



# RAFT SUMI: polymers from the bottom-up

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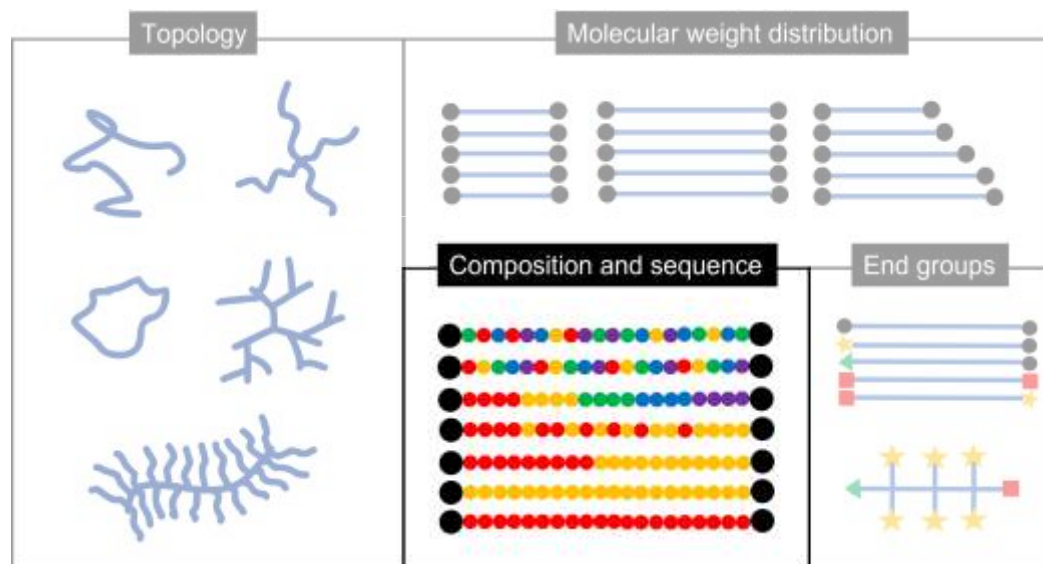


**38APS**

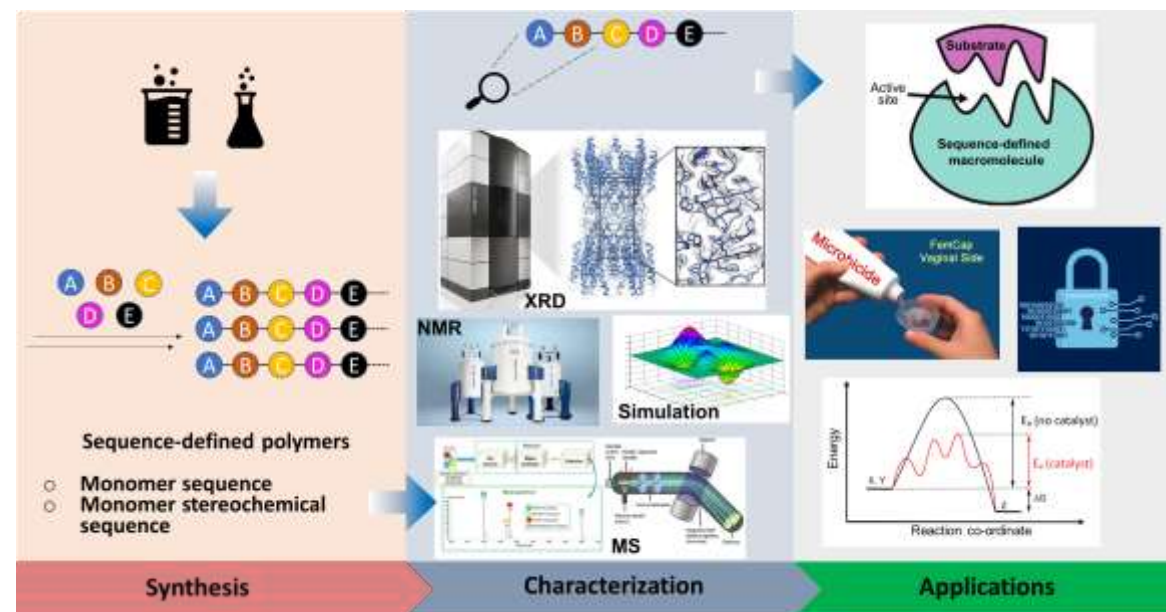
# Intro: polymer sequence control

How well does organic chemistry translate to polymers?

Iterative monomer additions: the middle ground.



*Polym. Chem.*, 2022,13, 5431-5446



*Prog. Polym. Sci.* 2023, 147, 101754.

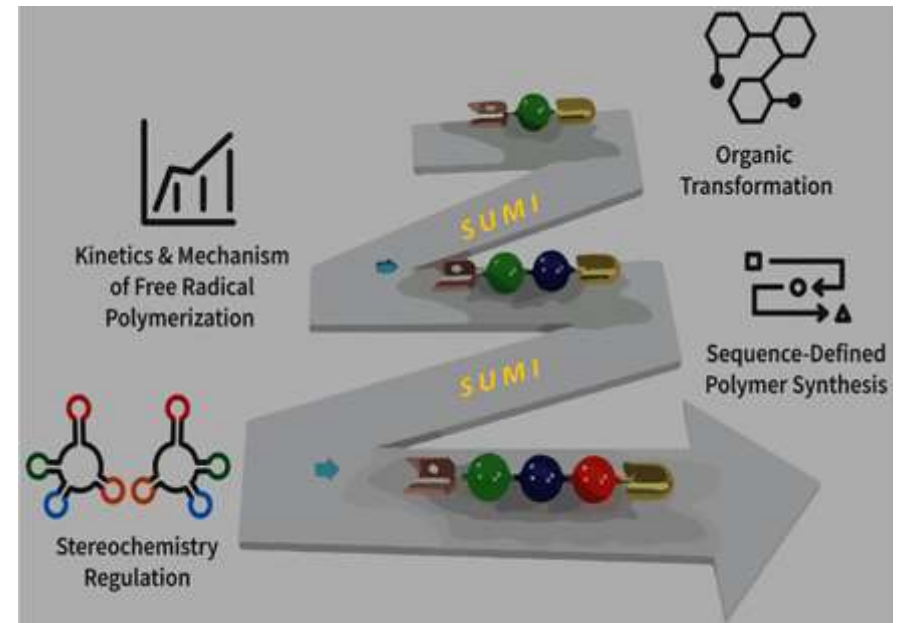
# Intro: challenges of controlling sequence of vinyl polymers

*Practical challenge:* lower yield/turnover with more purification steps.

*Conceptual challenge:* find monomers only adding once at a time.

SUMI: Chain-growth-like vs step-growth-like.

Balance single-addition vs polymerisation & termination.



*Macromolecules* 2019, **52**, 23, 9068–9093

# Intro: solid-phase RAFT single unit monomer insertion (SUMI)

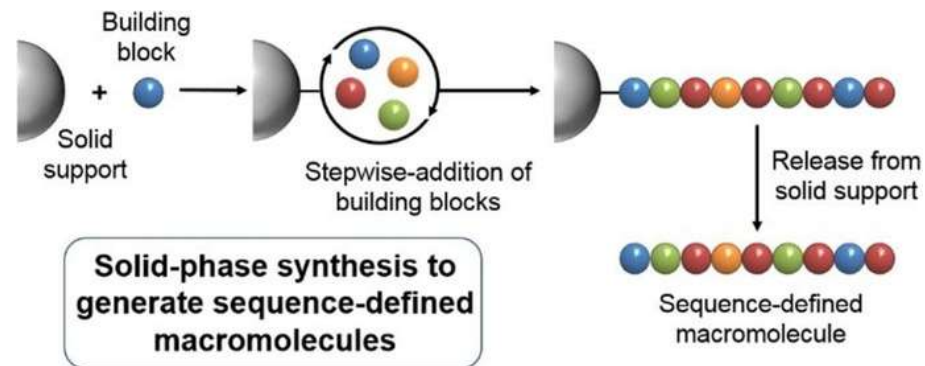
Addressed the practical challenge with solid-phase synthesis.

*Brief:* Operationally simple & versatile  
Oxygen-tolerant PET-RAFT SUMI

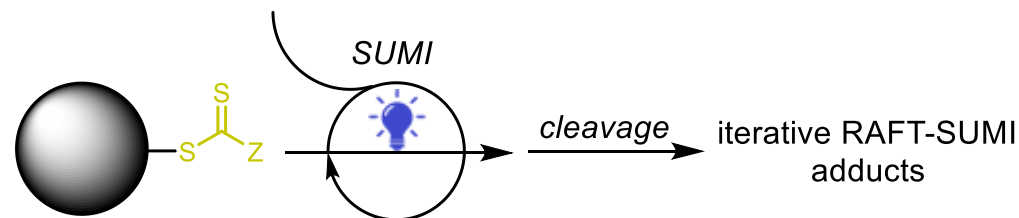
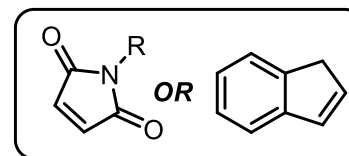
Dithiocarbonyl: a “radical protecting group”.

ZnTPP gives oxygen tolerance.

Indefinite additions by alternating radical polarity

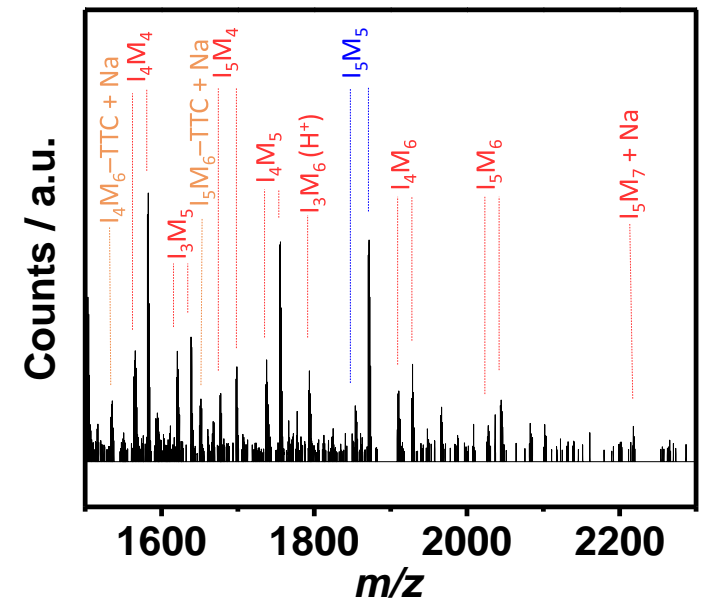
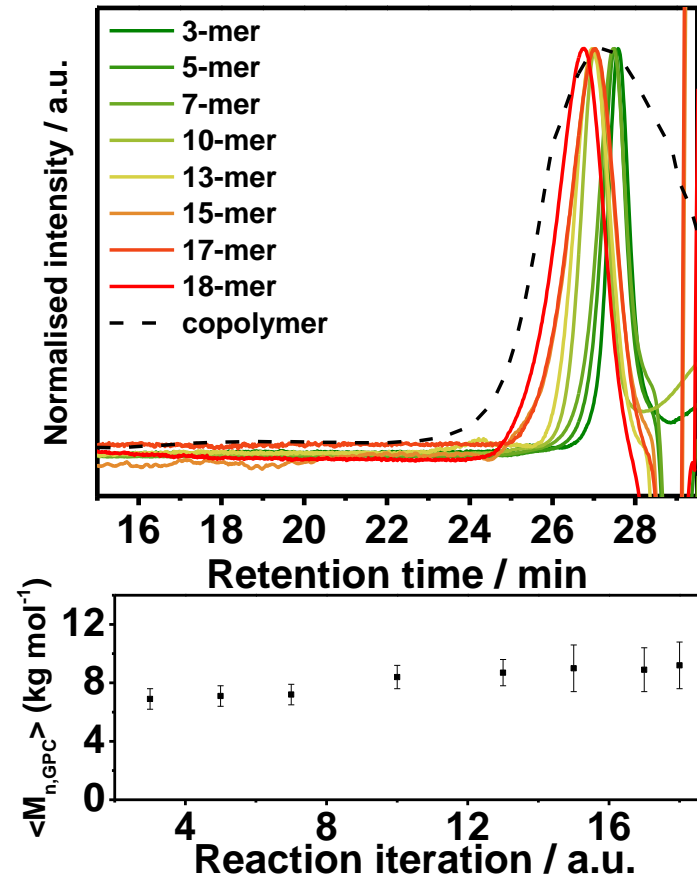
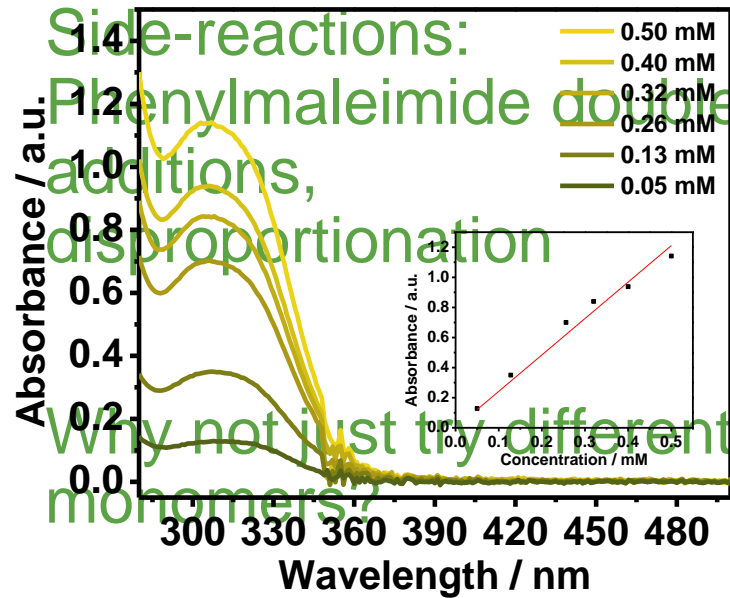
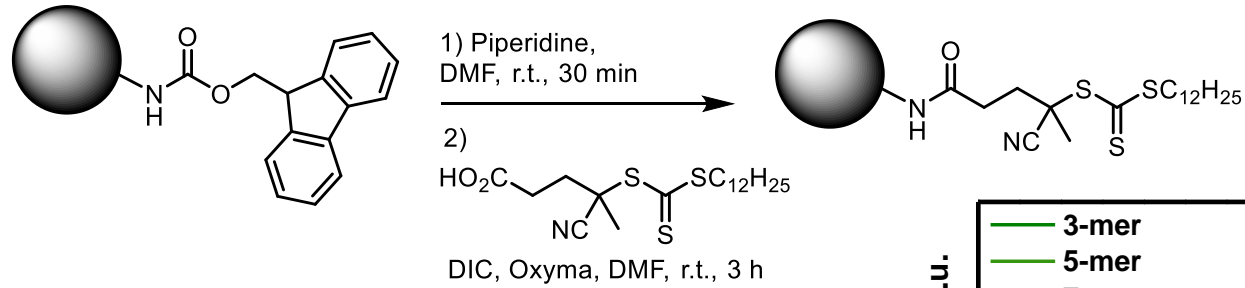


*Chem. Asian J.* **2018**, 13, 3611 – 3622



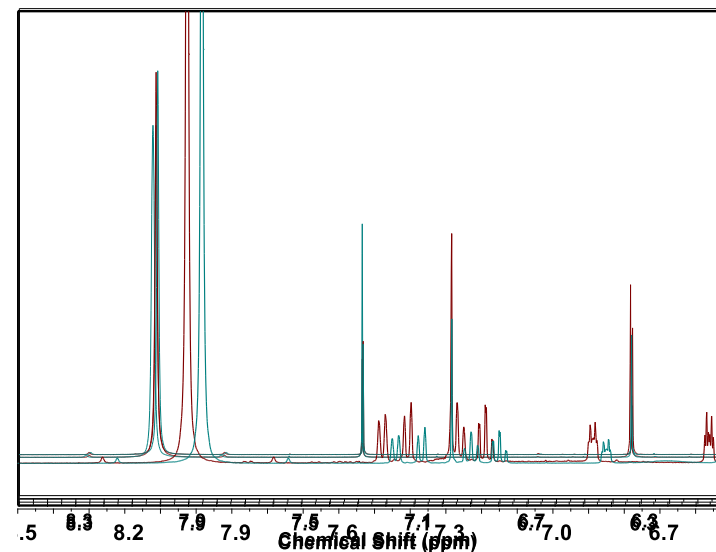
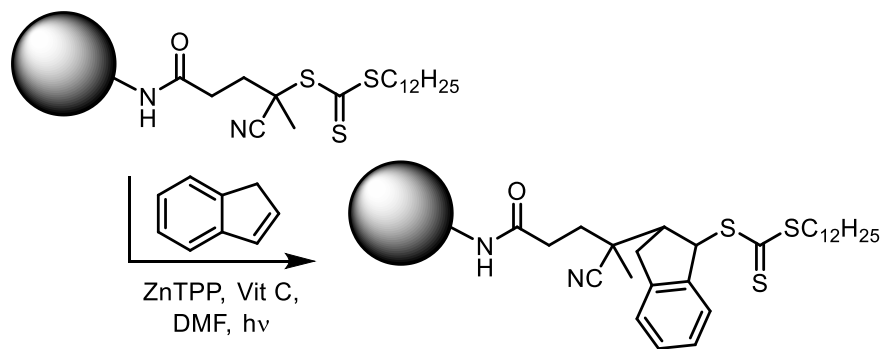
*Polym. Chem.*, 2023, **14**, 4116-4125

# PET RAFT SUMI on resin: summary of previous work

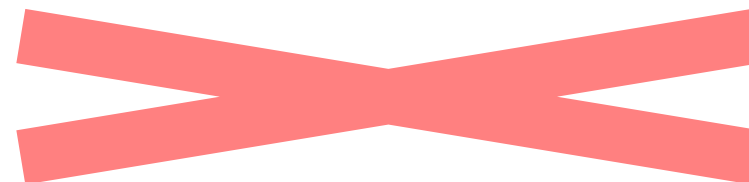




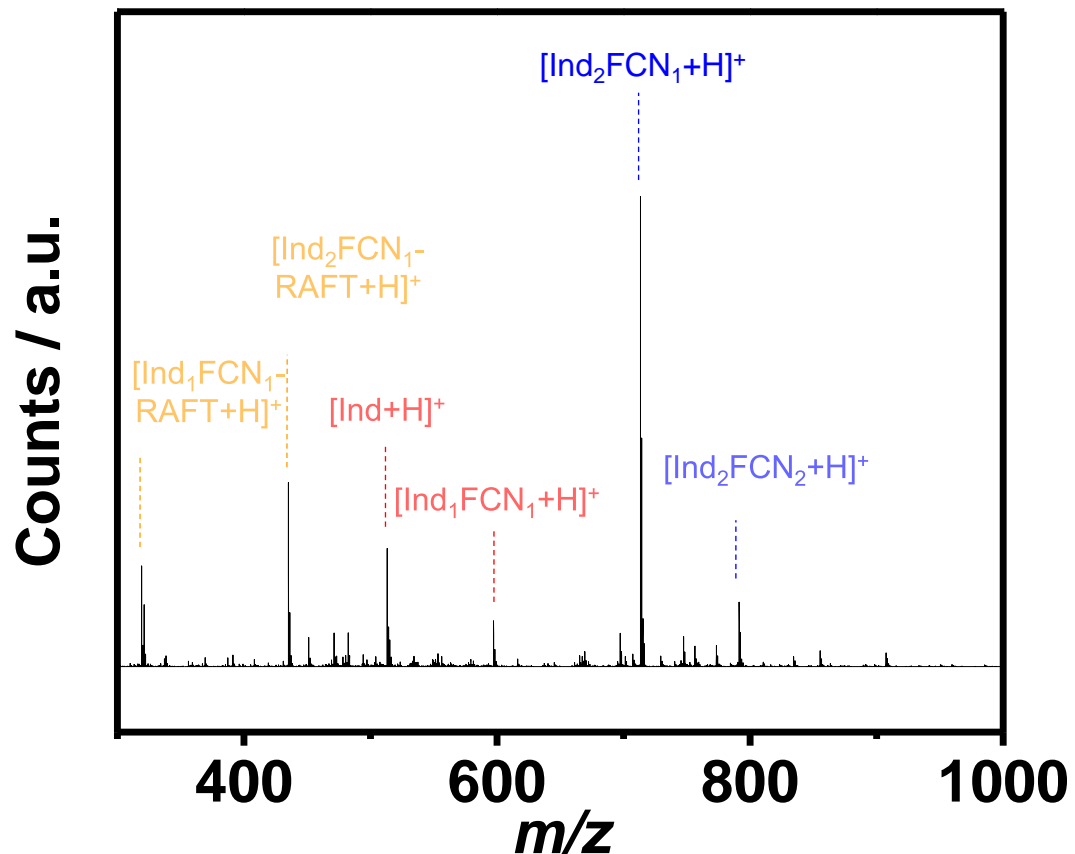
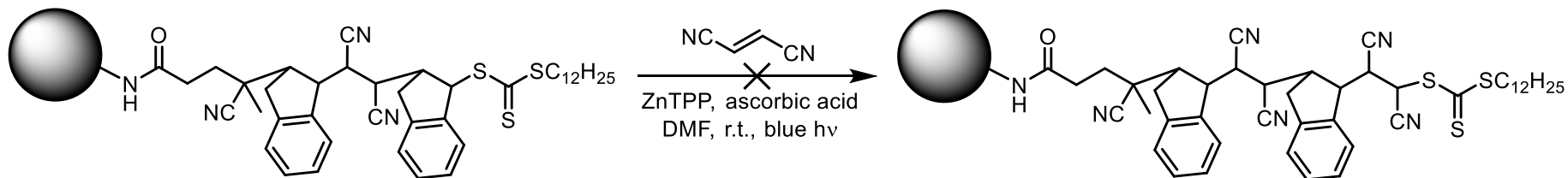
# Solid-phase SUMI of fumaronitrile-indene



Fumaronitrile can be used to synthesize  
addition polymers with the thiocarbonate-  
driven RAFT SUMI



# Solid-phase SUMI of fumaronitrile-indene



No double addition.

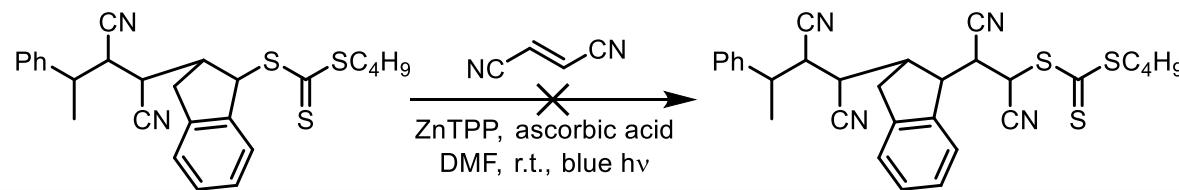
Remaining sequence error is incomplete addition

Addition or PET considered rate-limiting.

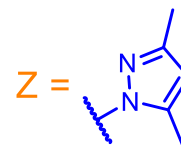
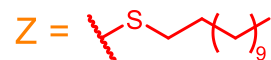
Penultimate unit effects?

Unlikely to be sterics

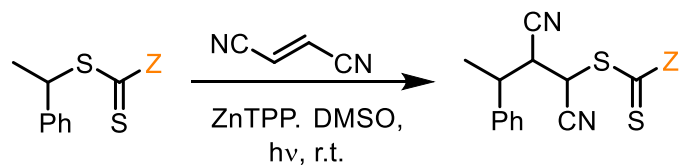
Maybe electronics...



# Penultimate unit effects and pyrazole carbodithiolates



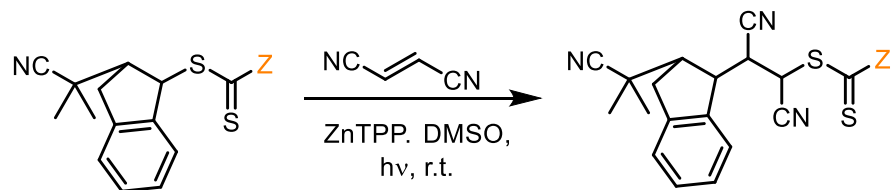
Pyrazole carbodithiolates as “universal RAFT agents”.



$$k_{\text{SUMI, app}} = 0.084 \text{ h}^{-1} \pm 0.002$$

$$k_{\text{SUMI, app}} = 0.62 \text{ h}^{-1} \pm 0.2$$

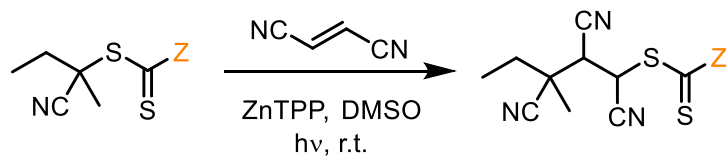
Sped up basic fumaronitrile SUMI



$$k_{\text{SUMI, app}} = 0.085 \text{ h}^{-1} \pm 0.001$$

$$k_{\text{SUMI, app}} = 0.60 \text{ h}^{-1} \pm 0.09$$

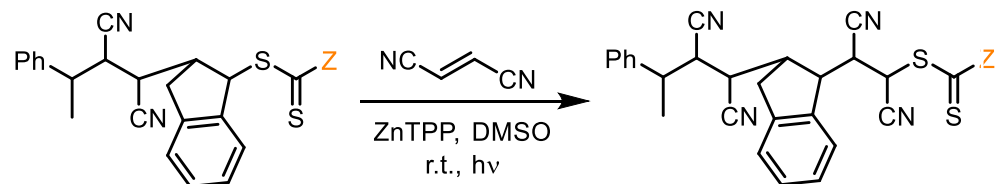
Rotatable bond mitigated CN–CN strain



<10% yield  
(7, 24 or 48 h)

60% conversion  
40% yield  
(10 h)

Unconventional SUMI was possible with pyrazole carbodithiolates



0% conversion  
0% yield  
(48 h)

>95% conversion  
85% yield  
(2 h)

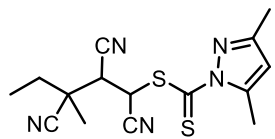
Penultimate unit effects *promoted* pyrazole carbodithiolate SUMI!



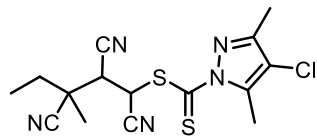


# Substrate scope

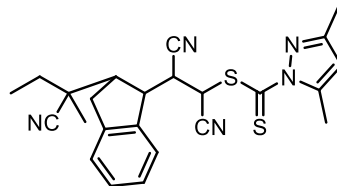
FUMARONITRILE  
TERMINAL  
UNIT



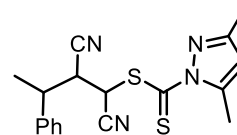
IPN-FCN-PCDT



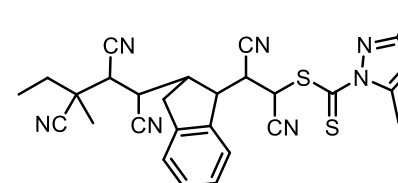
IPN-FCN-(Cl)PCDT



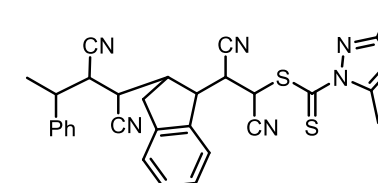
IPN-Ind-FCN-PCDT



PhMeCH-FCN-PCDT

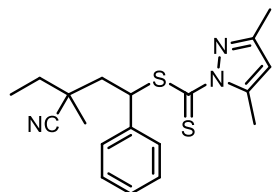


IPN-FCN-Ind-FCN-PCDT

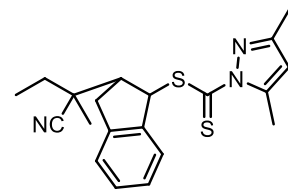


PhMeCH-FCN-Ind-FCN-PCDT

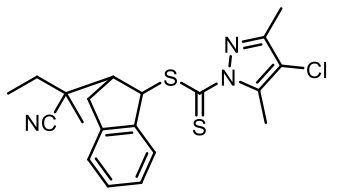
STYRENIC  
TERMINAL  
UNIT



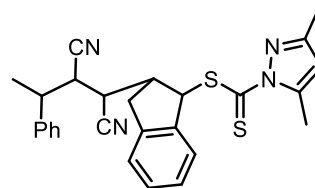
IPN-St-PCDT



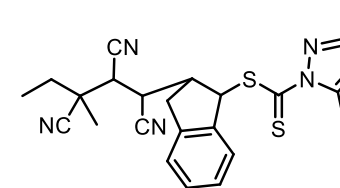
IPN-Ind-PCDT



IPN-Ind-(Cl)PCDT

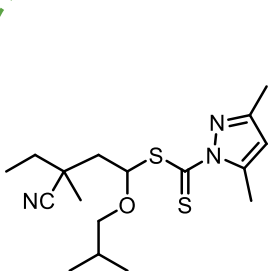


PhMeCH-FCN-Ind-PCDT

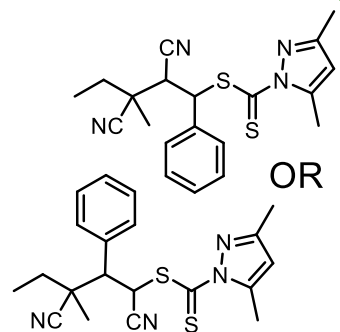


IPN-FCN-Ind-PCDT

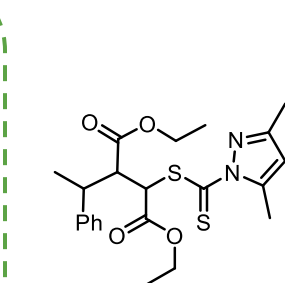
OTHER  
TERMINAL  
UNIT



IPN-IBVE-PCDT

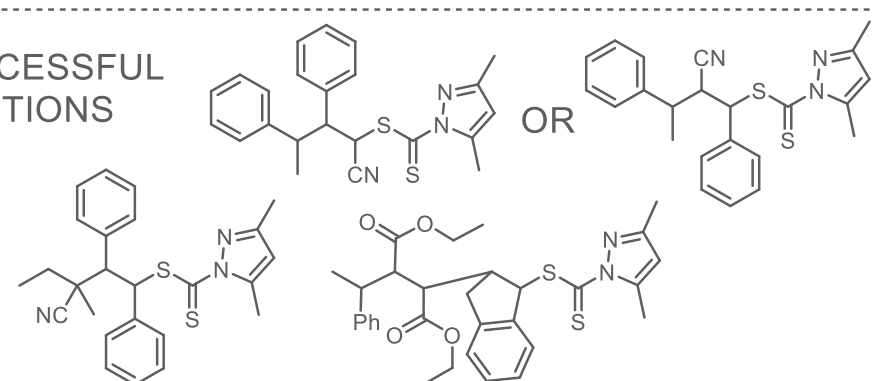


IPN-CCN-PCDT

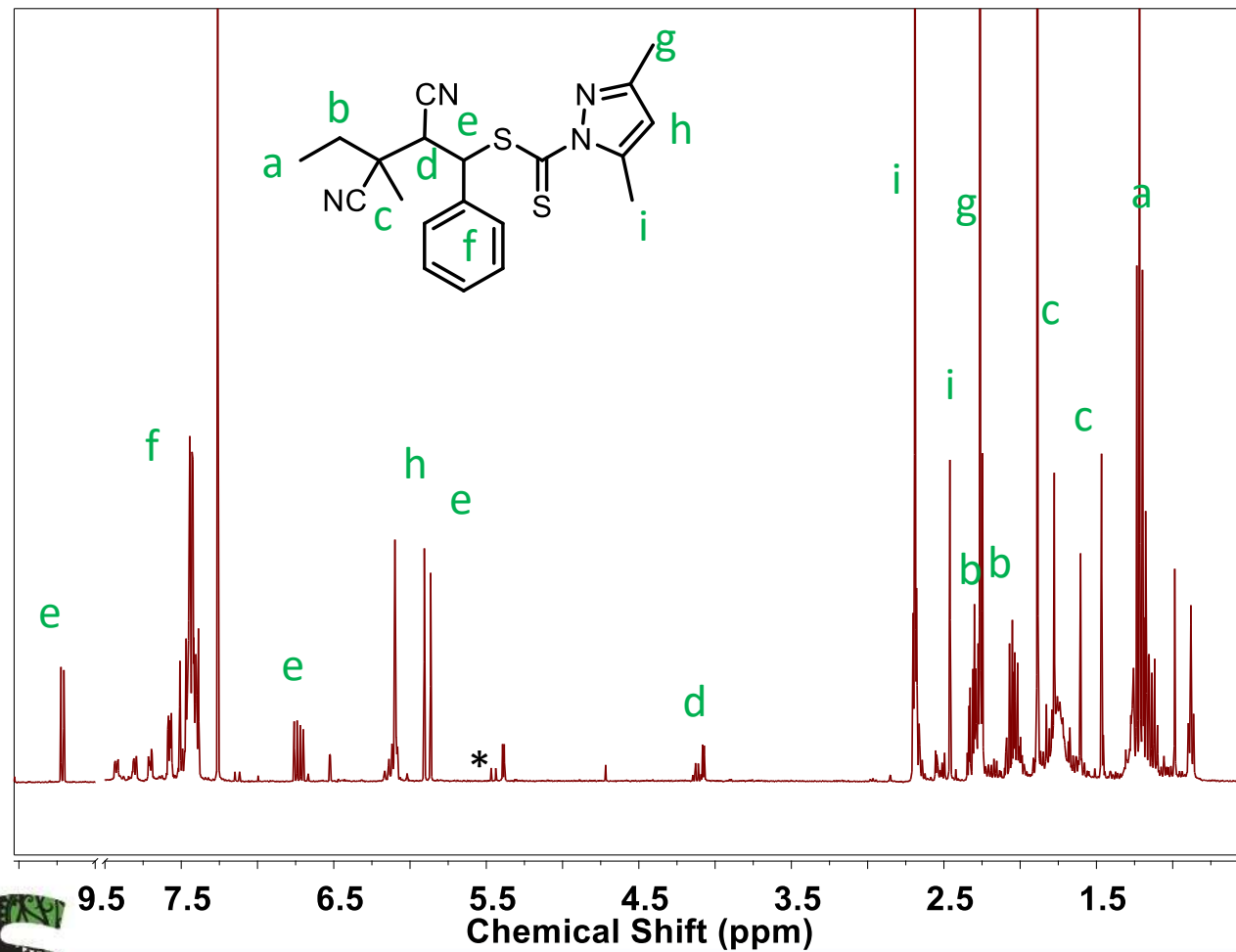
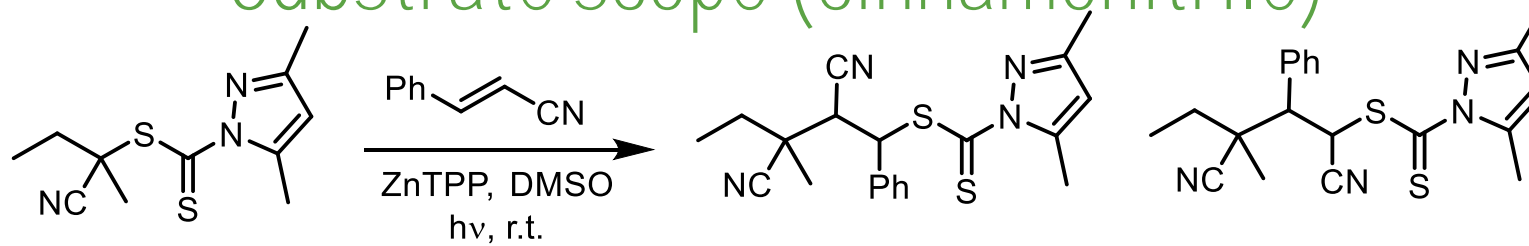


PhMeCH-DiMeFum-PCDT

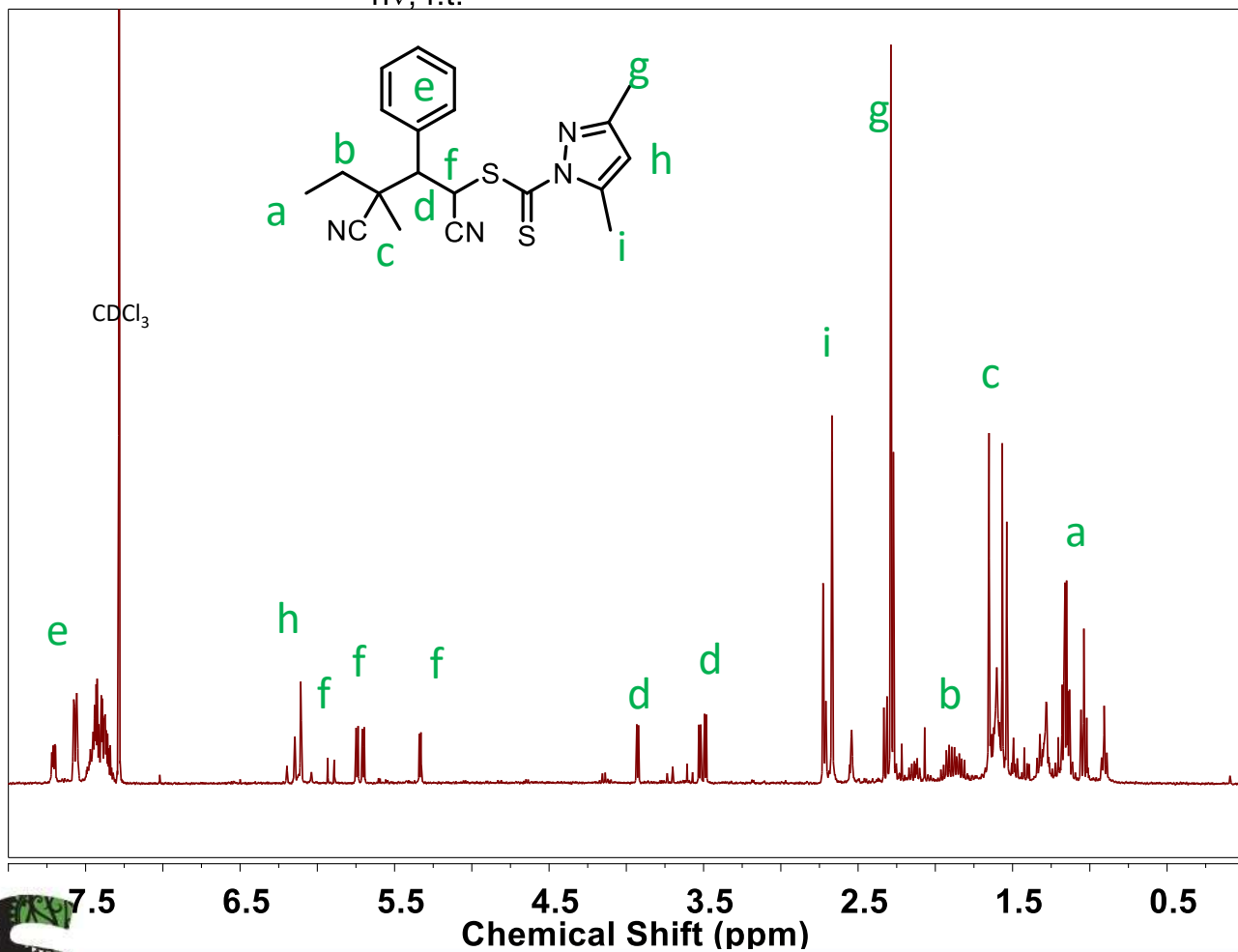
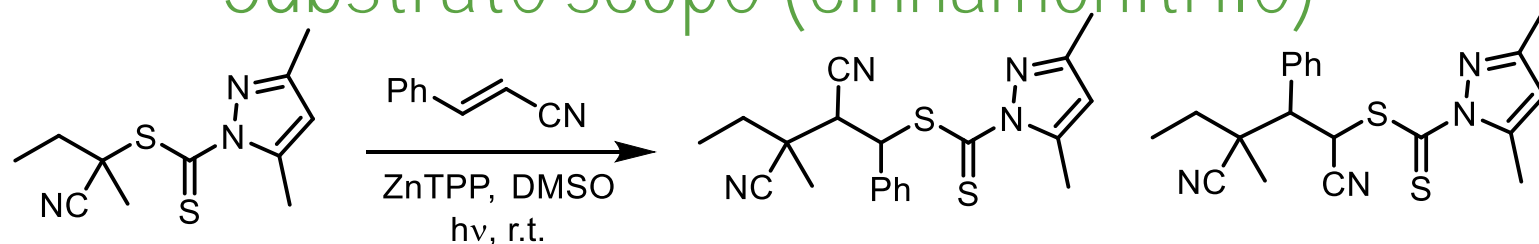
UNSUCCESSFUL  
ADDITIONS



# Substrate scope (cinnamionitrile)



# Substrate scope (cinnamionitrile)

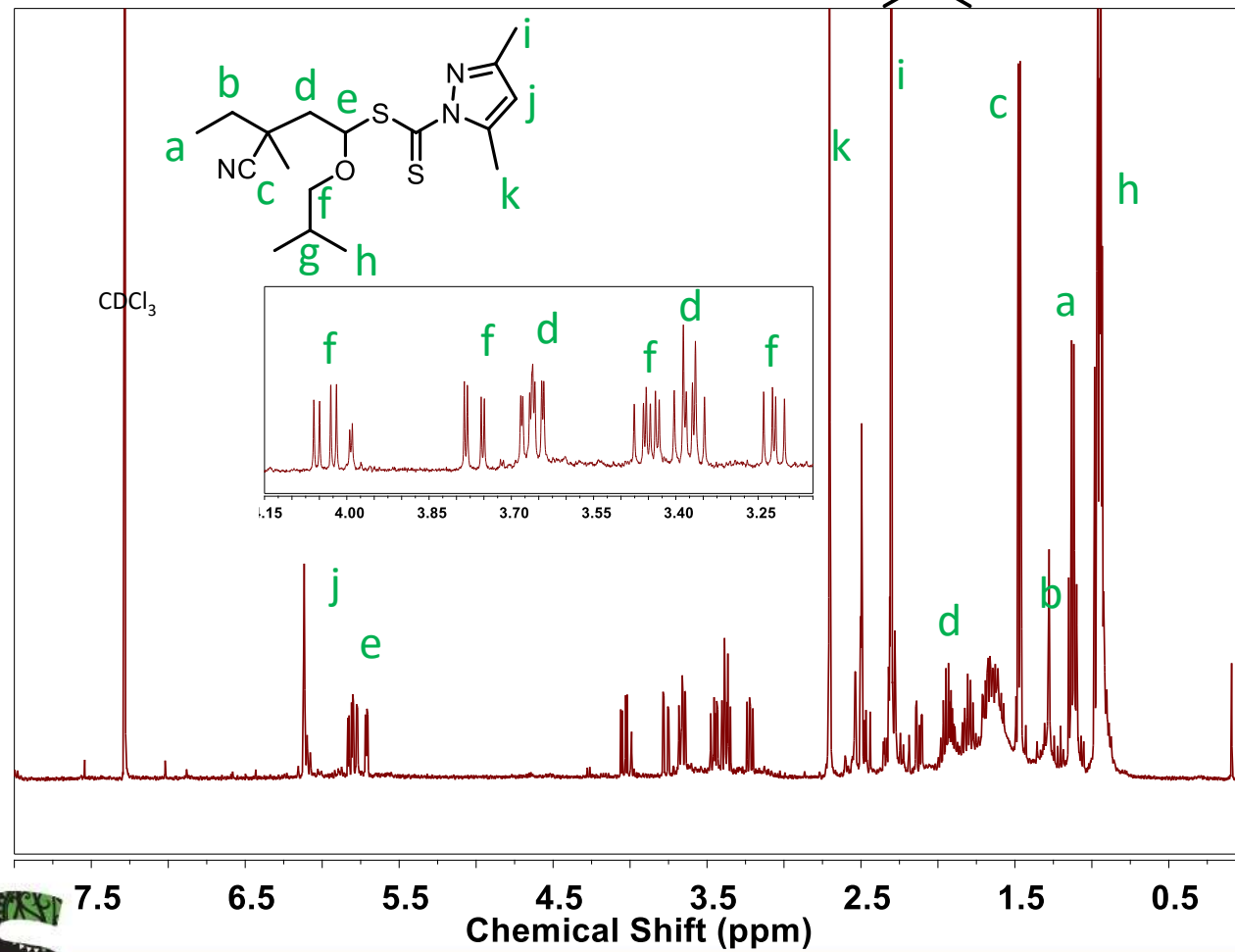
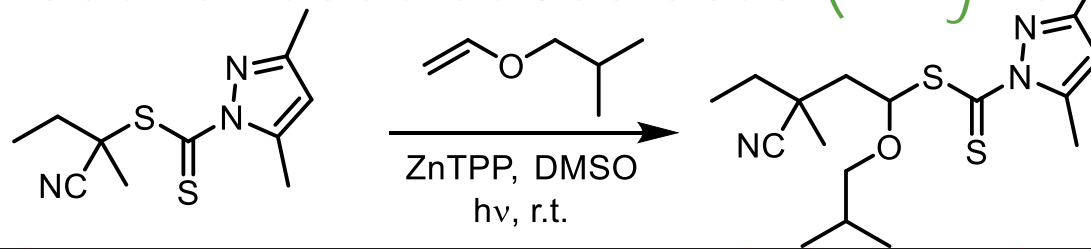


1,2/1,3-dinitrile  
strain vs terminal  
unit polarity match

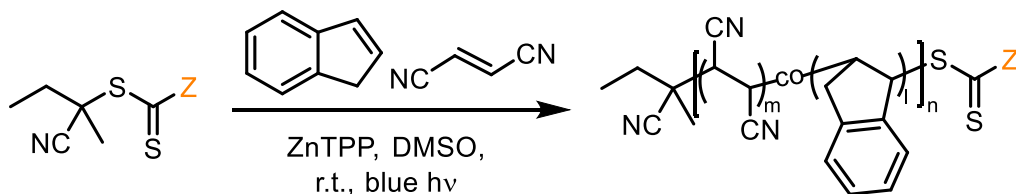
3:1 regioisomer ratio

Reaction not  
feasible with  
trithiocarbonate "Z-  
group" or  
methylbenzyl "R-  
group"

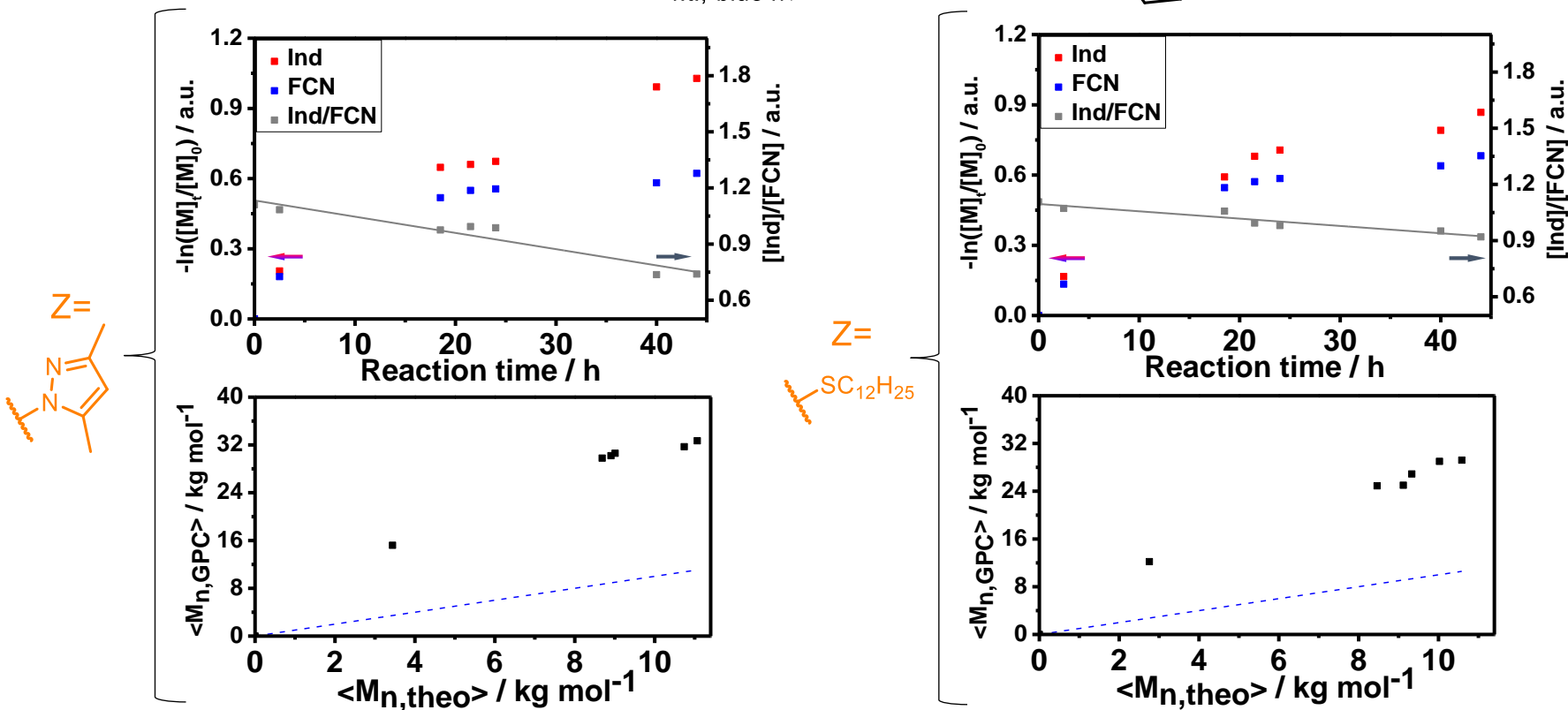
# Miscellaneous substrates (vinyl ether)



# Alternating copolymerisation



More conventional RAFT behaviour in copolymerisation.



# Conclusions

Practical challenge of scaling SUMI to multiple iterations has been addressed.

Theoretical challenge of ideal monomer combinations remains elusive yet instructive.

Pyrazole carbodithiolates can expand the scope of SUMI to new sequences and monomer units.

Radical addition is not the main determining factor of RAFT SUMI

Principles of SUMI and alternating copolymerisation aren't always transferable.







# Acknowledgements

Research team:

Jiangtao Xu

Ben Noble (RMIT)

Characterisation & technical support:

UNSW BMSF – Lewis Adler

UNSW NMR facility

Eh Hau Pan



**UNSW**  
SYDNEY



**Australian Government**

**Australian Research Council**



See poster #11 tonight!  
(...and #42 and #53)

