Acid Amplifiers Designed For EUV Resists Can Help Beat the RLS Trade-off

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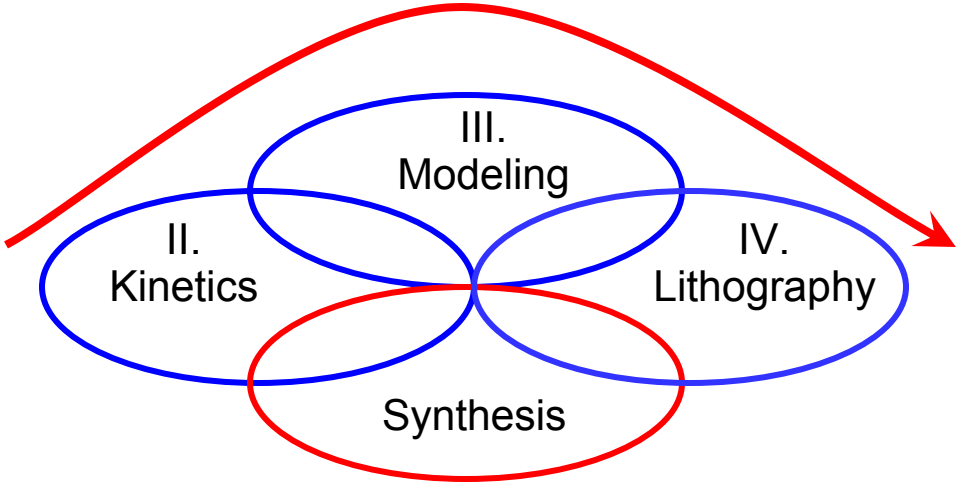
I. Introduction
II. Kinetics
III. Modeling
IV. Lithography
V. Conclusions



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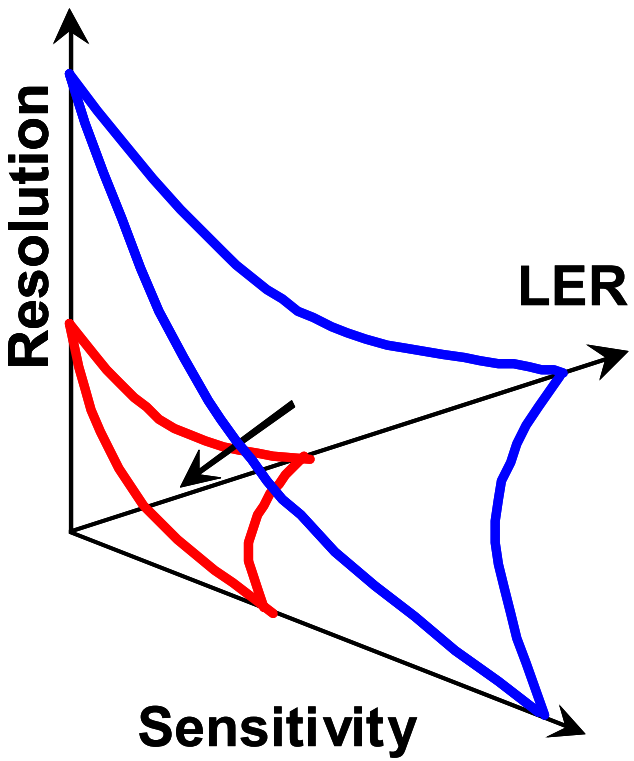
I. EUV Resist Goals



Resolution

Line Edge Roughness (LER)

Sensitivity

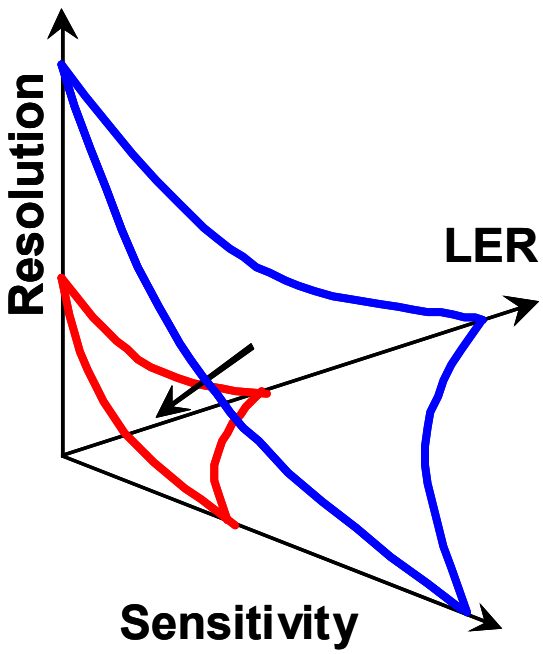
RLS Tradeoff

Minimize:

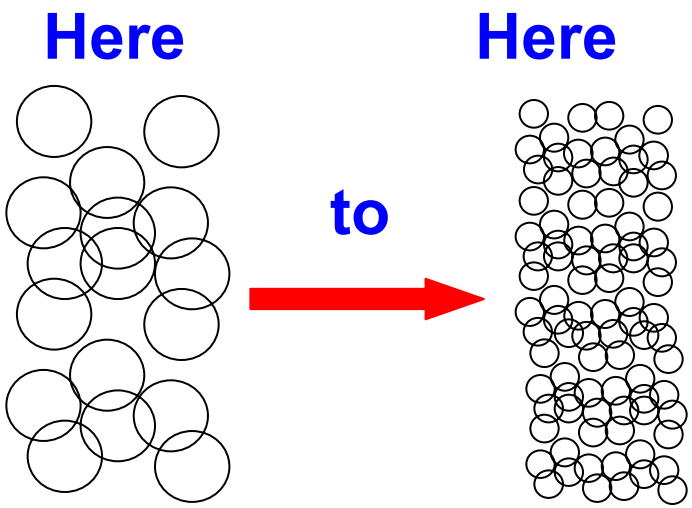
(Resolution)^3 x (LER)^2 x Esize = Z-Parameter

T. Wallow, C. Higgins, R. Brainard *et al. Proc. SPIE* **6921** (2008)

How to Simultaneously Improve Resolution, LER and Sensitivity?



We propose that higher quantum yield will allow us to go from…



…with no penalty to sensitivity.

$$\text{Film Quantum Yield} \equiv \frac{\text{Moles of Acids Generated in the Film}}{\text{Moles of Photons Absorbed by the Film}}$$

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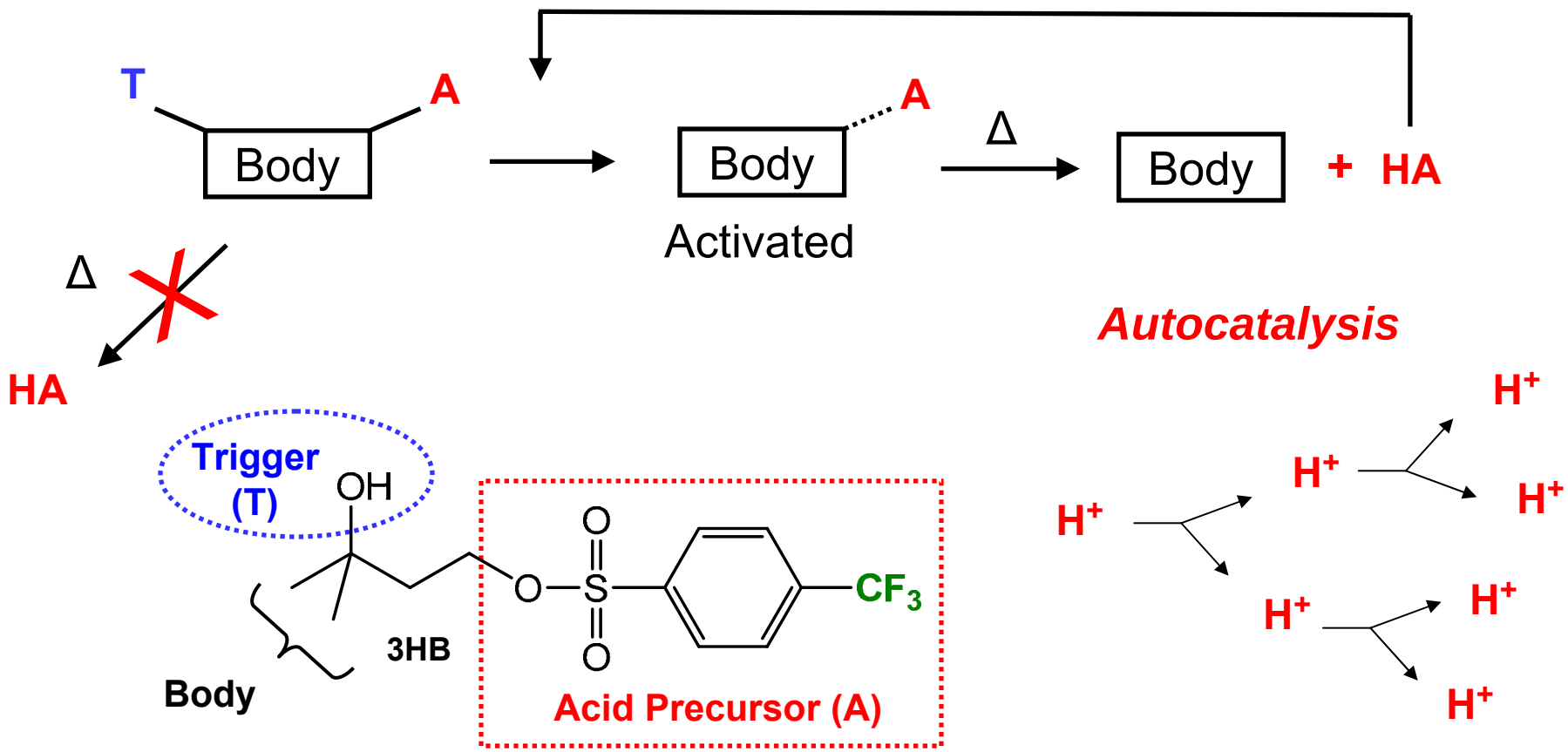
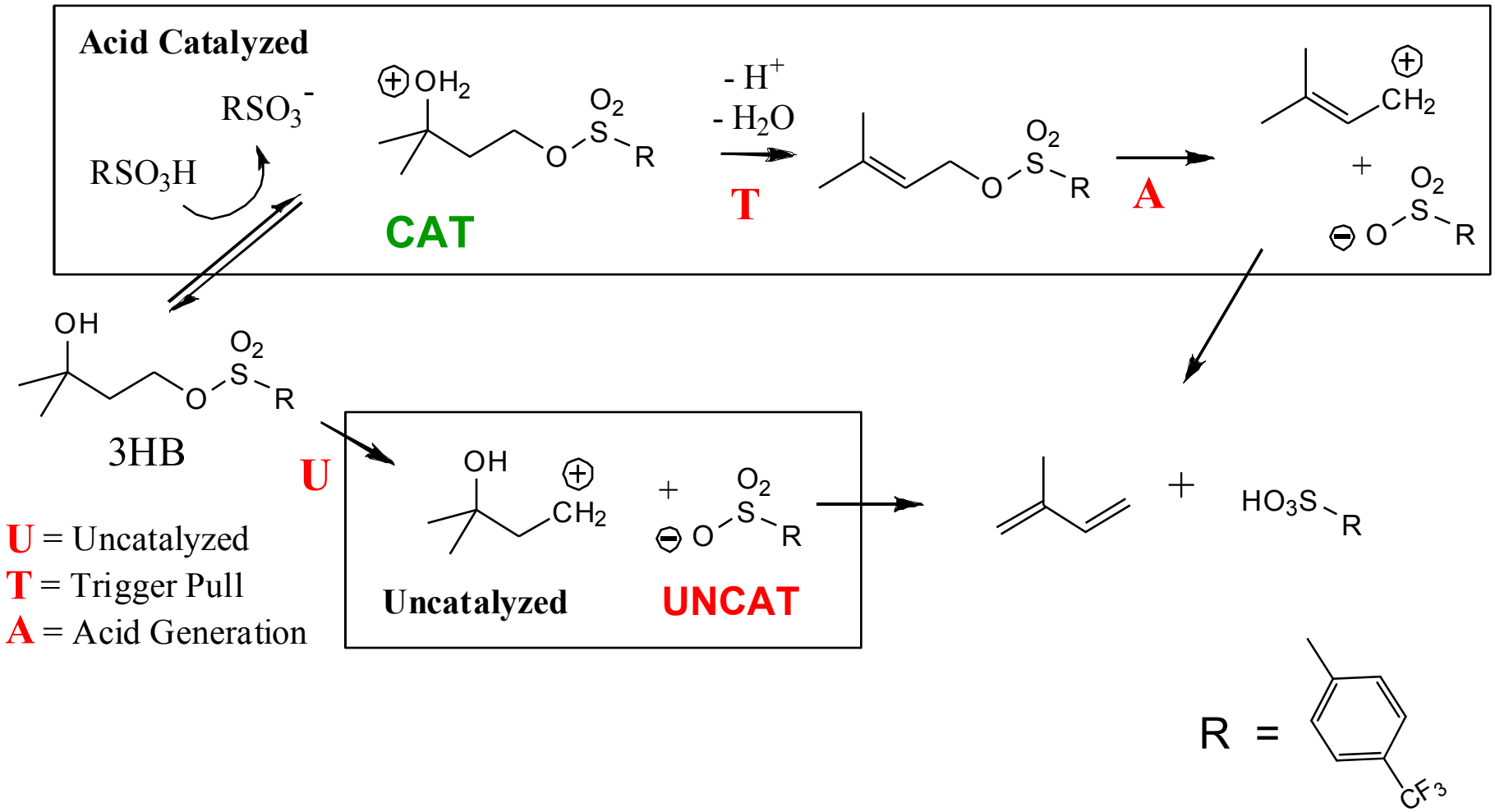
Acid Amplifiers

One possible way to *effectively* increase the quantum yield of the resist is through the use of acid amplifiers (AAs).



Proposed Mechanism



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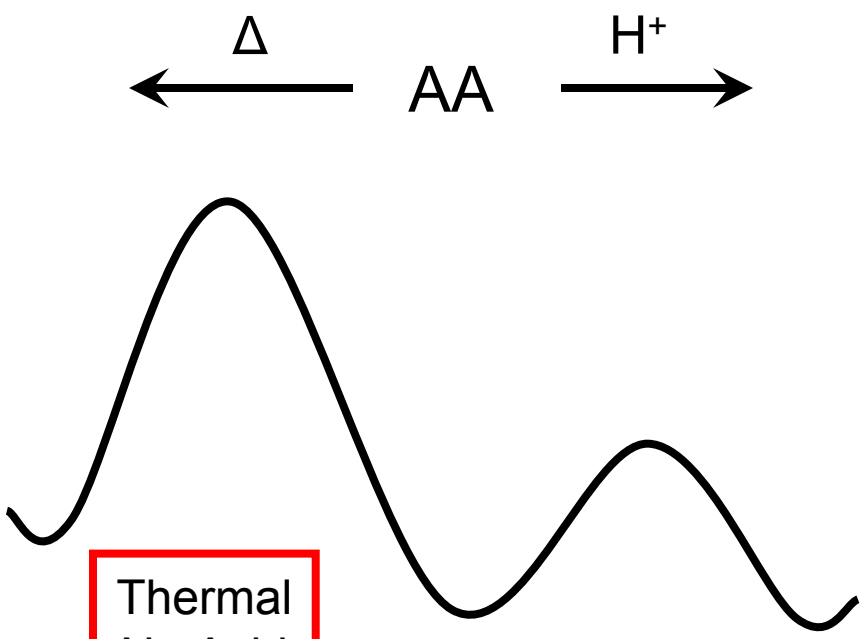
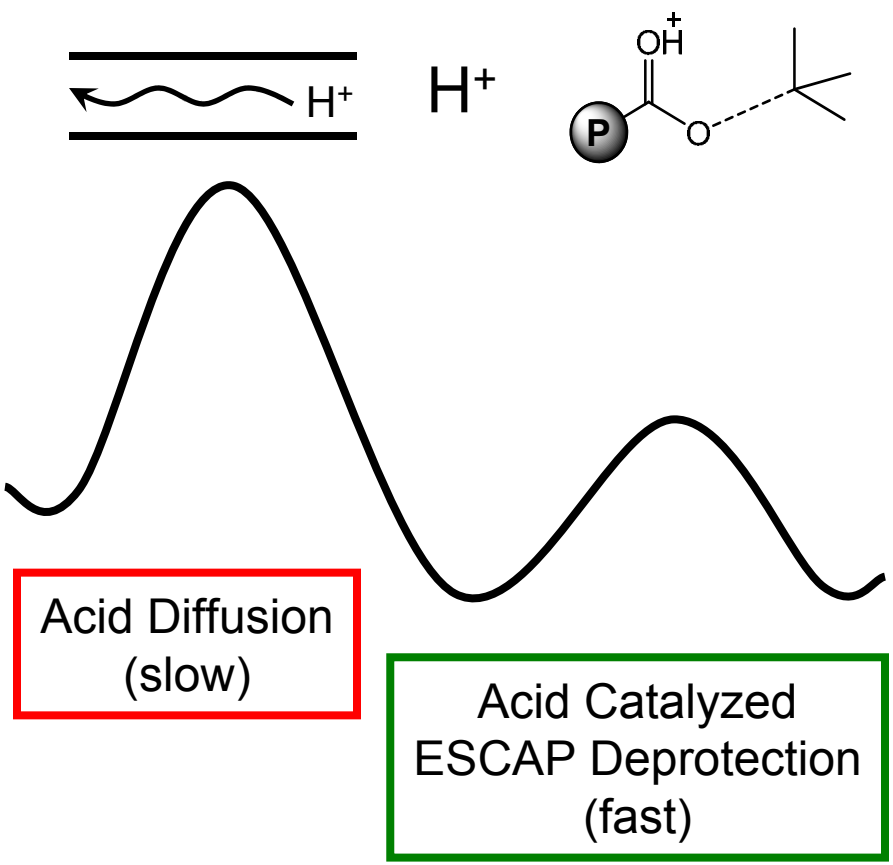
AA Decomposition and Behavior in Resist

AA Decomposition Kinetics



Acid Behavior in Resist



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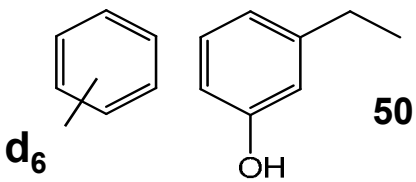
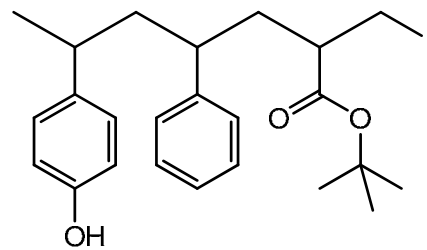
II. AA Decomposition Kinetics using ^{19}F-NMR Spectroscopy

Solvent System for Kinetics



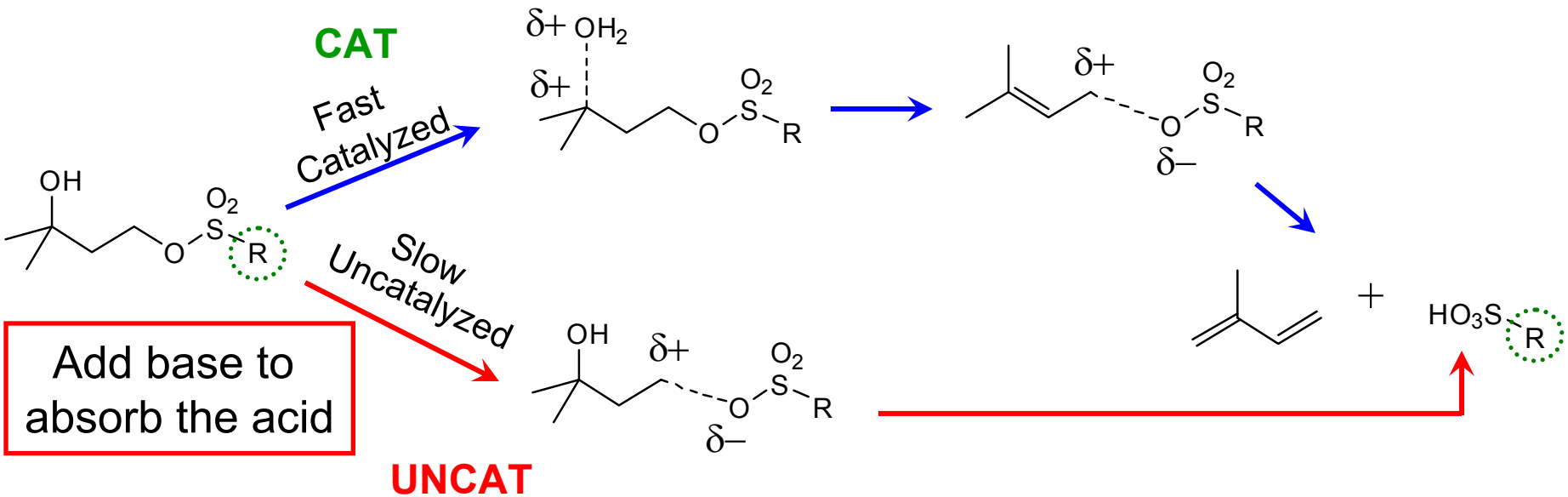
50 / 50 wt %

Resist Polymer



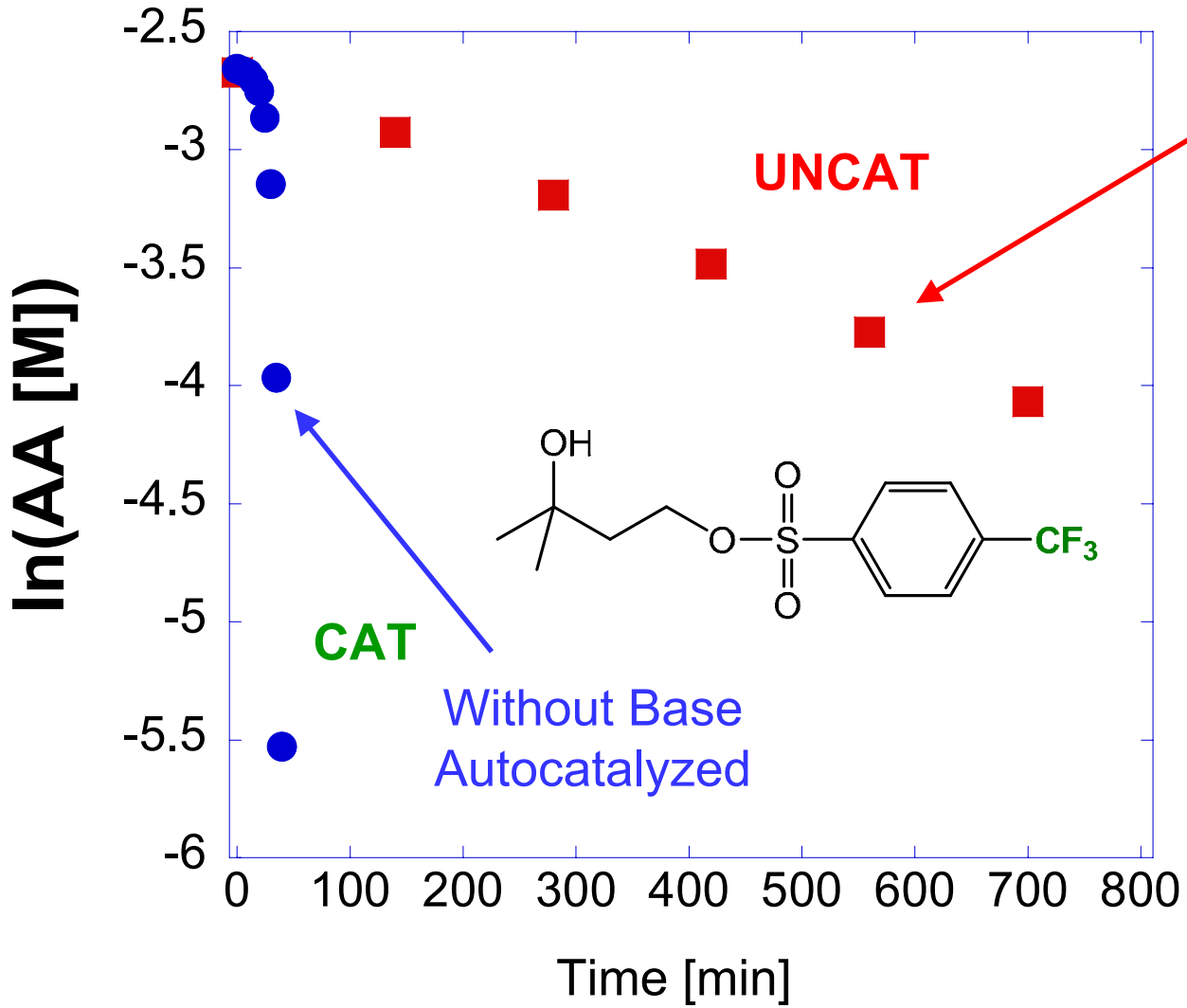
65/20/15

Solvent system is a good model for resist environment

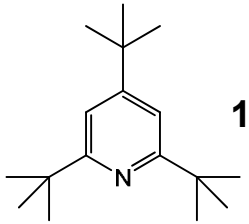


Add base to absorb the acid

With and Without Base



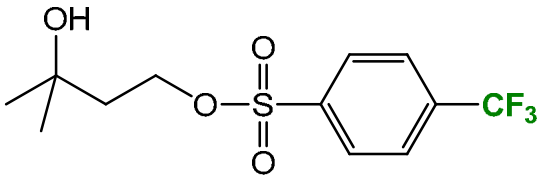
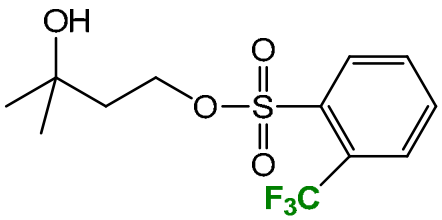
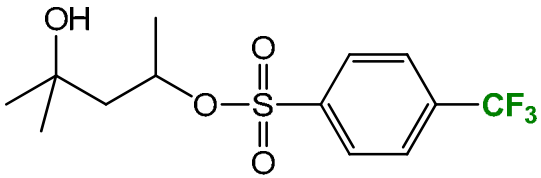
With Base
(Uncatalyzed
& First-Order)

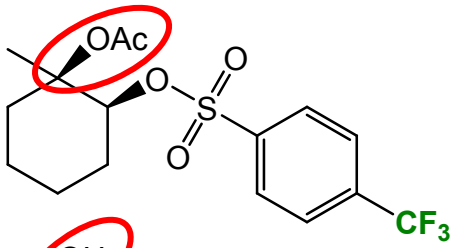
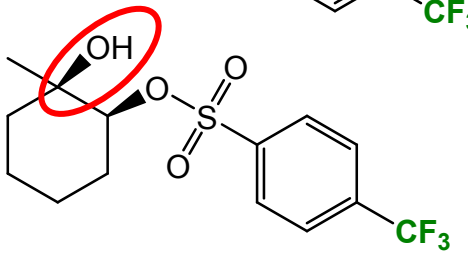


1.2 eq.

Decomposition at 100 °C

Reaction Rates Ratios at 100 °C

	$\frac{k_{CAT}}{k_{UNCAT}}$
	1425
	1359
	25

	$\frac{k_{CAT}}{k_{UNCAT}}$
	490
	1

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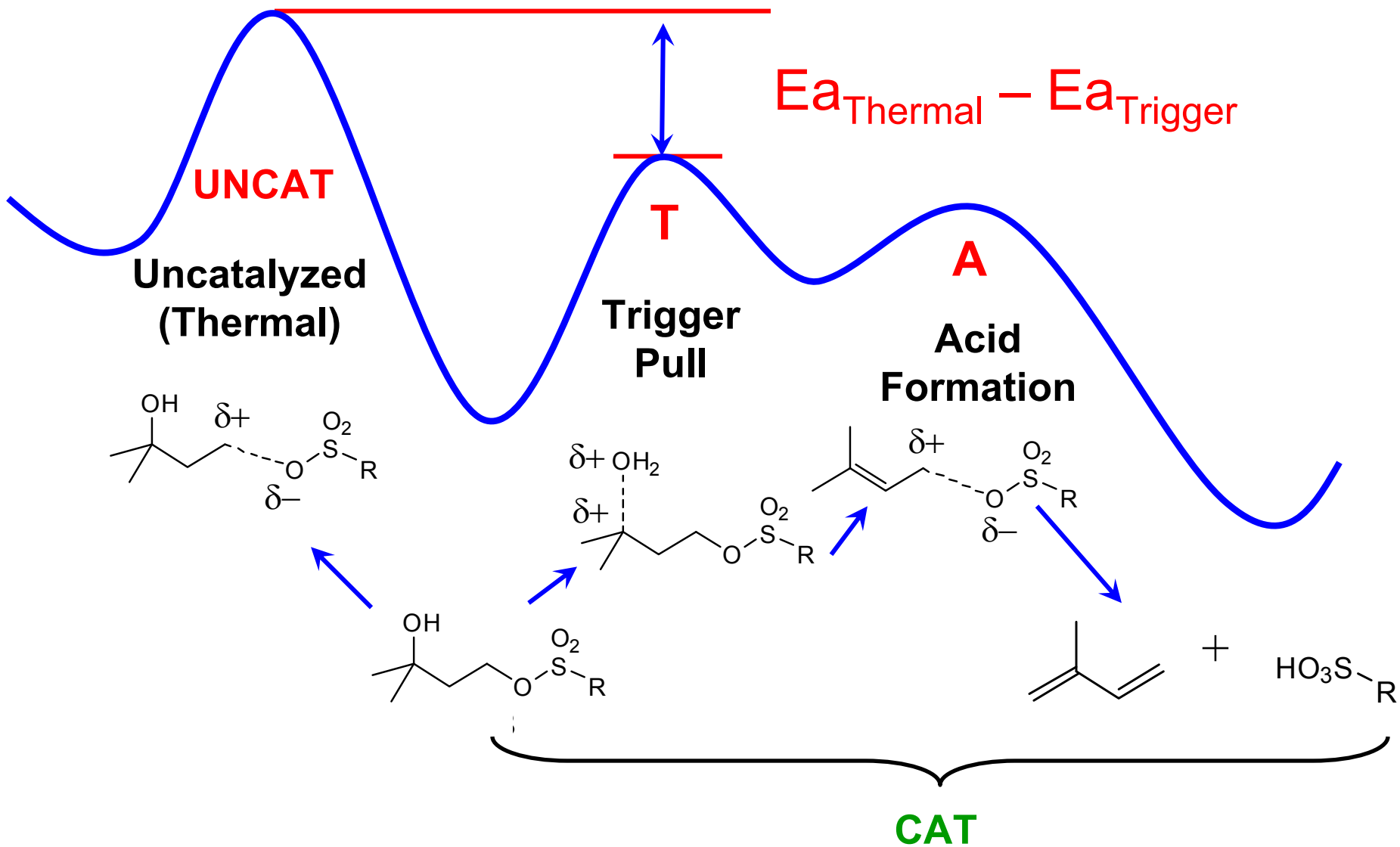
III. Kinetic Modeling



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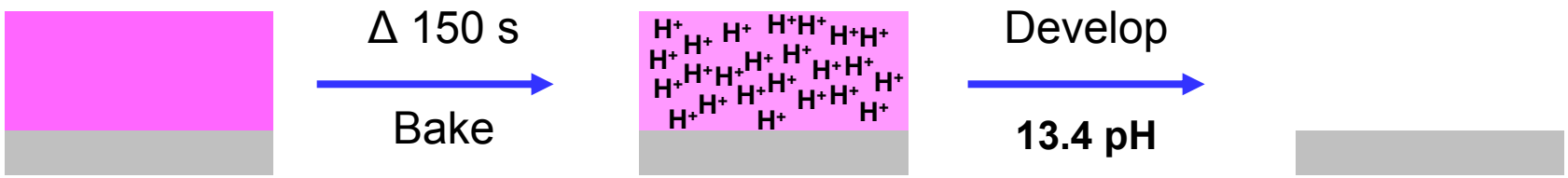
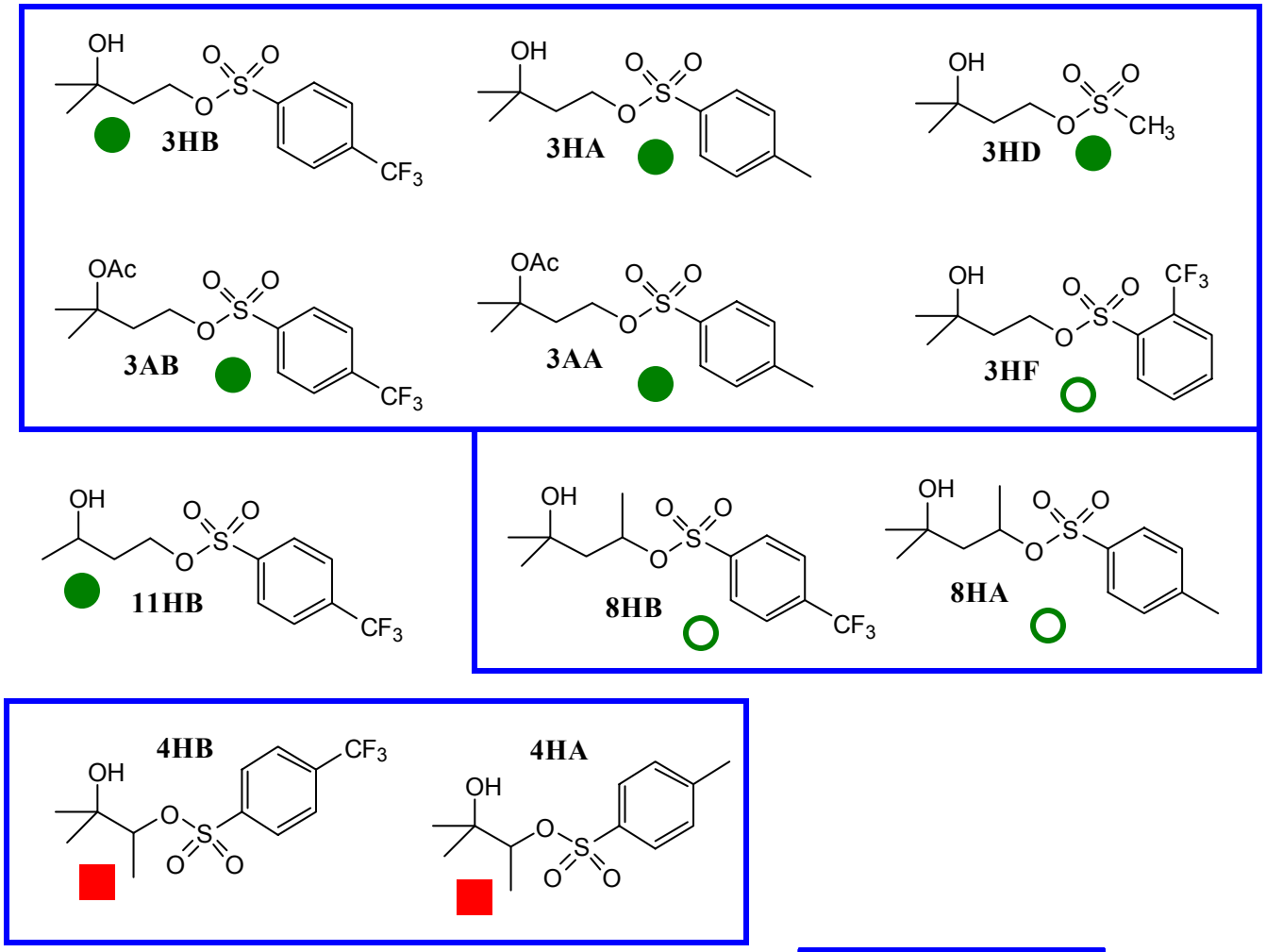
Thermal Stability Test

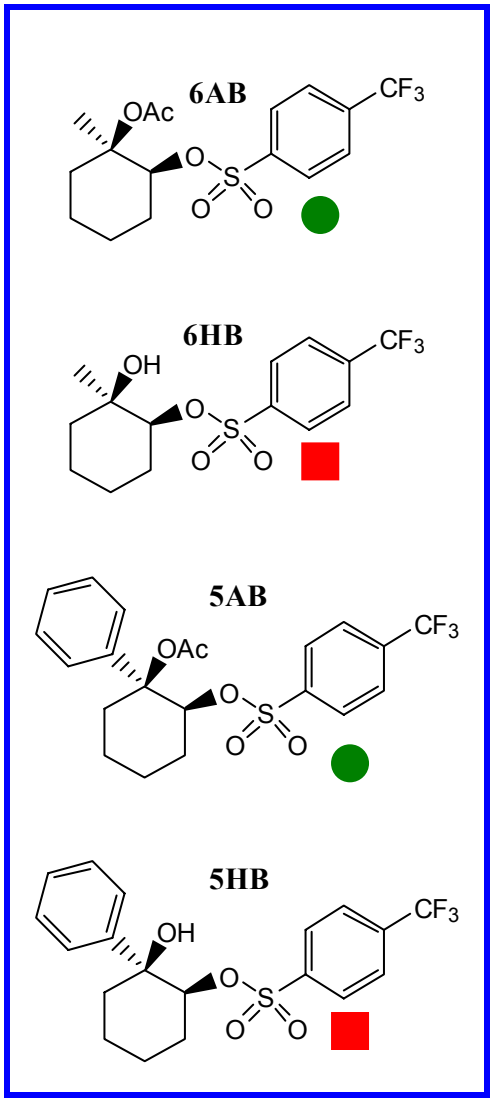
Thermal Acid Generator (TAG)



- Passed 110 °C
- Passed 70 °C
- Failed

Acid Amplifier Examples





Unexposed Film Thickness Loss (UFTL) Test Results

- Passed 110 °C
- Passed 70 °C
- Failed

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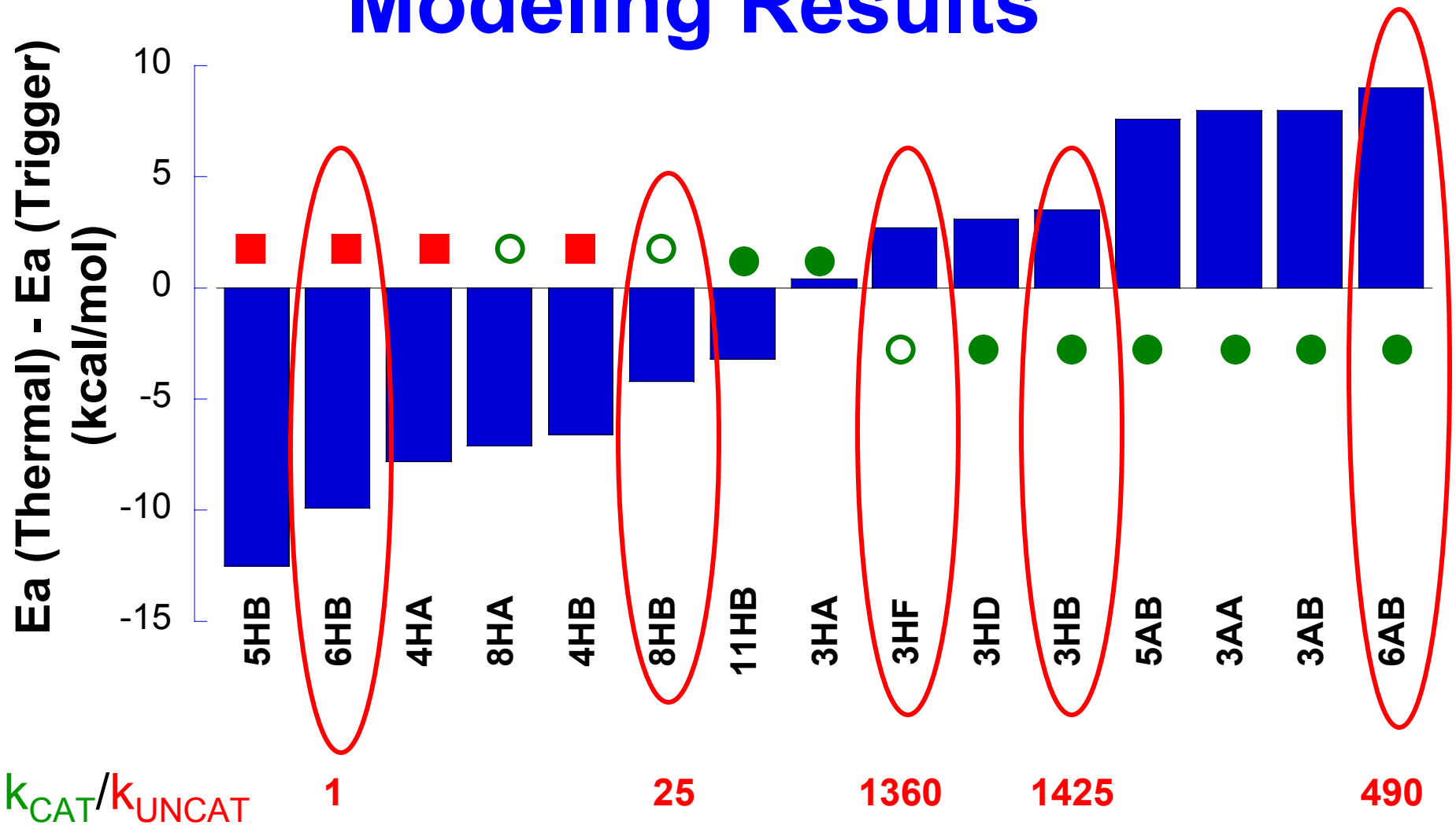
Modeling Results



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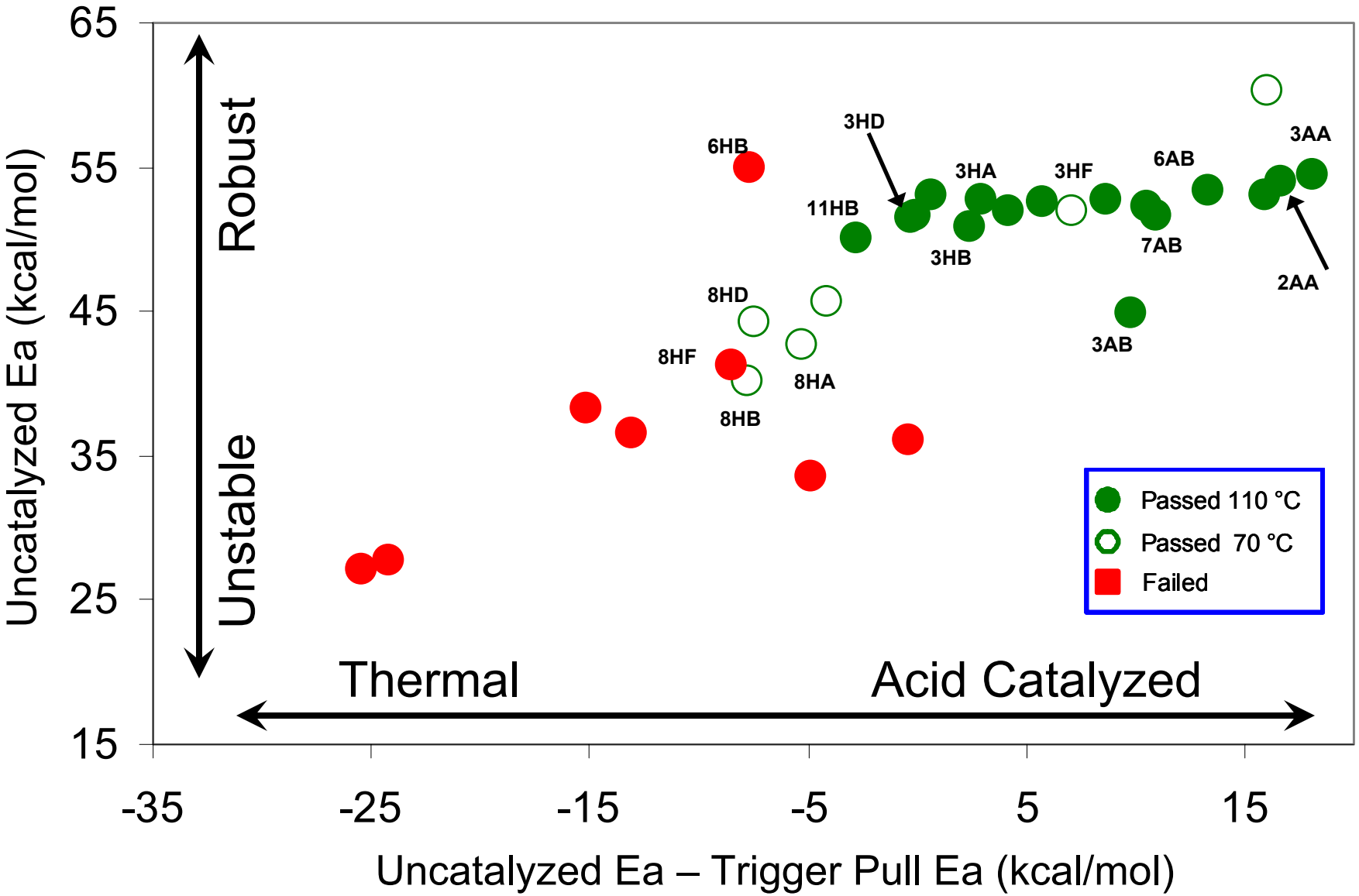
Thermal Stability and Modeled Activation Energy



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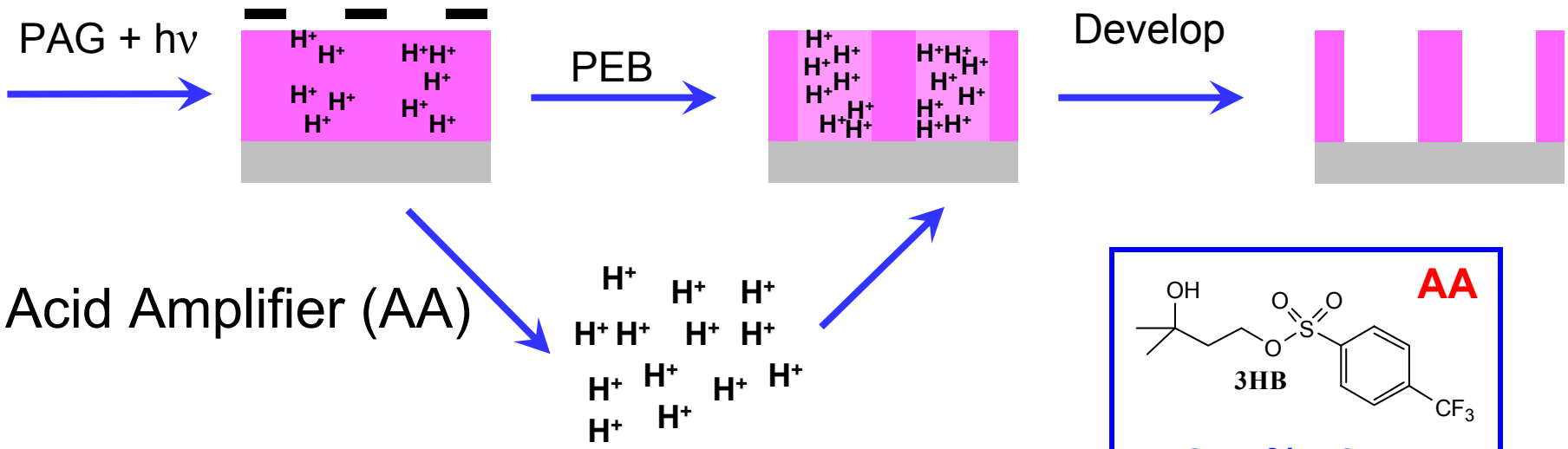
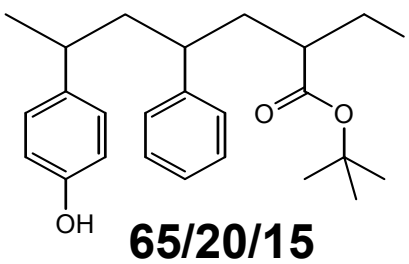
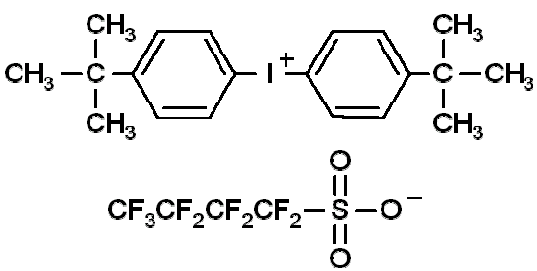
IV. Lithography

Resist Chemistry and Process

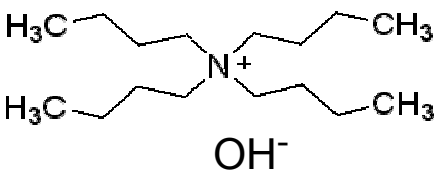




Polymer



7.5 wt% PAG



0.5 or 1 wt % Base

Resist Thickness 125 nm

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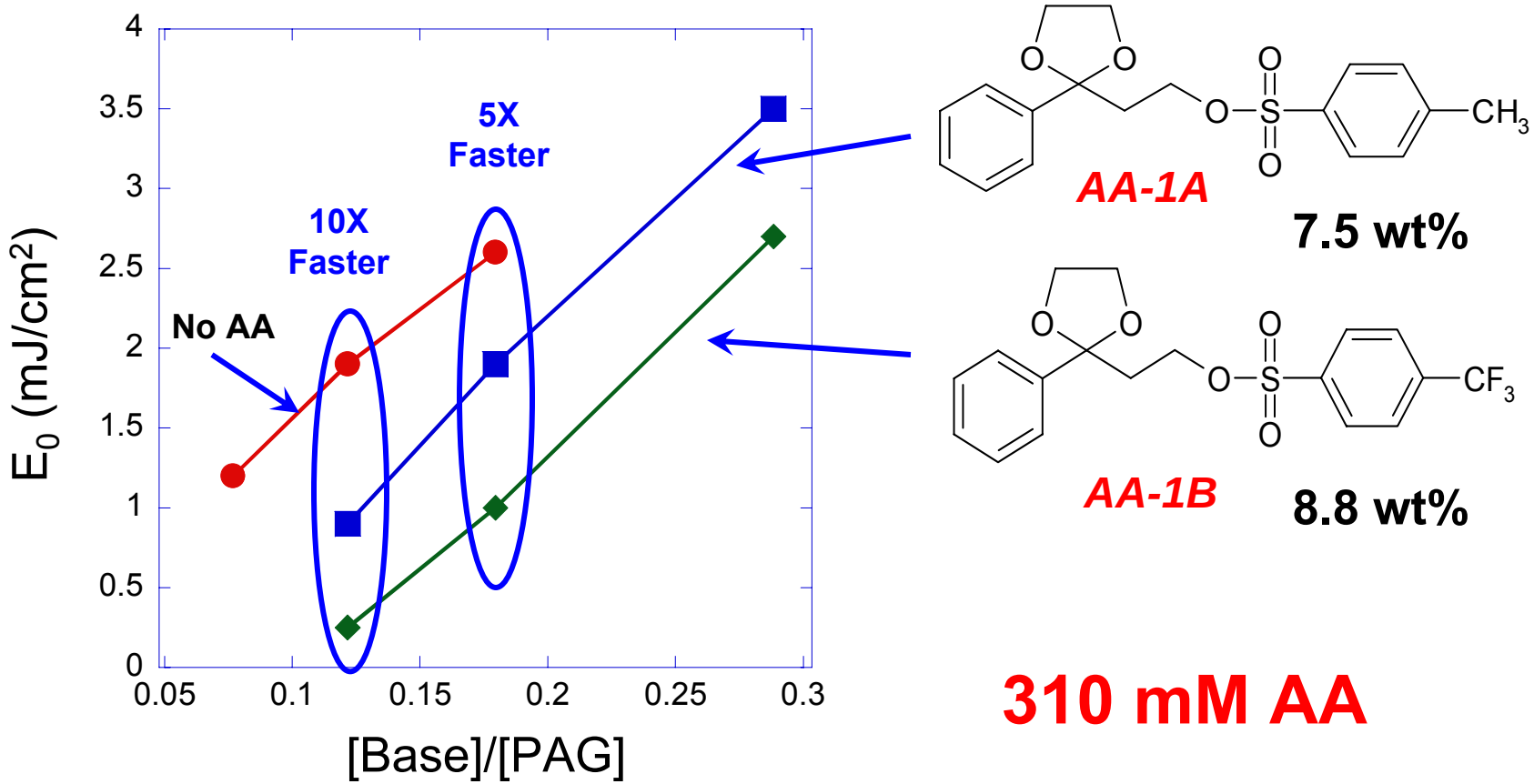
Fluorinated AAs Give Better Sensitivity than Nonfluorinated

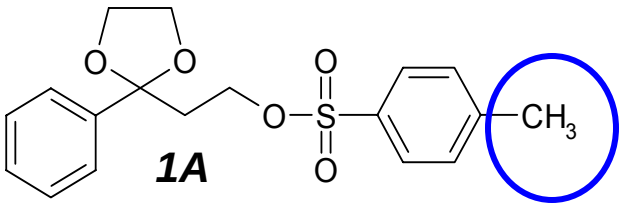


310 mM AA

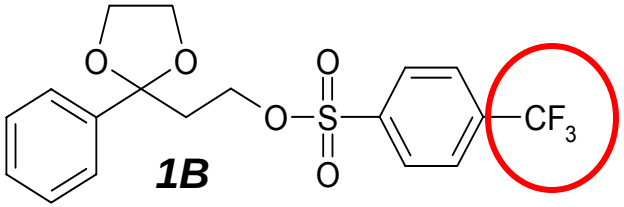
Process:
Tool: BMET
7.5 wt% PAG

PAB: 130˚C / 60
PEB: 130˚C / 90
Develop: 45 sec

Fluorinated Tosic Acid Shows Better Controlled Acid Diffusion than Tosic Acid



1A

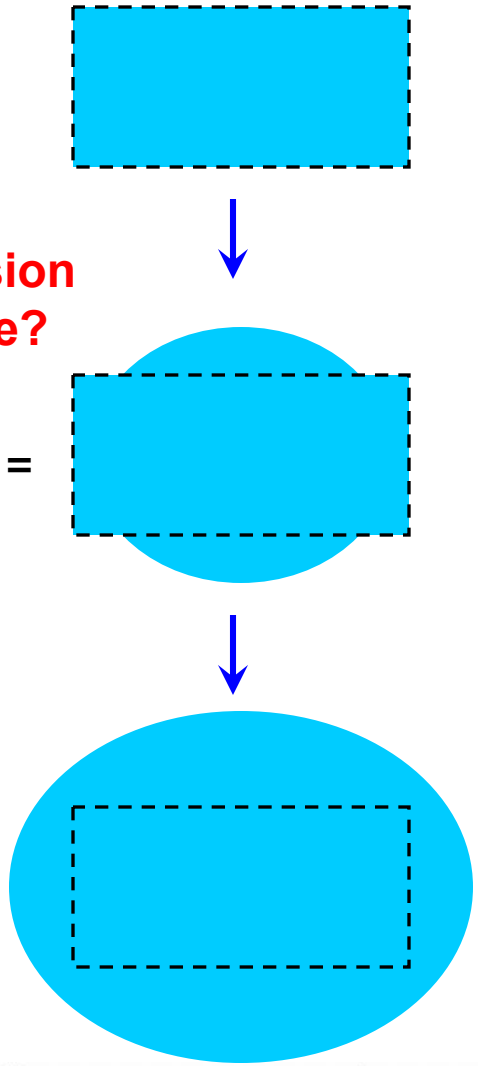


1B

	Ec / E0	
Base (wt %)	***1A***	***1B***
0.35	1.1	6.8
0.5	1.1	> 3.5*
0.8	1.2	> 1.9*

Diffusion Issue?

Ec =



Ec ≡ Critical Dose

Dose resist starts to clear outside the open frame

Using ***AA-1A***
2-3 wafers cleared completely

*Did not reach Ec

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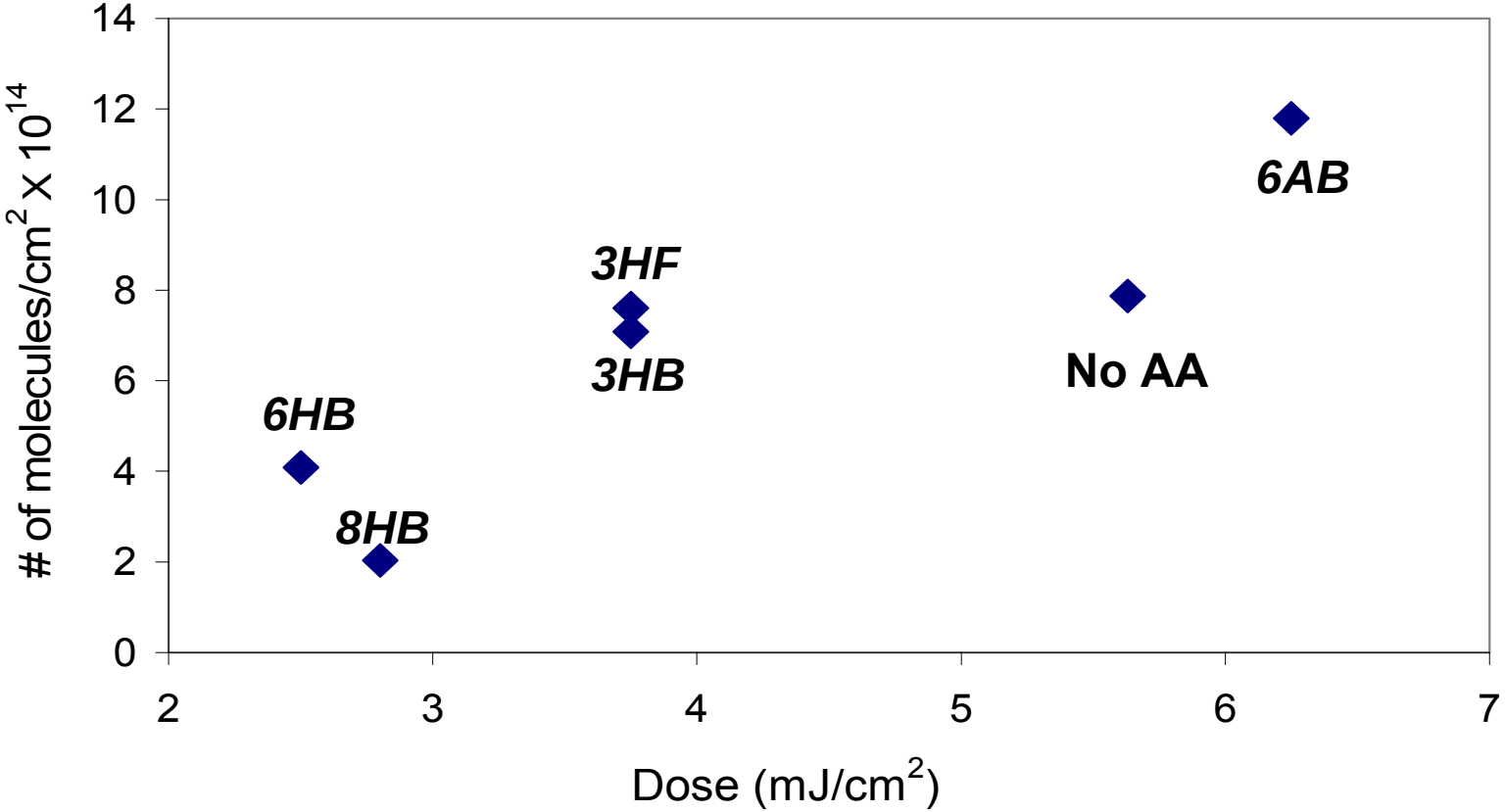
Outgassing *vs*. Dose



Outgassing increases with dose as expected

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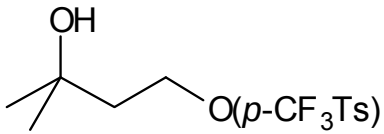
Acid Amplifiers Improve Sensitivity And Are Not Photosensitive

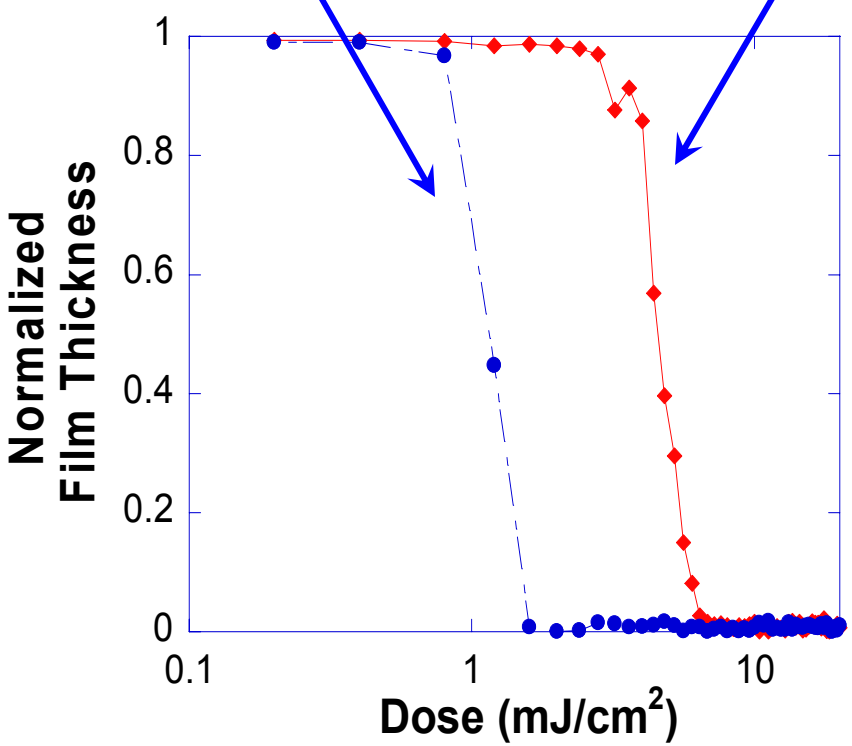
70 m*M*



Eo = 1.6 mJ/cm²

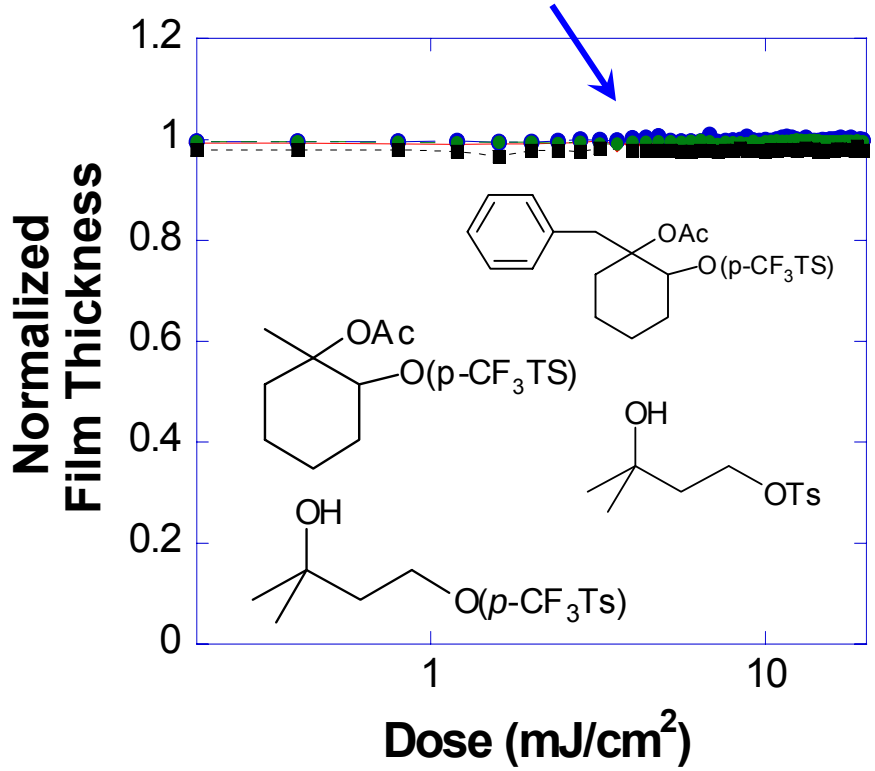
Control
No Acid Amplifier

Eo = 6.4 mJ/cm²



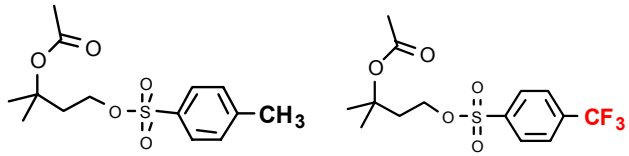
AA resists without PAG

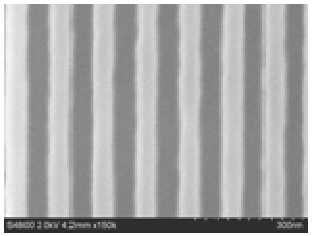
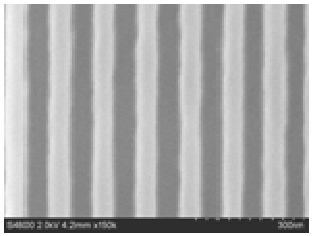
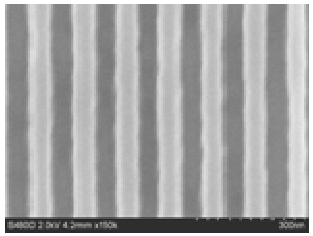
No change in dissolution rate ≤ 20 mJ/cm²



Tool: AMET
Base 0.5 wt %
PAB 110 °C / 60 s
PEB 110 °C / 60 s

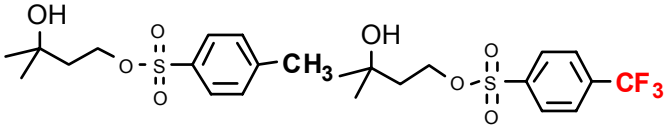
Effect of Trigger and Acid Precursor



	No AA	CH_3	CF_3
60 nm L/S			
E_{size} (mJ/cm^2)	7.6	5.4	4.9
LER (nm)	4.0	4.7	4.2
Z-Parameter	26	26	19

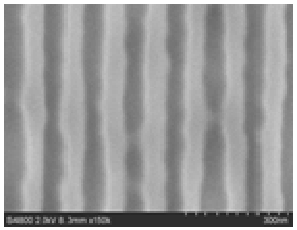
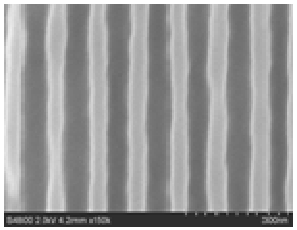
Acid Precursors:

-CF_3 gives better sensitivity, LER and exposure latitude



Triggers: -OH *vs.* -OAc

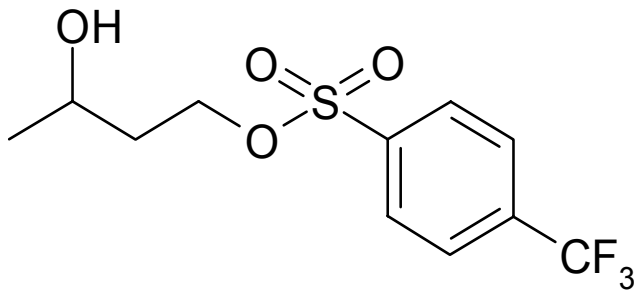
-OH gives better sensitivity than -OAc

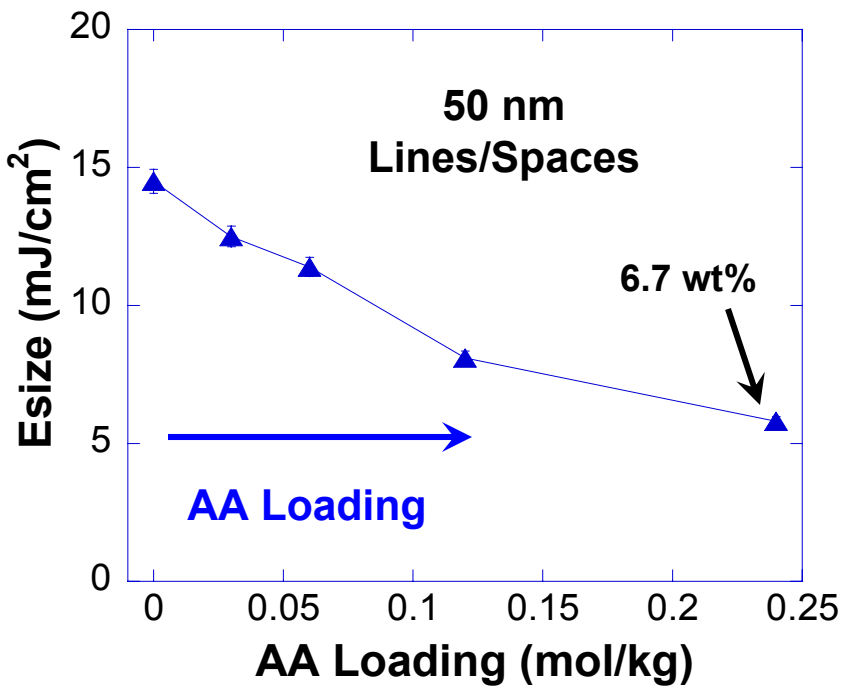
	CH_3	CF_3
		
E_{size} (mJ/cm^2)	3.5	1.9
LER (nm)	9.1	7.9
Z-Parameter	63	26

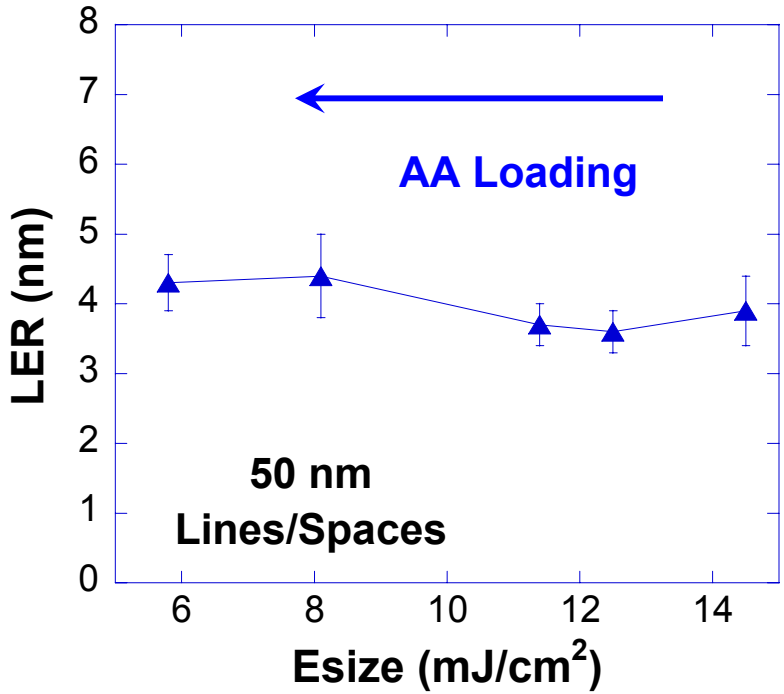
Process:
Tool: BMET
Base 0.5 wt%
70 mM AA

PAB: 130˚C / 60
PEB: 130˚C / 90
Develop: 45 sec

Secondary-Trigger Acid Amplifier







Increased sensitivity without penalty to LER.

Tool: BMET
Base 1 wt %
PAB 110 °C / 60 s
PEB 110 °C / 60 s

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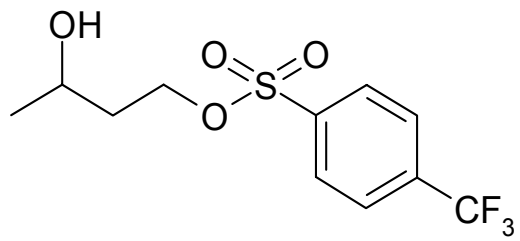
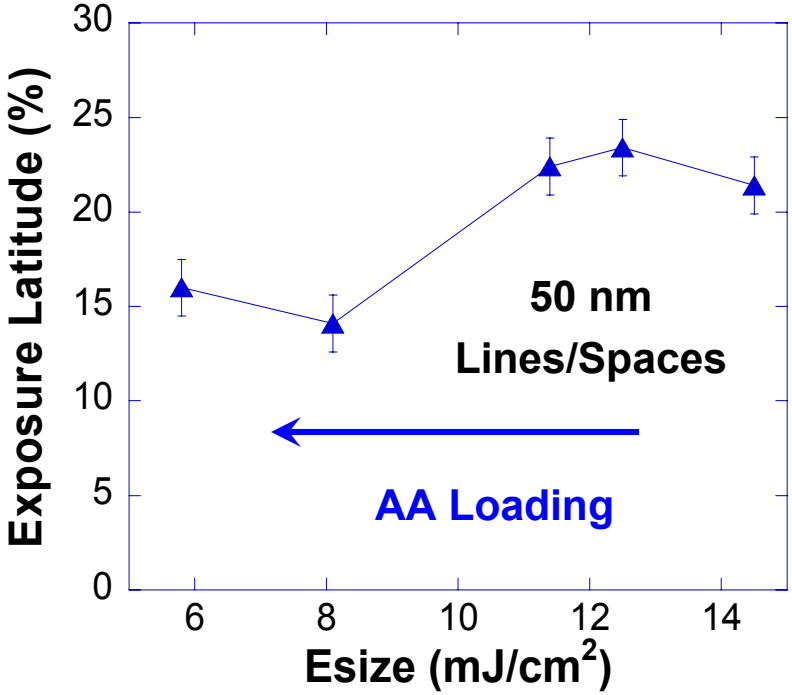
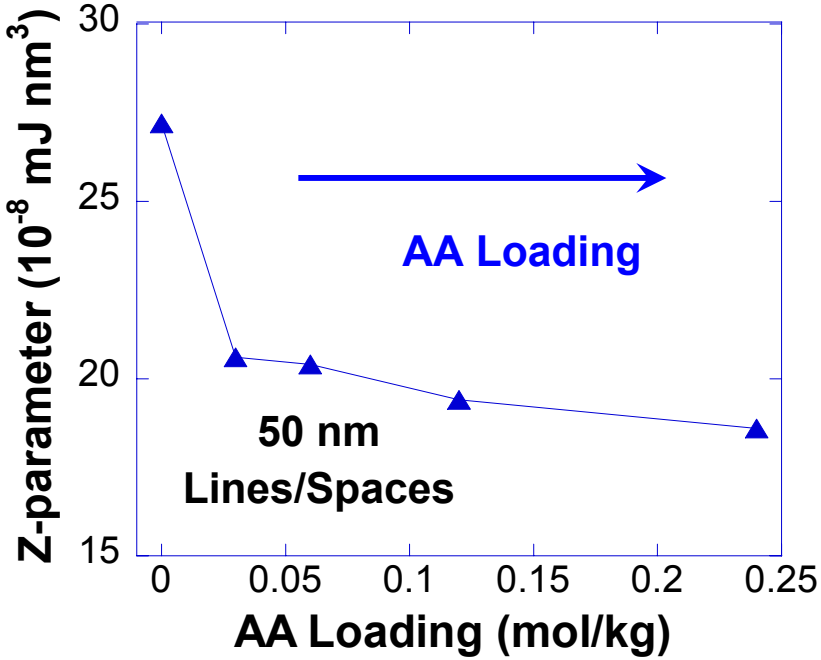
EL & Z-Parameter







Despite some loss in exposure latitude,

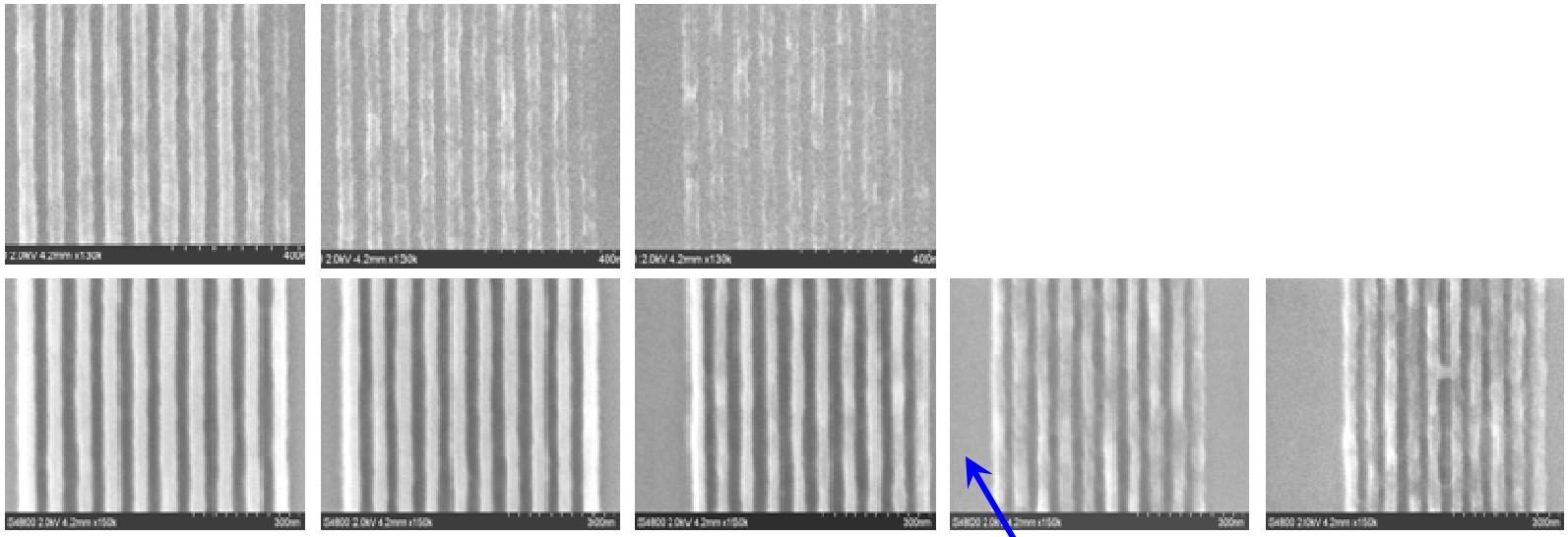
Overall gains in Z-parameter quite strong.

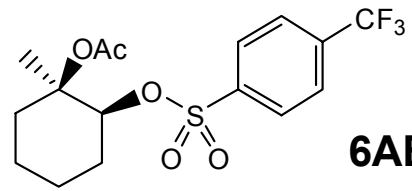
Tool: BMET
Base 1 wt %
PAB 110 °C / 60 s
PEB 110 °C / 60 s

Acid Amplifier: Improved Image Quality

Resolution

	40 nm	38 nm	36 nm	32 nm	30 nm
E_{size} (mJ/cm^2)		21.7			
LER (nm)		8.6	9.4		
No AA					
With AA					
E_{size} (mJ/cm^2)		16.6			
LER (nm)		4.9	5.8		





6AB

Tool: BMET
Base 1 wt %
PAB 90 °C / 60 s
PEB 90 °C / 60 s

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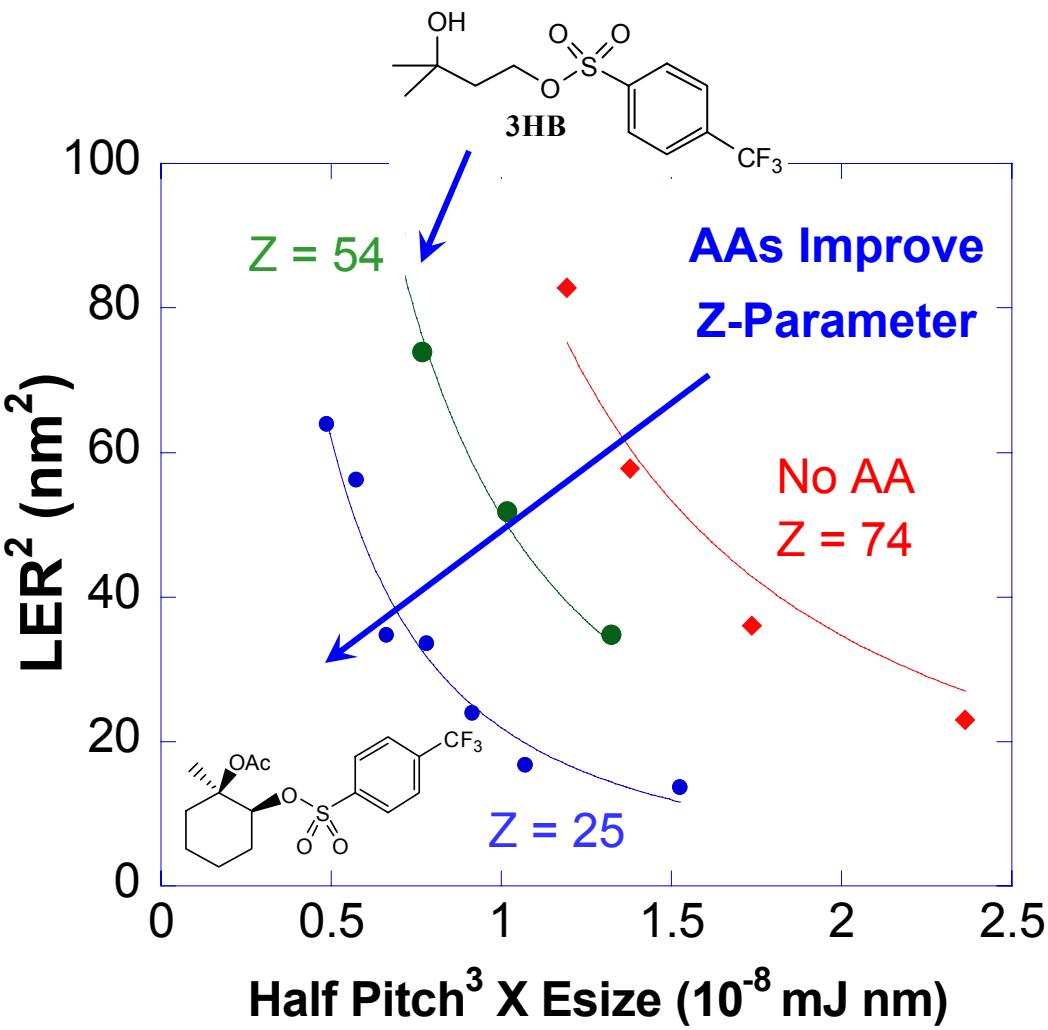
Improved Combined Performance

Z-Parameter = (Resolution)^3 x (LER)^2 x Esize



V. Conclusions

Kinetics

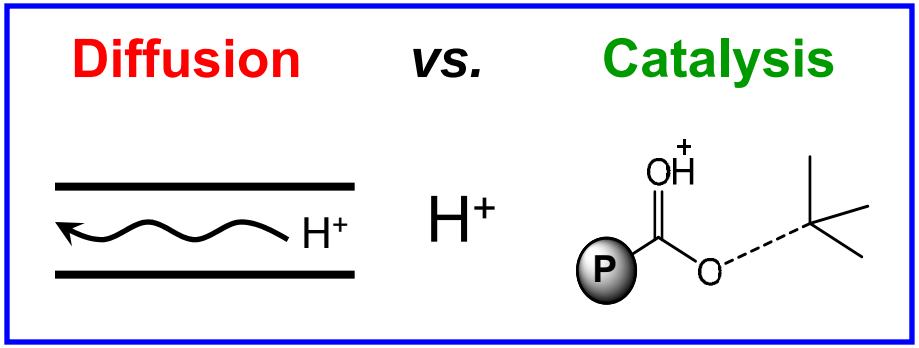
- Added base allows the comparisons between catalyzed and uncatalyzed reactions.
- AA triggers significantly modify reactivity of AAs.

Modeling

- Predictions of the chemical reactivity.

Lithography

- Fluorinated acids give better performance than non-fluorinated acids.
- No outgassing problems.



Acid Amplifiers are Capable of Simultaneously Improving Resolution, LER and Sensitivity in EUV Resists

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