Lecture 18

Chemical Engineering for Micro/Nano Fabrication

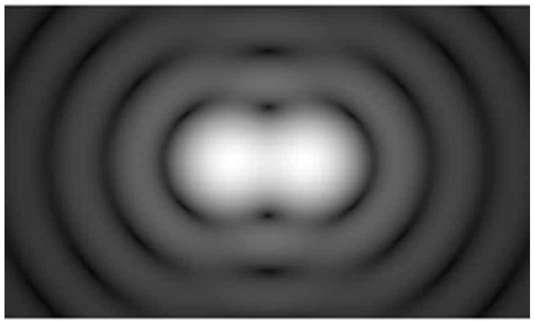
John William Strutt, third Baron Rayleigh, 1842-1919

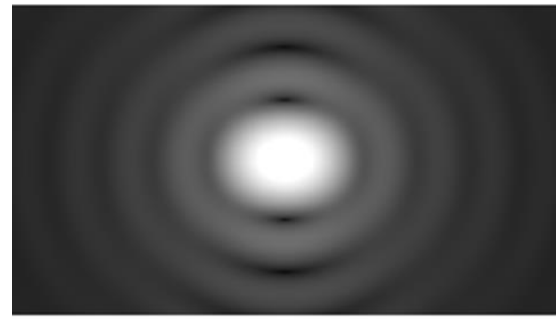
The Nobel Prize in Physics 1904

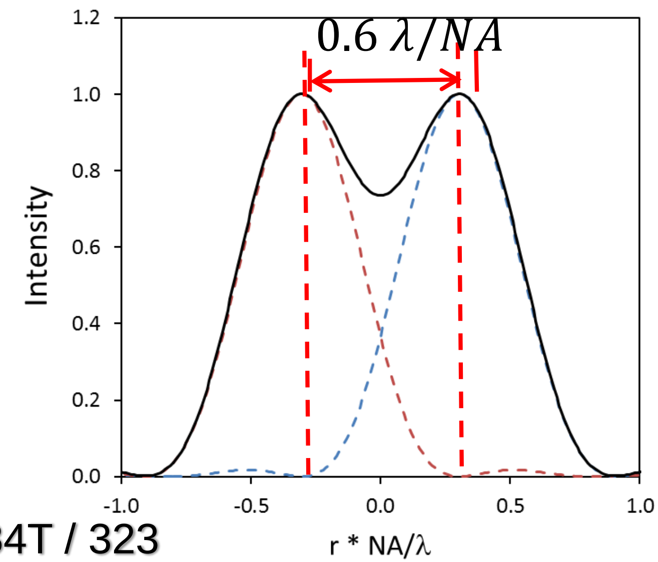
$$R = k_1 \frac{\lambda}{n \sin\theta}$$

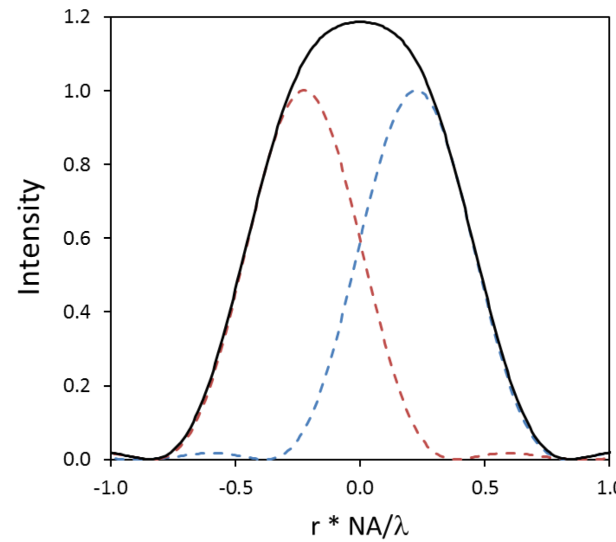
Rayleigh's Rule for Resolution

Lord Rayleigh defined this criterion: when the first minimum of one Airy disk coincides with the maximum of another -> $0.6\ \lambda/NA$





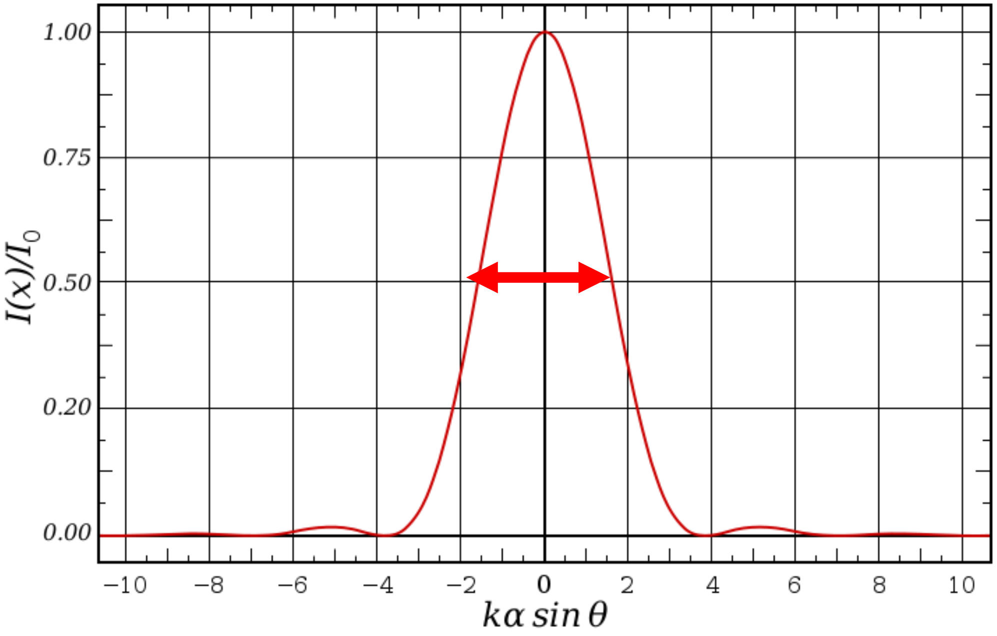


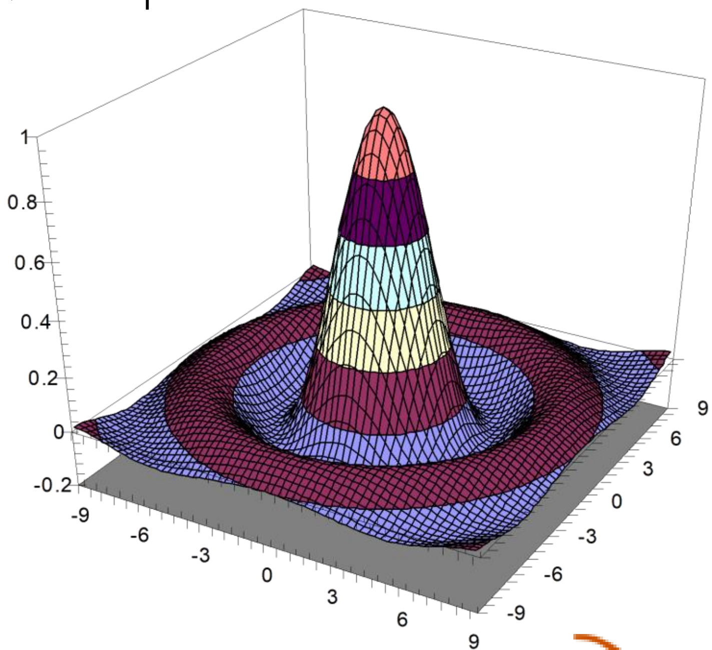


Defining the resolution of an imaging system

- When a single point of light is imaged it becomes the point spread function (PSF) of the lens system.
  - For an ideal, circular imaging system, the PSF is called the Airy disk:
  - The FWHM of the Airy disk is **0.5 λ/NA**, which defines the smallest image of a point source

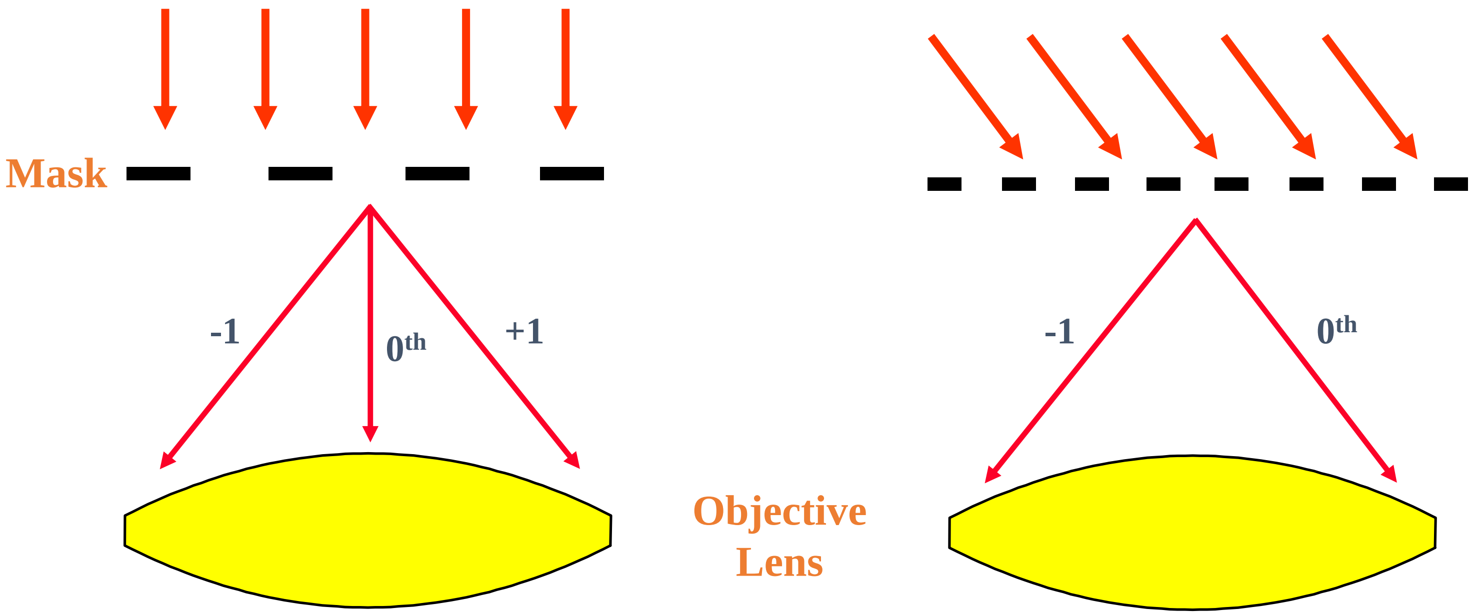
$$PSF = \left| J_1(2\pi r NA/\lambda)/\pi r \right|^2$$





Lithography breaks Rayleigh's rule

Normal Incidence **Oblique Incidence**



$$\sin\theta_{max} = NA = \lambda/p_{min}$$

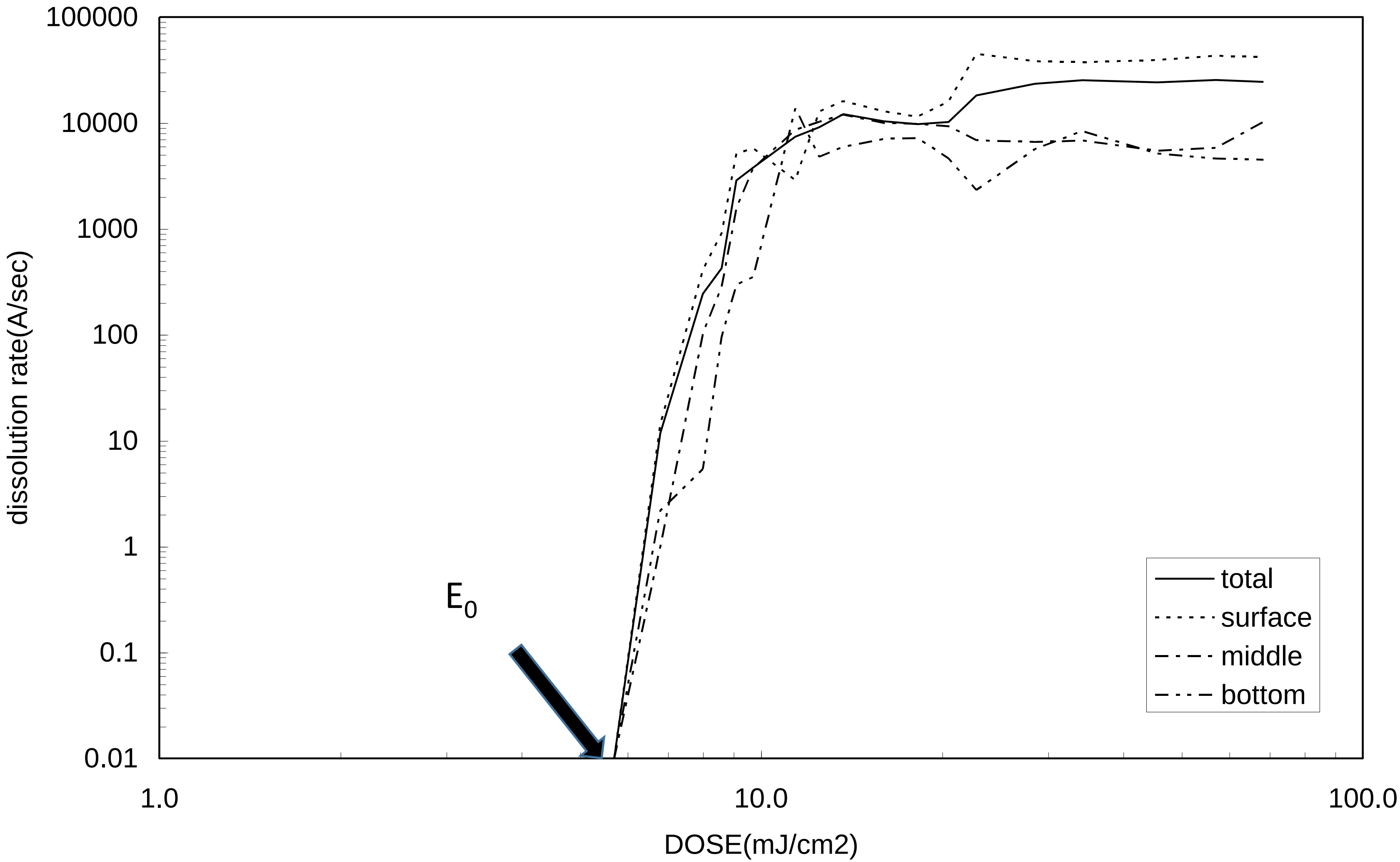
$$R = \frac{p_{min}}{2} = 0.5\frac{\lambda}{NA}$$

$$\sin\theta_{max} = 2NA = \lambda/p_{min}$$

$$R = \frac{p_{min}}{2} = 0.25\frac{\lambda}{NA}$$

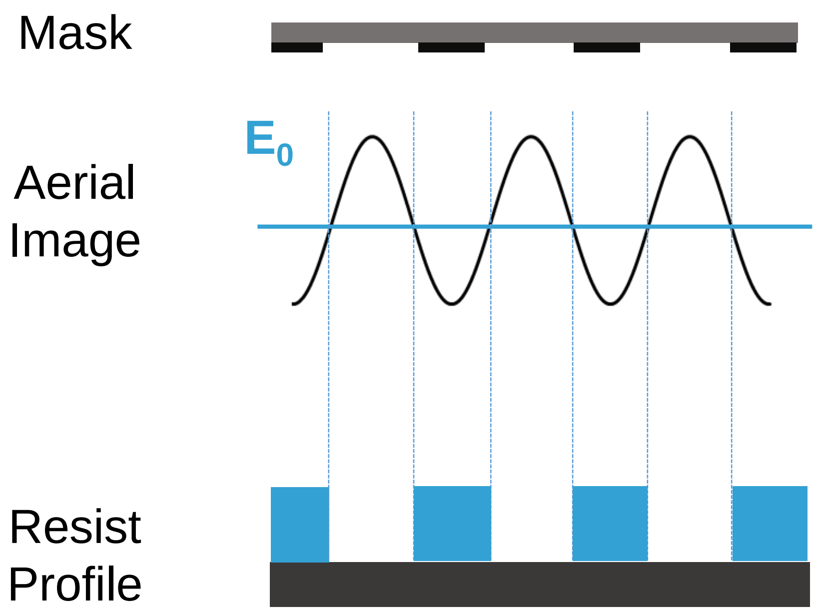
Threshold like Response of ArF Resist

enables breaking Rayleigh's rule



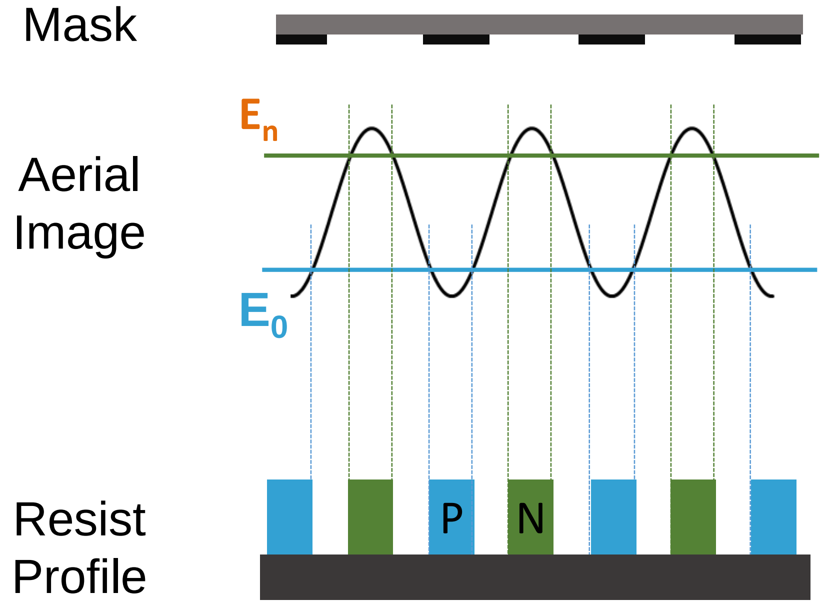
Pitch division …..Breaking Rayleigh's Rule!

Conventional Resist System



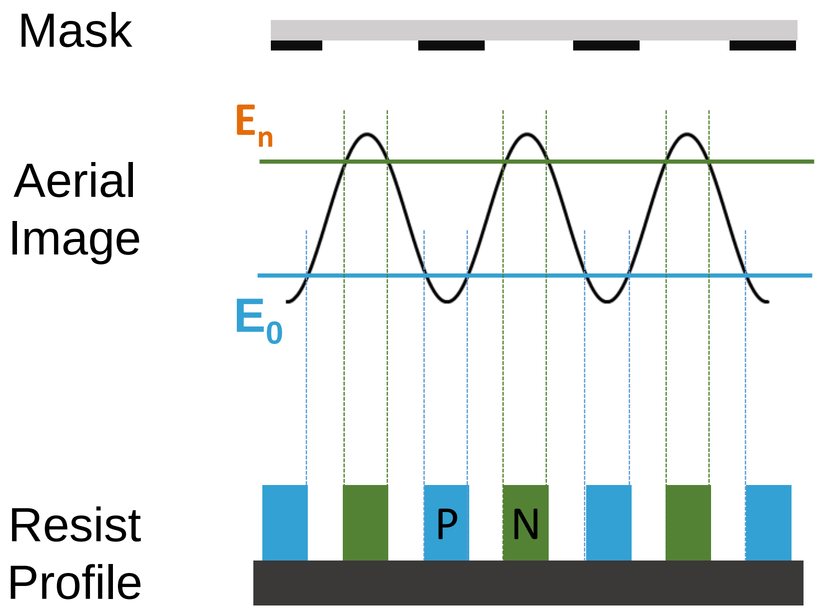
The frequency on the wafer plane is **SAME** as that on the mask.

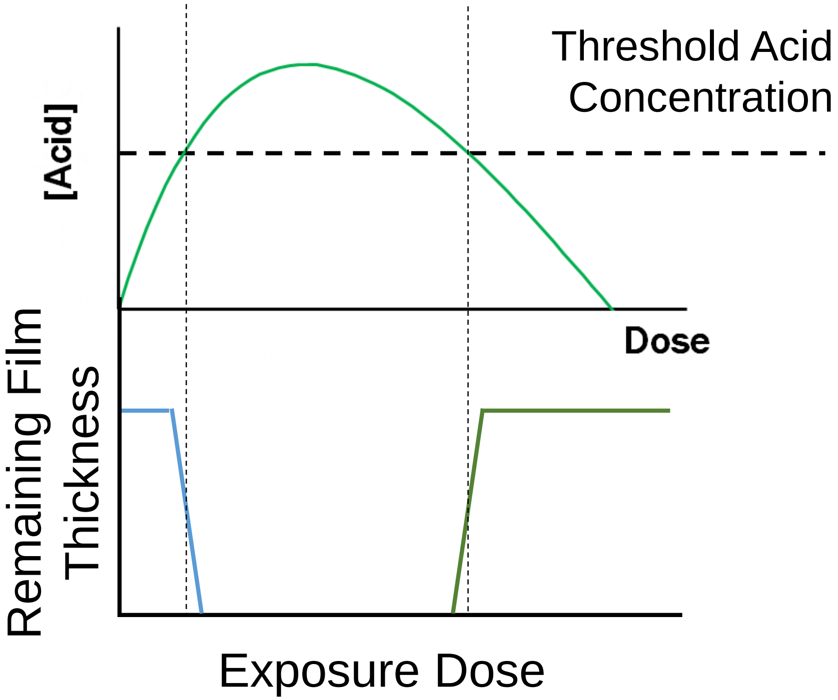
Pitch Division Approach



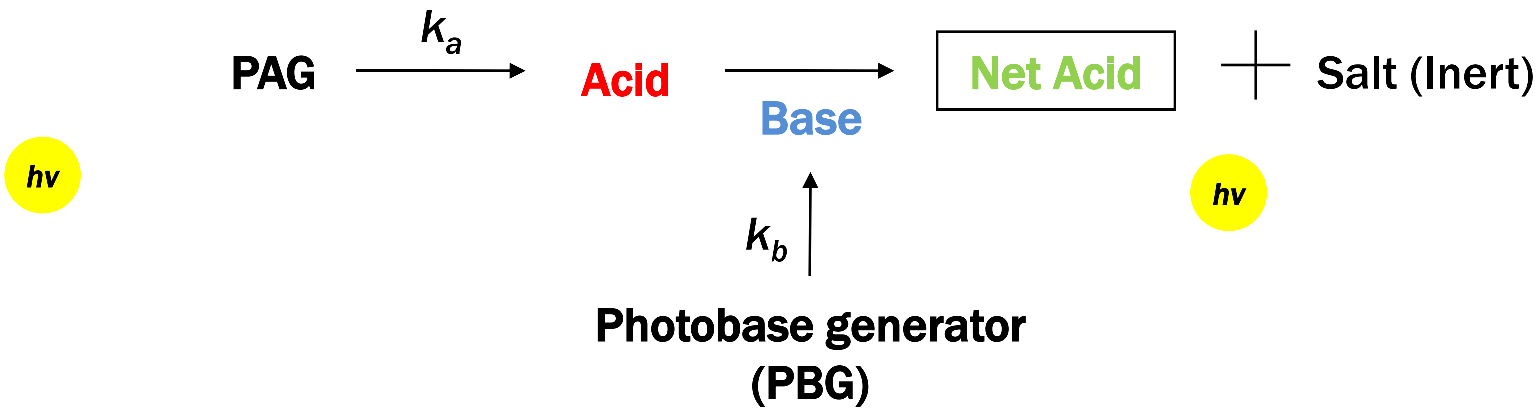
One space on the mask prints **TWO** spaces on the wafer plane.

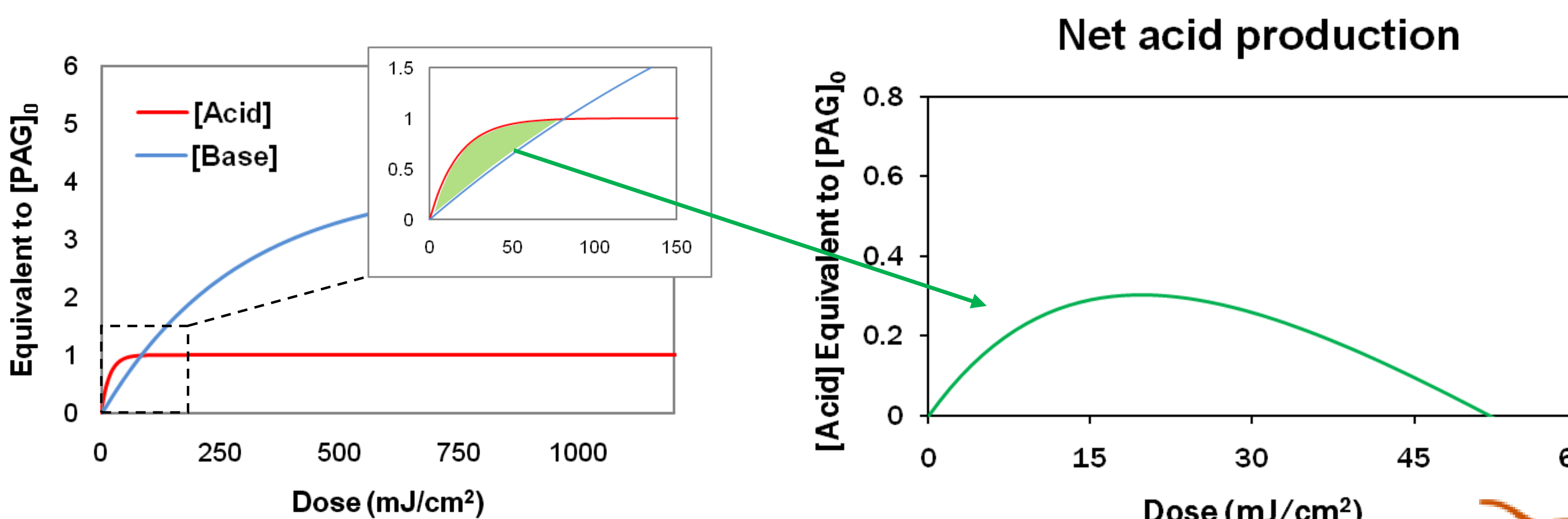
Dual Tone Resist- an unusual response



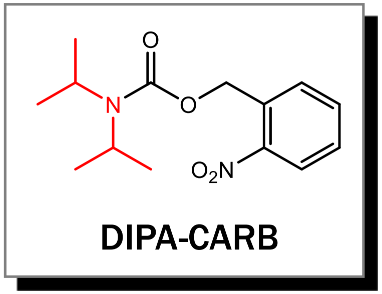


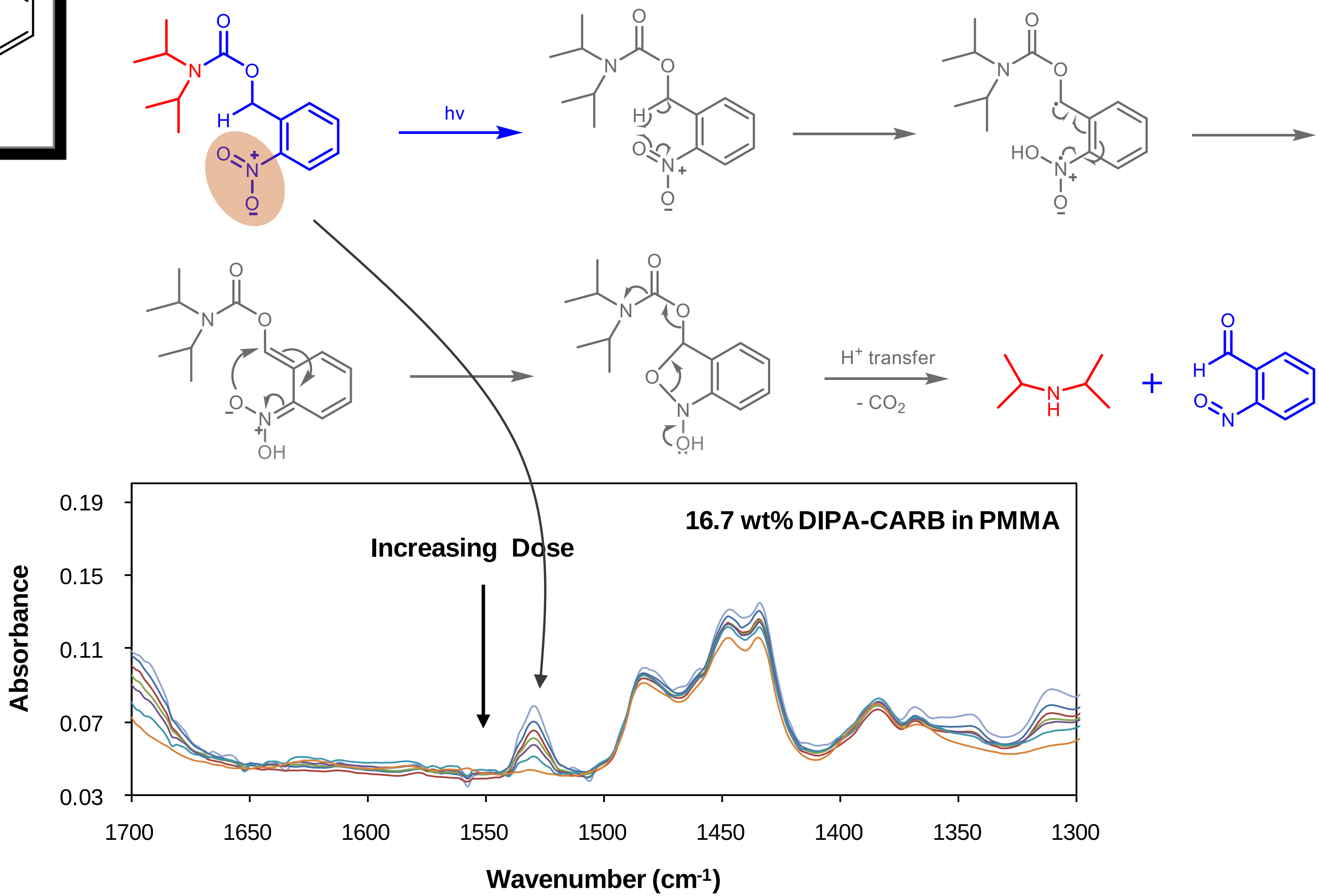
Photoactive System And Mechanism





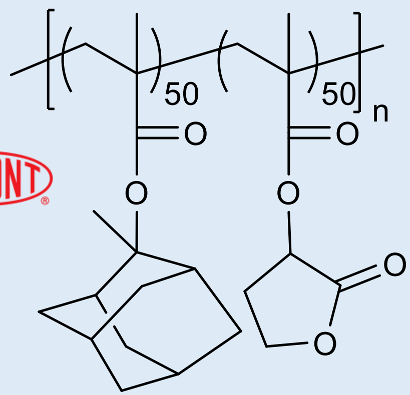
Photobase Generator (PBG)



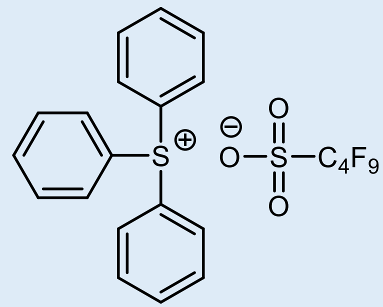


Suyama et al., *Progress in Polymer Science*, **34** (2009) 194-209.
Houlihan et al., *Macromolecules*, **21** (1988) 2001-2006.
Cameron et al., *J. Am. Chem. Soc.*, **113** (1991) 4303-4313.

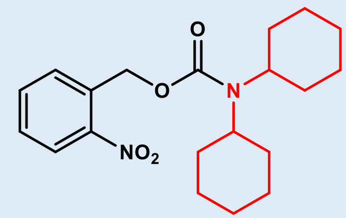
A Test Formulation



MAdMA:GBLMA (50/50)



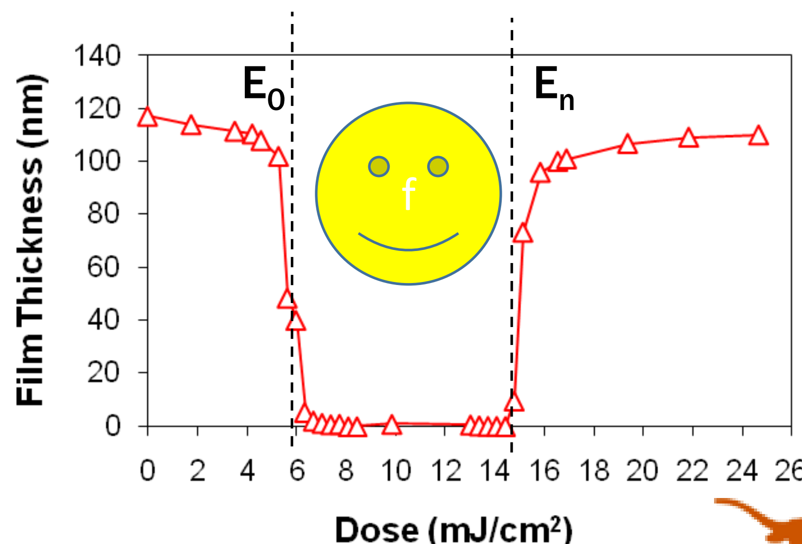
Photoacid generator (PAG)



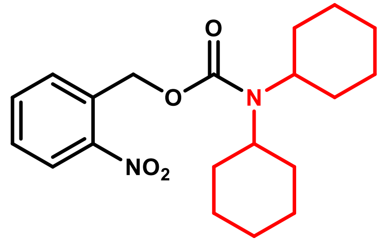
Photobase generator (PBG)

CONDITIONS:

- 6.5 wt% of PAG to polymer
- PBG/PAG molar ratio = 3
- PEB: 121.5 ºC, 60 sec
- BARC (89 nm)



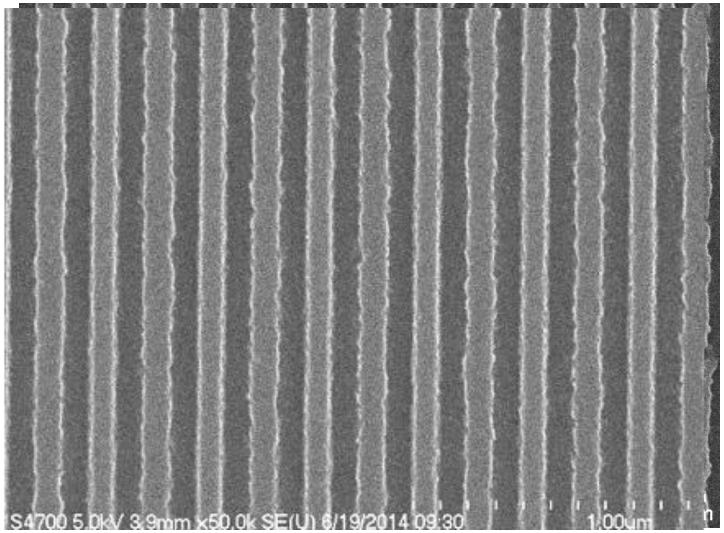
Lithography Result

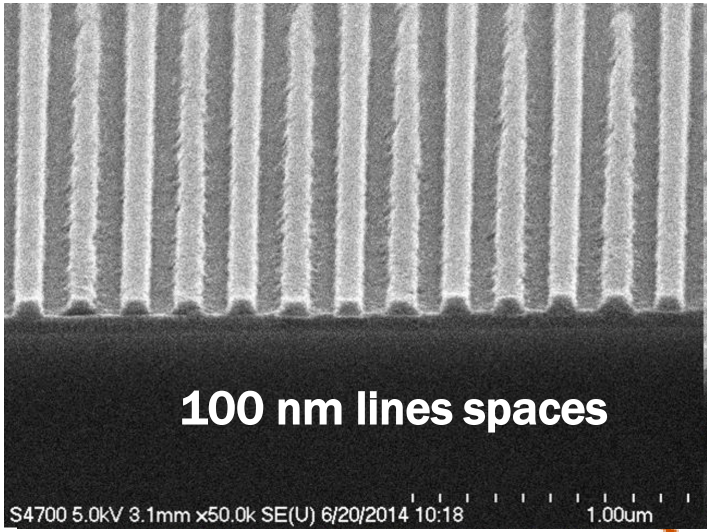


DCHA-CARB

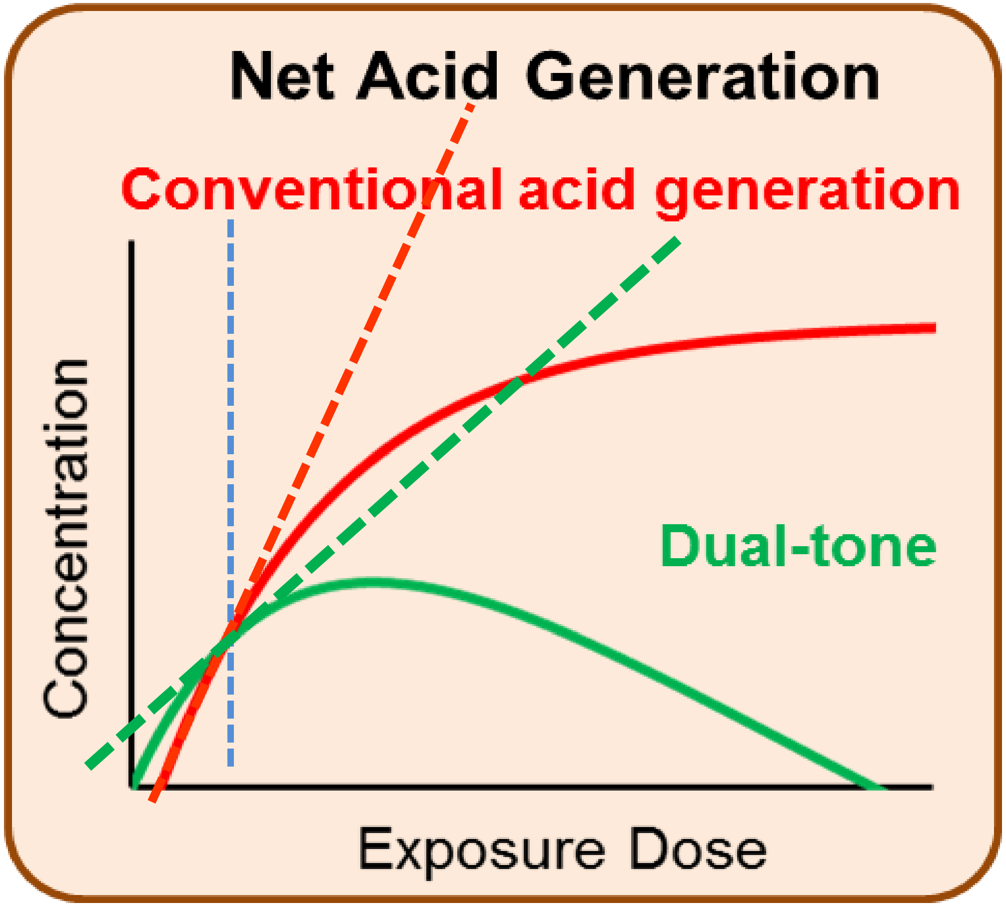
$$R = k \frac{\lambda}{NA}$$

k_1 = 0.15!!!





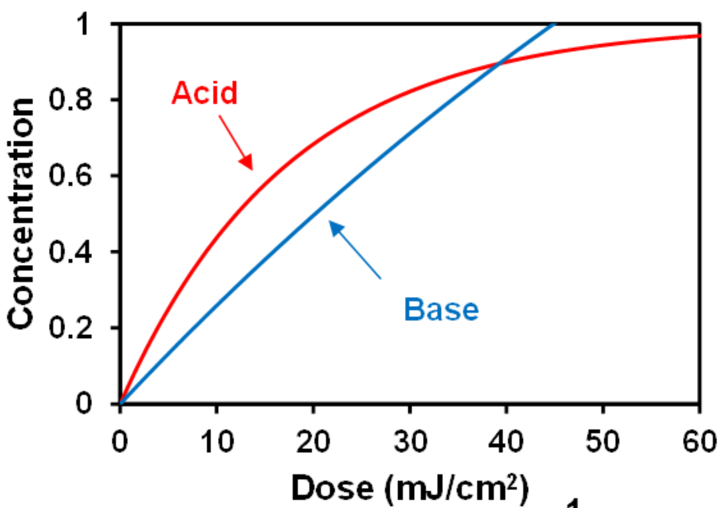
Poor edge definition due to Low chemical contrast?



Increase Chemical Contrast (Acid Gradient)

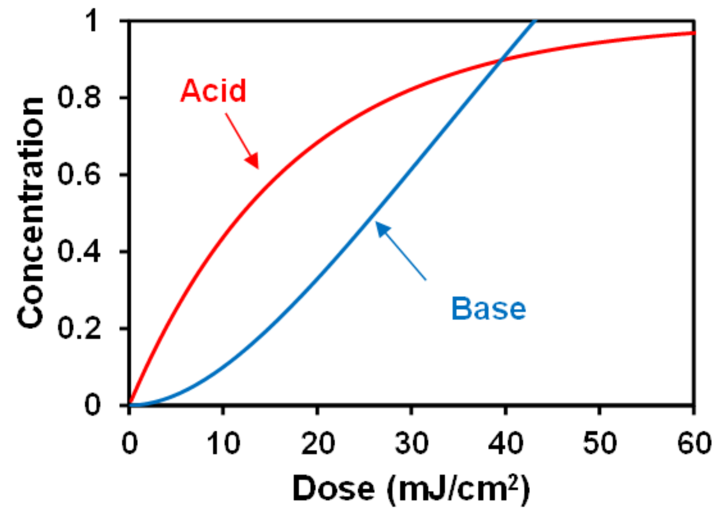
Conventional PBG

$$PBG \xrightarrow{h\nu} Base$$

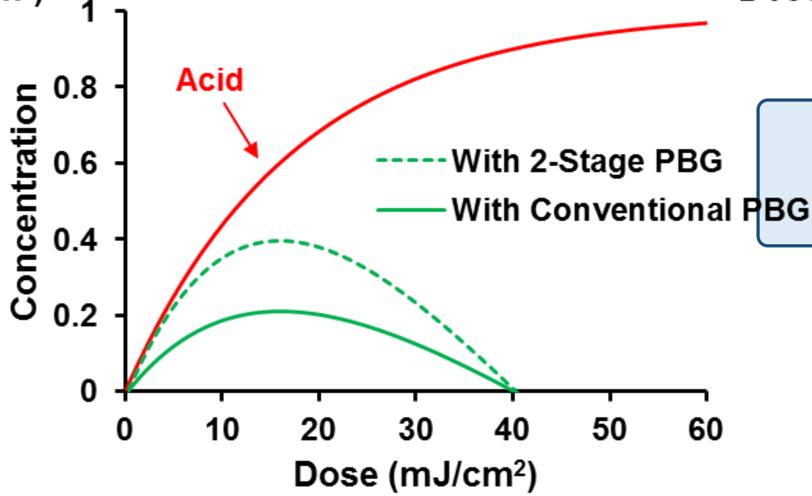


2-Stage PBG

$$L-PBG \xrightarrow{h\nu} PBG \xrightarrow{h\nu} Base$$



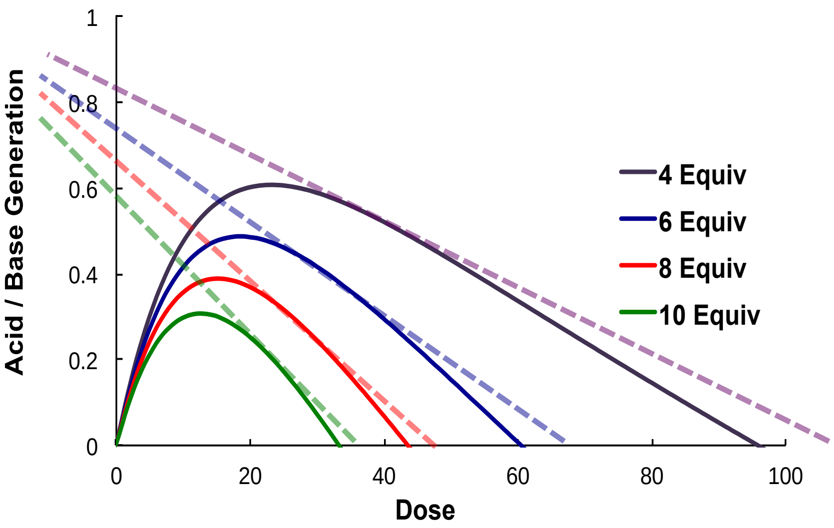
With Nick Turro from Columbia



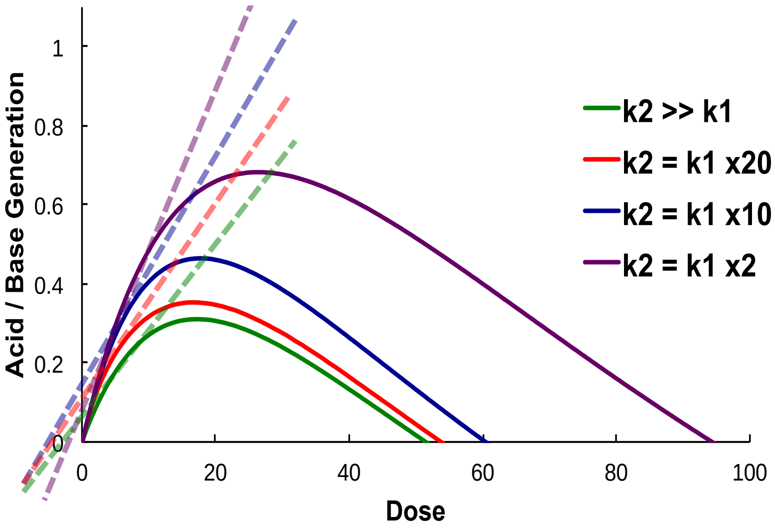
2-Stage PBG improves chemical contrast!!

Improving Chemical Contrast

Increase PBG Loading



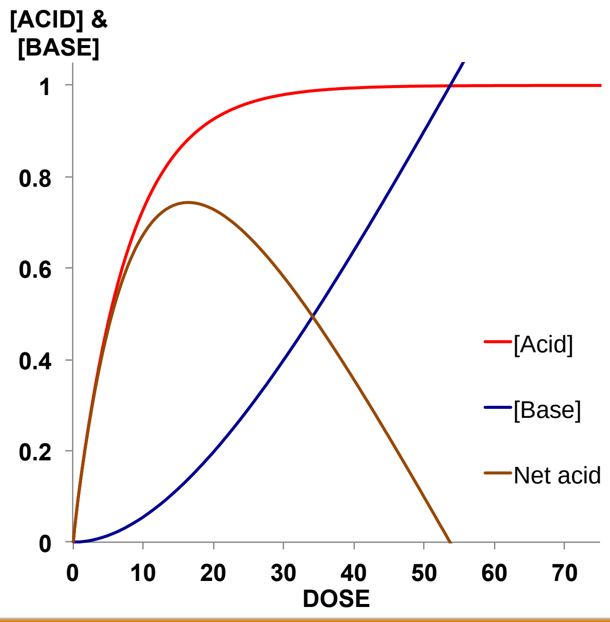
2-Stage PBG



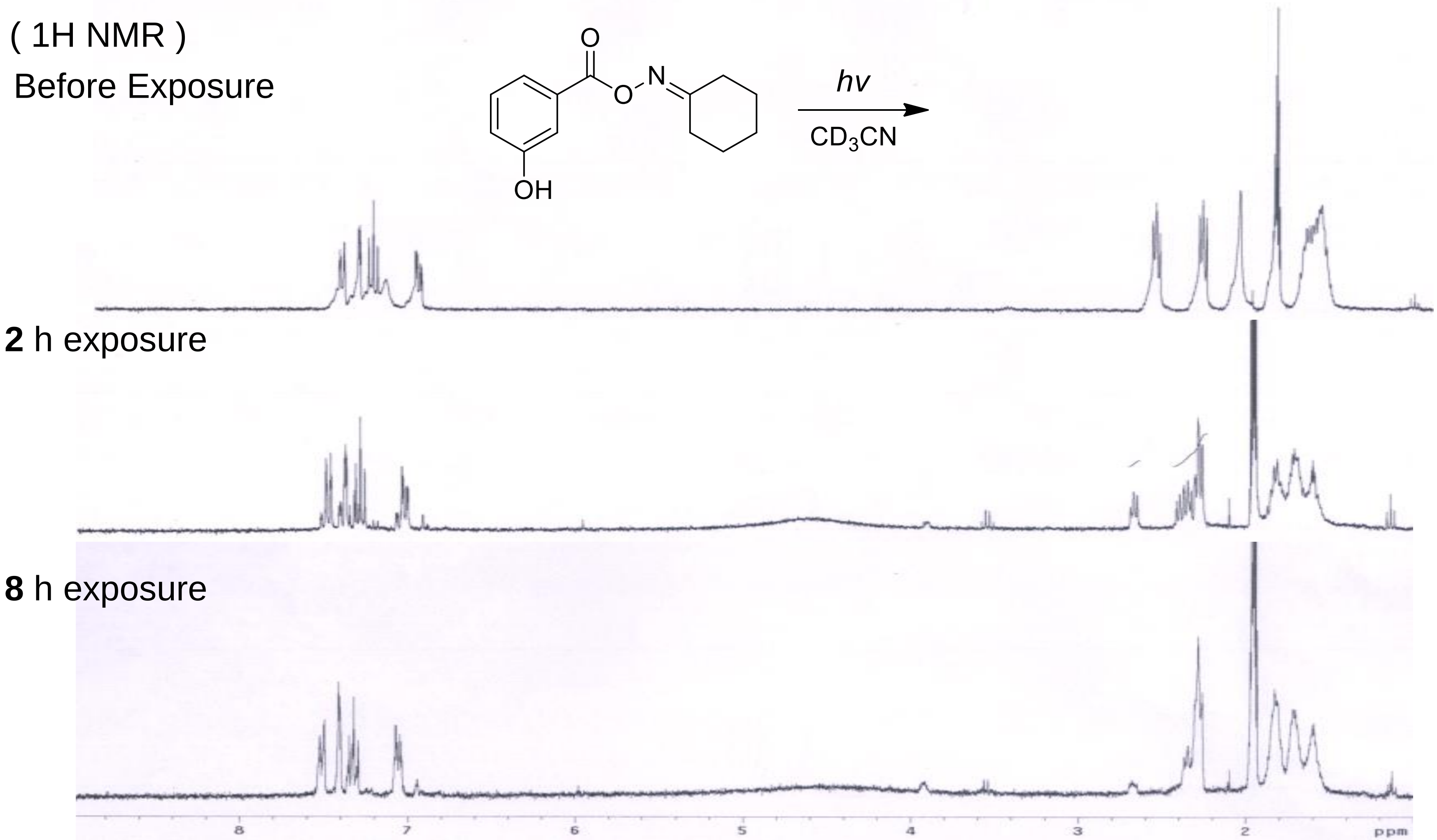
<u>Combination:</u>

[PBG] / [PAG] = 4.5

k2 ≈ k1



An interesting observation on oxime esters: Aromatic Undergoes Rapid Photolysis at 248nm

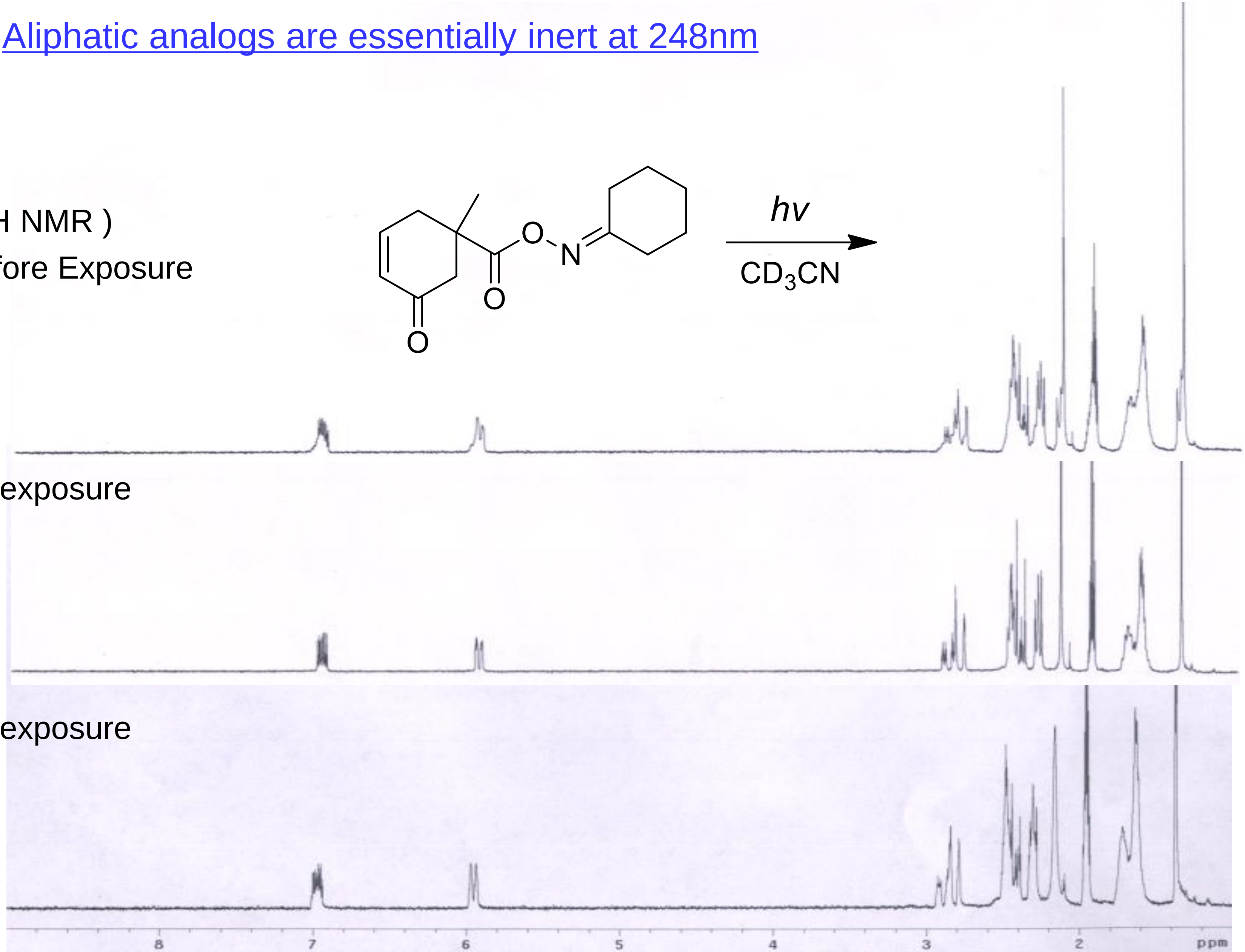


Aliphatic analogs are essentially inert at 248nm

(1H NMR)
Before Exposure

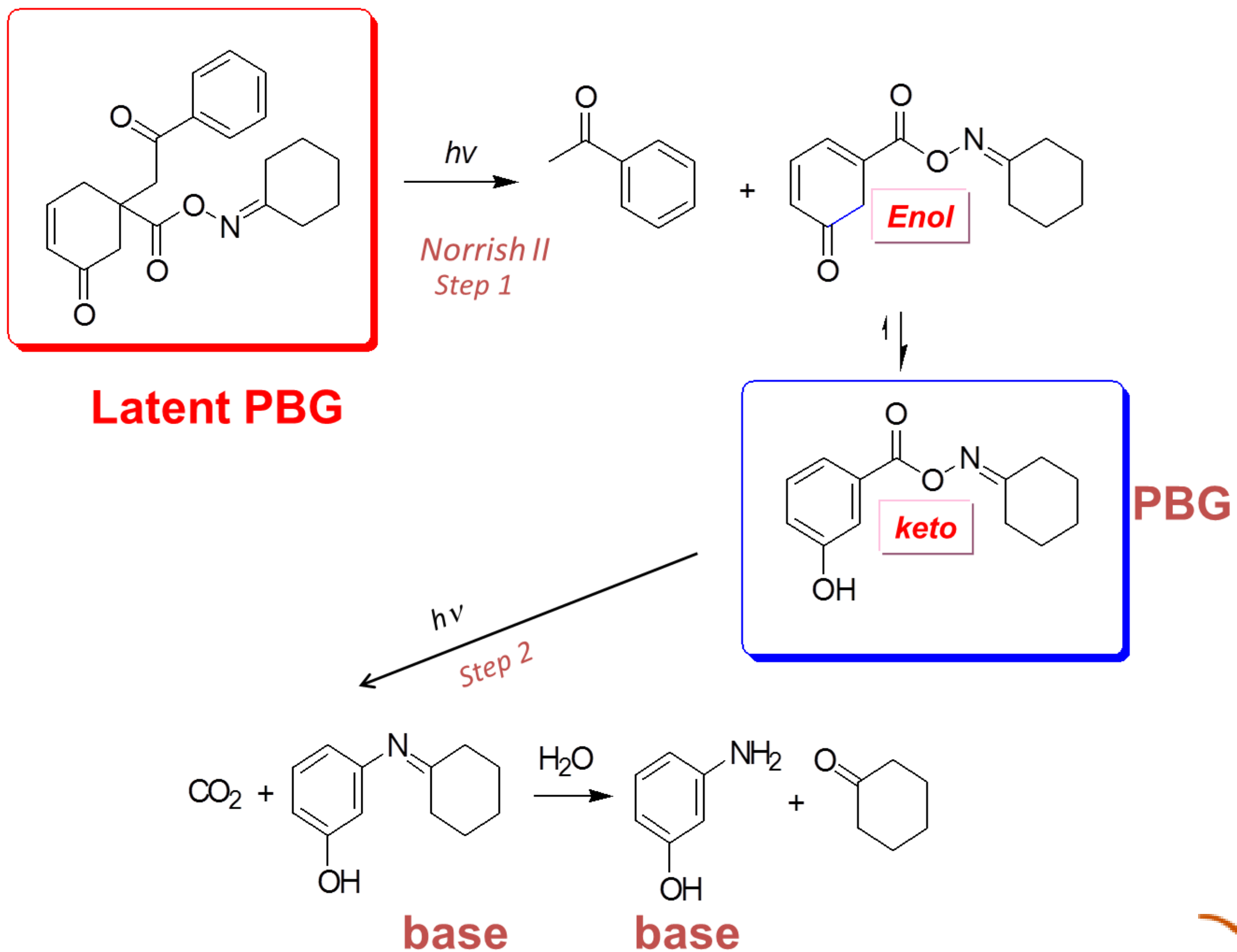
2 h exposure

8 h exposure

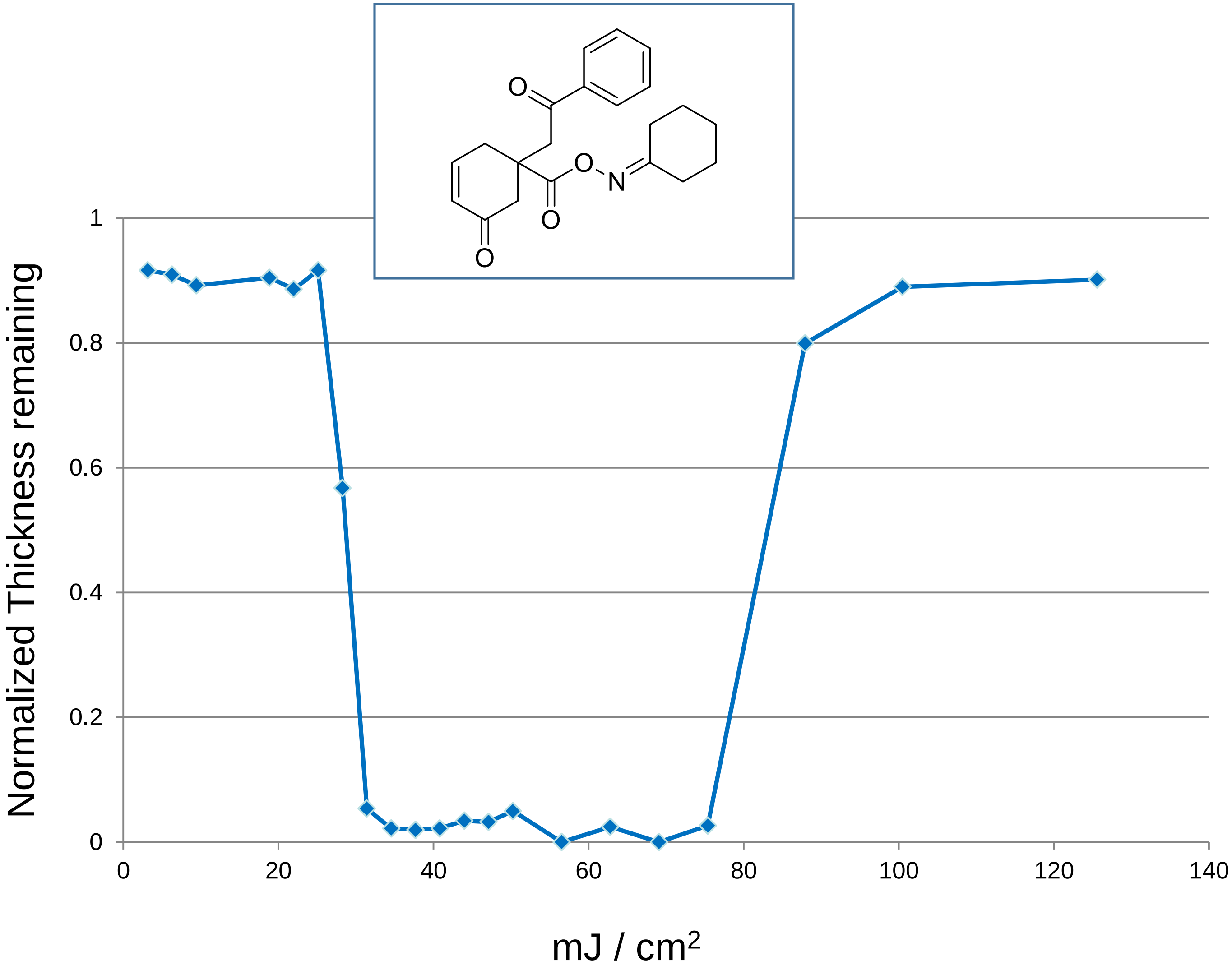


No Reaction !!

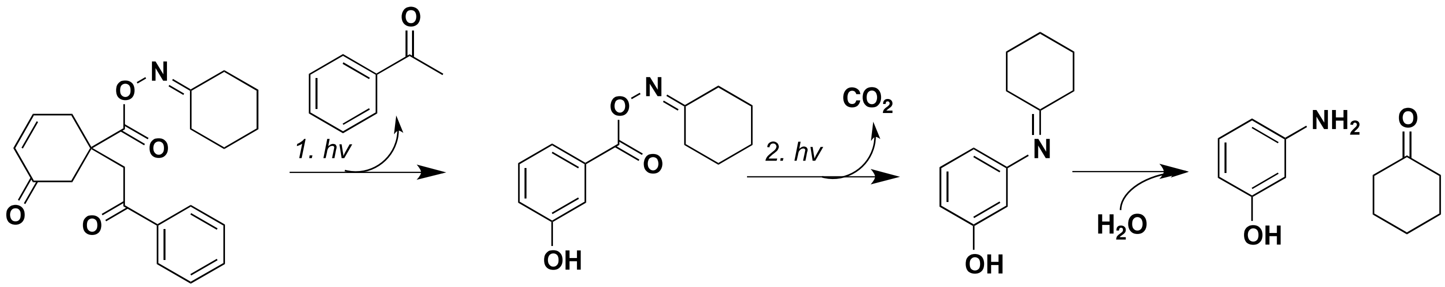
Photoaromatization

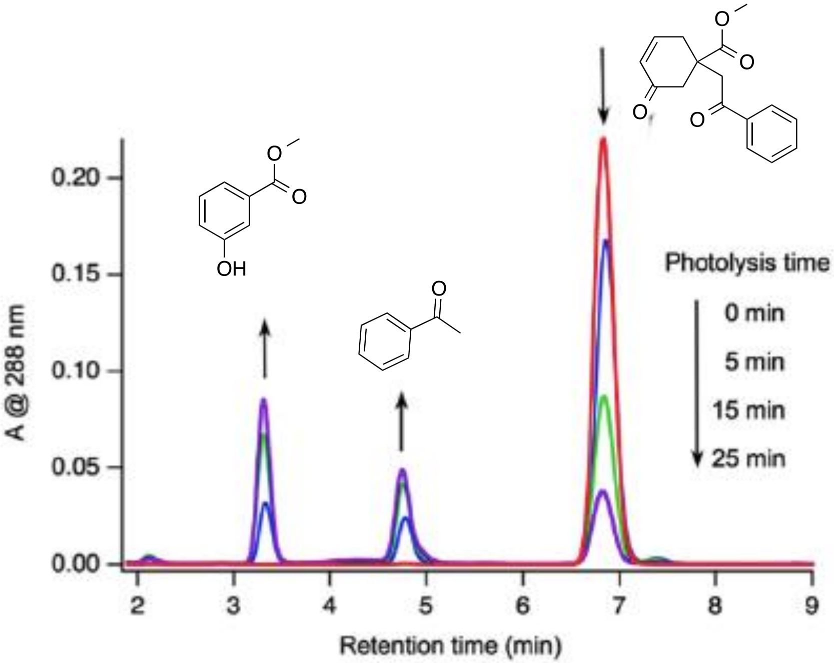


Contrast curve under 193nm

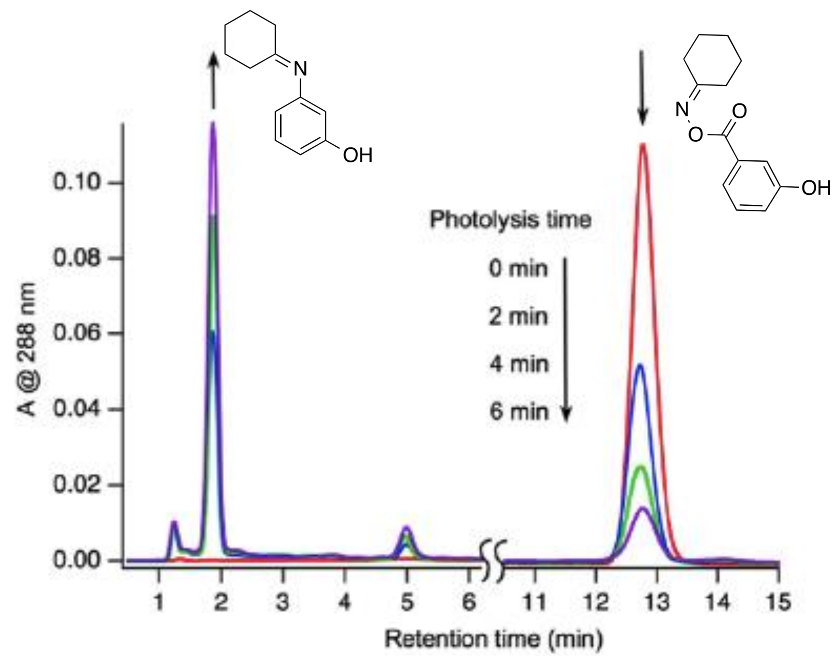


Hagiwara, Y; **Mesch, R;** Kawakami, T; Okazaki, M; Jockusch, S; Li, Y, Turro, NJ; and Willson, CG. *JOC* Vol. 78(5), p1730-1734, 2
Turro, NJ; Li, Y; Jockusch, S. Hagiwara, Y; Okazaki, M; **Mesch, R**; Schuster, D and Willson, CG. *JOC* Vol. 78(5) p1735-1741, **201**





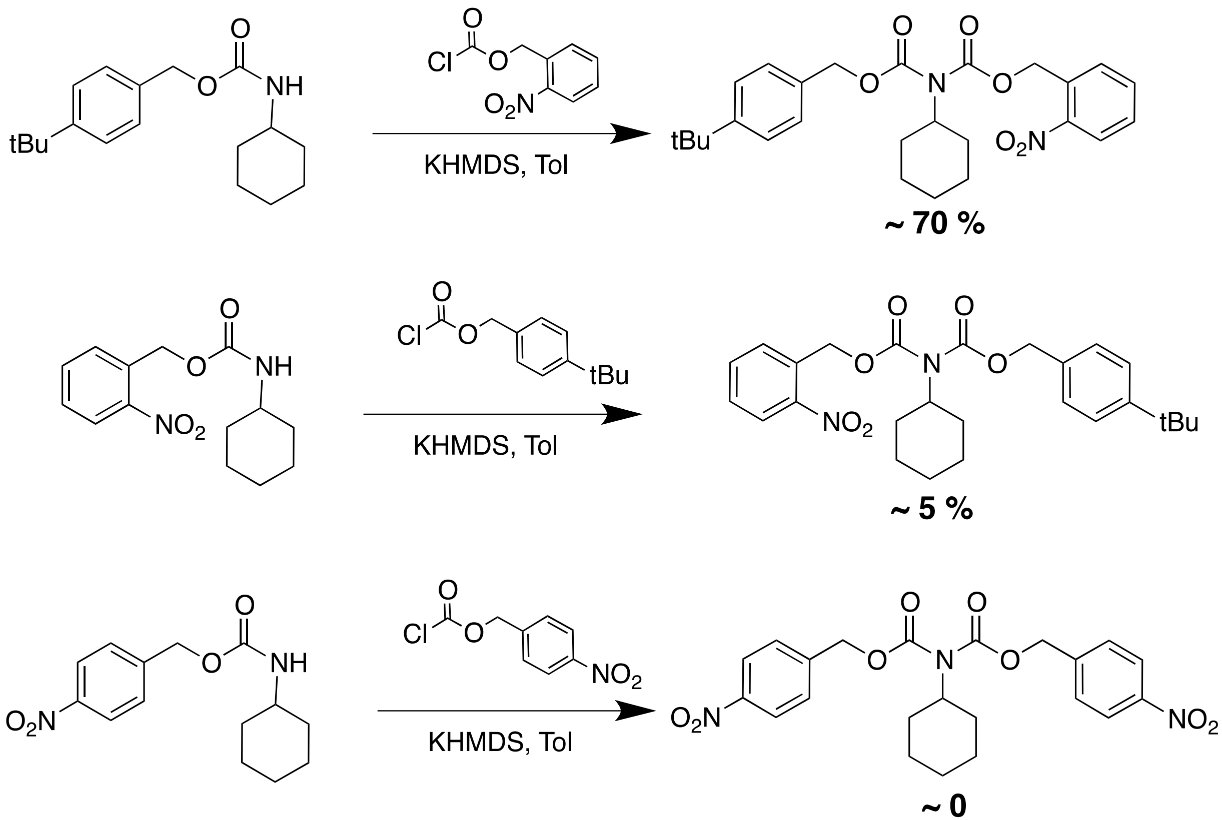
$\Phi_{1st\text{-}stage} = 0.04$

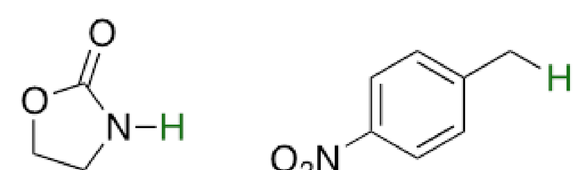


$\Phi_{2nd\text{-}stage} = 0.56$

Sadly quantum efficiencies lead to pseudo 1st order kinetics.

Toward the difunctional PBG

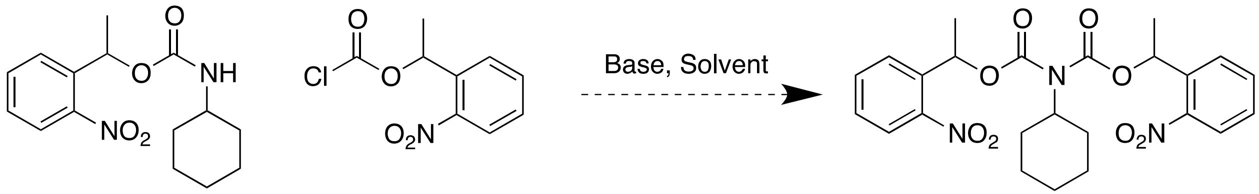




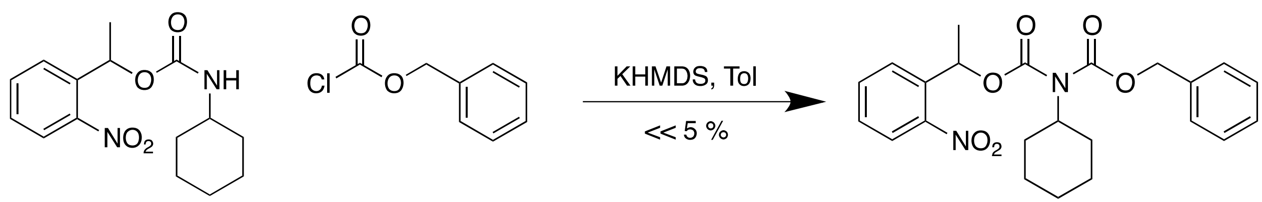
pK$_a$: 20.8

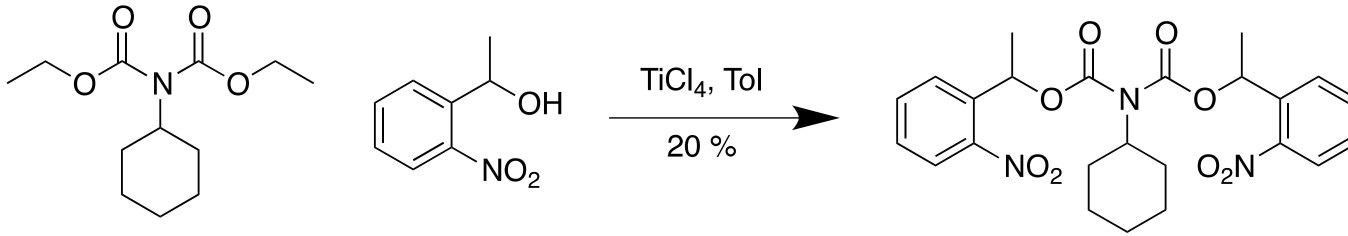
pK$_a$: 20.4

Close pK_a presents a synthetic challenge



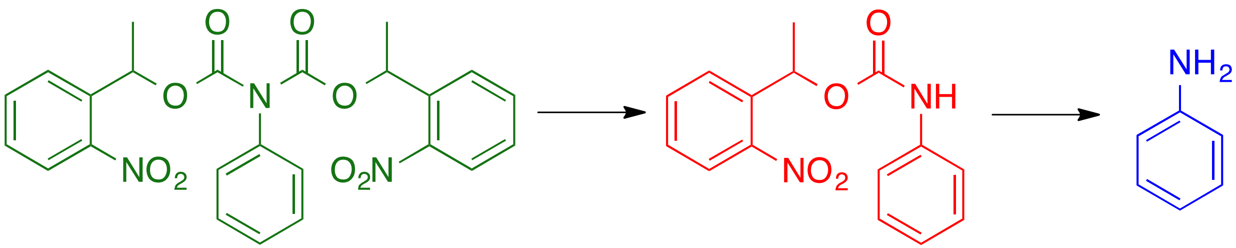
Entry	Base	Solvent (M)	E^+ (equiv)	T ^{o}C	% Yield
1	KHMDS	tol	2.0	0 - RT	0
2	KHMDS	THF	1.5	0 - RT	0
3	KHMDS	tol	4.0	RT	0
4	sec-BuLi	THF	1.5	-78 - RT	0
5	n-BuLi	tol	1.5	-78 - RT	0
6	TEA	tol	1.1	110	0
7	DBU	tol	2.0	110	0



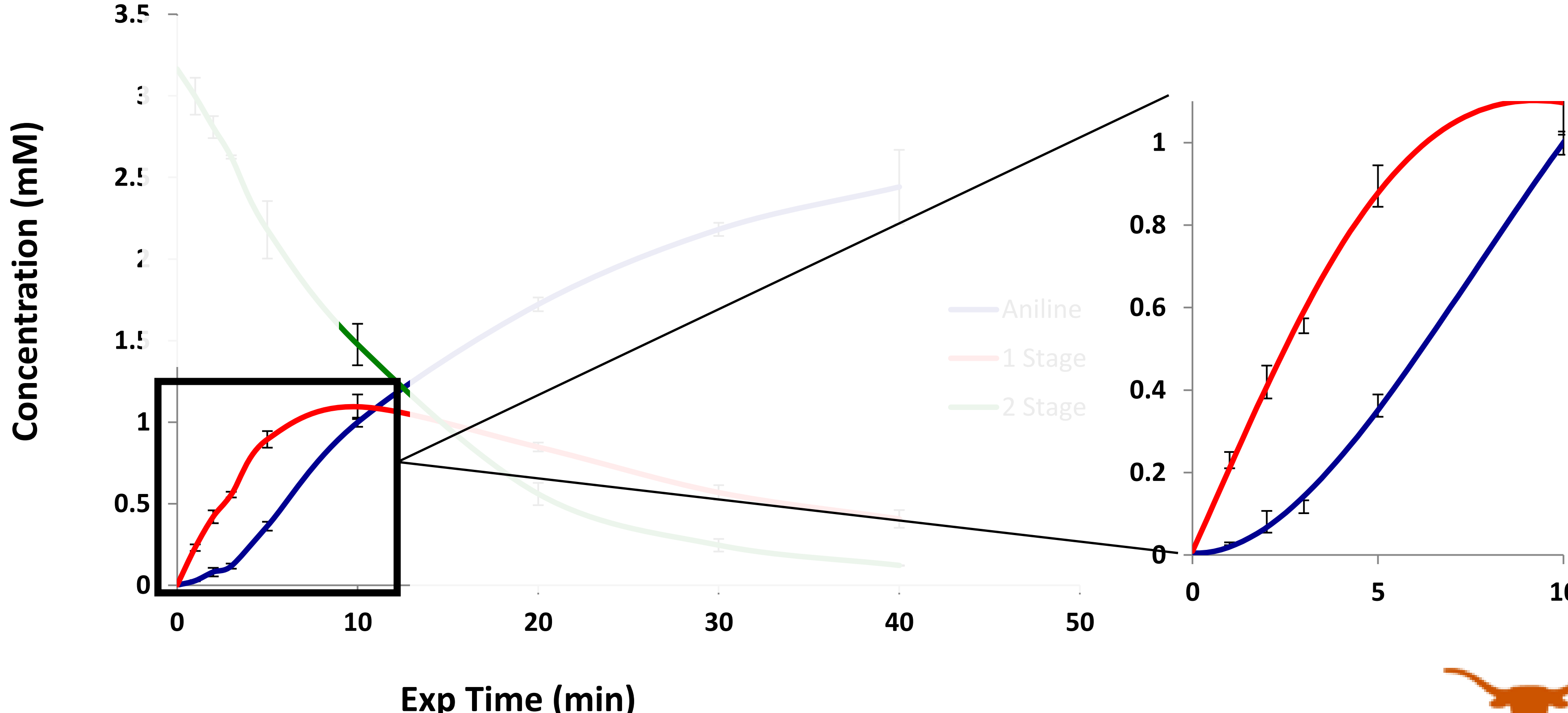


CHA-BisMeNO2

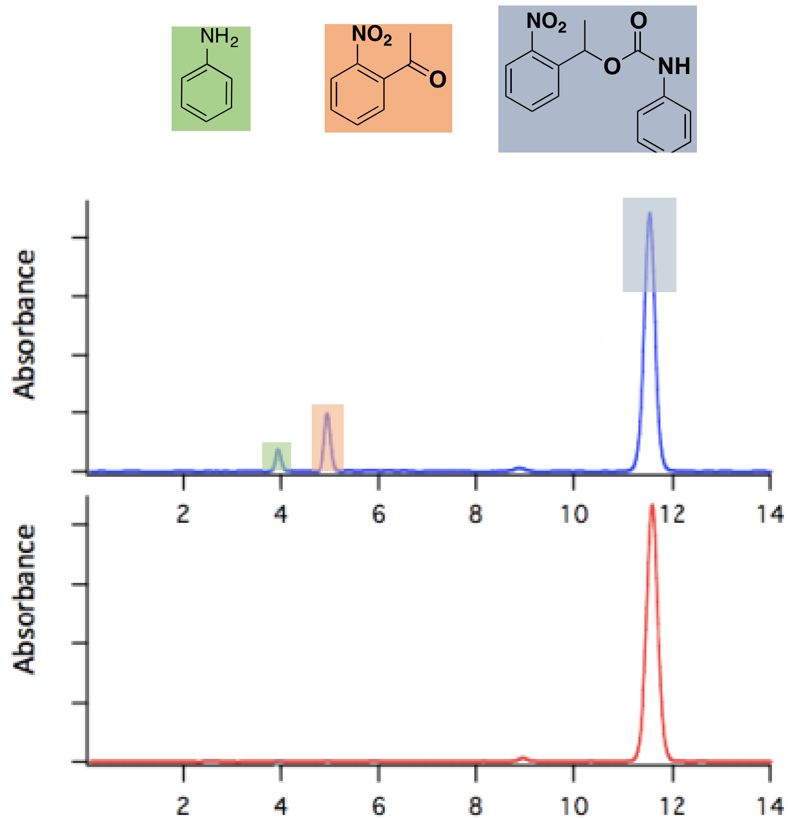
Base Generation

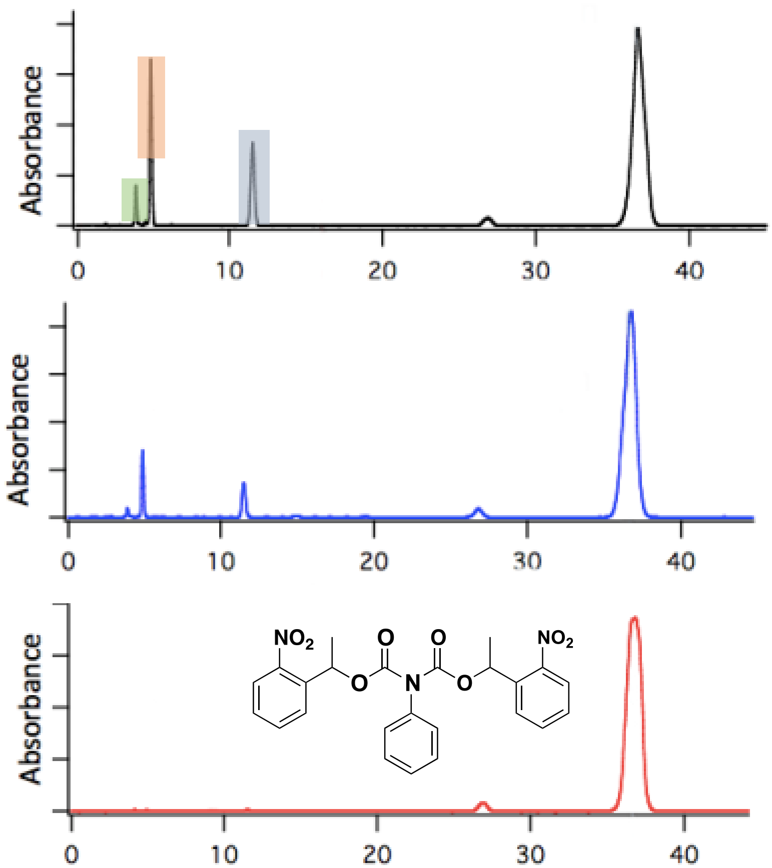


CHA-BisMeNO2 **A-MeNO2**



Quantum efficiency by HPLC analysis





$\Phi_{1\text{-PBG}} = 0.21$

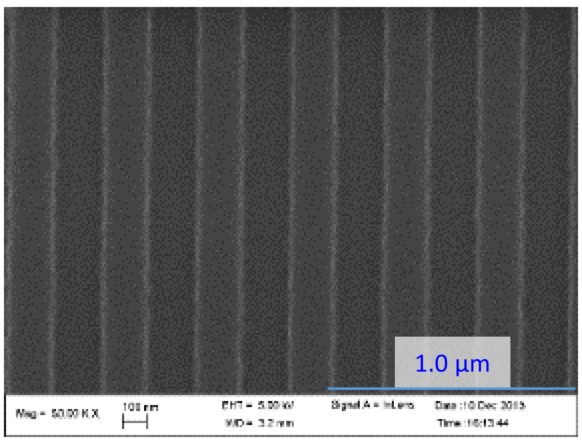
$\Phi_{2\text{-PBG}} = 0.12$

Quantum efficiency for first stage is only ~1.3x the second

Efficiency based upon valerophenone standard.

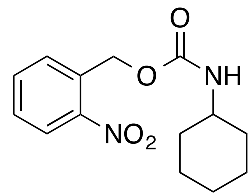
Lithographic Demonstration of Principle

Plain Resist

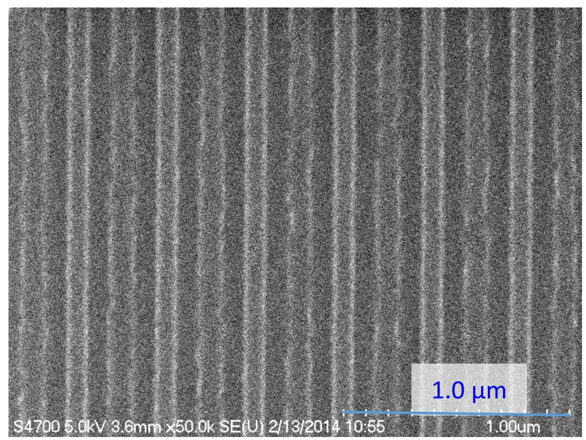


PEB=110ºC E_{op}= 1.6mJ)

	CD	LWR	LER
P	202	12	8

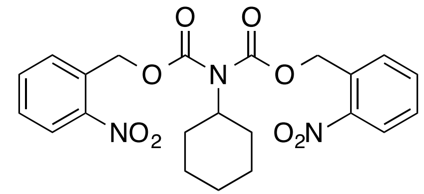


1-Stage PBG (4.5 m)

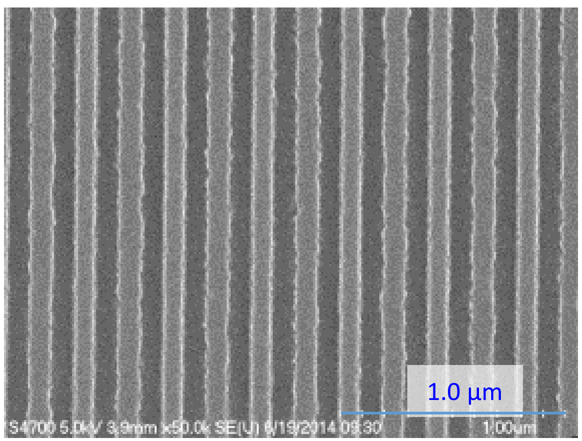


PEB=109ºC E_{op}= 16 mJ

	CD	LWR	LER
P	103	12	9
N	113	44	23



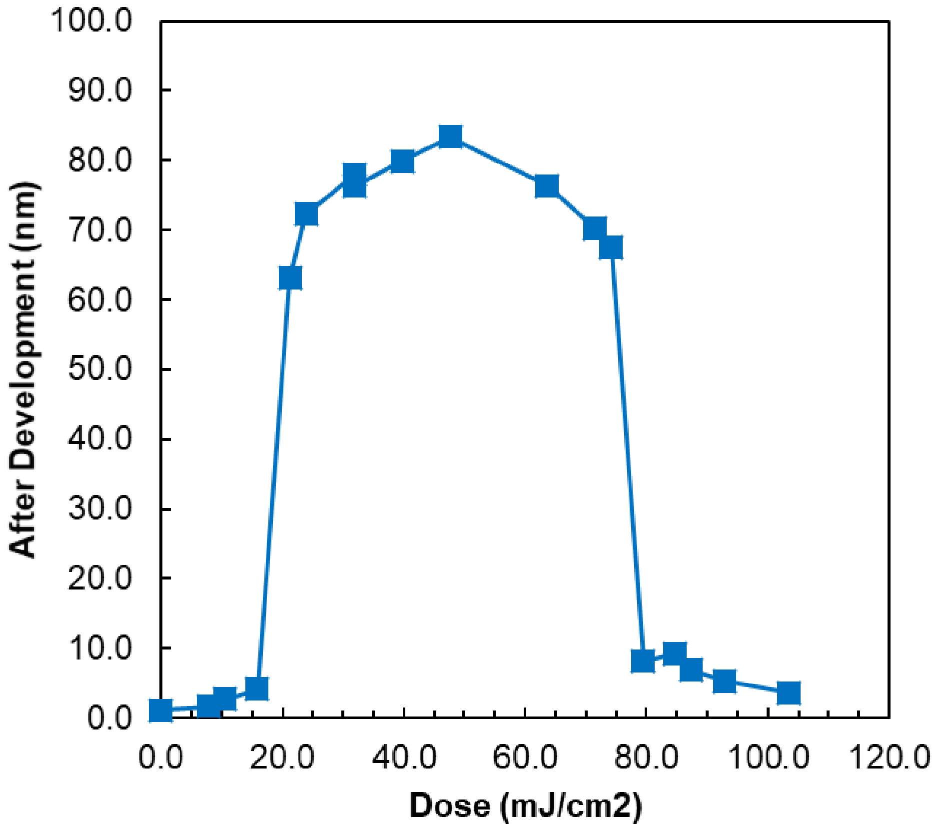
2-Stage PBGb



PEB=100ºC E_{op}= 10.9 mJ

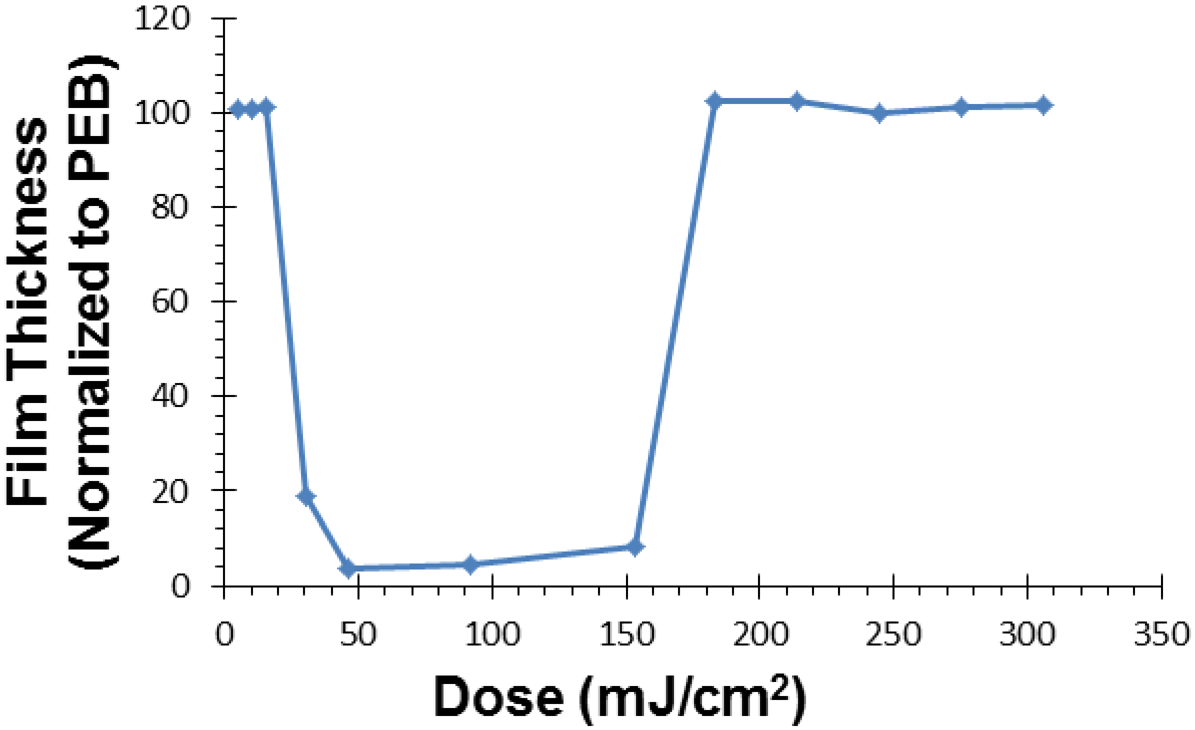
	CD	LWR	LER
P	100	9	6
N	110	17	12

Pitch Doubling in Negative Tone at i-Line



Early proof of concept data
Ji Yeon Kim

Pitch Doubling in Positive Tone at i-Line



Early proof of concept data
Paul Meyer