Synthetic Studies toward Conjugated Carbon Nanobelts

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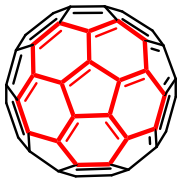
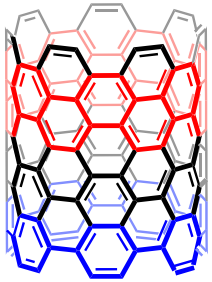
Nanohoops: Fragment Structures of CNT

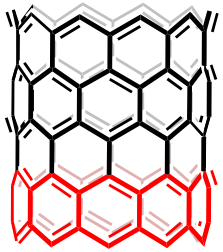
- Fullerenes and carbon nanotubes – "curved conjugation"



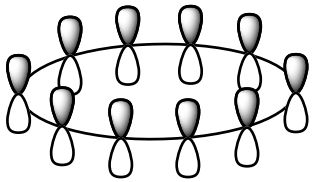
C_{60}



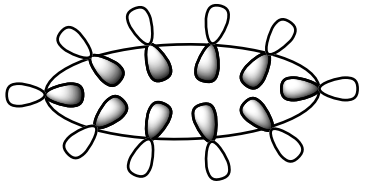
Armchair CNT



Zig-zag CNT

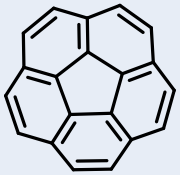
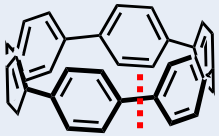
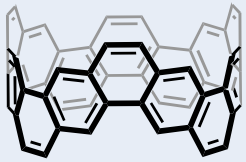


p orbital perpendicular to molecular plane



Radially oriented p orbitals

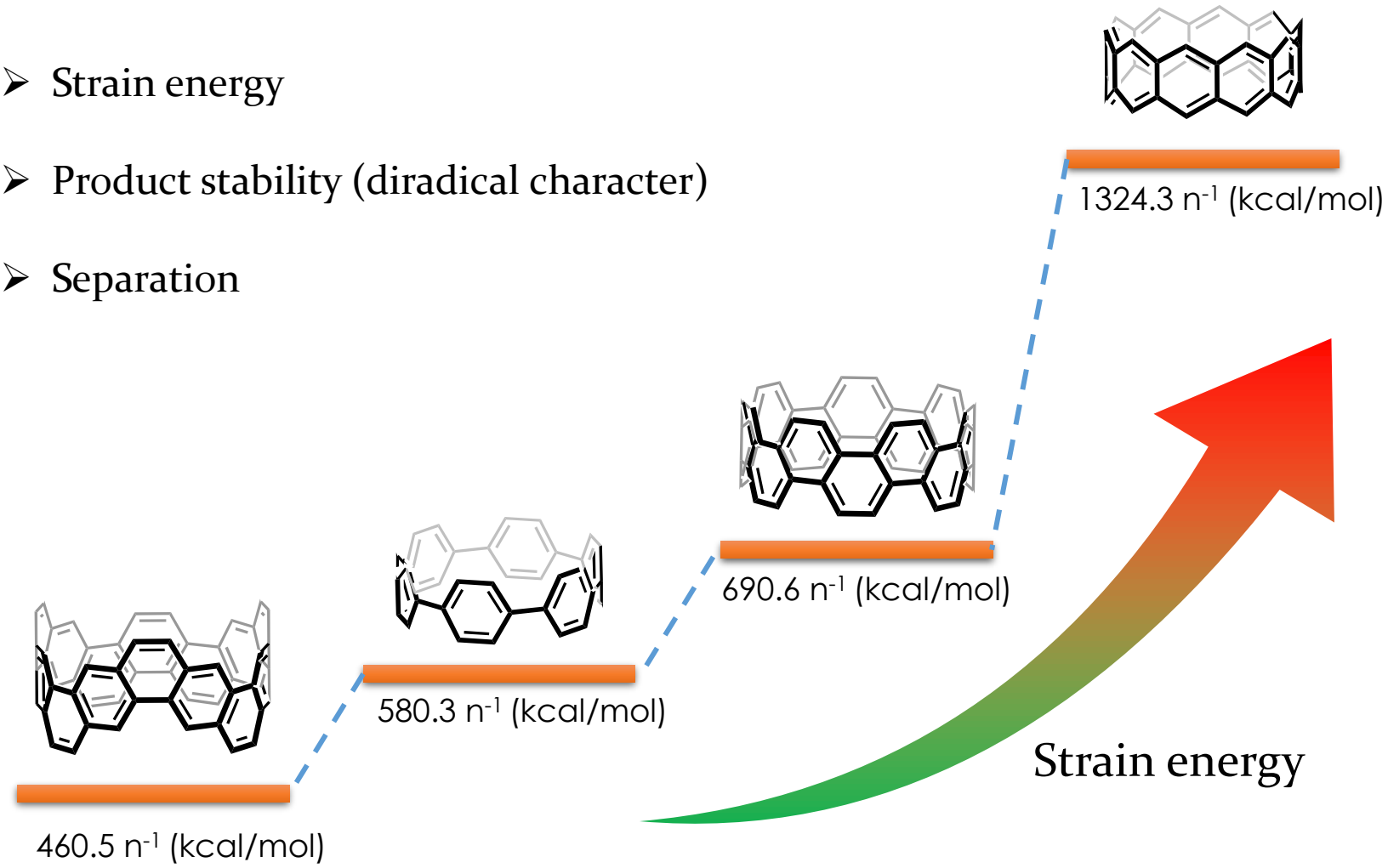
- Fragment structures

Buckybowl	Carbon Nanorings	Carbon Nanobelts	
 Corannulene	 Cycloparaphenylene	 Cyclophenacene isomer	 Cyclacene
synthesized in 1966	*synthesized in 2008*	*synthesized in 2017*	*proposed in 1954* *not synthesized*

(1) Barth, W. E.; Lawton, R. G. J. Am. Chem. Soc. 1966, 88, 380–381.
(2) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. J. Am. Chem. Soc. 2008, 130, 17646-17647.
(3) Povie, G.; Segawa, Y.; Nishihara, T.; Miyauchi, Y.; Itami, K. Science, 2017, 356, 172–175.

General challenges in Carbon Nanobelt Synthesis

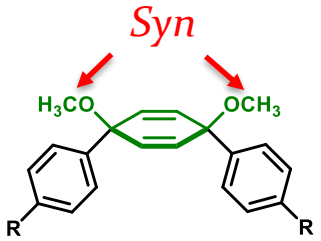
- Strain energy
- Product stability (diradical character)
- Separation



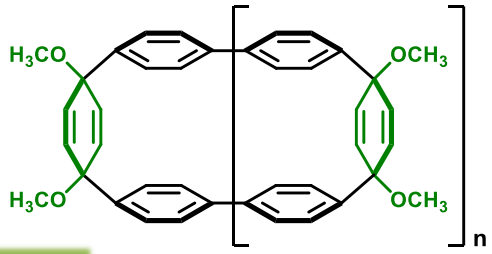
(1) Segawa, Y.; Yagi, A.; Ito, H.; Itami, K. Org. Lett. 2016, 18, 1430–1433.

Synthetic Strategies for Carbon Nanorings and Nanobelts

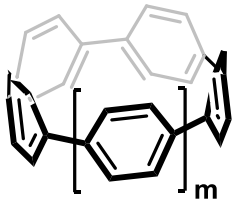
Cycloparaphenylenes



Suzuki coupling macrocyclization



Reductive aromatization

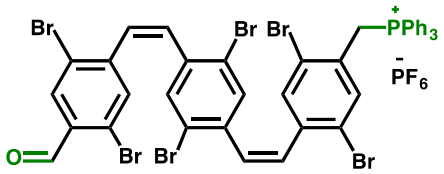


Curved/unstrained synthons

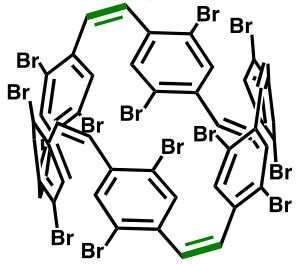
Macrocycle

End-game (aromatization)

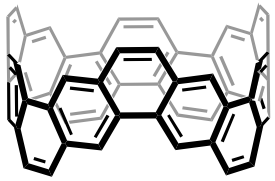
Chiral CNB



Cyclodimerization



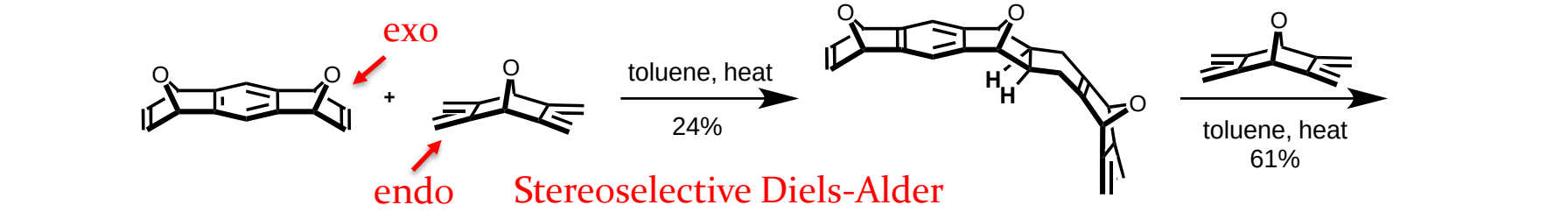
Aryl–aryl coupling



(1) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646-17647.
(2) Povie, G.; Segawa, Y.; Nishihara, T.; Miyauchi, Y.; Itami, K. *Science*, **2017**, *356*, 172–175.
(3) Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem., Int. Ed.* **2010**,*49*, 757–759.
(4) Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**,*48*, 6112–6116.

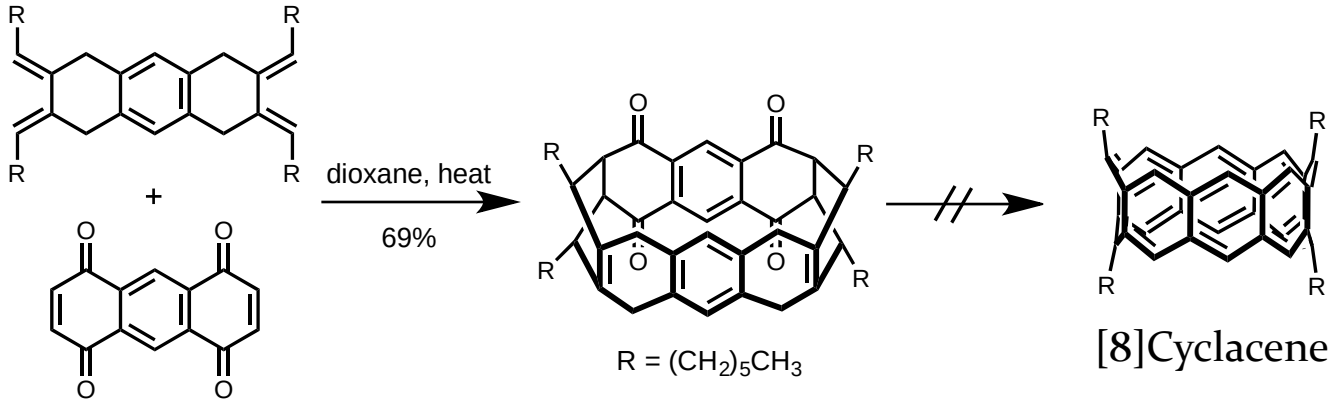
Synthetic precedence to [n]Cyclacene derivatives

- Stoddart's approach to [12]cyclacene



[12]Cyclacene

- Cory's approach to [8]cyclacene



[8]Cyclacene

(1) Kohnke, F. H.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed.* **1987**, *26*, 892-894
(2) Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Philp, D.; Stoddart, J. F. *Pure Appl. Chem.* **1993**, *65*, 119-125.
(3) Cory, R. M.; McPhail, C. L.; Dikmans, A. J.; Vittal, J. J. *Tetrahedron Lett.* **1996**, *37*, 1983-1986.

The Strategy for Macrocycle Synthesis– The Douglas Approach

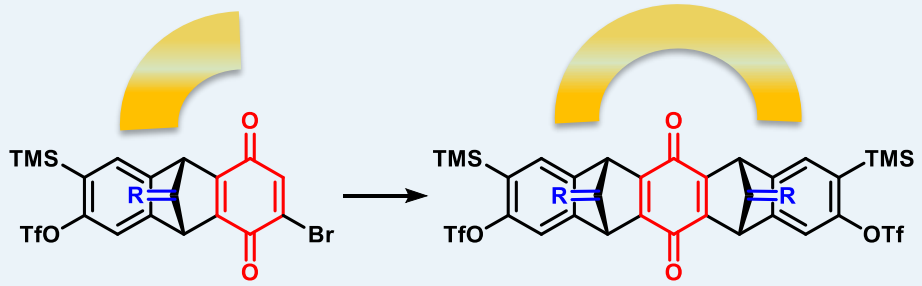
Curved/unstrained synthons

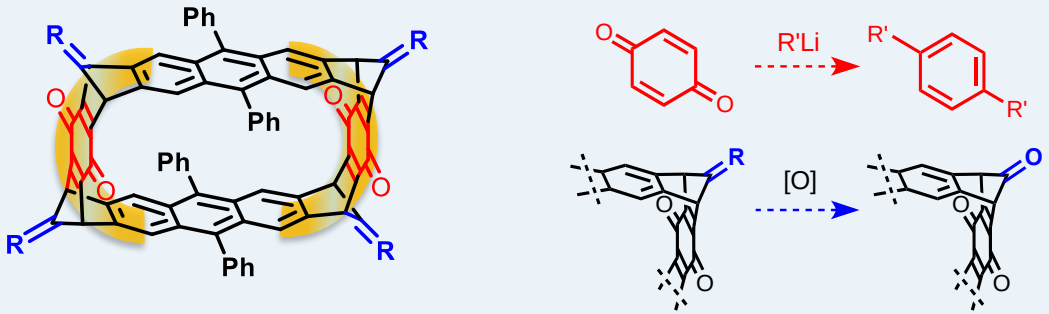
Stereoselective Diels–Alder reaction

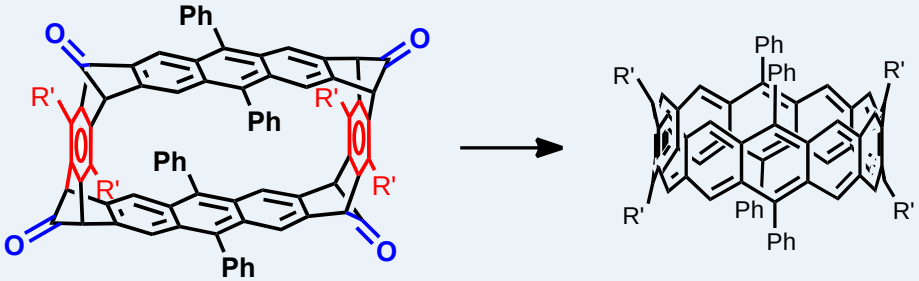
Macrocycle

decarbonylation

End-game (aromatization)

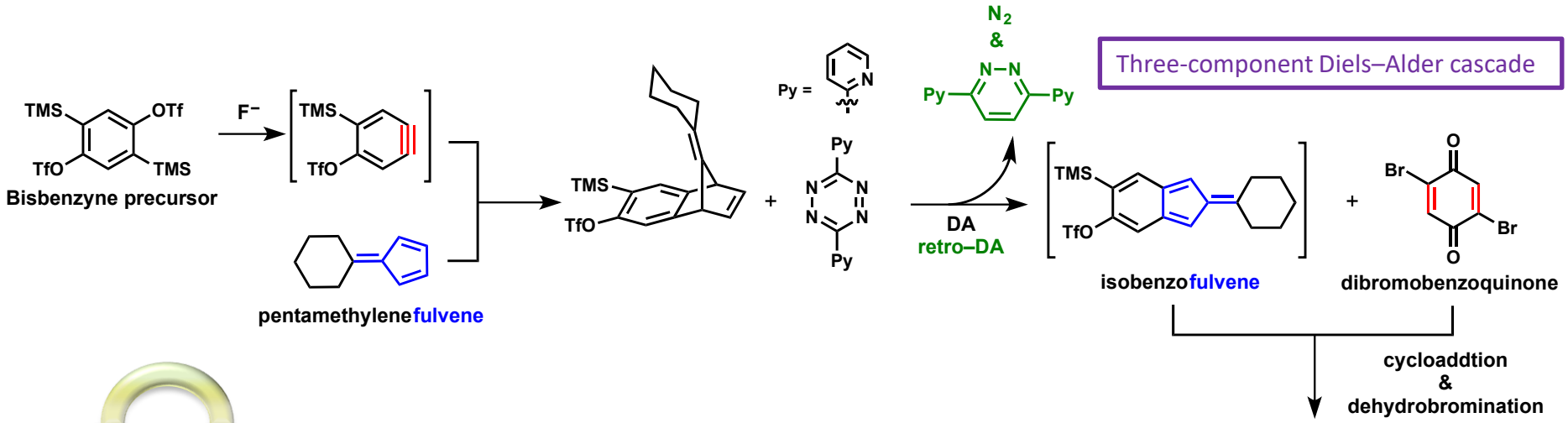


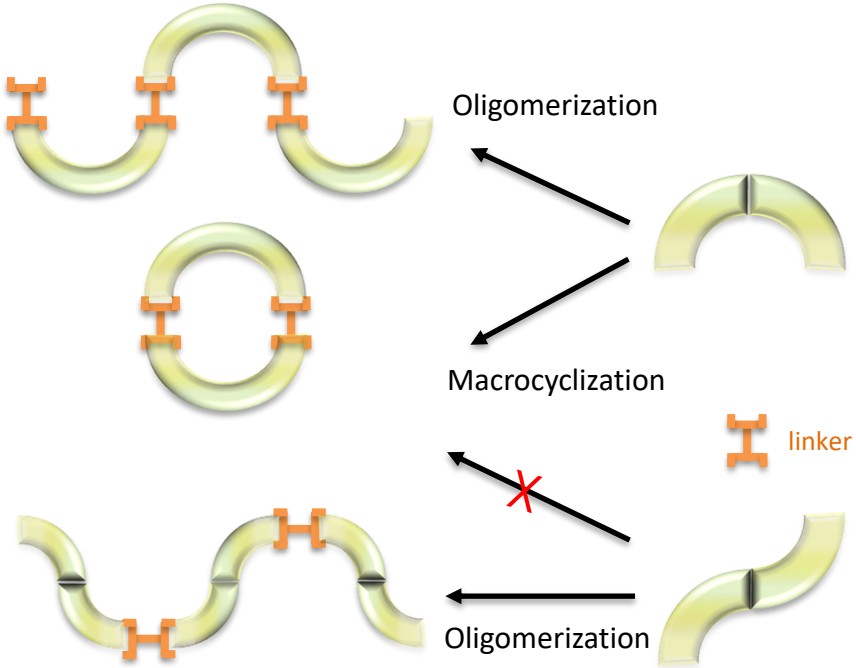


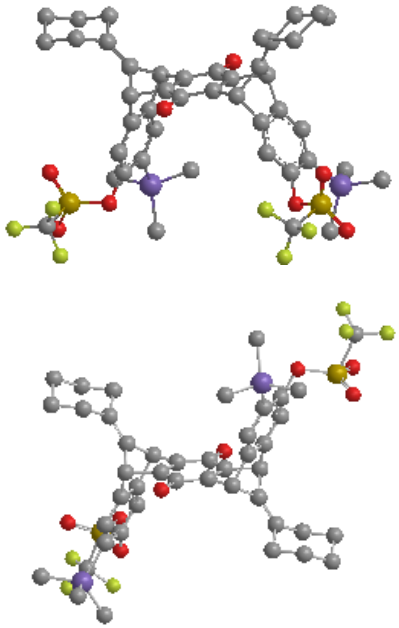


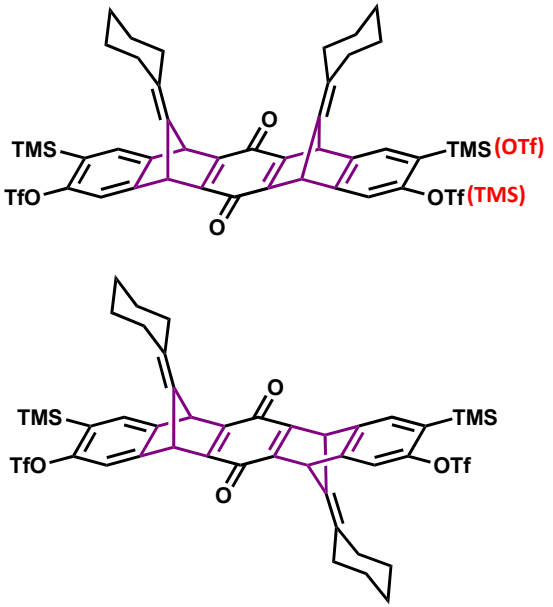
Proposed Synthesis

- Challenge: stereoselective synthesis of cyclization precursor (half cycle)



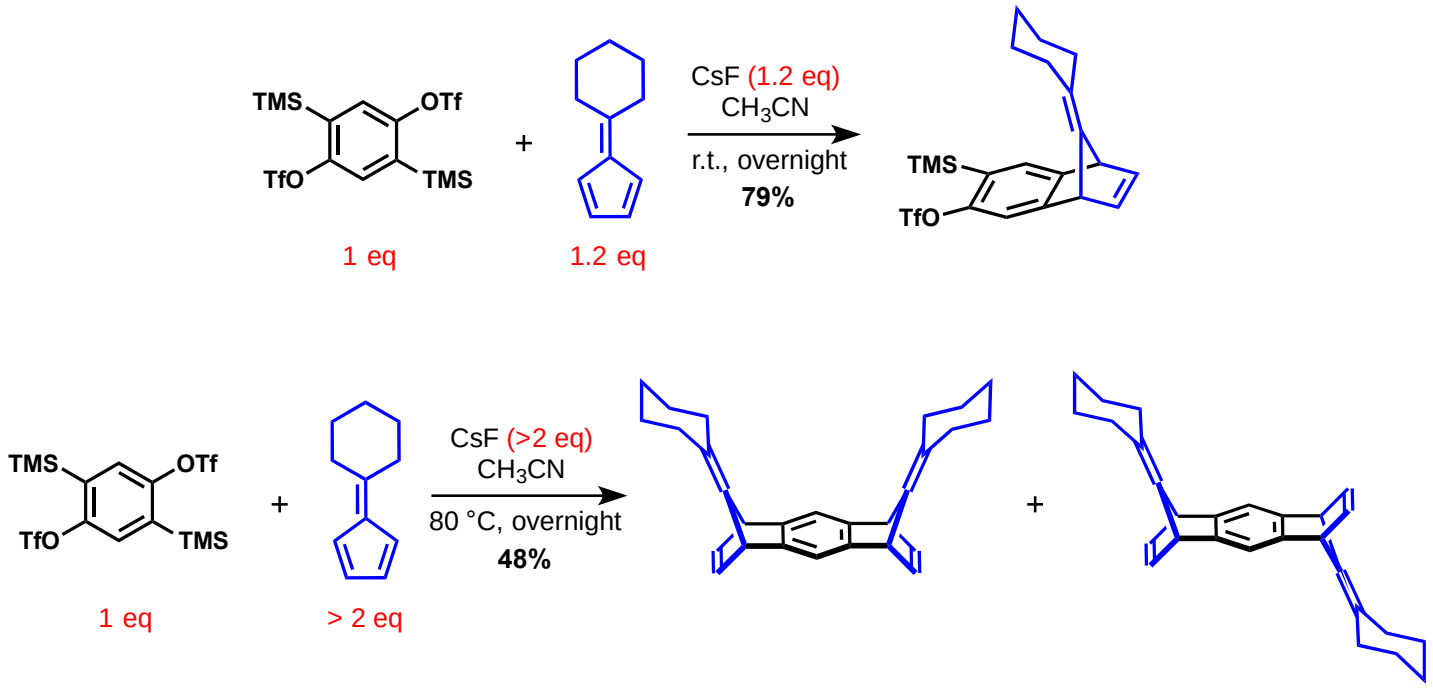






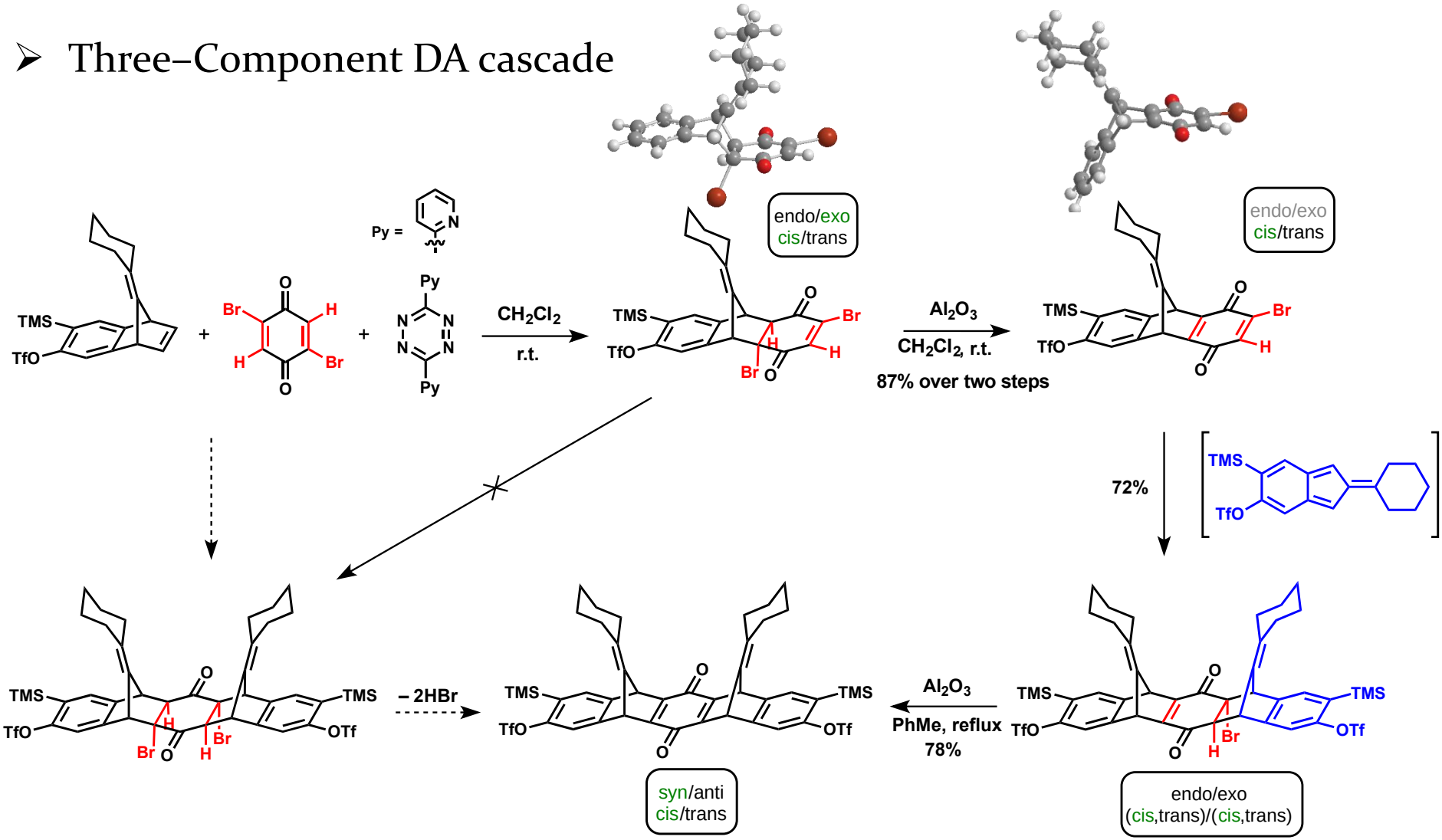
Synthesis of Mono-bridged Precursor (1/4 cycle)

- Controlled benzyne Diels–Alder reaction



Synthesis Attempts toward Syn-isomer (Half Cycle)

- Three–Component DA cascade



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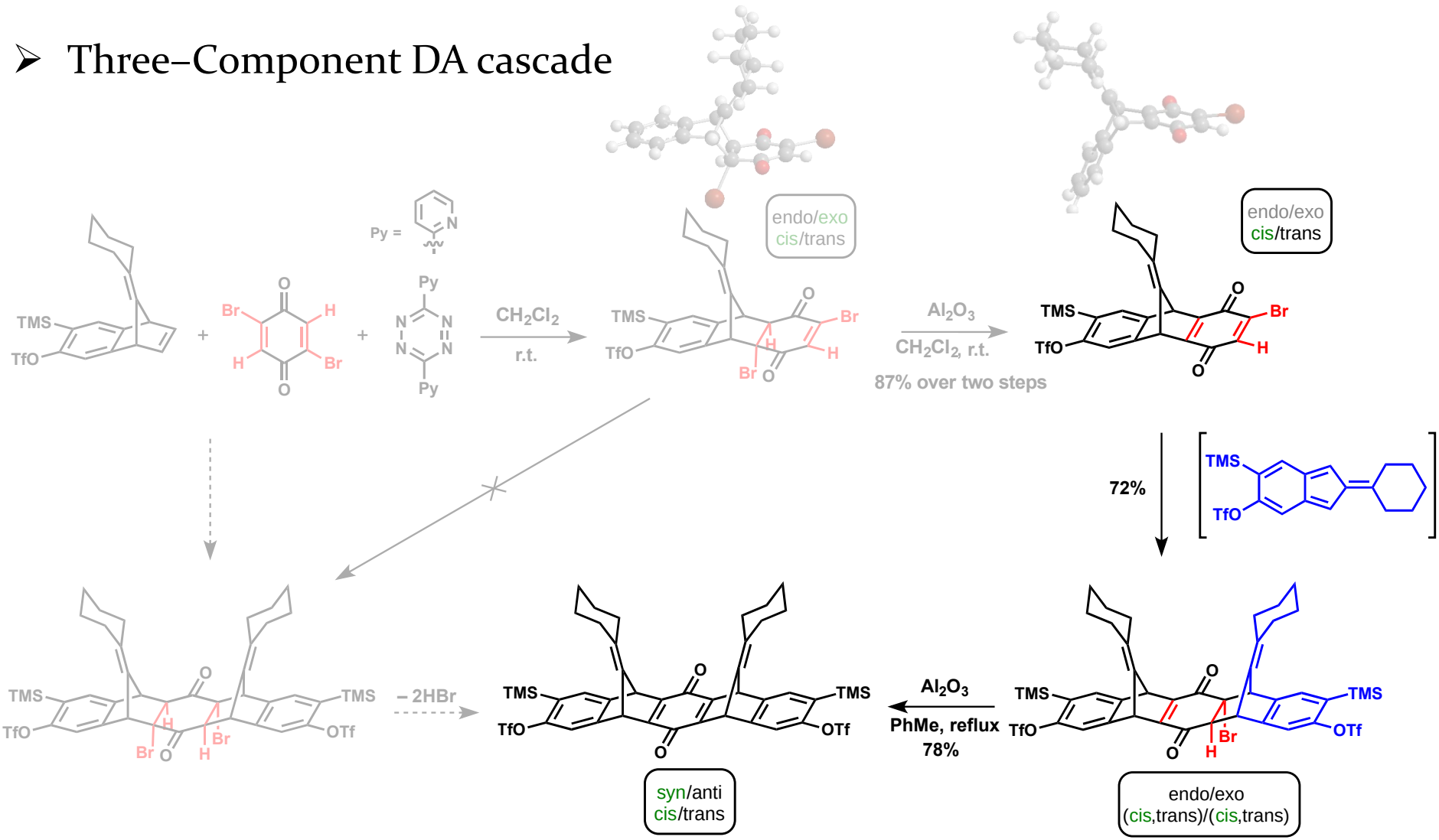
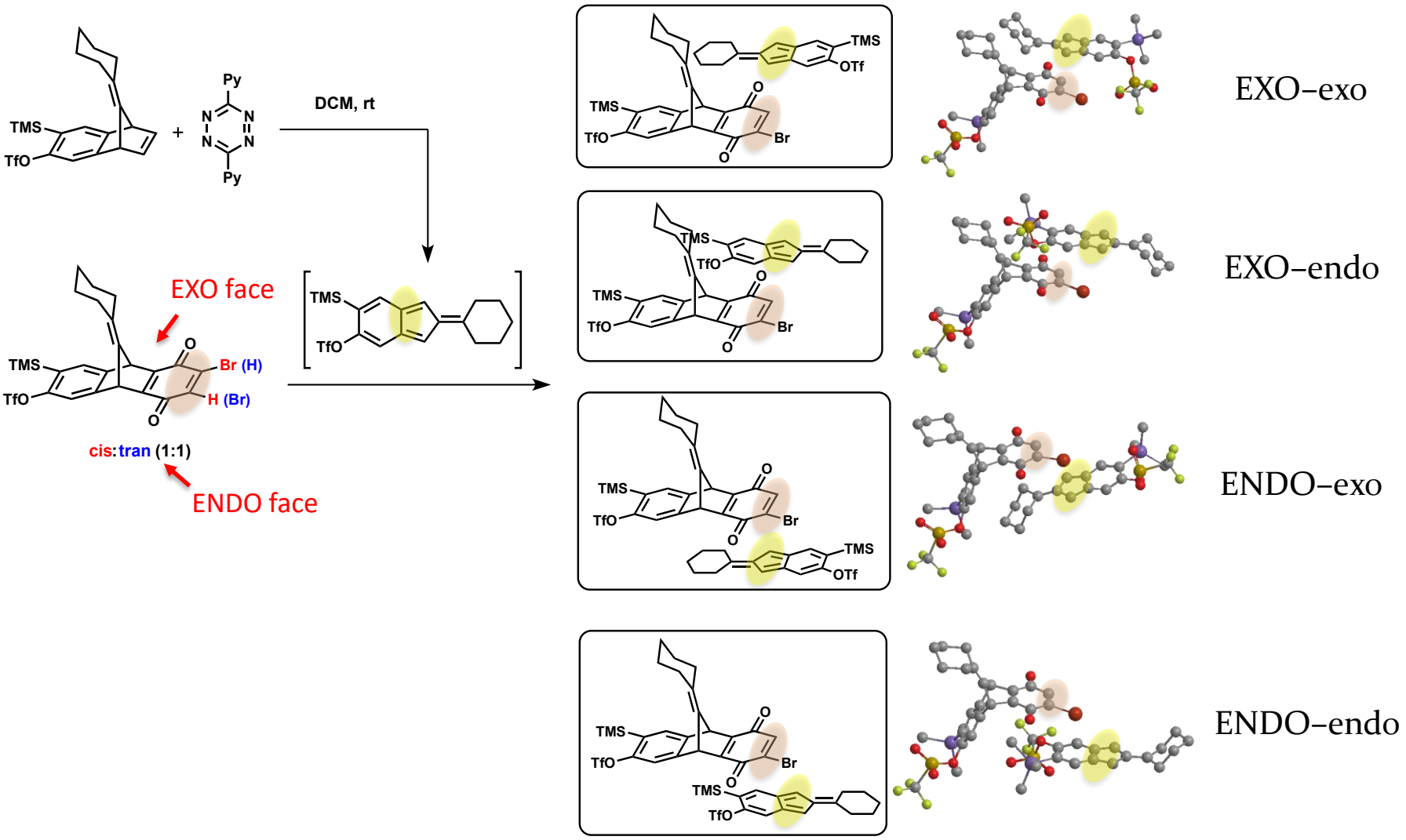


Steric Analysis

- Stereoselective Diels–Alder reactions –– "*EXO–exo* selectivity"



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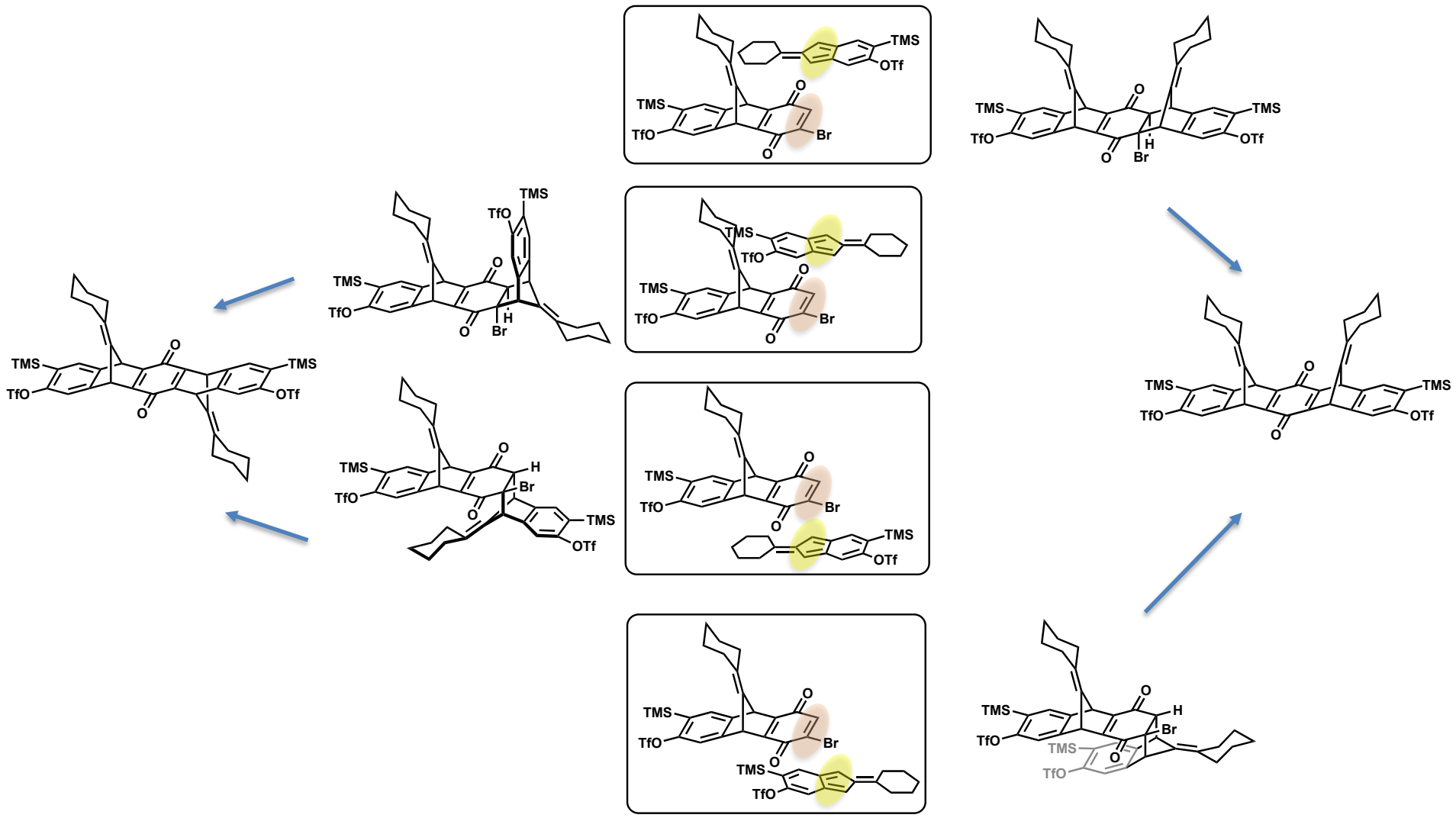
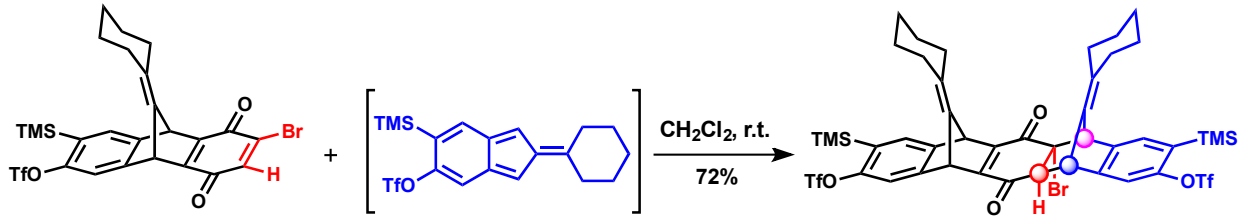


Stereoselective Diels–Alder Reaction

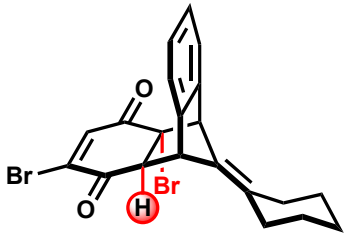
- Stereoselectivity observed in ^{1}H–NMR spectrum!

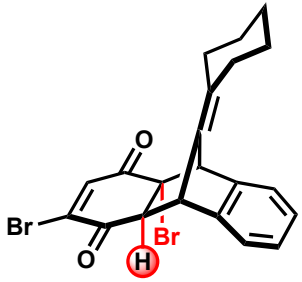


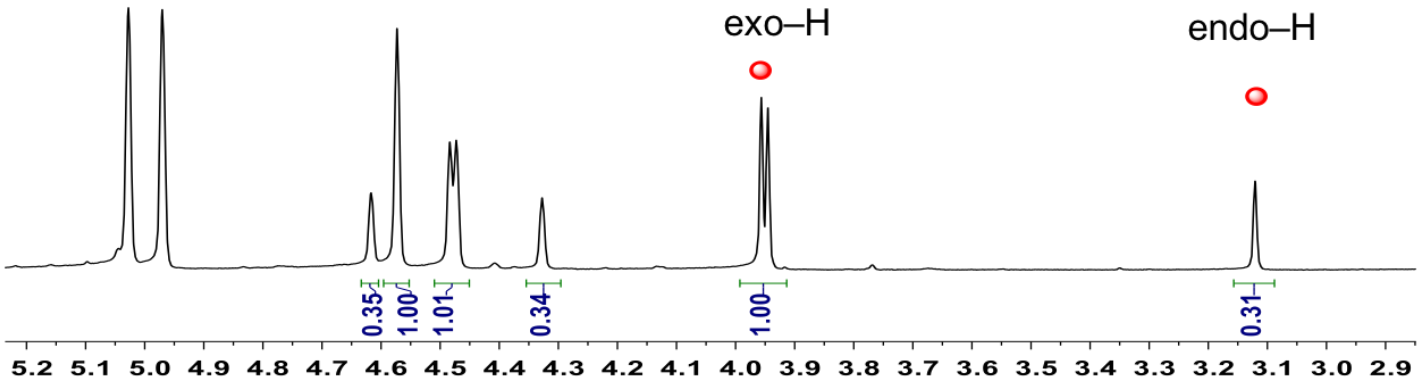
Stereoselective Diels–Alder Reaction

- Model study

Dr. Sarah Wegwerth







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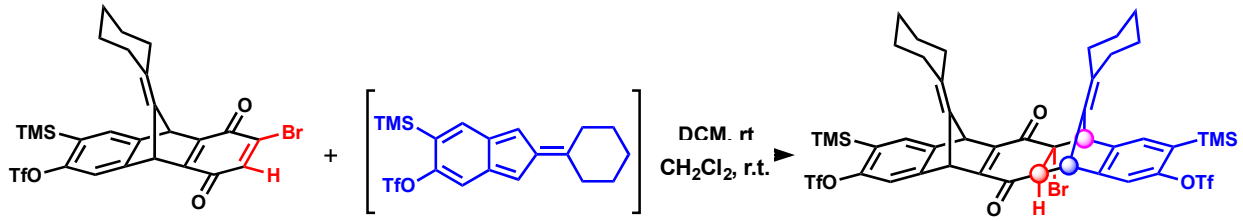
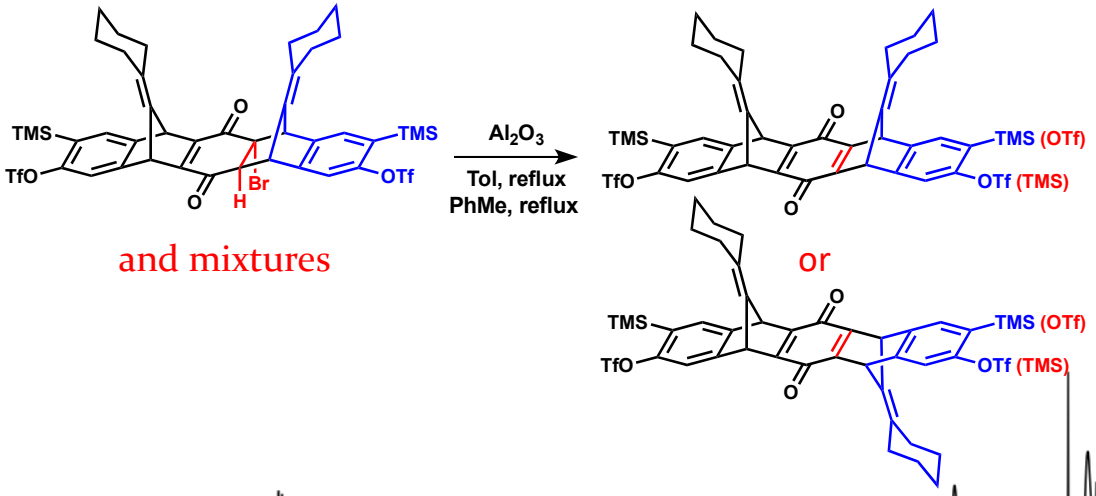


Synthesis Attempts toward Syn-isomer

- Dehydrobromination of stereoisomers

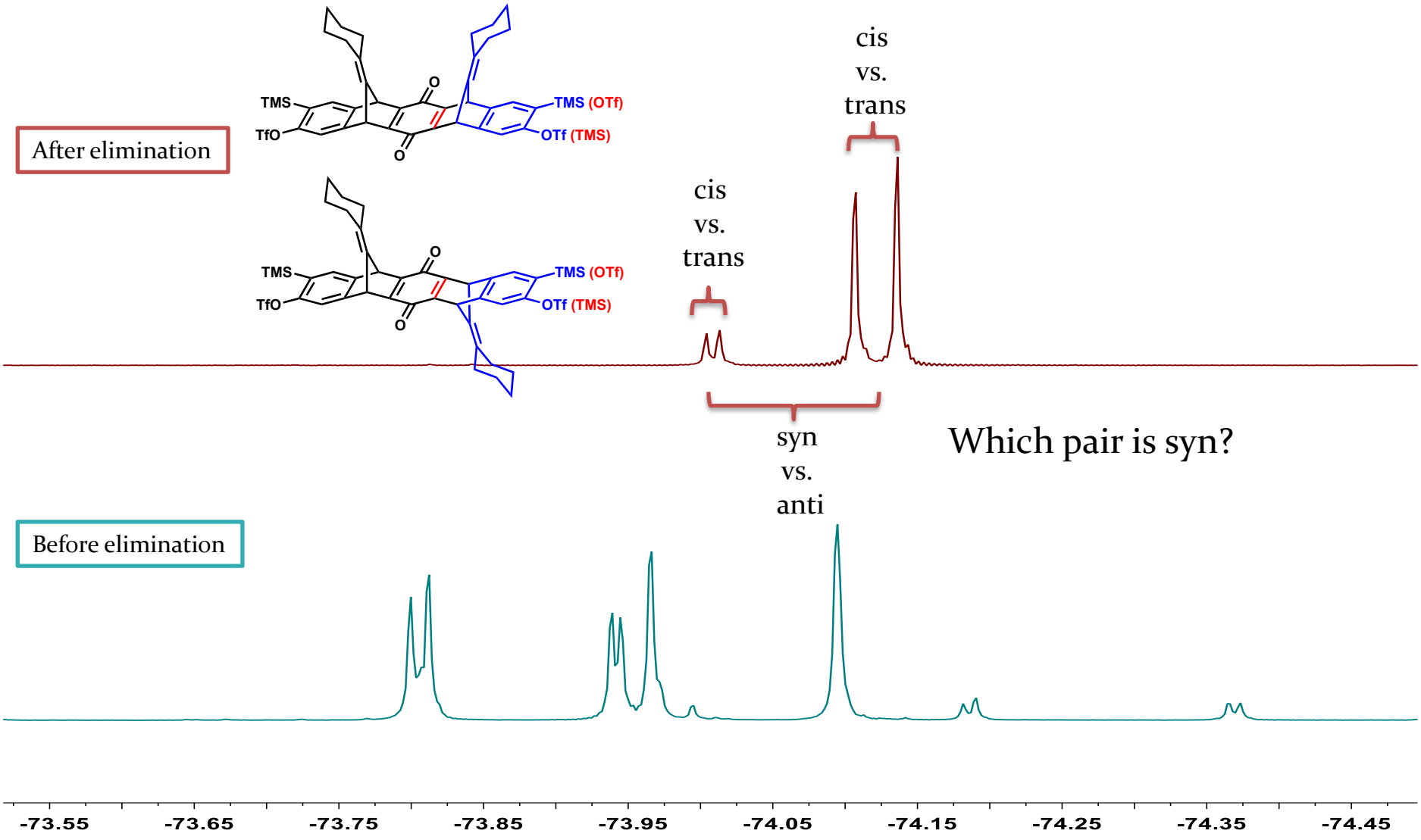


After elimination

Before elimination

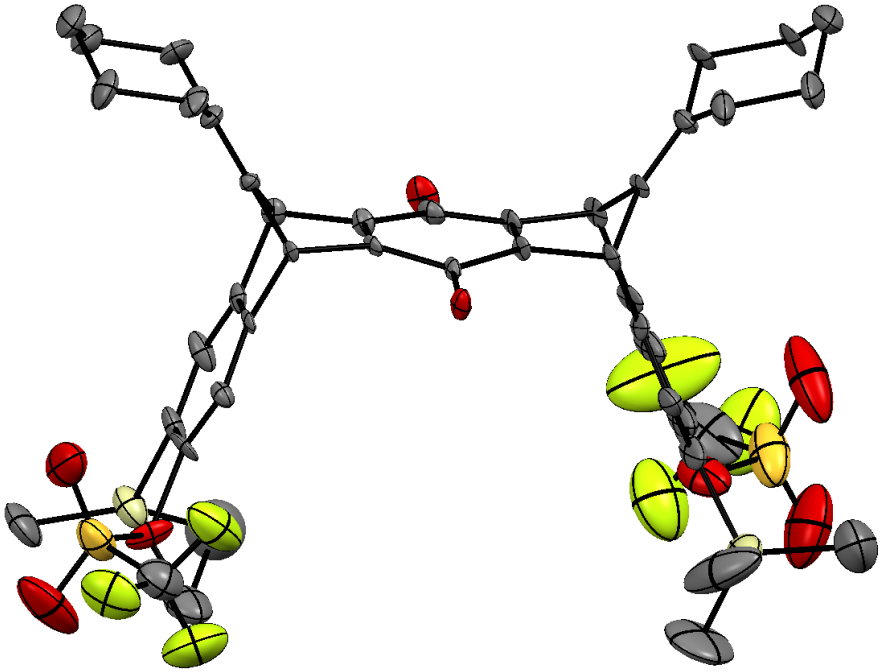
Synthesis Attempts toward Syn-isomer

- Dehydrobromination of stereoisomers by ^{19}F–NMR



Crystal Structure of *Syn*-isomer

- *Syn*-isomer as the major product!

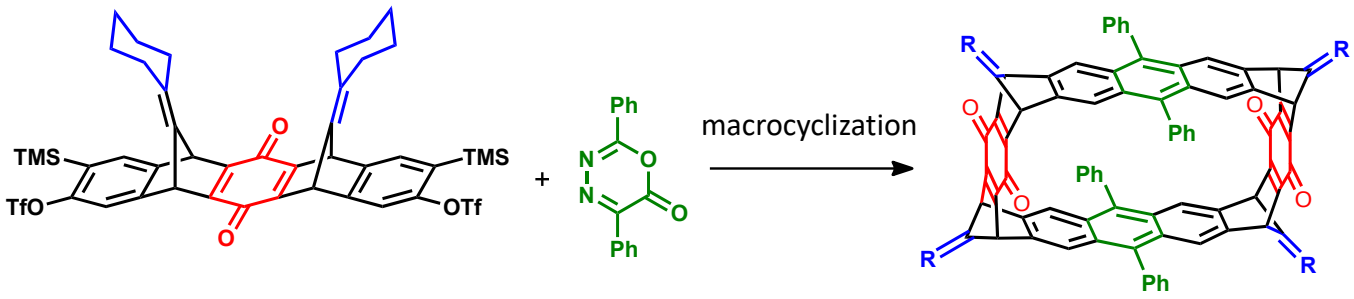


Steven Underwood

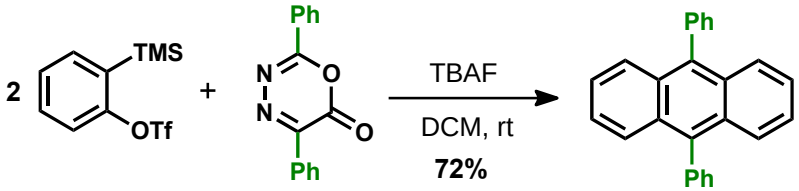
Dr. Victor Young

Future Work – Advance to the Macrocycle

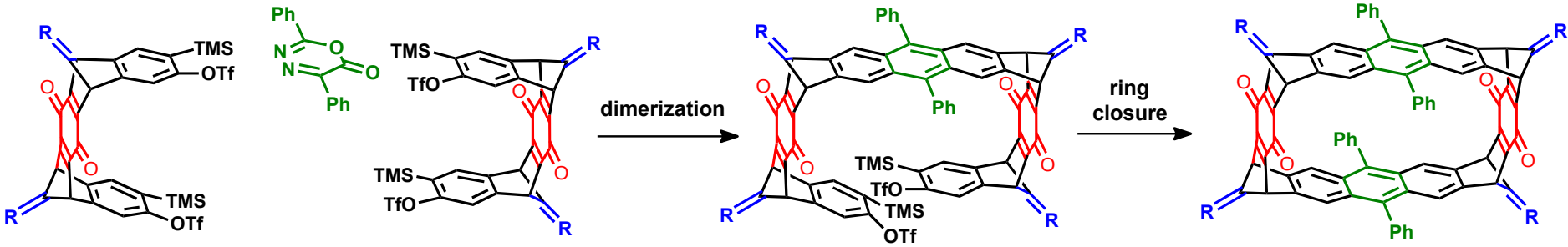
- Macrocyclization and late-stage functionalization



Model reaction

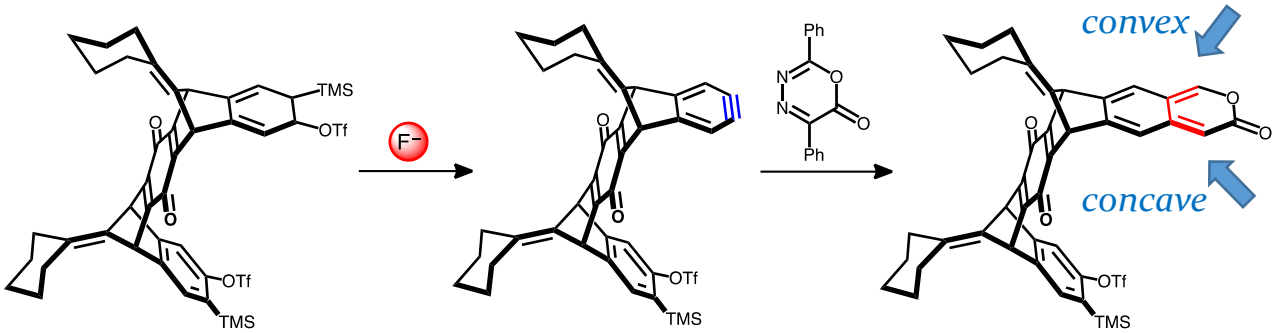


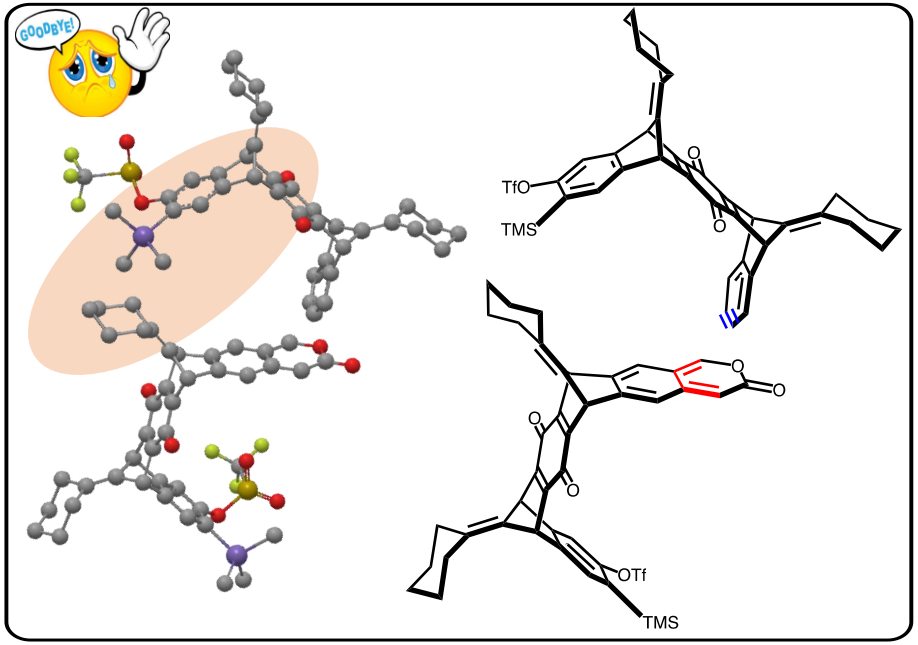
Real system –– "AA + BB"

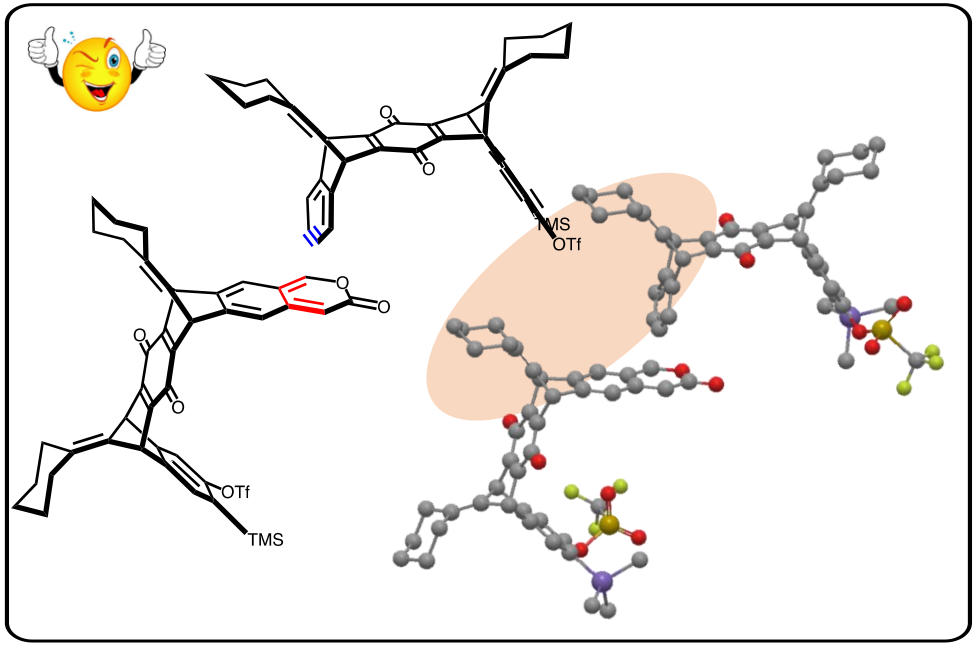


Steglich, W.; Buschmann, E.; Gansen, G.; Wilschowitz, L. *Synthesis* **1977**, *1977(4)*, 252-253.

Vision into the Dimerization Intermediate







Acknowledgements

- Prof. Chris Douglas
- Team Cyclacene: Dr. Sarah Wegwerth, Steve Underwood, Casey Carpenter
- NMR lab and XCL @ University of Minnesota

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