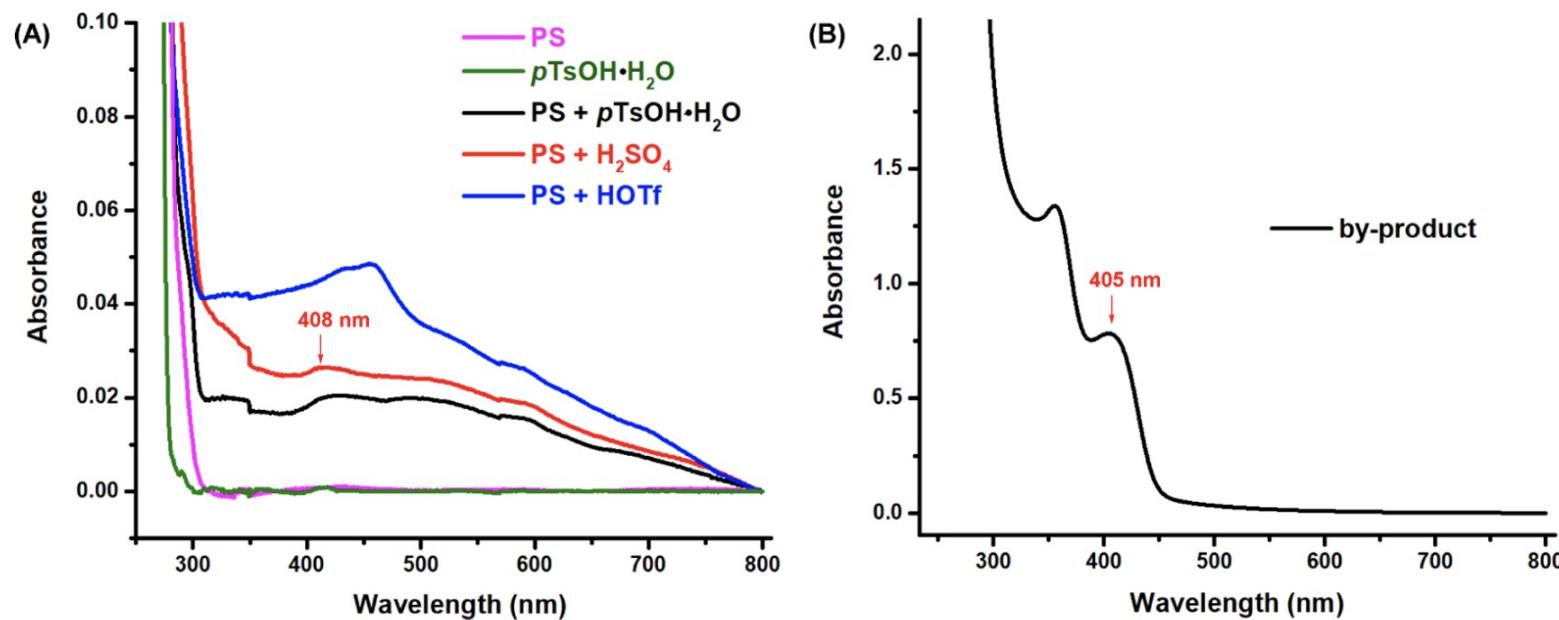
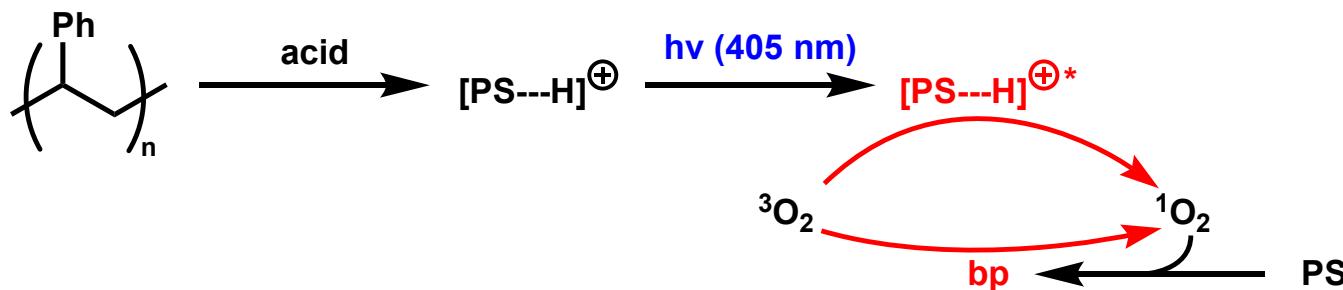
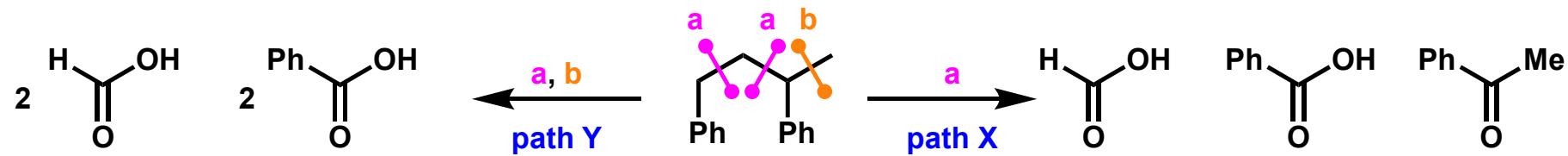
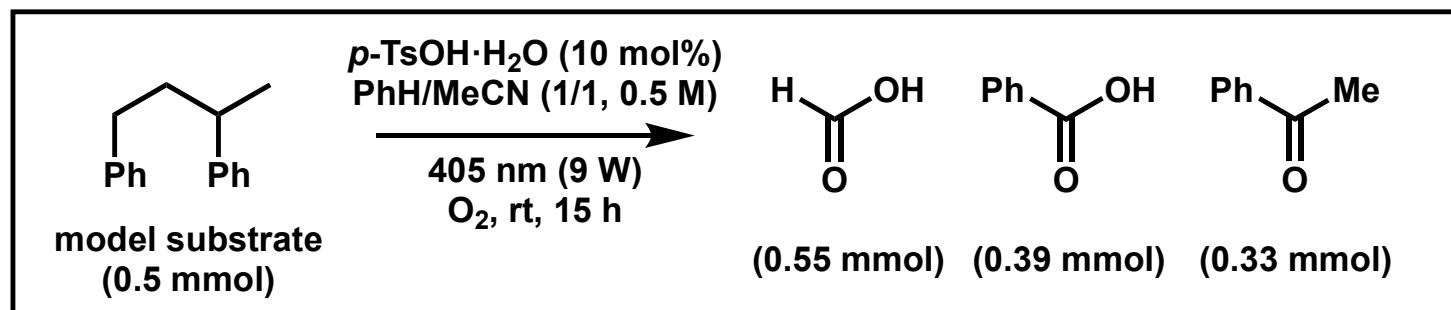
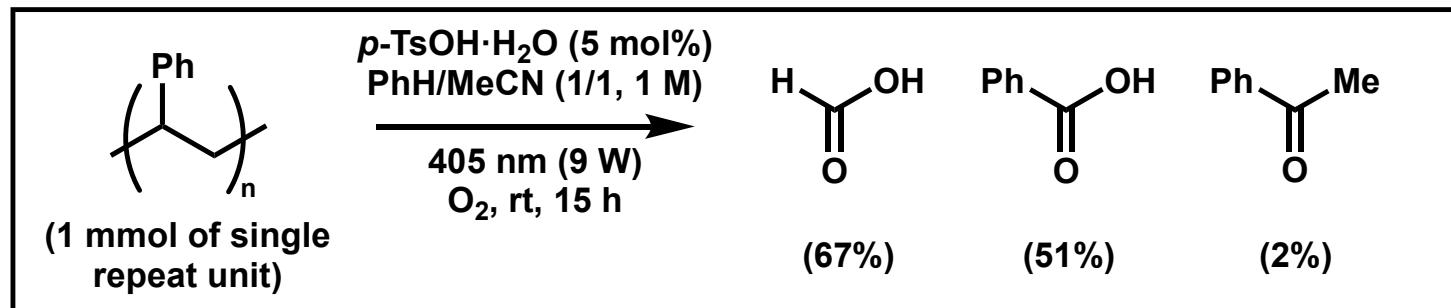


Figure 2. UV-vis spectra of PS,  $p\text{TsOH}\cdot\text{H}_2\text{O}$ , the mixture of PS and acid ( $p\text{TsOH}\cdot\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , or HOTf), and the byproduct ([PS]: 10 mM (based on single repeat unit); [acid]: 10 mM; [byproduct]: 1 mg/mL, in DCE).

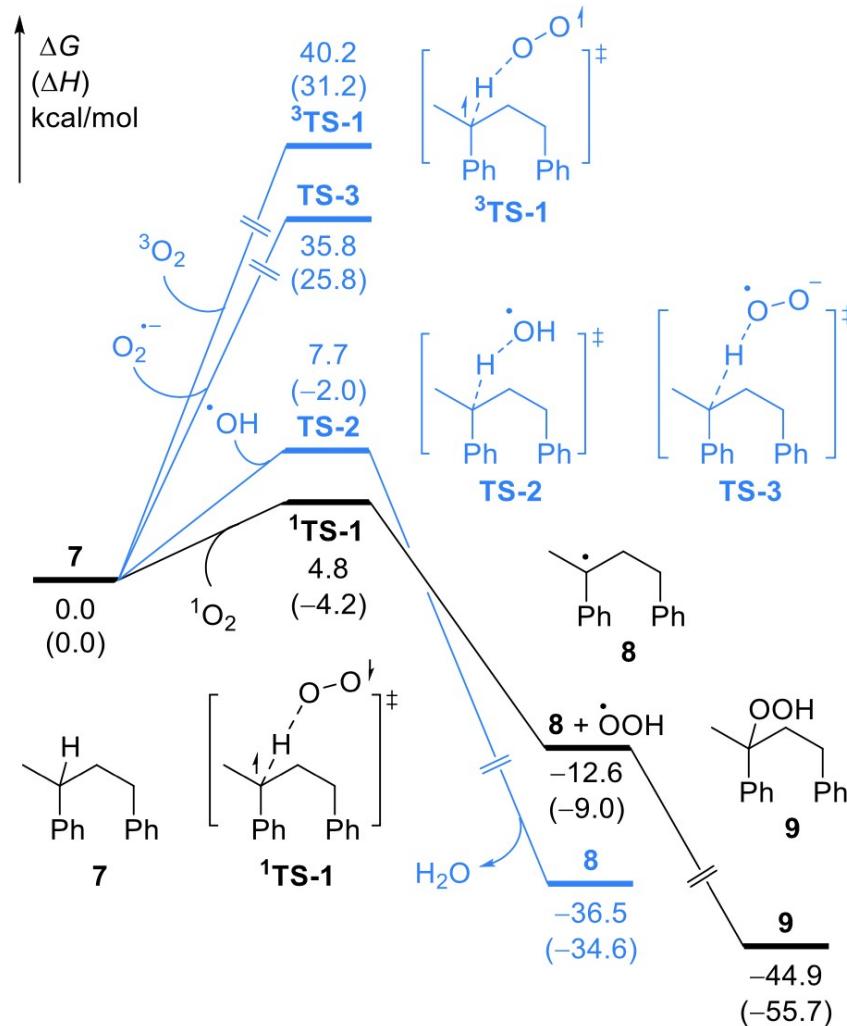


# Oxidation of 1,3-Diphenylbutane



1) Huang, Z.; Shanmugam, M.; Liu, Z.; Brookfield, A.; Bennett, E. L.; Guan, R.; Herrera, D. E. V.; Lopez-Sanchez, J. A.; Slater, A. G.; McInnes, E. J. L.; Qi, X.; Xiao, J. *J. Am. Chem. Soc.* **2022**, DOI: 10.1021/jacs.2c01410. 20

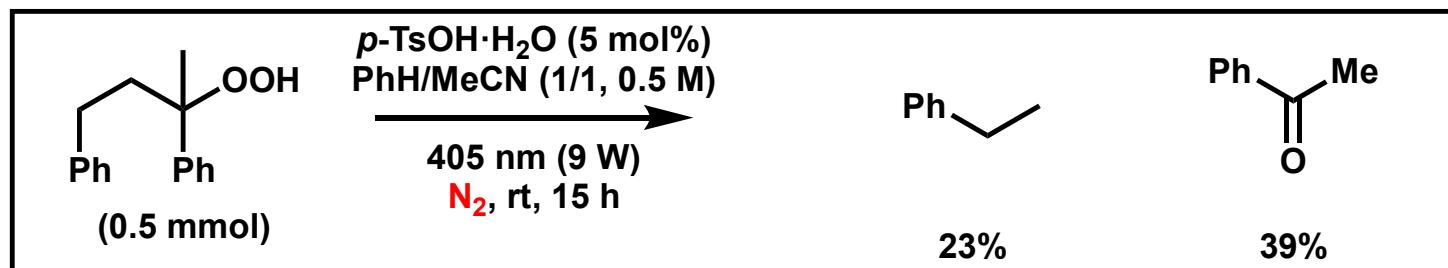
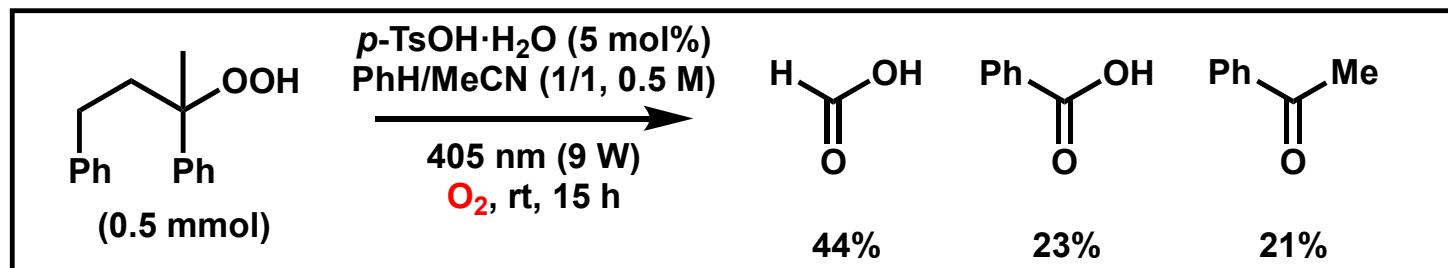
# DFT Calculation for Conformation of Peroxide



<sup>a</sup>All energies were calculated at the B3LYP-D3/6-311+G(d,p)/SMD(acetonitrile<sup>75</sup>)//B3LYP -D3/6-31G(d) level of theory.

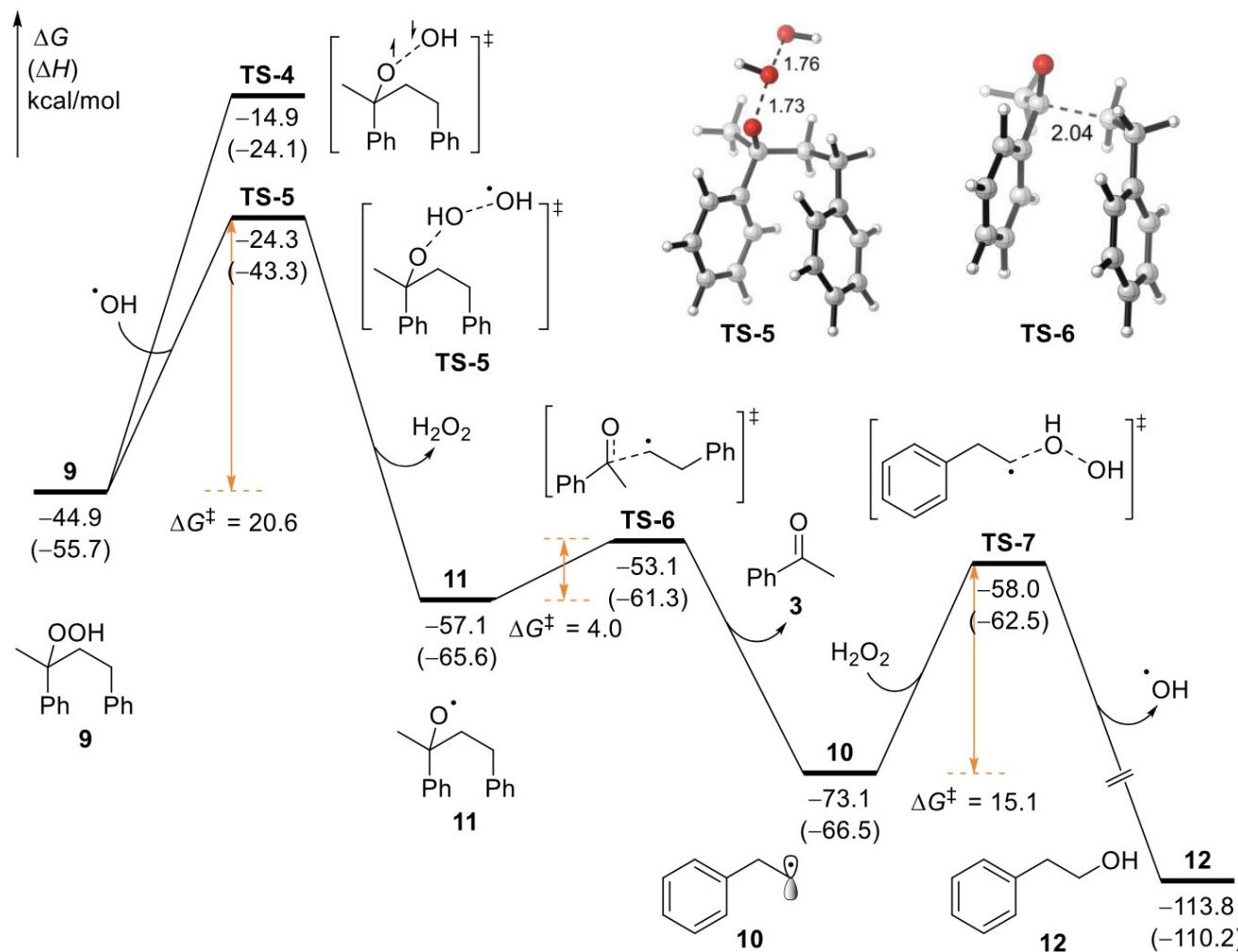
- 1) Huang, Z.; Shanmugam, M.; Liu, Z.; Brookfield, A.; Bennett, E. L.; Guan, R.; Herrera, D. E. V.; Lopez-Sanchez, J. A.; Slater, A. G.; McInnes, E. J. L.; Qi, X.; Xiao, J. *J. Am. Chem. Soc.* **2022**, DOI: 10.1021/jacs.2c01410. 21

# Decomposition of Peroxide



1) Huang, Z.; Shanmugam, M.; Liu, Z.; Brookfield, A.; Bennett, E. L.; Guan, R.; Herrera, D. E. V.; Lopez-Sanchez, J. A.; Slater, A. G.; McInnes, E. J. L.; Qi, X.; Xiao, J. *J. Am. Chem. Soc.* **2022**, DOI: 10.1021/jacs.2c01410. 22

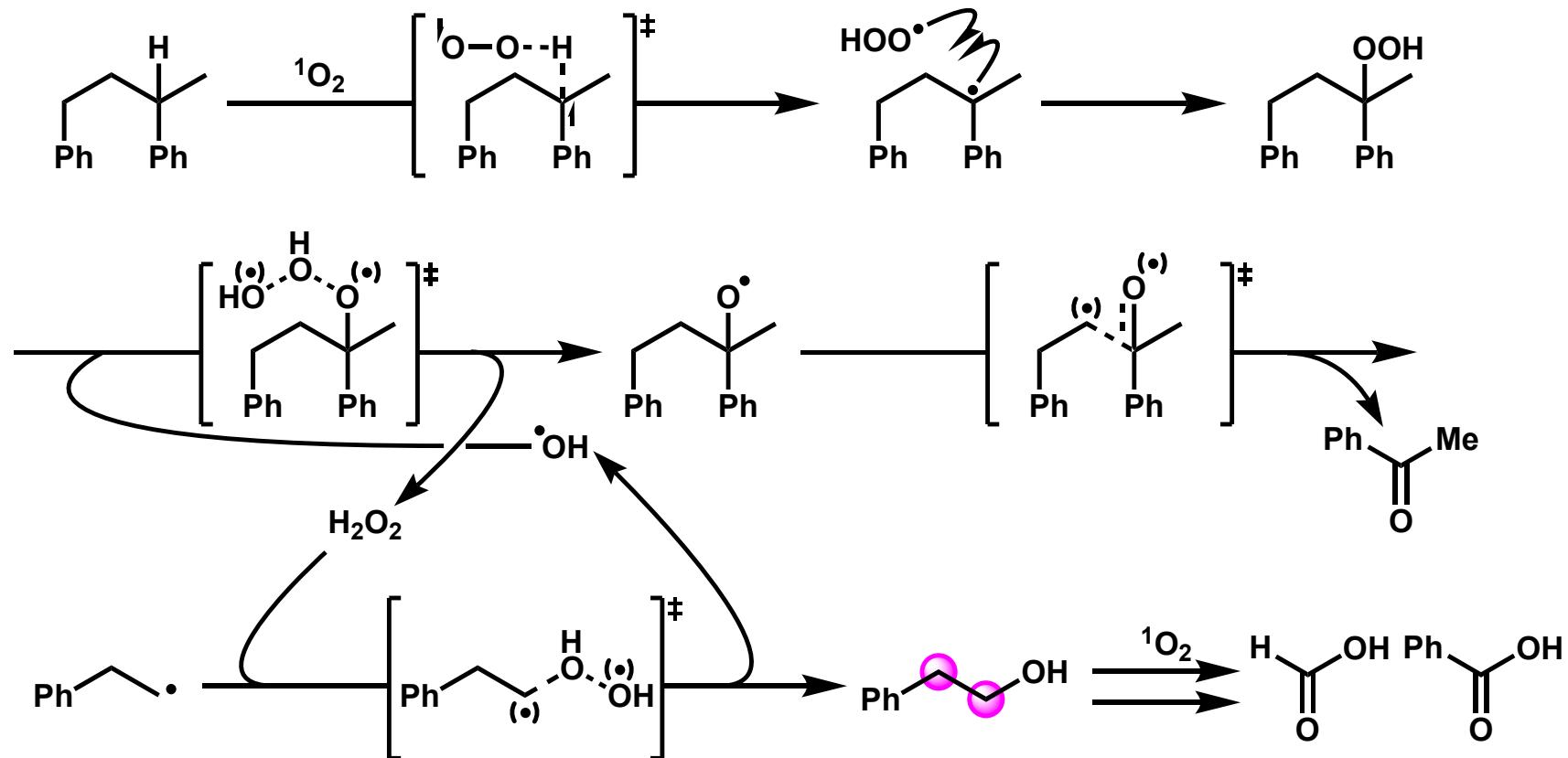
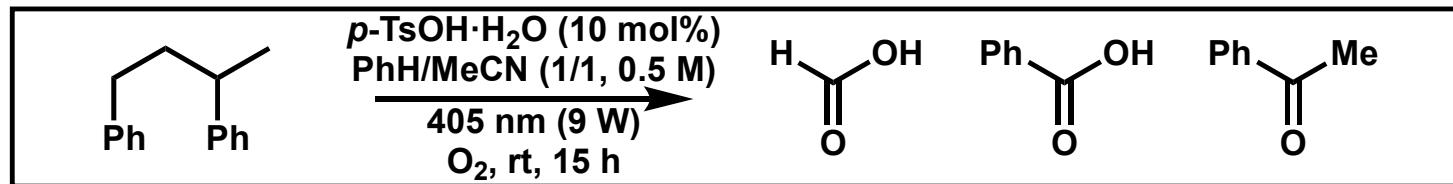
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# Reaction Mechanism

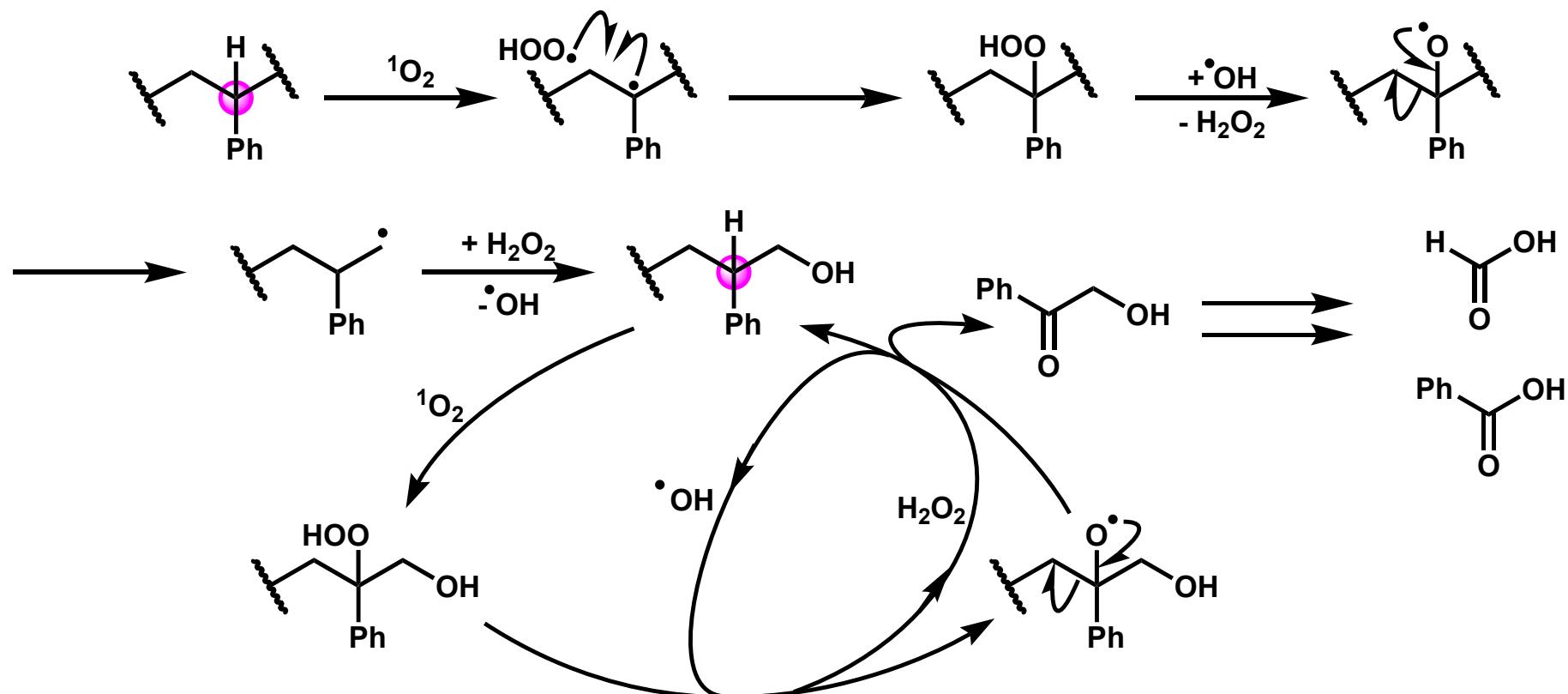
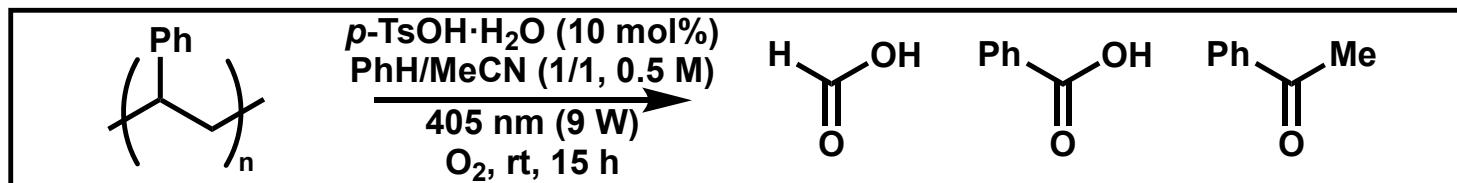
## -Oxidation of 1,3-Diphenylbutane-



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# Proposed Reaction Mechanism

## -Recycling of Polystyrene-

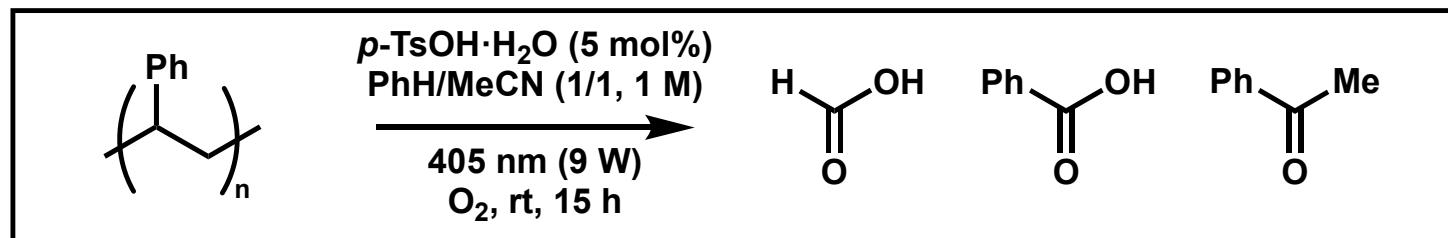


1) Huang, Z.; Shanmugam, M.; Liu, Z.; Brookfield, A.; Bennett, E. L.; Guan, R.; Herrera, D. E. V.; Lopez-Sanchez, J. A.; Slater, A. G.; McInnes, E. J. L.; Qi, X.; Xiao, J. *J. Am. Chem. Soc.* **2022**, DOI: 10.1021/jacs.2c01410. 25

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# Summary



· Low cost · Mild reaction conditions

New  ${}^1\text{O}_2$  generation mechanism

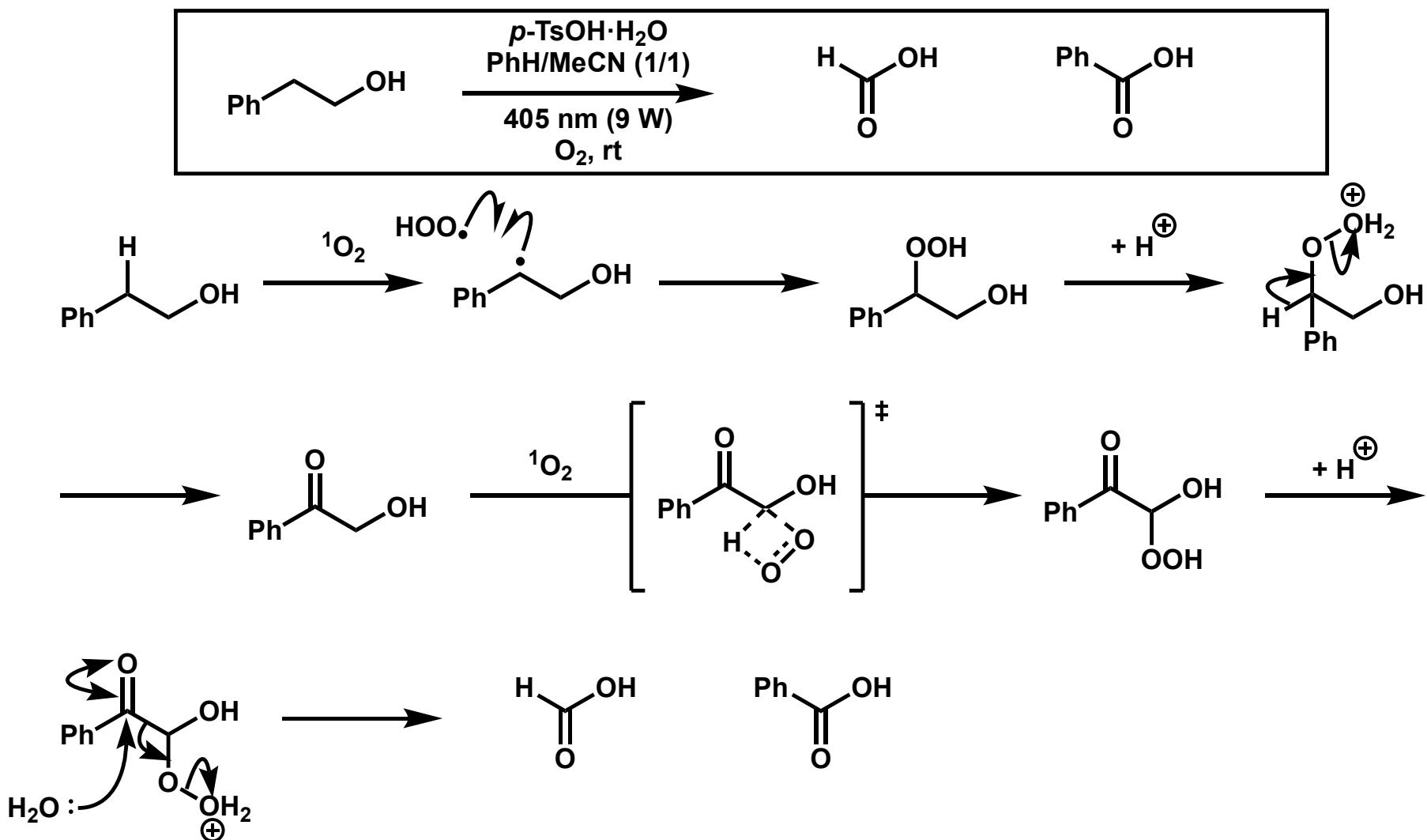


## -Remaining Tasks-

- Application to **larger scale**
- Chemical recycling of **other plastics or mixture**

# **Appendix**

# Oxidation of Phenethylalcohol



1) Sagadevan, A.; Hwang, K. C.; Su, M.-D. *Nat. Commun.* **2017**, *8*, 1812.