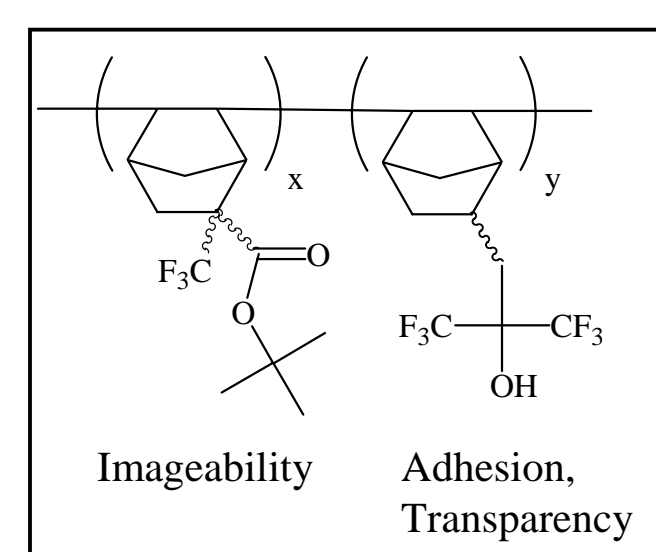


Tricyclononenes: New Alicyclic Monomers for 157 nm Photoresists

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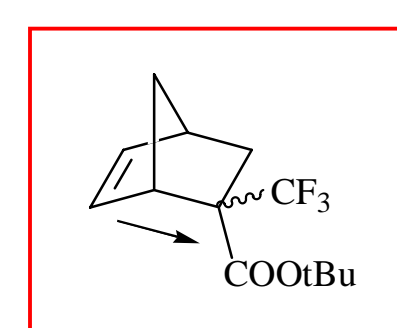
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Departments of Chemistry and Chemical Engineering
University of Texas - Austin

Norbornene Copolymers for 157 nm Photoresists



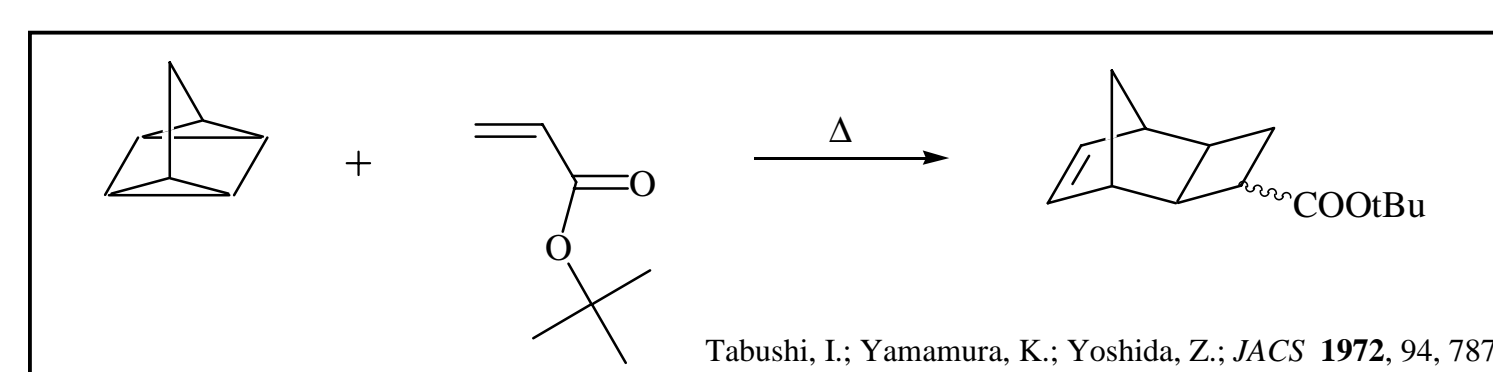
Features of Norbornene Copolymers
α-trifluoromethyl group increases transparency of the ester

Imageability Adhesion, Transparency



Unfortunately,
Proximity of strongly electron withdrawing groups deactivates olefin towards polymerization
∴ Monomer difficult to polymerize using cationic nickel and palladium catalysts

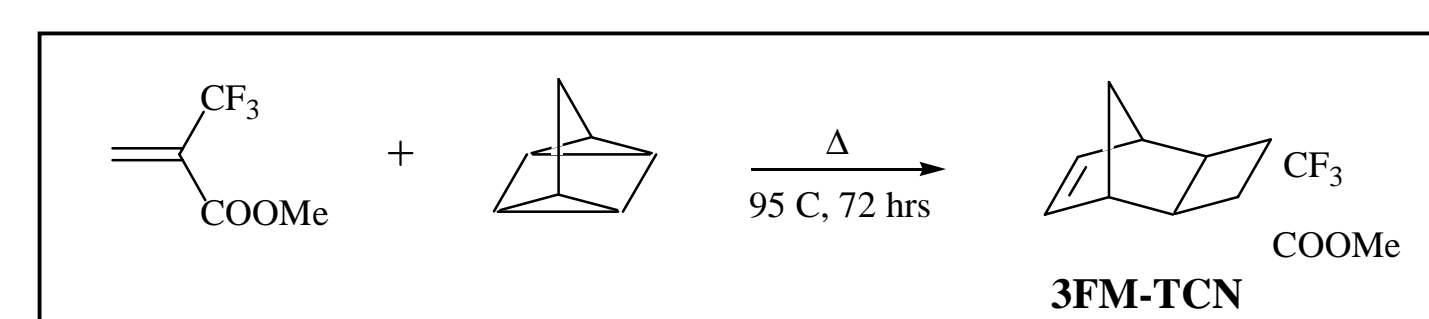
Tricyclononene Chemistry



Benefits of TCN Chemistry:

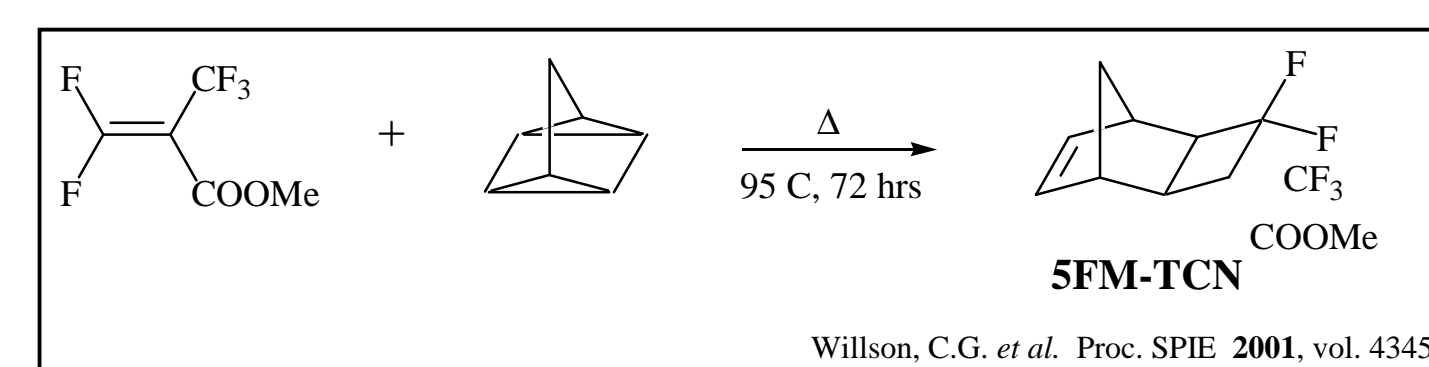
Electron withdrawing groups positioned further away from double bond
Easy synthesis and purification
Compatible with a wide range of alkene and alkyne starting materials

Fluorinated TCN Monomers



Isolated yield: 80-90%

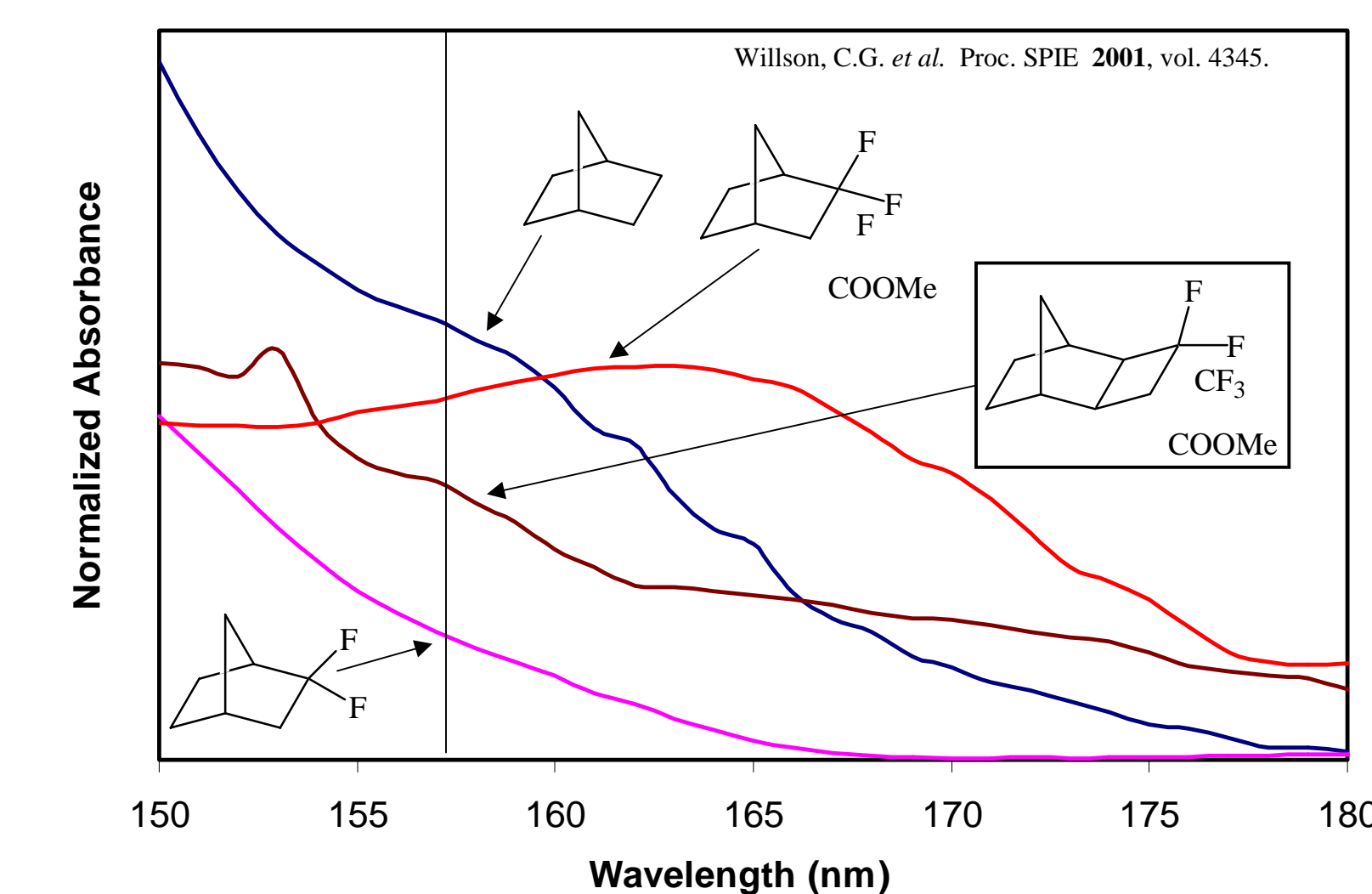
Clean reaction, high yield, easy purification



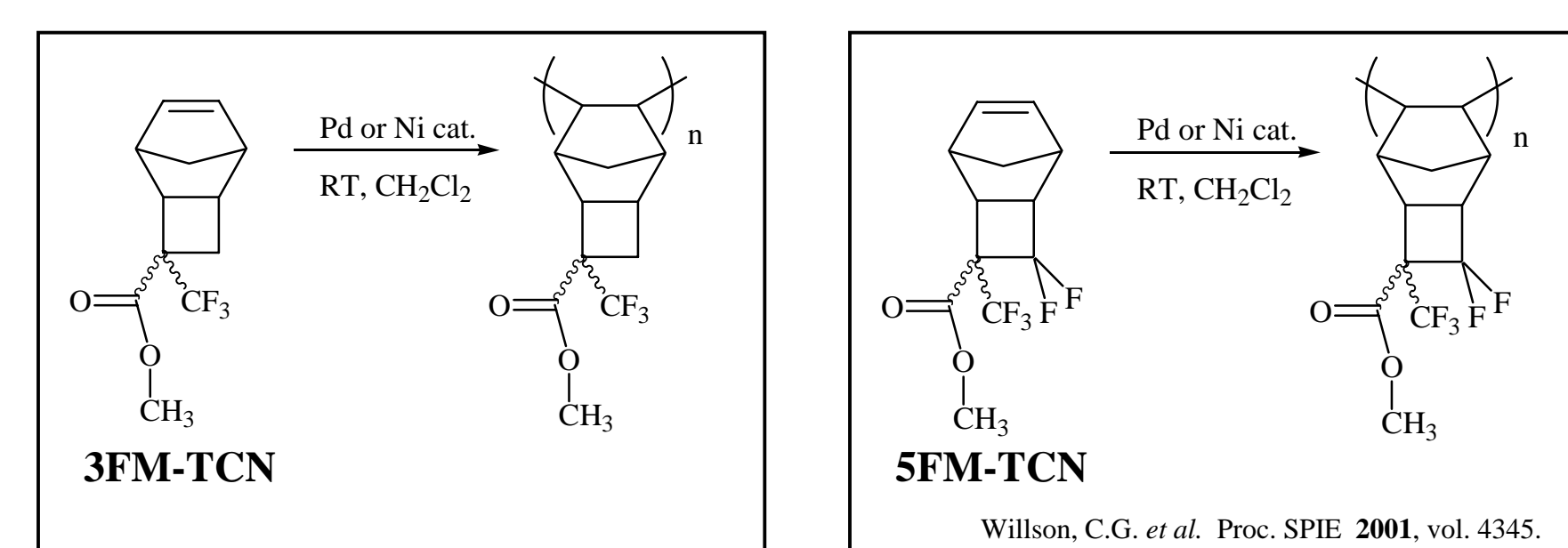
Isolated yield: 20%

Higher fluorine content...but lower yield
Currently, optimizing conditions to improve yield

Gas Phase V-UV Spectra



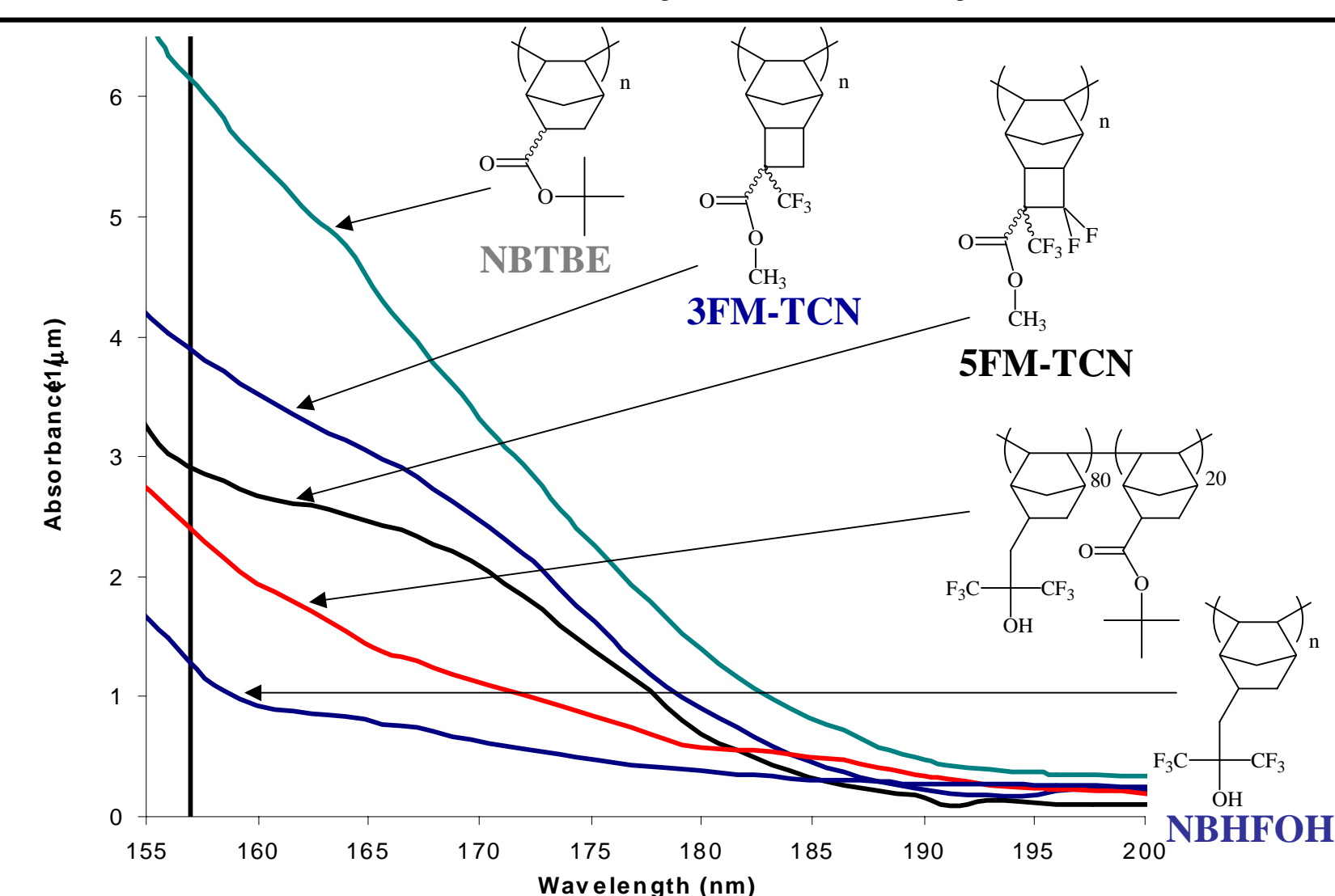
Successful Synthesis of TCN Model Resist Polymers



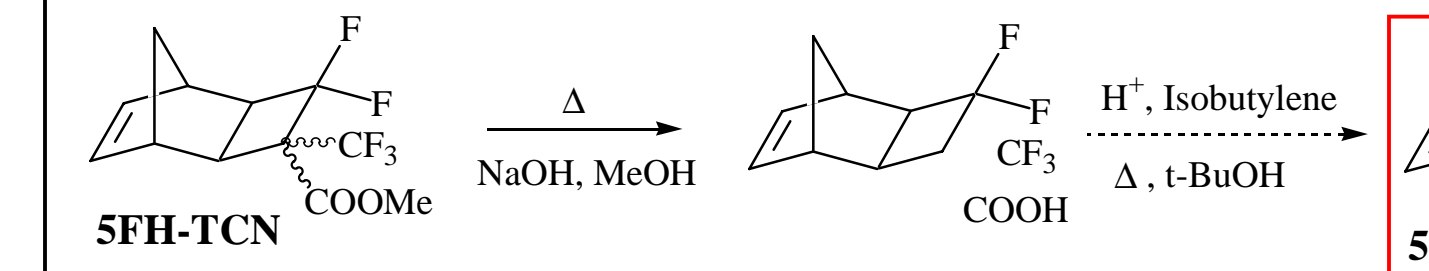
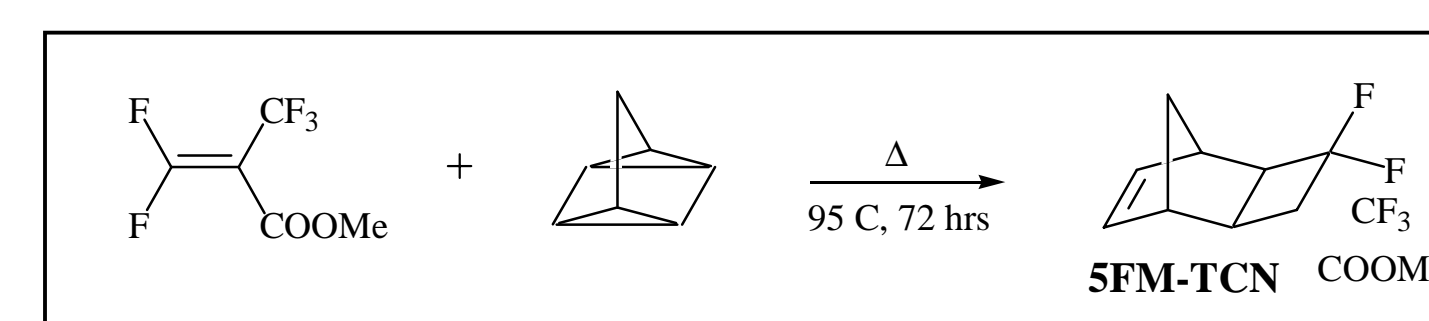
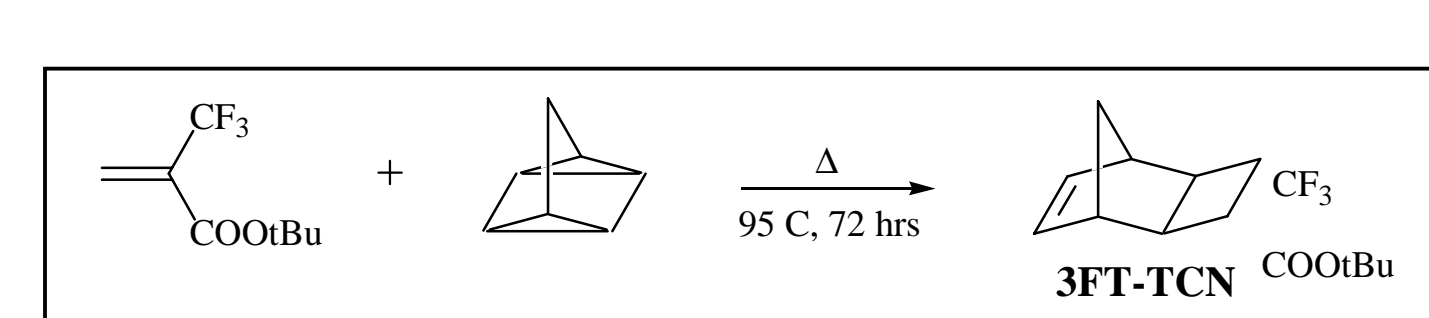
TCN framework allows polymerization of monomer containing the α-CF₃/t-butyl ester functionality

Polymerization and work-up identical to norbornene-based vinyl addition polymers

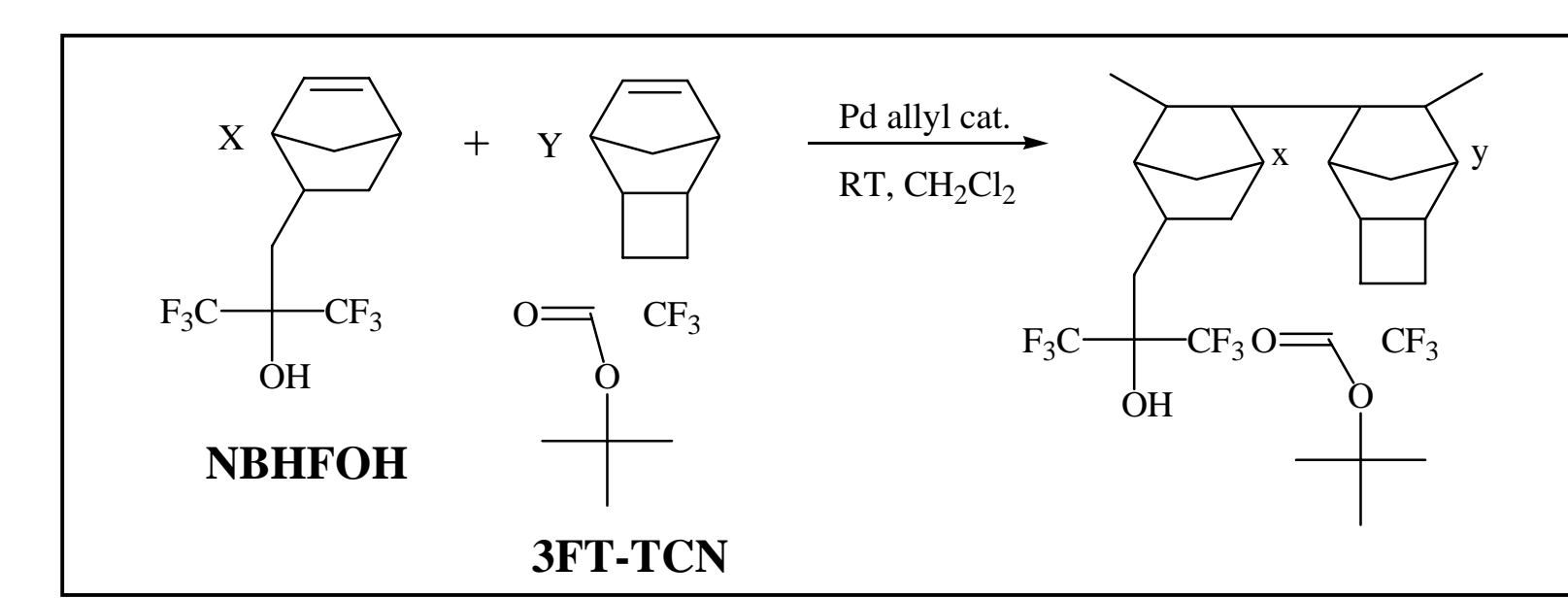
VASE Analysis of Polymers



Fluorinated TCN Monomers Synthesis

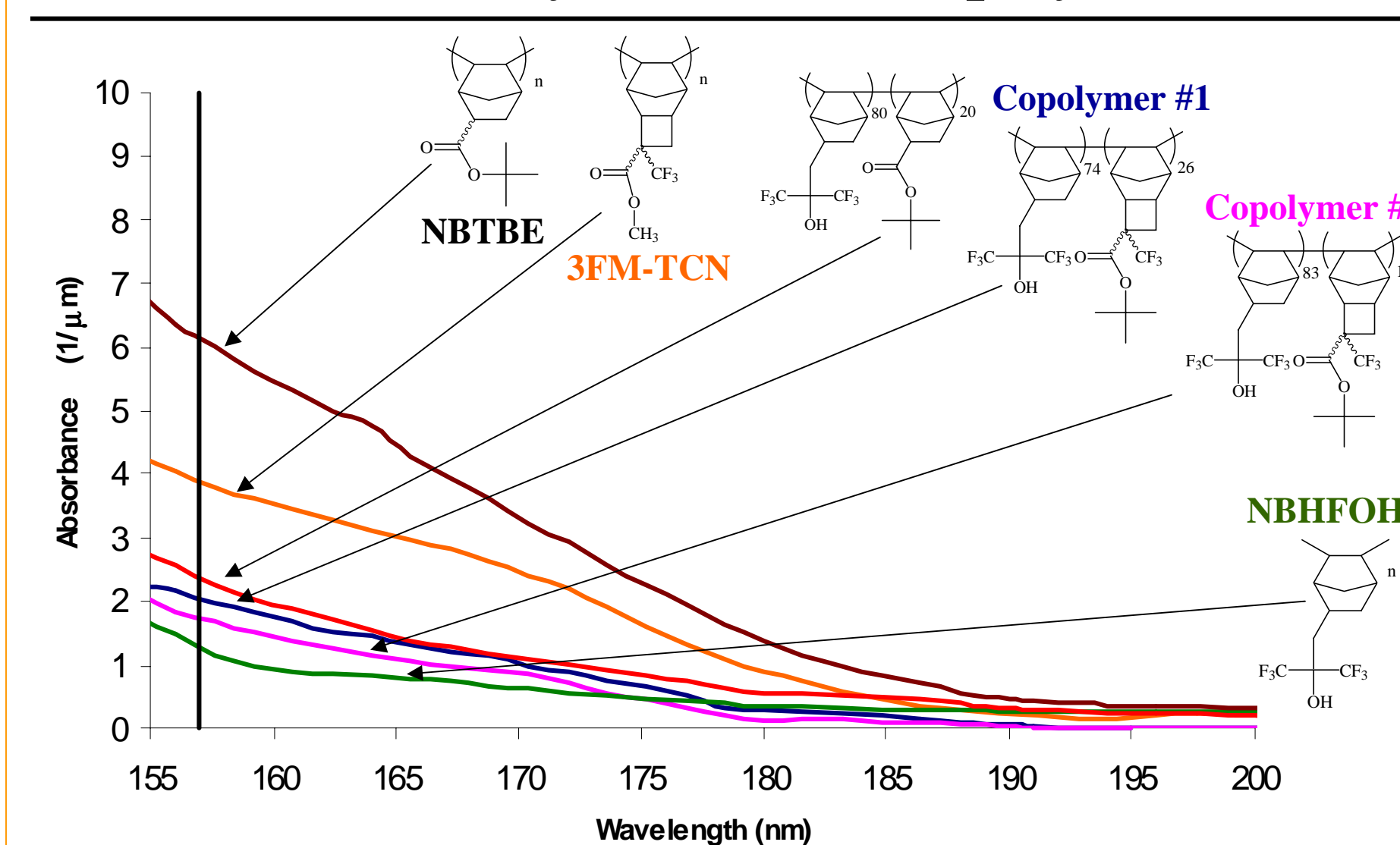


TCN Copolymers for 157 nm Photoresists

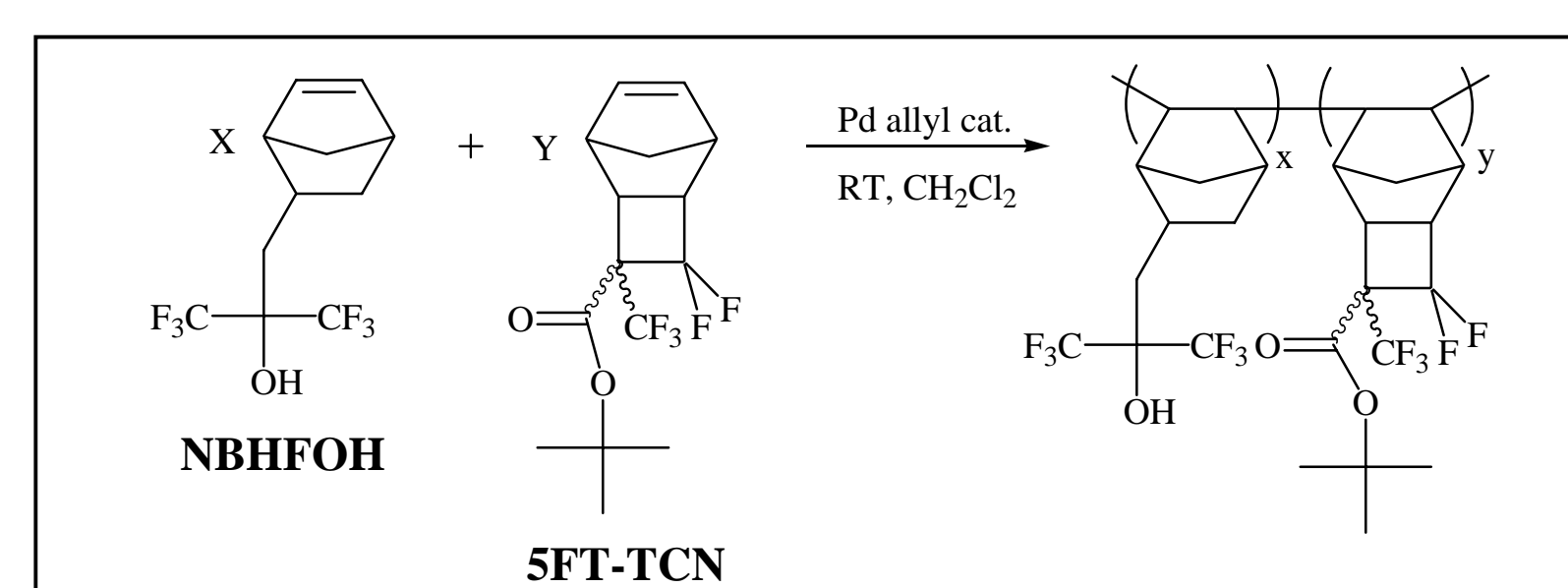


α-trifluoromethyl group increases transparency of the ester
TCN framework allows for facile polymerization of monomer containing the α-CF₃/t-butyl ester functionality
Copolymerize with hexafluoroisopropyl alcohol-functionalized norbornene for increased transparency and adhesion

VASE Analysis of TCN Copolymers



Coming Attractions



Increased fluorine content decreases absorbance of ester monomer at 157 nm
Expect significant increases in transparency of copolymers of 5FT-TCN compared to copolymers with more heavily absorbing 3FT-TCN.
Working on scaling-up polymers for image work

Conclusions

Tricyclononene monomers offer a route to vinyl addition polymers containing esters with α-CF₃ groups.
V-UV and VASE analysis on model monomeric and polymeric TCN systems indicate promising transparency at 157 nm.
Functional resist copolymers using TCN monomers show good transparency at 157nm and are being evaluated for imaging performance.
More heavily fluorinated TCN copolymers are being synthesized with the potential for increased transparency.
Additional TCN-based monomers are being evaluated for resist comonomers.

Acknowledgements

The authors gratefully acknowledge the generous financial support of the *International SEMATECH* and its member companies.

