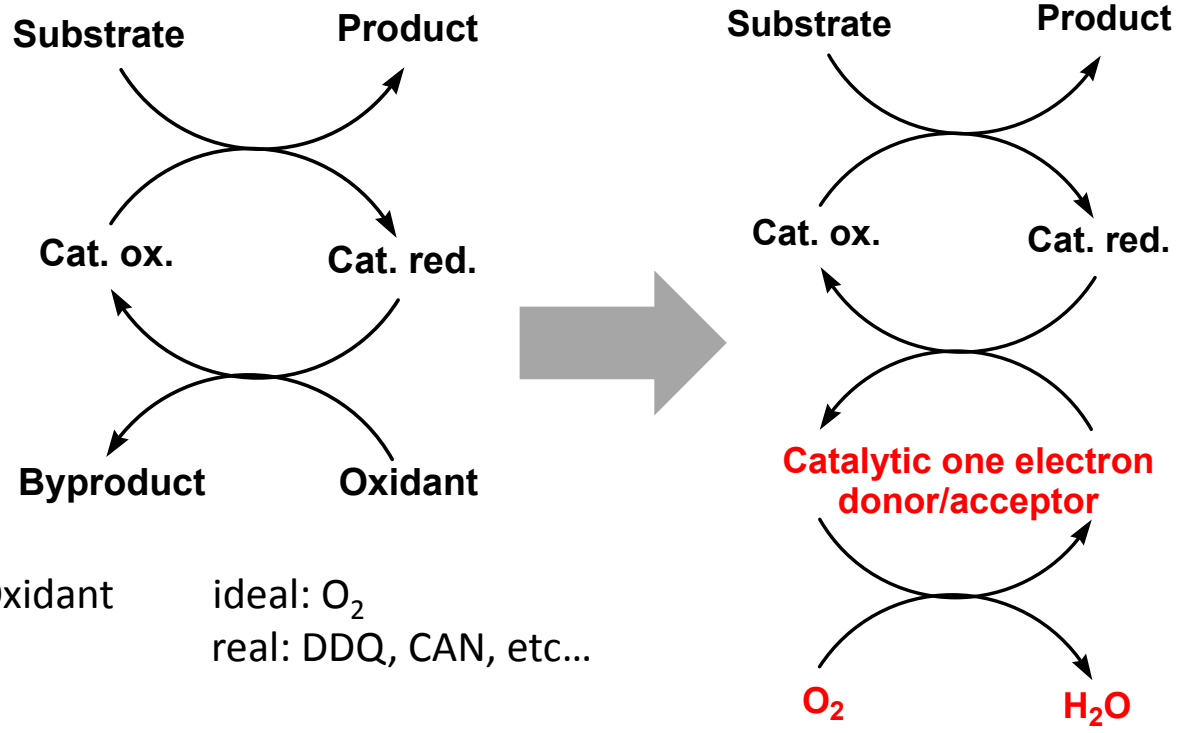
Lit. seminar

# Aerobic Catalytic Oxidative Radical Reactions

Y. Tanaka (D2)
10. 5. 19

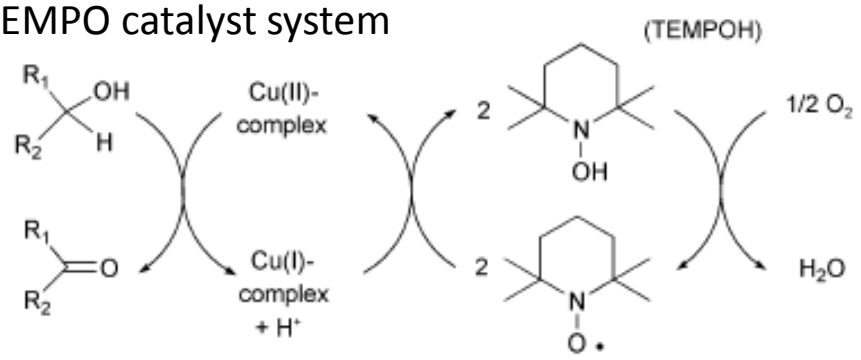
## Use of Molecular Oxygen in Catalytic Cycle



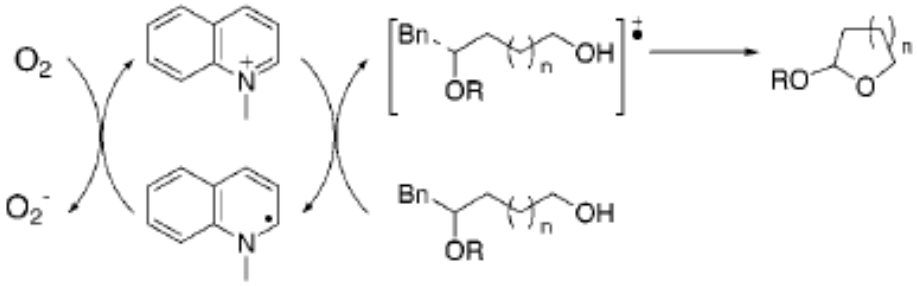

Oxidant ideal: $O_2$
real: DDQ, CAN, etc…

## Contents

1. Cu-TEMPO catalyst system

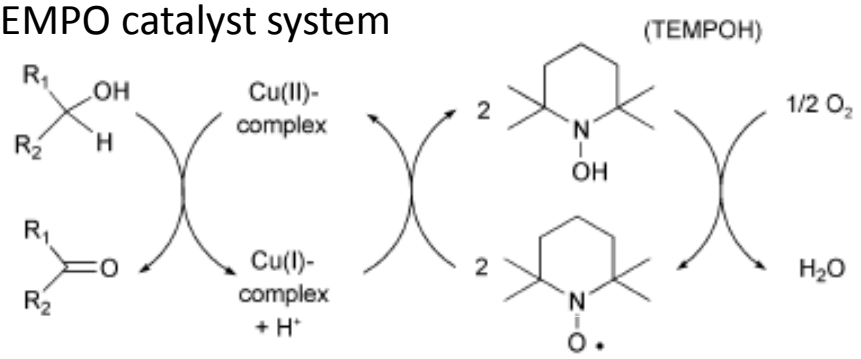



2. Organic photo catalyst system




## 1. Cu-TEMPO catalyzed Aerobic Oxidation of Alcohols

1. Cu-TEMPO catalyst system

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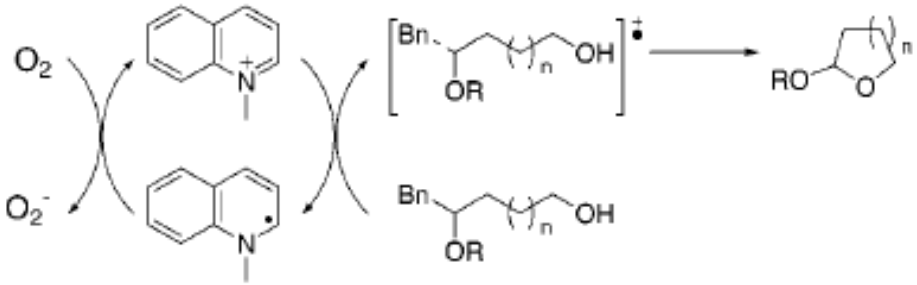


# Cu-TEMPO catalyzed Aerobic Oxidation of Alcohols

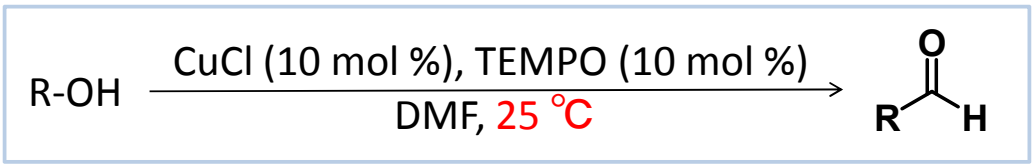
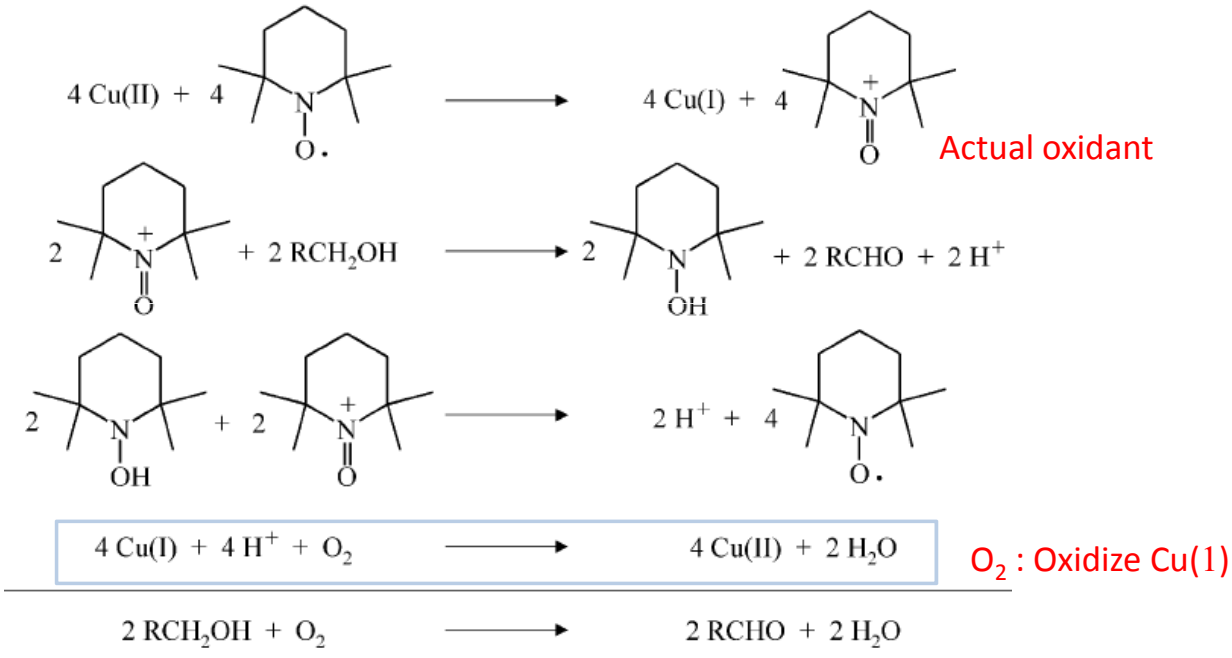



**Table I.** Conversion of Alcohols to Aldehydes with Oxygen[a]

| entry | alcohol | aldehyde | time, h | yield[b] |
|---|---|---|---|---|
| 1 | *p*-$MeOC_6H_4CH_2OH$ | *p*-$MeOC_6H_4CHO$ | 1.0 | 96% |
| 2 | *p*-$MeOC_6H_4CH_2OH$ | *p*-$MeOC_6H_4CHO$ | 24.0[c,e] | 97% |
| 3 | *p*-$MeOC_6H_4CH_2OH$ | *p*-$MeOC_6H_4CHO$ | 1.0[e,f] | 92% |
| 4 | *p*-$MeOC_6H_4CH_2OH$ | *p*-$MeOC_6H_4CHO$ | 2.0[f,g] | 91% |
| 5 | *p*-$MeOC_6H_4CH_2OH$ | *p*-$MeOC_6H_4CHO$ | 6.0[h] | 80% |
| 6 | *p*-$MeOC_6H_4CH_2OH$ | *p*-$MeOC_6H_4CHO$ | 7.0[i] | 25%[j] |
| 7 | $C_6H_5CH_2OH$ | $C_6H_5CHO$ | 4.0[k] | 94%[d] |
| 8 | *p*-$NO_2C_6H_5CH_2OH$ | *p*-$NO_2C_6H_4CHO$ | 7.0 | 85% |
| 9 | piperonyl alcohol | piperonal | 16.0[l,m] | 85% |
| 10 | (*E*)-hex-2-en-1-ol | (*E*)-2-hexenal | 1.75 | 100%[d] |
| 11 | geraniol | geranial | 1.75 | 92% |
| 12 | cinammyl alcohol | cinammaldehyde | 2.75 | 93% |
| 13 | myrtenol | myrtenal | 2.0 | 92% |
| 14 | 2-cyclohexenol | 2-cyclohexenone | 18.5[n] | 0% |

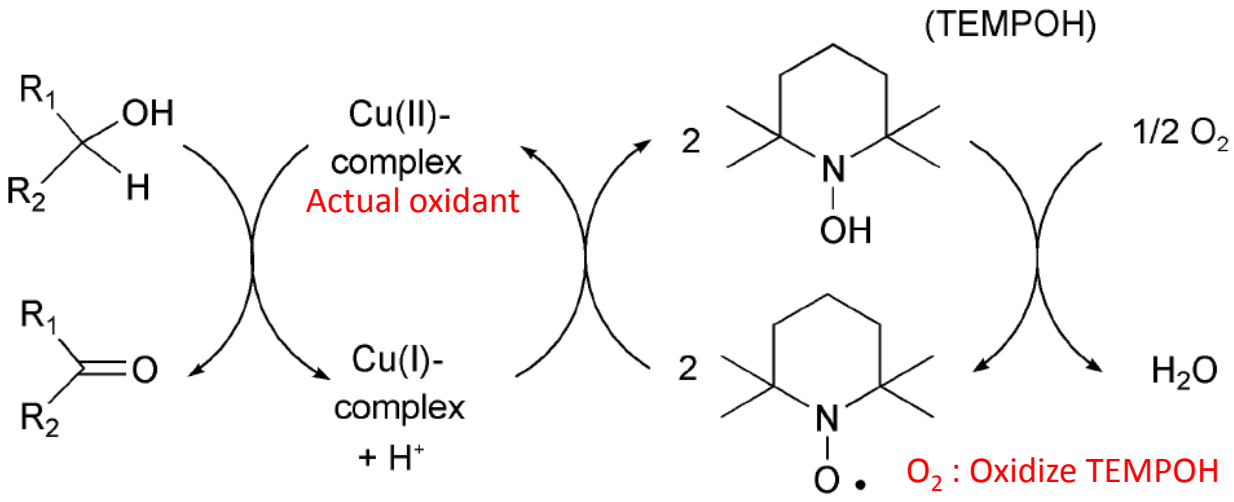
Semmelhack *et al. J. Am. Chem. Soc.* **1984**, *106*, 3376.

# Proposed Reaction Mechanism by Semmelhack



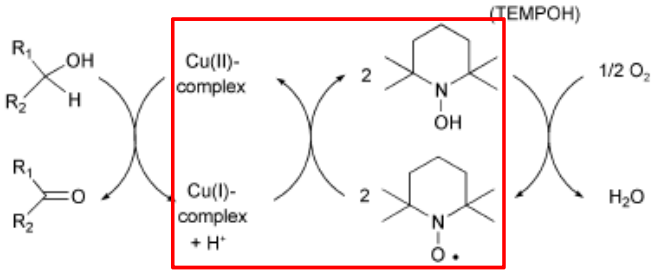

Semmelhack *et al. J. Am. Chem. Soc.* **1984**, *106*, 3376.

# Proposed Reaction Mechanism by Sheldon




Sheldon *et al. Org. Biomol. Chem.* **2003**, *1*, 3232.

# Verification of the Mechanism 1




Cu(1) + TEMPO

↓ $N_2$, rt, 24 h

Cu(2) + TEMPOH

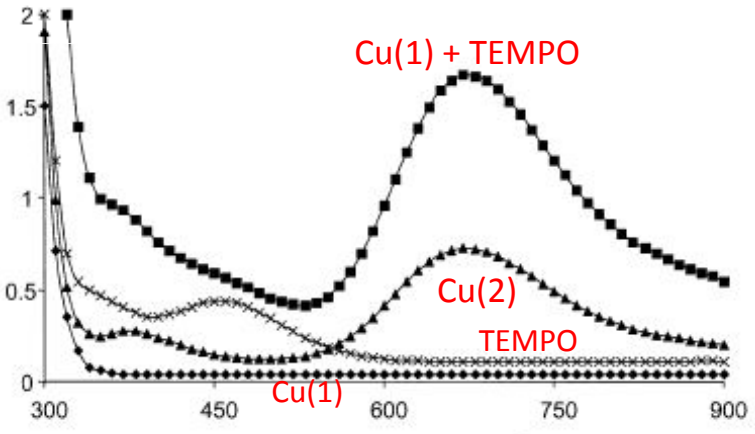
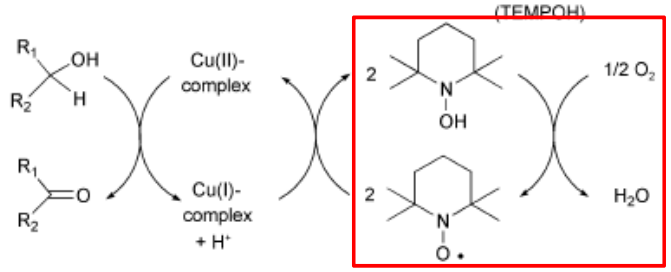
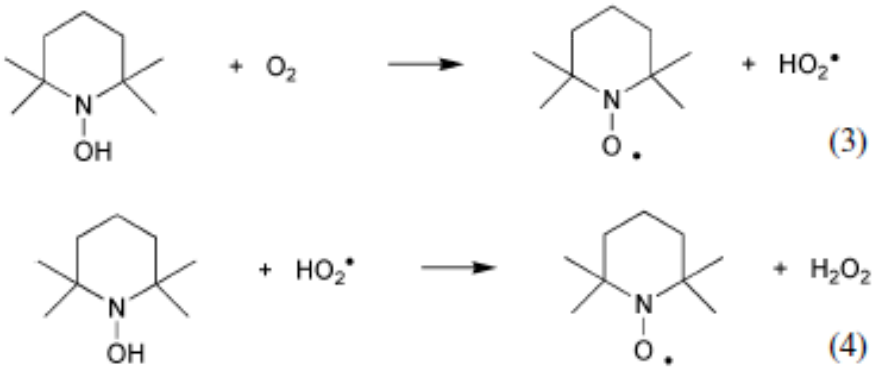



**Fig. 4** UV spectra of 2 mM solutions of $Cu^{(I)}(OAc)$–TEMPO (■), $Cu^{(II)}(OAc)_2$ (▲), TEMPO (x) and $Cu^{(I)}OAc$ (◆) in acetonitrile under an inert atmosphere.

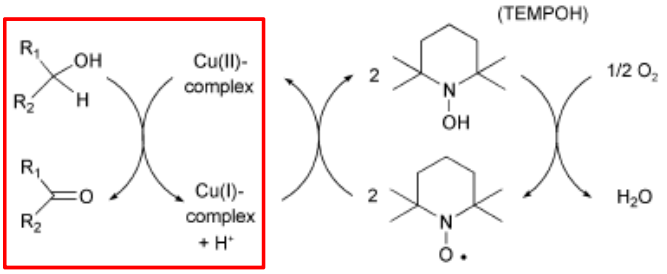
# Verification of the Mechanism 2



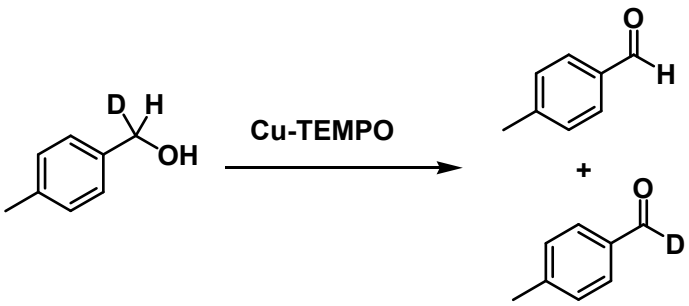

Instantaneously occur in basic $H_2O$ (checked by the color)

# Verification of the Mechanism 3




KIE Hammet → Compared with other reactions

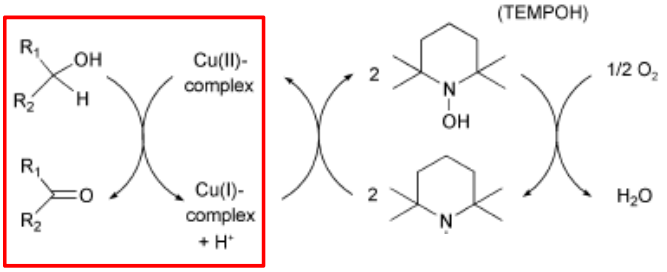
Kinetic isotope effect



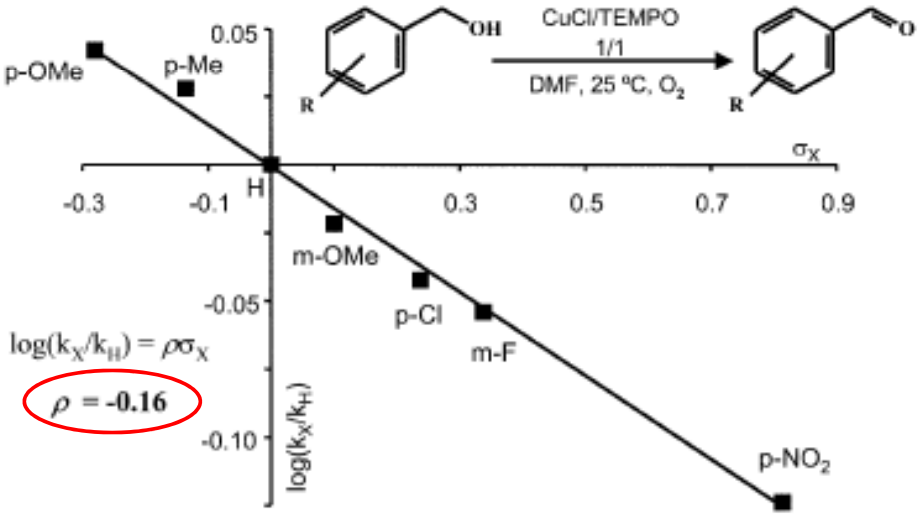

**catalytic under $O_2$: $k_H/k_D$ = 5.42**

**Stoichio. under $N_2$: $k_H/k_D$ = 5.77**

# Verification of the Mechanism 3

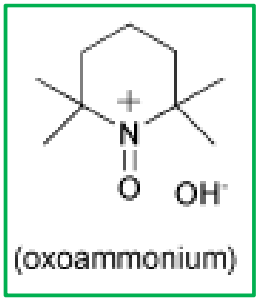


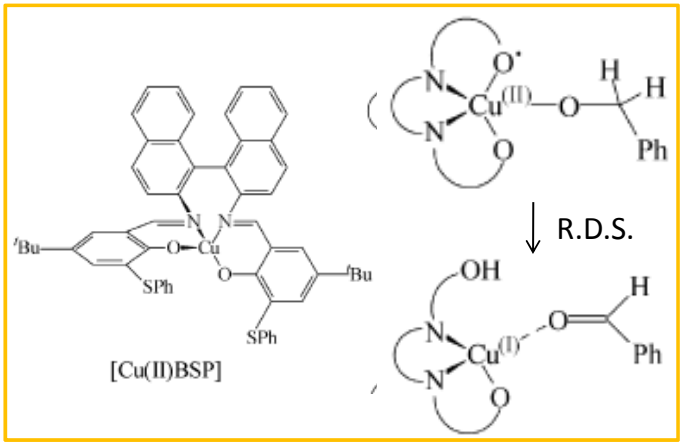

Hammett plot




# Verification of the Mechanism 3

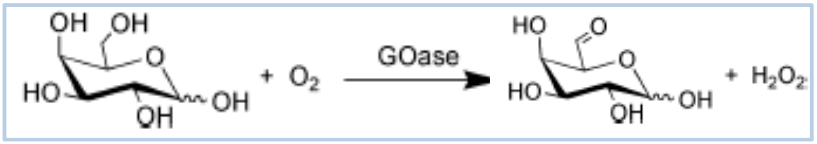
| System | Kinetic isotope effect ($k_H/k_D$)[b] | Hammett $\rho$-value |
|---|---|---|
| CuCl–TEMPO–$O_2$ | 5.42 | −0.16 |
| Oxoammonium chloride | 1.7–2.3 | −0.3 |
| $RuCl_2(PPh_3)_3$–TEMPO–$O_2$ | 5.12 | −0.58 |
| CuCl–TEMPO–$N_2$[a] | 5.77 | — |
| [Cu(II)BSP]–$O_2$ | 5.3 | −0.14 |
| Galactose oxidase | 5.02 | −0.09 |

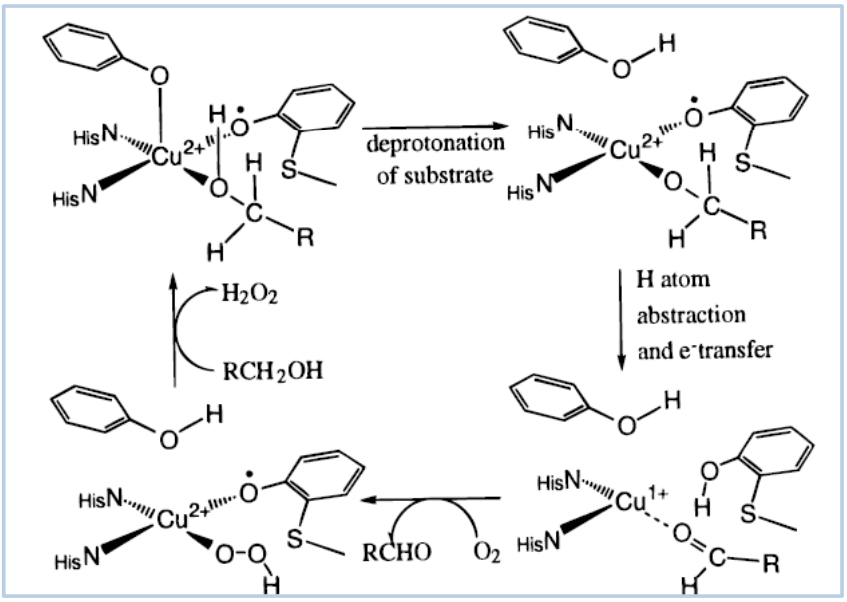


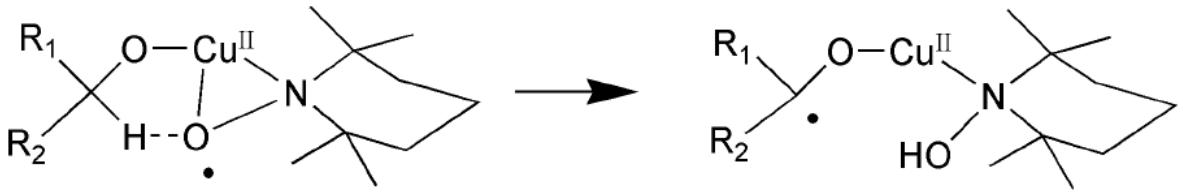
# Verification of the Mechanism 3

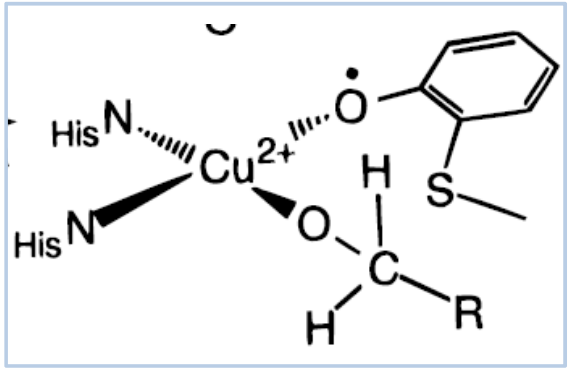
cf. Galactose oxidase

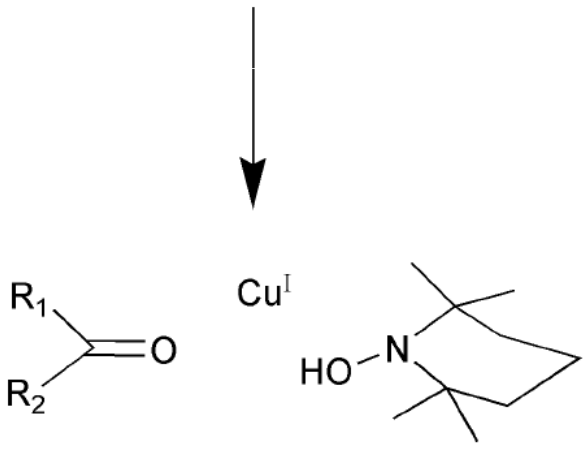



# Proposed Hydrogen Abstraction Mechanism

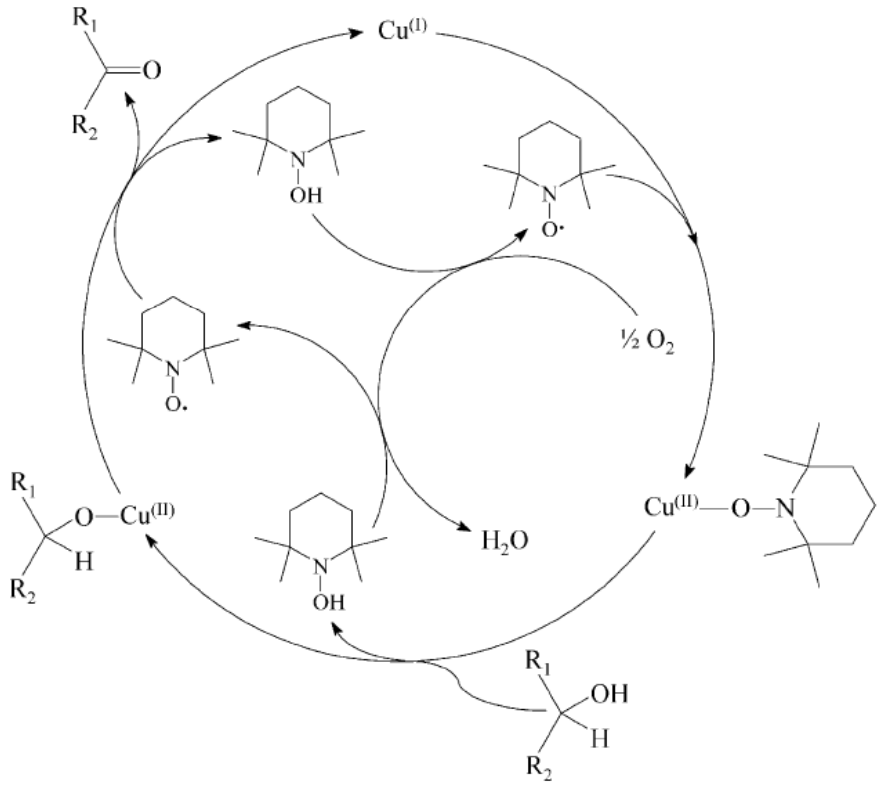




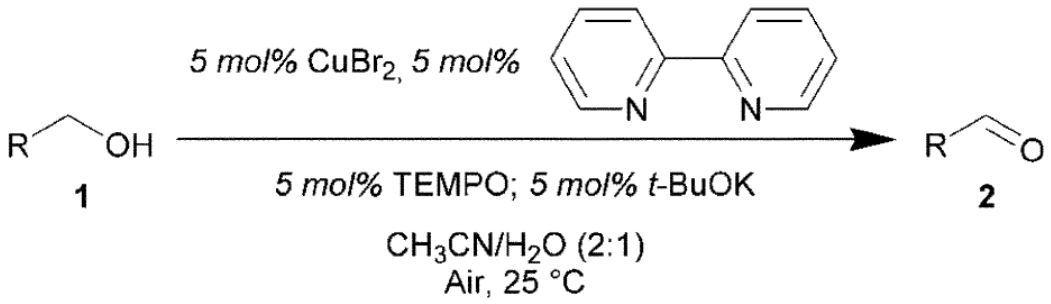


By analogy with galactose oxidase

## Proposed Catalytic Cycle




## Further Improvement through Condition Optimization

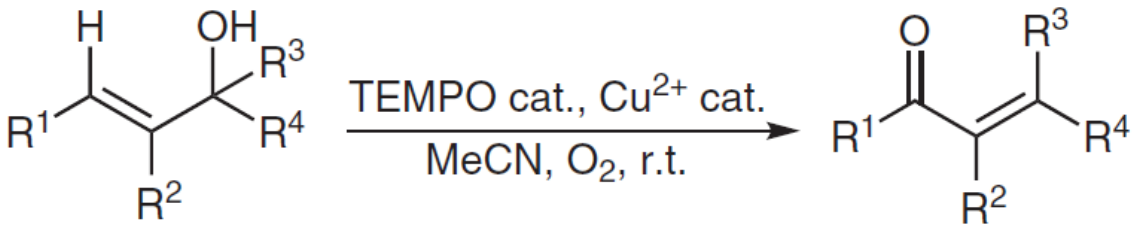



| | | | | Conversion (%) | |
|---|---|---|---|---|---|
| Entry | Bipy | TEMPO | *t*-BuOK | 0.5 h | 1.5 h |
| 1 | no | yes | yes | <1 | 6 |
| 2 | yes | no | yes | No reaction | |
| 3 | yes | yes | no | 10 | 27[b] |
| 4 | yes | yes | yes | 38 | 83[c] |

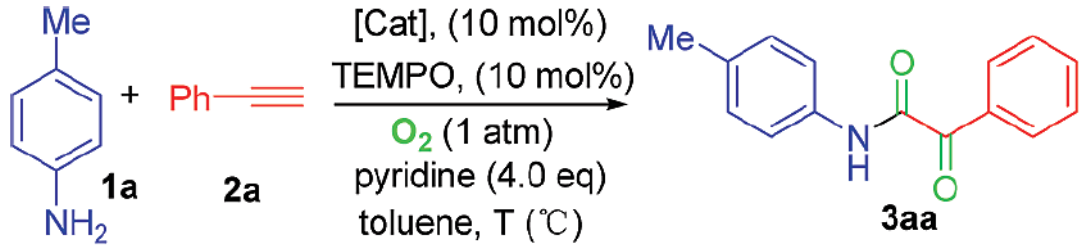
[a] Selectivity >99% based on GC. [b] 100% Conversion after 24 h. [c] 100% Conversion after 2.5 h.

Sheldon *et al. Chem. Comm.* **2003**, 2414.

## Other Examples of Cu-TEMPO Catalyzed Reactions




Vatele *SYNLETT* **2009**, *13*, 2143.

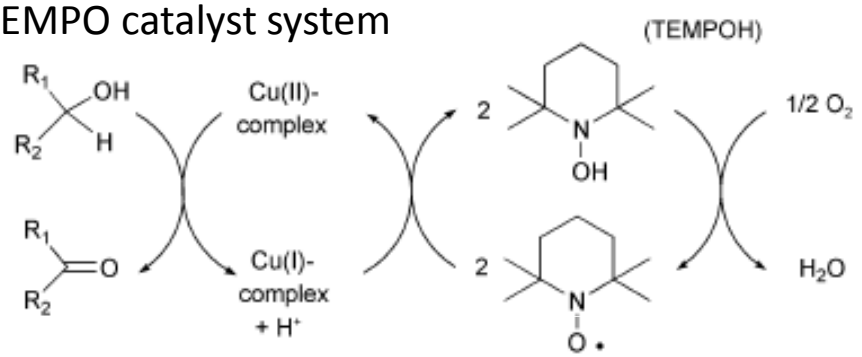



[Cat] = $CuBr_2$
T = 60 ℃

Jiao *et al. J. Am. Chem. Soc.* **2010**, *132*, 28.

## 2. Organic Photo Catalyst System

### 1. Cu-TEMPO catalyst system

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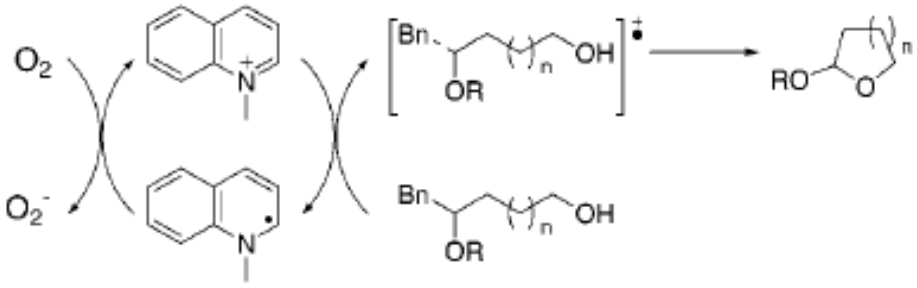
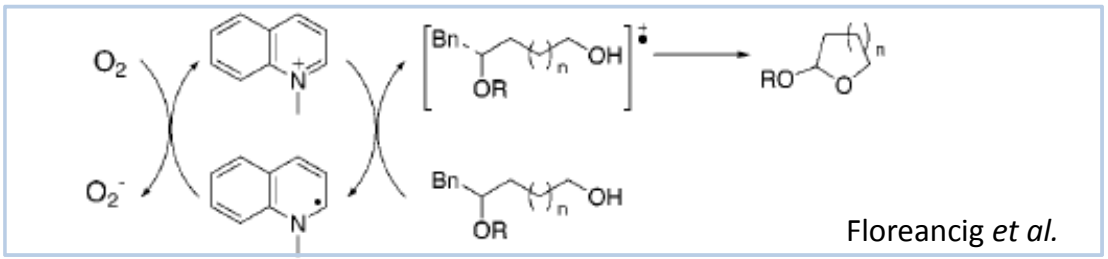
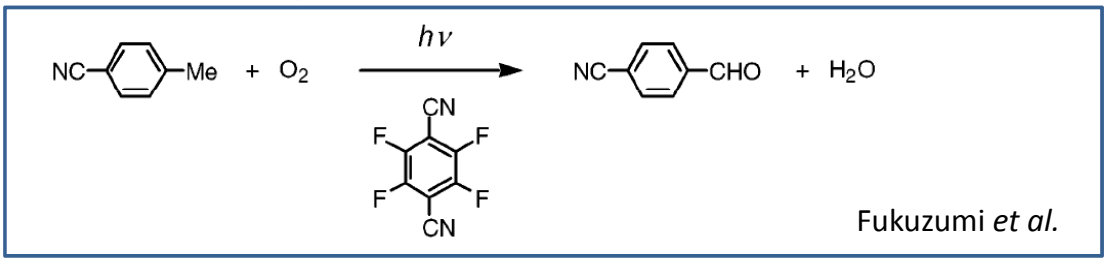
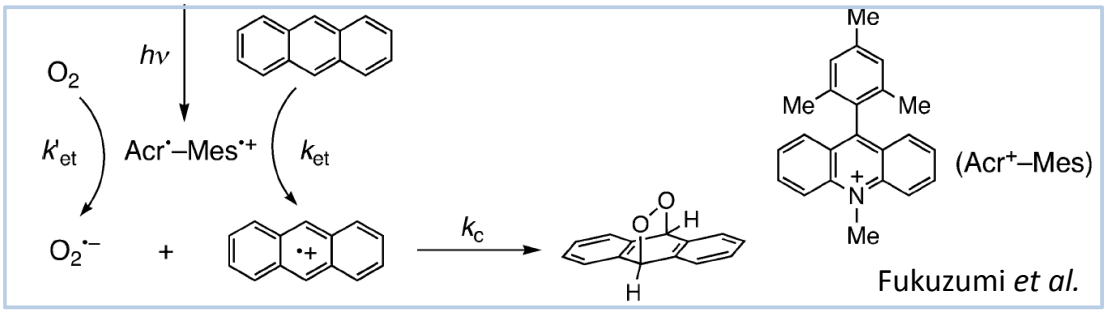


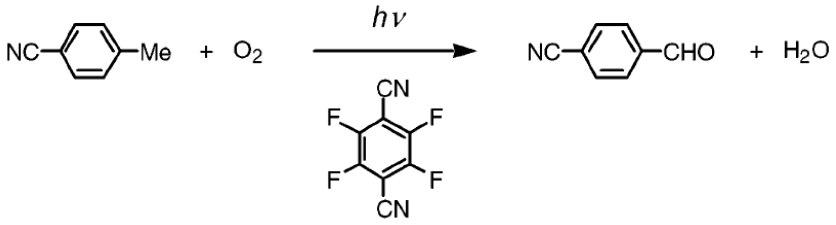
# Aerobic Photocatalytic Reactions



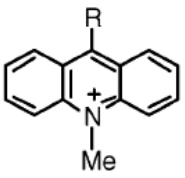




# Aerobic Oxidation of Toluene with Photo Catalyst



| | conversion | yield | |
|---|---|---|---|
| | | CHO | OHC, CHO |
| *p*-xylene | 100 % | 100 % | 0 % |
| *m*-xylene | 67 % | 99 % | 1 % |
| *o*-xylene | 70 % | 94 % | 6 % |
| toluene | 3 %[b] | 100 %[b] | |
| *p*-tolualdehyde | 0 % | | 0 % |

Conditions

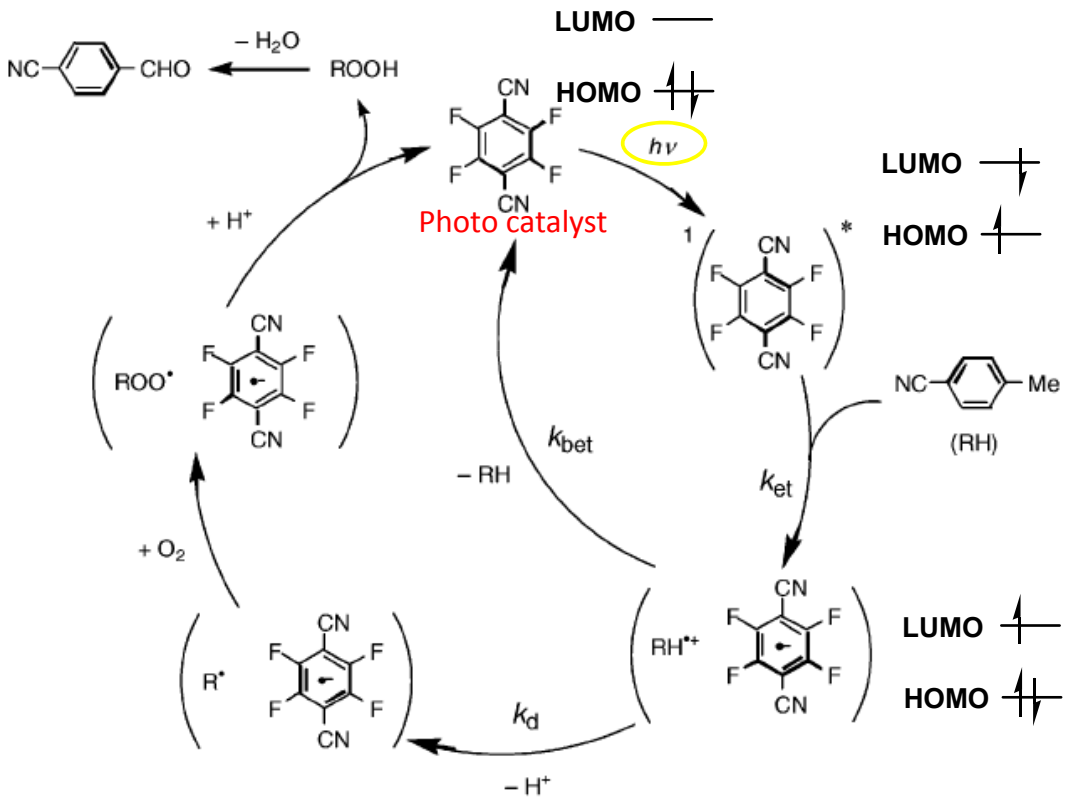


$AcrR^+$ (R = Ph) 33 mol %

$O_2$, $CHCl_3$, 25 °C

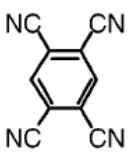
Fukuzumi *et al. J. Am. Chem. Soc.* **2003**, *125*, 12850.

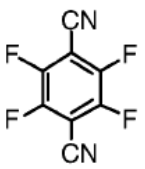
# Proposed Catalytic Cycle




# Organic Photo Catalysts

| | photosensitizer | $E^0_{red}$[a] (V) vs SCE | $E^{0*}_{red}$[b] (V) vs SCE | $\tau$[c] (ns) | $E_{00}$(S)[d] (eV) | $k_q$[e] ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 1,2,4,5-tetracyanobenzene | −0.74 | 3.17 | 4.3 | 3.81 | $1.5 \times 10^{10}$ |
| 2 | 1-methyl-3-cyanoquinolinium ion | −0.60[f] | 2.72[f] | 45[f] | 3.32[f] | $7.3 \times 10^{9}$ |
| 3 | tetrafluoro-*p*-dicyanobenzene | −1.10 | 2.66 | 3.2 | 3.76 | $4.9 \times 10^{9}$ |
| 4 | tetrafluoro-*o*-dicyanobenzene | −1.62 | 2.66 | 2.6 | 4.18 | $3.4 \times 10^{9}$ |
| 5 | tetrafluoro-*m*-dicyanobenzene | −1.33 | 2.61 | 3.9 | 3.99 | $3.3 \times 10^{9}$ |
| 6 | 1,4-dicyanobenzene | −1.46 | 2.55 | 9.7 | 4.01 | $7.4 \times 10^{8}$ |
| 7 | 1-methylquinolinium ion | −0.96[f] | 2.54[f] | 20[f] | 3.50[f] | $2.2 \times 10^{8}$ |
| 8 | 1,4-dimethylquinolinium ion | −1.07[f] | 2.51[f] | 19[f] | 3.58[f] | $1.2 \times 10^{8}$ |
| 9 | 1,2-dimethylquinolinium ion | −1.05[f] | 2.46[f] | 15[f] | 3.51[f] | $8.7 \times 10^{7}$ |
| 10 | 10-methylacridinium ion | −0.43[g] | 2.32[g] | 37[g] | 2.75[g] | *h* |
| 11 | tetrachloro-*p*-dicyanobenzene | −0.95 | 2.55 | 0.25 | 3.50 | *i* |
| 12 | tetrachloro-*m*-dicyanobenzene | *j* | | 0.20 | 3.71 | *i* |


1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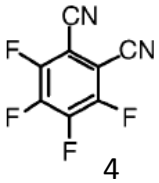
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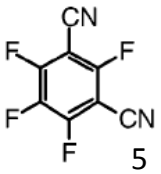
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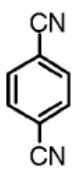
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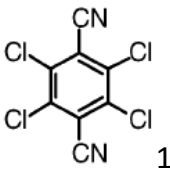
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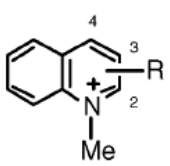
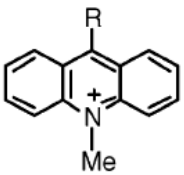
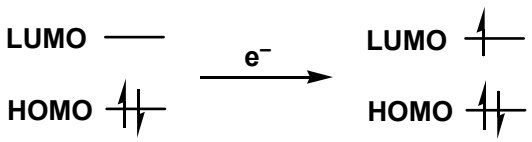

RQuH+
(R = H, 2-Me, 4-Me, 3-CN)
7 9 8 2


AcrR+
(R = H, Ph)
10

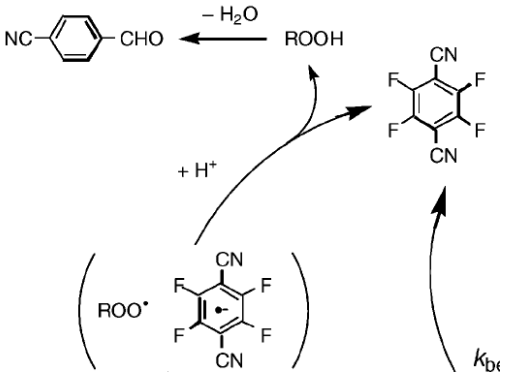
# Organic Photo Catalysts

| | photosensitizer | $E^0_{red}$[a] (V) vs SCE | $E^{0*}_{red}$[b] (V) vs SCE | $\tau$[c] (ns) | $E_{00}$(S)[d] (eV) | $k_q$[e] ($M^{-1}\,s^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 1,2,4,5-tetracyanobenzene | −0.74 | 3.17 | 4.3 | 3.81 | $1.5 \times 10^{10}$ |
| 2 | 1-methyl-3-cyanoquinolinium ion | −0.60[f] | 2.72[f] | 45[f] | 3.32[f] | $7.3 \times 10^{9}$ |
| 3 | tetrafluoro-*p*-dicyanobenzene | −1.10 | 2.66 | 3.2 | 3.76 | $4.9 \times 10^{9}$ |
| 4 | tetrafluoro-*o*-dicyanobenzene | −1.62 | 2.66 | 2.6 | 4.18 | $3.4 \times 10^{9}$ |
| 5 | tetrafluoro-*m*-dicyanobenzene | −1.33 | 2.61 | 3.9 | 3.99 | $3.3 \times 10^{9}$ |
| 6 | 1,4-dicyanobenzene | −1.46 | 2.55 | 9.7 | 4.01 | $7.4 \times 10^{8}$ |
| 7 | 1-methylquinolinium ion | −0.96[f] | 2.54[f] | 20[f] | 3.50[f] | $2.2 \times 10^{8}$ |
| 8 | 1,4-dimethylquinolinium ion | −1.07[f] | 2.51[f] | 19[f] | 3.58[f] | $1.2 \times 10^{8}$ |
| 9 | 1,2-dimethylquinolinium ion | −1.05[f] | 2.46[f] | 15[f] | 3.51[f] | $8.7 \times 10^{7}$ |
| 10 | 10-methylacridinium ion | −0.43[g] | 2.32[g] | 37[g] | 2.75[g] | *h* |
| 11 | tetrachloro-*p*-dicyanobenzene | −0.95 | 2.55 | 0.25 | 3.50 | *i* |
| 12 | tetrachloro-*m*-dicyanobenzene | *j* | | 0.20 | 3.71 | *i* |

One electron reduction potential of ground state




cf. $O_2 + e^- \longrightarrow O_2^{\bullet -}$ : –0.72 eV




# Organic Photo Catalysts

| | photosensitizer | $E^0_{red}$[a] (V) vs SCE | $E^{0*}_{red}$[b] (V) vs SCE | $\tau$[c] (ns) | $E_{00}$(S)[d] (eV) | $k_q$[e] ($M^{-1}\,s^{-1}$) |
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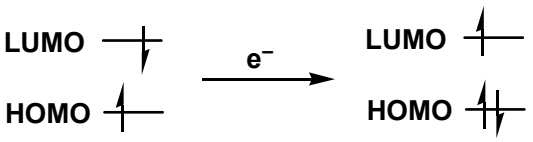
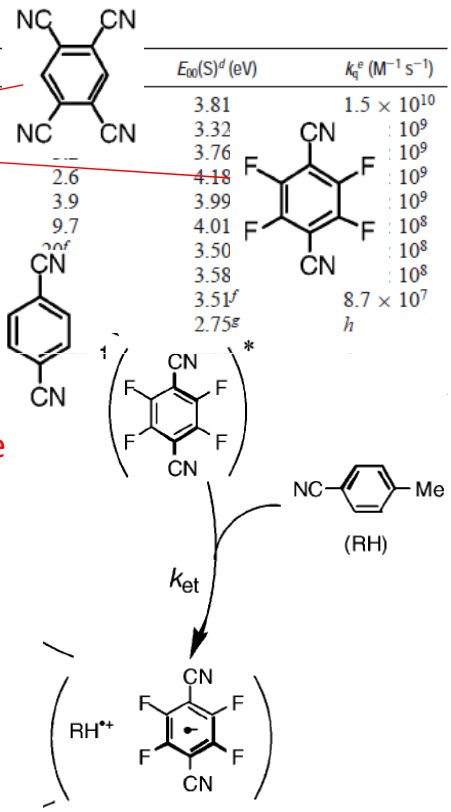
| 11 | tetrachloro-*p*-dicyanobenzene | −0.95 | 2.55 | | | |
| 12 | tetrachloro-*m*-dicyanobenzene | *j* | | | | |

One electron reduction potential of singlet exited state




cf. DDQ: +0.56 V



# Organic Photo Catalysts

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| 11 | tetrachloro-*p*-dicyanobenzene | −0.95 | 2.55 | 0.25 | 3.50 | *i* |
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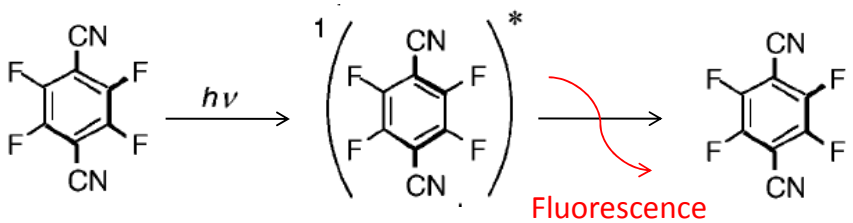
Fluorescence life time





# Organic Photo Catalysts

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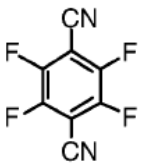
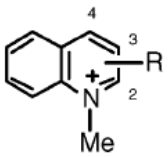
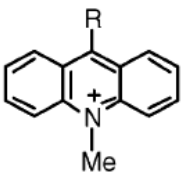



RQuH$^+$
(R = H, 2-Me, 4-Me, 3-CN)




AcrR$^+$
(R = H, Ph)

Singlet exited energy $E^0_{red}$–$E^0_{red}$*

Nearly HOMO-LUMO gap

1 eV = ca. 1200/λ ($nm^{-1}$) = 23 kcal/mol

1: 3.81 eV
$\lambda_{max}$ = 312 nm

8: 3.58 eV

10: 2.75 eV
$\lambda_{max}$ = 417nm

# Organic Photo Catalysts

| | photosensitizer | $E^0_{red}$[a] (V) vs SCE | $E^0_{red}$*[b] (V) vs SCE | $\tau$[c] (ns) | $E_{00}$(S)[d] (eV) | $k_q$[e] ($M^{-1}$ $s^{-1}$) |
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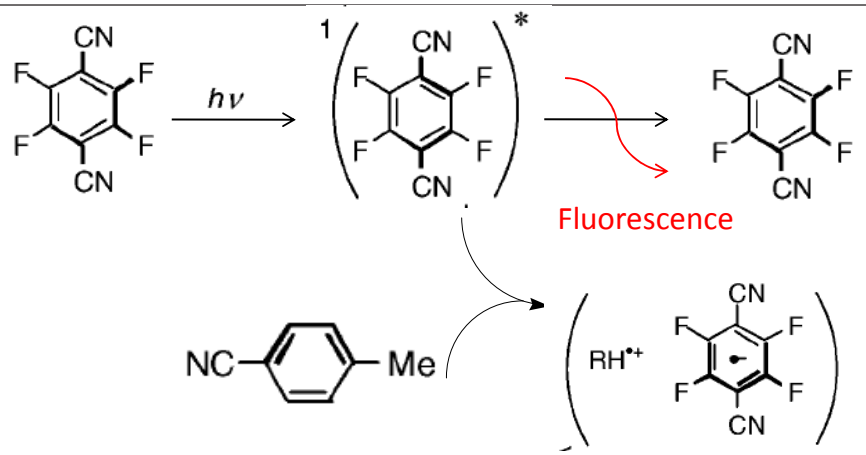
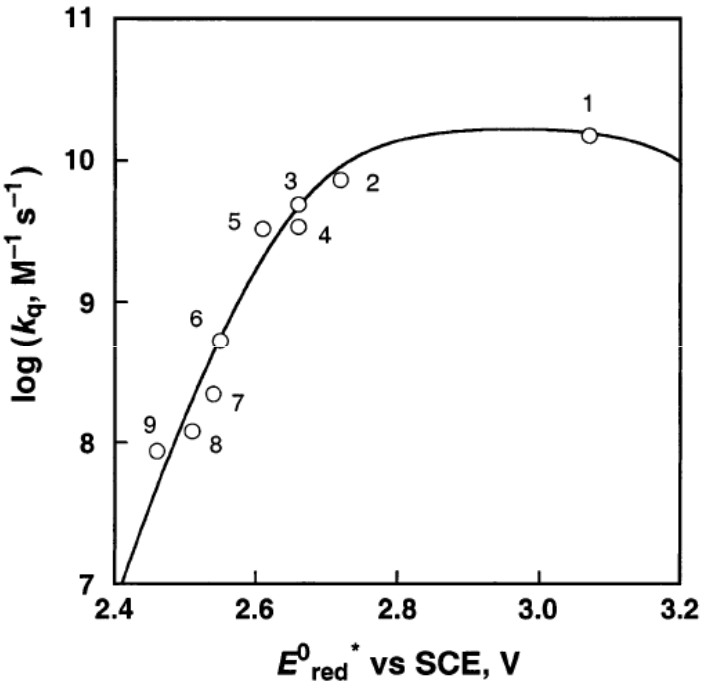
| 11 | tetrachloro-*p*-dicyanobenzene | −0.95 | 2.55 | 0.25 | 3.50 | *i* |
| 12 | tetrachloro-*m*-dicyanobenzene | *j* | | 0.20 | 3.71 | *i* |

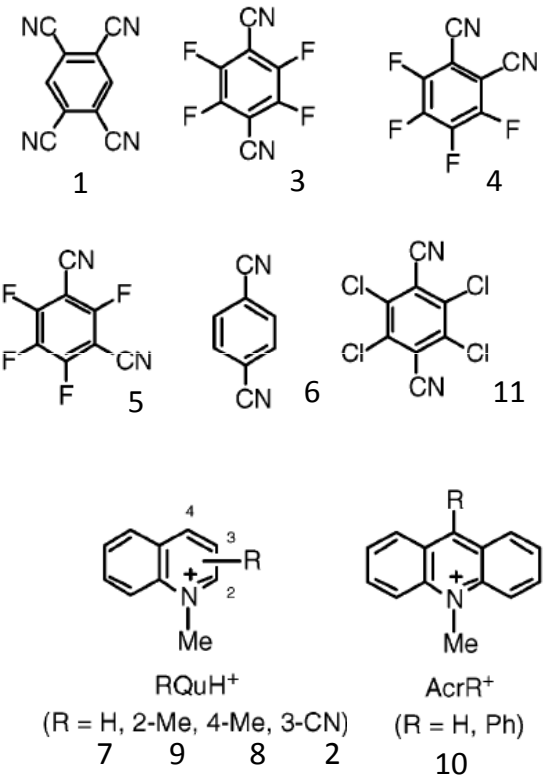



Quenching rate constants

# $E^0_{red}$ vs Reactivity




0.1 eV difference: ca. 50 times faster reaction




1 3 4 5 6 11

7 9 8 2

10

# Reaction with *p*-tolunitrile

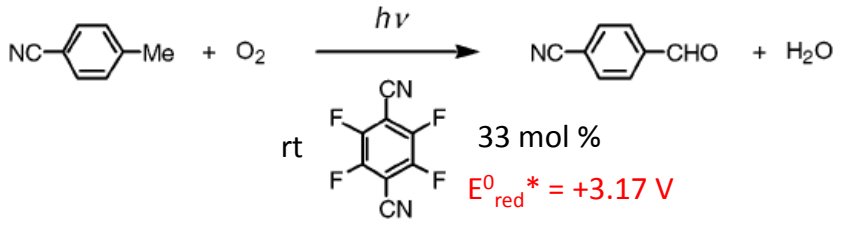
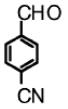
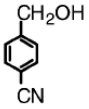



***Table 2.*** Reactant Conversion and Product Yields in Photooxygenation of *p*-Tolunitrile ($3.0 \times 10^{-2}$ M), Catalyzed by Tetrafluoro-*p*-Dicyanobenzene ($1.0 \times 10^{-2}$ M) in $O_2$-Saturated MeCN

| time, h | conversion, % | yield, % | |
|---|---|---|---|
| | |  |  |
| 0 | 0 | 0 | 0 |
| 1 | 6 | 6 | 0 |
| 2 | 9 | 9 | 1 |
| 4 | 18 | 15 | 3 |
| 8 | 27 | 22 | 4 |

254, 365, 405, 436, 546, 577, 579 nm

Mercury lamp through acetophenone –methanol filter (>300 nm)

# Reaction with Xylens

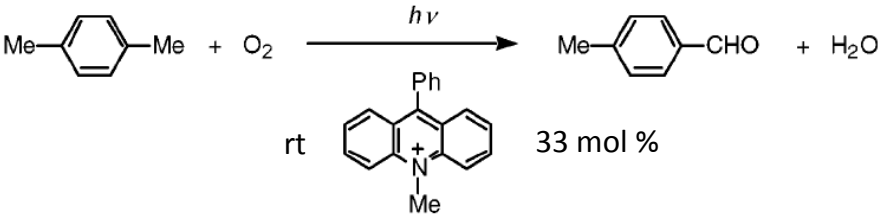
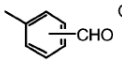
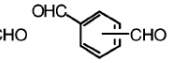
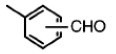



***Table 3.*** Photooxygenation Yields of Xylenes and Toluene ($3.0 \times 10^{-2}$ M), Catalyzed by $AcrPh^+$ ($1.0 \times 10^{-2}$ M) with $O_2$ in $O_2$-Saturated Chloroform at 298 K[a]

| | conversion | yield | |
|---|---|---|---|
| | |  |  |
| *p*-xylene | 100 % | 100 % | 0 % |
| *m*-xylene | 67 % | 99 % | 1 % |
| *o*-xylene | 70 % | 94 % | 6 % |
| toluene | 3 %[b] | 100 %[b] | |
| *p*-tolualdehyde | 0 % | | 0 % |

[a] Irradiation time is 10 h. [b] Benzaldehyde.

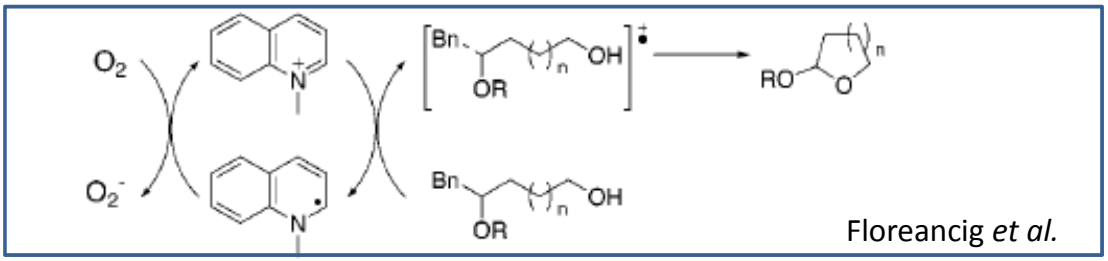
***Table 4.*** Fluorescence Quenching Rate Constants of $AcrH^+$ and $AcrPh^+$ by Ring-Substituted Toluenes and Aldehydes in Deaerated MeCN at 298 K

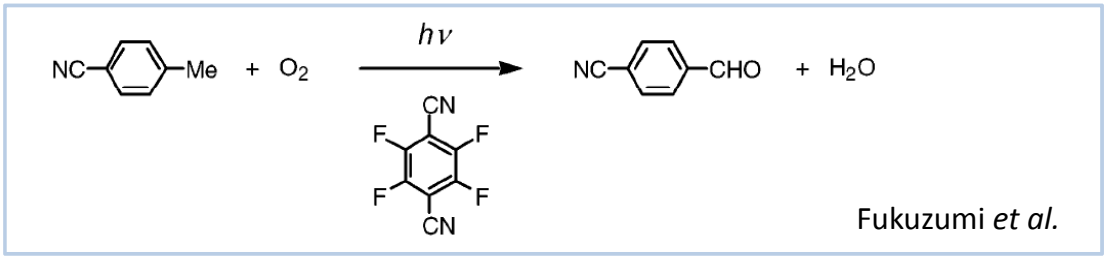
| | $k_q$, $M^{-1} s^{-1}$ | | | |
|---|---|---|---|---|
| | $AcrH^+$ | | $AcrPh^+$ | |
| |  |  |  |  |
| *p*-xylene | $8.6 \times 10^9$ | $< 10^6$ | $1.4 \times 10^{10}$ | $< 10^8$ |
| | $(4.2 \times 10^9)$[a] | | $(6.9 \times 10^9)$[a] | |
| *m*-xylene | $7.7 \times 10^9$ | $5.2 \times 10^7$ | $4.7 \times 10^9$ | $< 10^8$ |
| *o*-xylene | $7.9 \times 10^9$ | $3.8 \times 10^8$ | $6.5 \times 10^9$ | $< 10^8$ |
| toluene | $2.4 \times 10^8$ | $< 10^6$[b] | $< 10^8$ | $< 10^8$[b] |

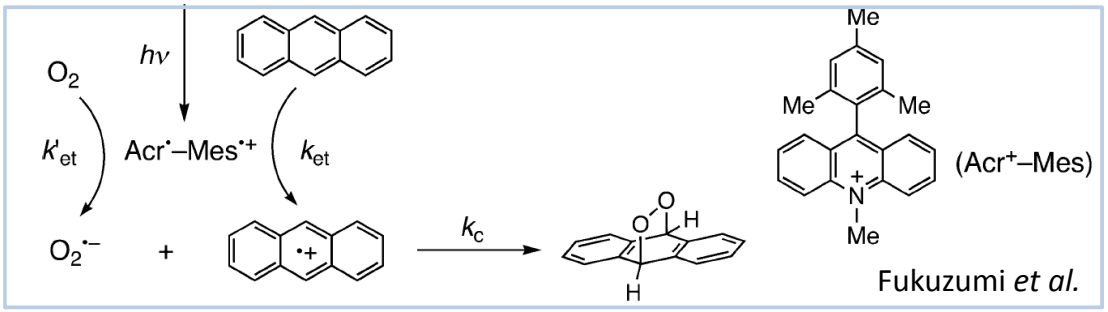
[a] Values in parentheses were determined in $CHCl_3$. [b] Benzaldehyde.

Xenon lamp through UV cutoff filter (> 310 nm)

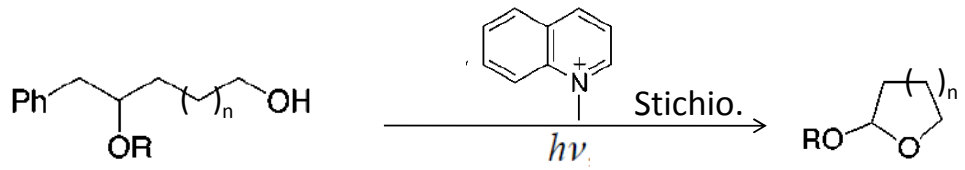
# Aerobic Photocatalytic Reactions



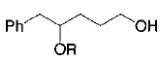
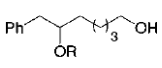
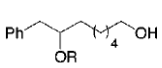
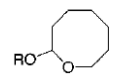
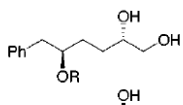
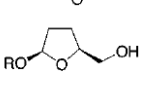
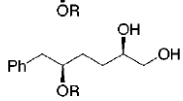
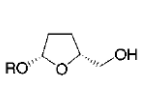
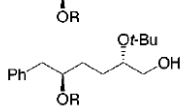
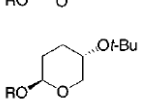



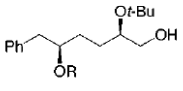
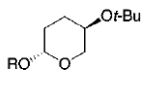
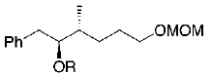
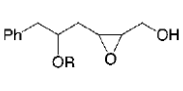




# Stichio. Reaction



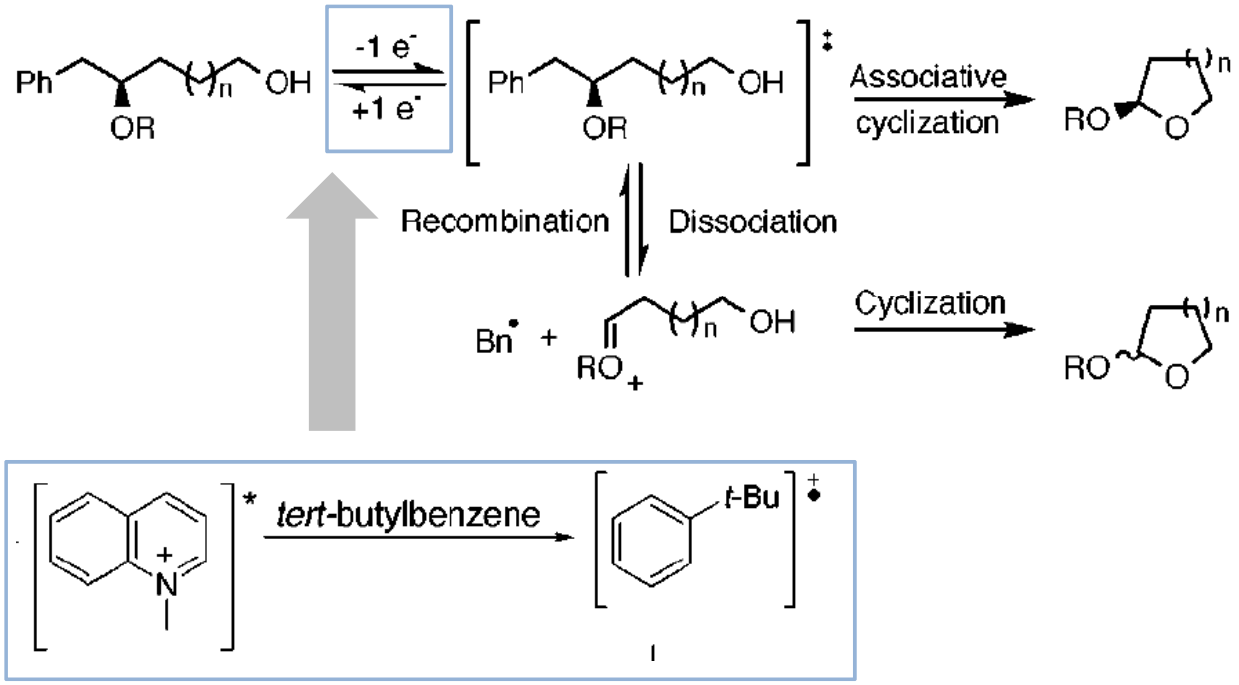

[a] Reaction conditions: *hν*, *N*-methylquinolinium tetrafluoroborate (1−2 equiv), NaOAc, DCE, *tert*-butylbenzene (4:1).

| Entry | Substrate[b] | Product | Yield (%) | D.R.[c] |
|---|---|---|---|---|
| 1 |  |  | 74 | - |
| 2 |  |  | 82 | - |
| 3 |  |  | 55 | - |
| 4 |  |  | 74 | 10:1[d] |
| 5 |  |  | 92 | 1.2:1[d] |
| 6 |  |  | 84 | 1.7:1 |

| Entry | Substrate[b] | Product | Yield (%) | D.R.[c] |
|---|---|---|---|---|
| 7 |  |  | 82 | 1.1:1 |
| 8 |  |  | 67[e] | 1.4:1 |
| 9[f] |  |  | 78[g] | 2.6:1 |

[a] Reaction conditions: *hν*, *N*-methylquinolinium tetrafluoroborate (1−2 equiv), NaOAc, DCE, *tert*-butylbenzene (4:1). [b] R = *n*-octyl. [c] Diastereomeric ratio. The major diastereomer is represented by the structure in the Product column. Stereochemical assignments were based on $^1$H NMR coupling constants except where noted. [d] Stereochemistry was determined by NOE analysis. [e] Yield at 88% conversion. [f] The relative stereochemistry of the starting material and the products was not determined. [g] Yield at 91% conversion.

## Proposed Reaction Mechanism

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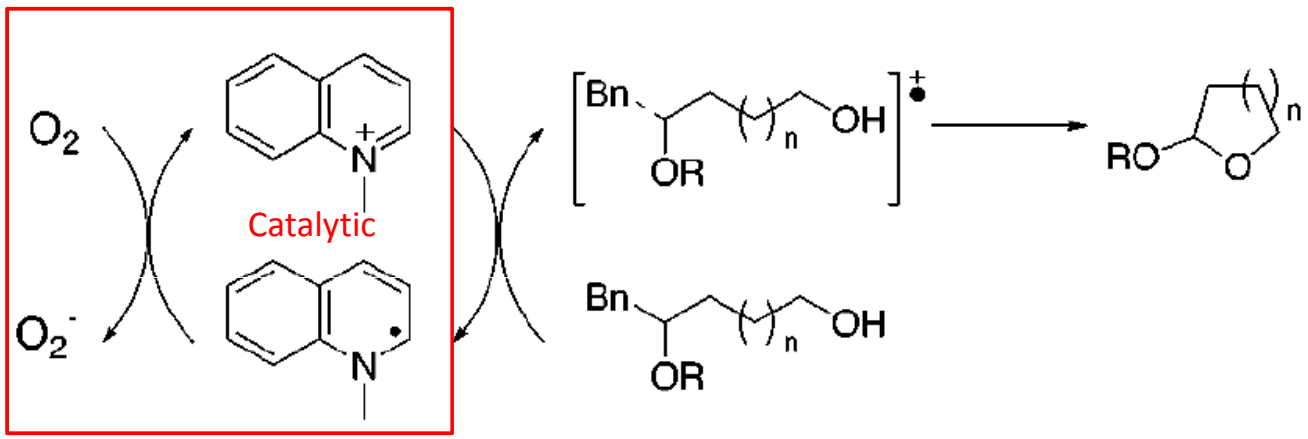
## Catalytic Reaction

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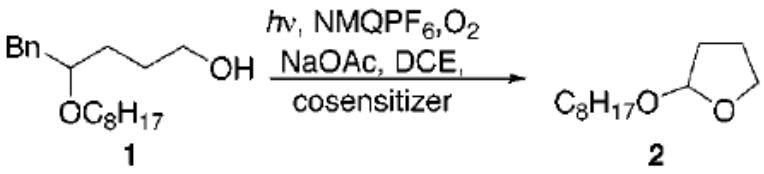
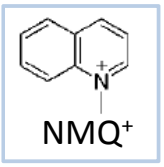
# Condition Optimization

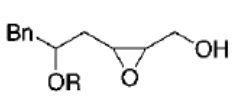
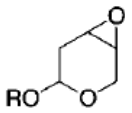
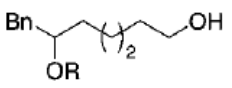
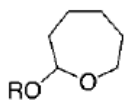
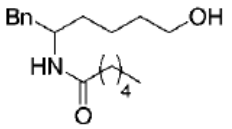
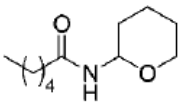
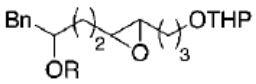
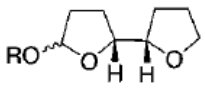


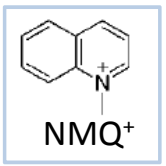




| entry | $NMQPF_6$ (mol %) | cosensitizer | time (h) | yield (%)[b] |
|---|---|---|---|---|
| 1 | 200[c] | TBB[d] | 4 | 55[e] |
| 2 | 50 | TBB | 1.5 | 79 |
| 3 | 10 | TBB | 1.5 | 82 |
| 4 | 2.5 | TBB | 2 | 86 |
| 5 | 2.5 | toluene | 3 | 82 |

[a] Reaction conditions: **1** (50 mg), $NMQPF_6$, NaOAc (100 mg), 1,2-dichloroethane (6 mL), cosensitizer (1 mL), gentle air bubbling, irradiation with a medium-pressure mercury lamp. [b] Reported yields are of isolated, purified products unless noted otherwise. [c] Air was not used in this example. [d] TBB = *tert*-butylbenzene. [e] 74% yield based on 76% conversion.

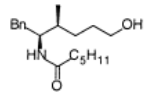
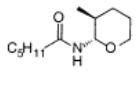
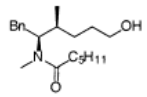
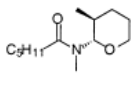
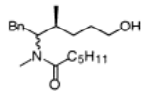
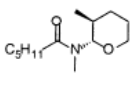
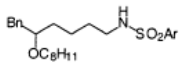
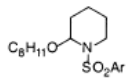
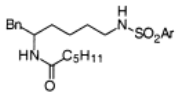
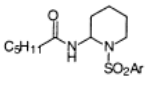
# Substrate Scope

| Entry | Substrate[b] | Product | Yield (cat.)[c] | Yield (stoic.)[d] |
|---|---|---|---|---|
| 1[e] |  |  | 90 | 78 |
| 2 |  |  | 85 | 82 |
| 3 |  |  | 75 | 78 |
| 4 |  |  | 73 | 82 |

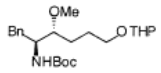
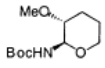
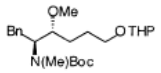
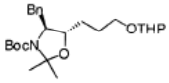
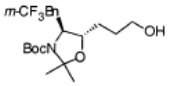



[a] Reaction conditions: 50−150 mg substrate, 2.5 mol % $NMQPF_6$, 2 wt equiv of NaOAc, 2 wt equiv of $Na_2S_2O_3$, DCE/toluene (6:1), gentle air bubbling, irradiation with a medium-pressure mercury lamp. [b] R = *n*-$C_8H_{17}$. [c] Reported yields are of isolated, purified products. [d] Procedures for the stoichiometric reactions in entries 1 and 2 can be found in ref 5. [e] A 1.3:1 ratio of diastereomers was isolated. The relative stereochemistry of the isomers was not determined.

# Other Examples of This Type Reaction

| Entry | Substrate | Product | Yield (%) | D.R.[b] |
|---|---|---|---|---|
| 1 |  **3** |  **4** | 75 | 2:1 |
| 2 |  **5** |  **6** | 67 | >19:1 |
| 3[c] |  **7** |  **6** | 56 | >19:1 |
| 4[d] |  **8** |  **9** | 68 | |
| 5[d] |  **10** |  **11** | 64 | |

[a] Reaction conditions: $h\nu$, $NMQPF_6$ (2.5 mol %), $O_2$, NaOAc, $Na_2S_2O_3$, DCE, PhMe. [b] Diastereomeric ratio. The major diastereomer is shown in the product column. Stereochemical assignments were based on $^1H$ NMR coupling constants. [c] 1:1 mixture of diastereomers. [d] Ar = *p*-$NO_2C_6H_4$.

| Entry | Substrate | Product | Yield (%) | D.R.[b] |
|---|---|---|---|---|
| 1 |  **14** |  **15** | 63 | 2:1 |
| 2 |  **16** | Decomposition | | |
| 3 |  **17** |  **18** | 88 | >19:1 |
| 4 |  **19** |  **18** | 56 | >19:1 |

[a] Reaction conditions: $h\nu$, $NMQPF_6$ (2.5 mol %), $O_2$, NaOAc, $Na_2S_2O_3$, DCE, PhMe. [b] Diastereomeric ratio. The major diastereomer is shown in the product column. Stereochemical assignments were based on $^1H$ NMR coupling constants.

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