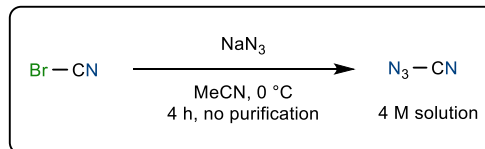


## Properties and synthesis

### Cyanogen azide

- Colorless oil
- Shock and heat sensitive
- $t_{1/2}$  (MeCN, RT) = 15 days
- Stored indefinitely between 0 °C and -20 °C.

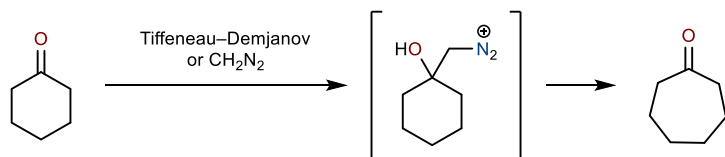


Hermes, M. E. *J. Am. Chem. Soc.* **1964**, *96*, 4506. <https://doi.org/10.1021/ja01074a071>

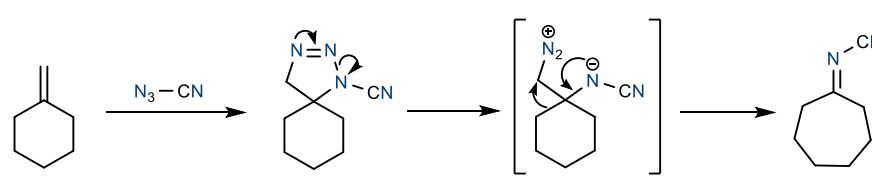
### Method of preparation

- Dissolve cyanogen bromide (1 eq., 4 M) in MeCN
- Cool to 0 °C
- Add finely powdered NaN<sub>3</sub> (1 eq.)
- Stir for 4 h at 0 °C
- Cease stirring, use supernatant (with a syringe)
- Reported procedure on 100 mmol scale

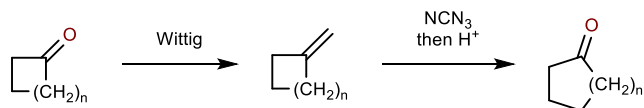
## Ring expansion of ketones



## Ring expansion of endocyclic olefins with NCN<sub>3</sub> (mechanism)

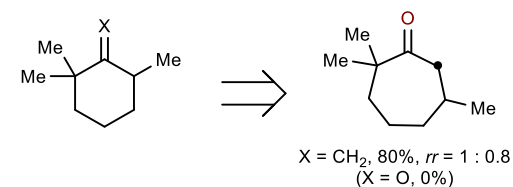
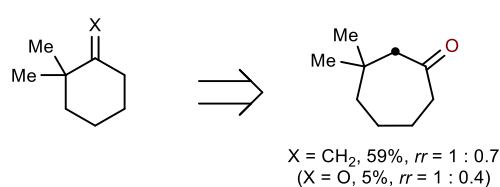
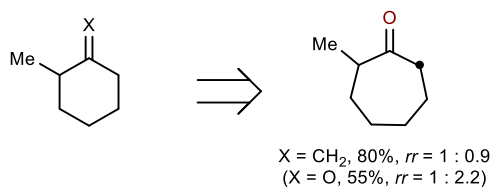


## Proof of concept and initial substrate scope

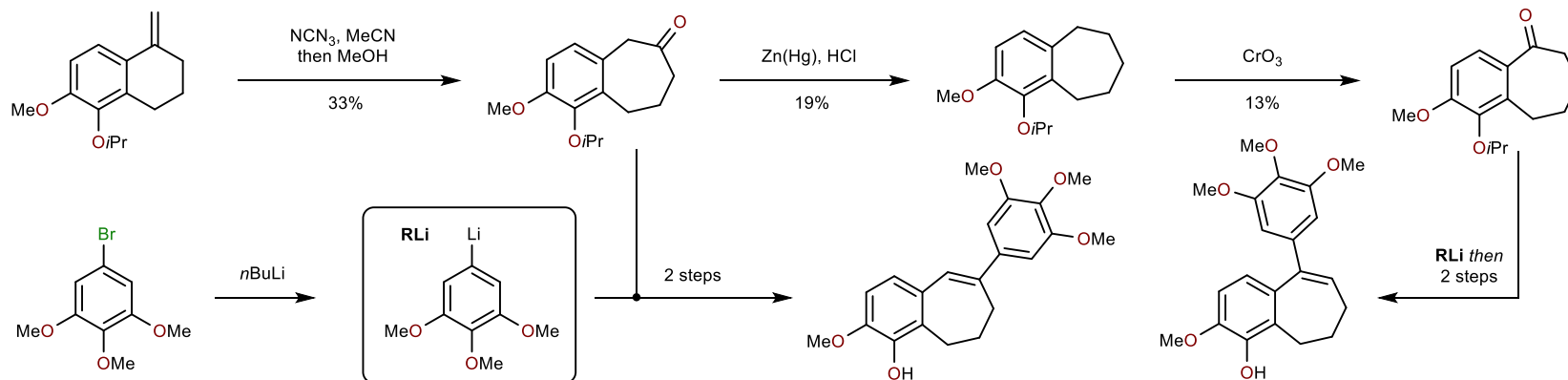
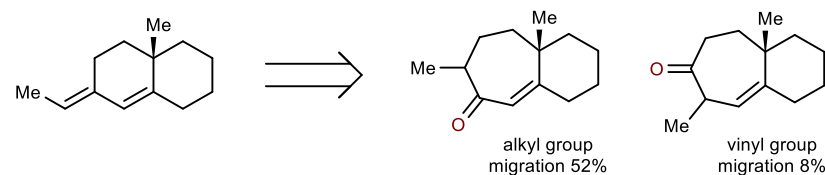
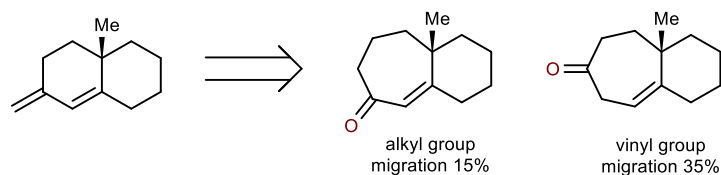
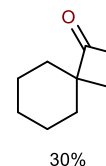
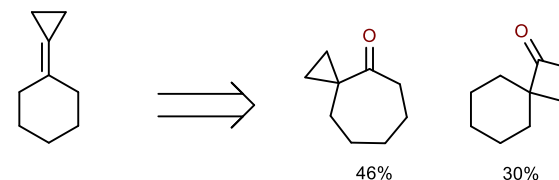
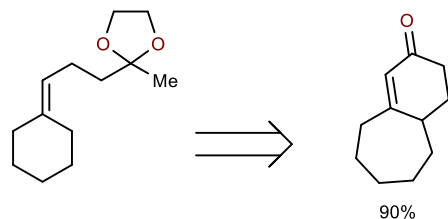
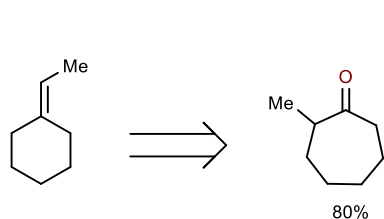
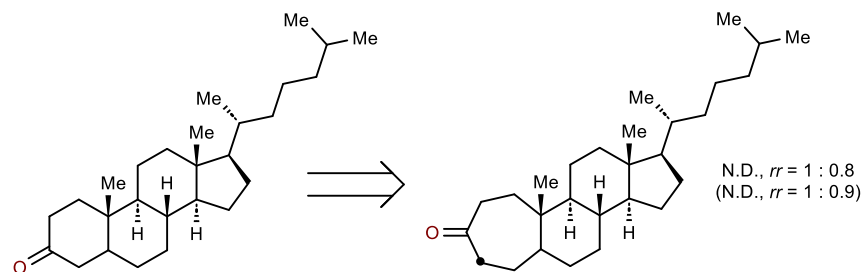
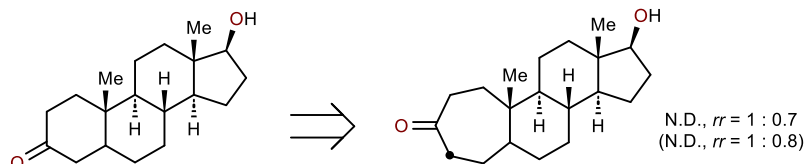


n	Yield [%]	n	Yield [%]	n	Yield [%]
3	52	5	80	7	38
4	44	6	41	11	60

## Substrate scope and comparison with CH<sub>2</sub>N<sub>2</sub>



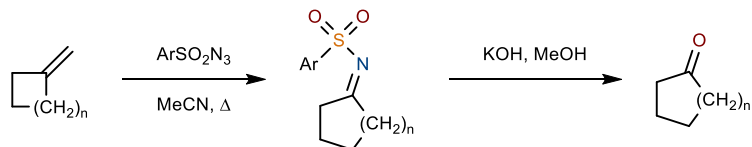
McMurry, J. *J. Am. Chem. Soc.* **1973**, *38*, 2821. <https://doi.org/10.1021/jo00956a019>



## Synthesis of tubulin polymerization inhibitors

Piney K. G. *Bioorg. Med. Chem.* **2008**, *16*, 8161. <https://doi.org/10.1016/j.bmc.2008.07.050>

## Arenesulfonyl azides

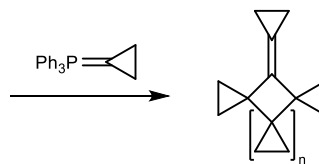
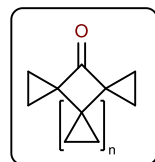
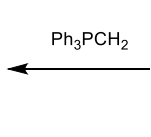
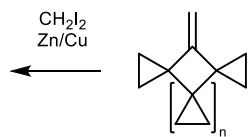
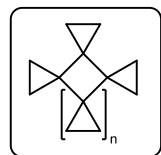


n	Yield [%]	n	Yield [%]	n	Yield [%]
4	99	5	quant.	6	99

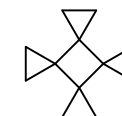
Wohl R. A. *J. Org. Chem.* **1973**, *16*, 8161. <https://doi.org/10.1021/jo00962a600>

if (n = desired): exit loop

start here

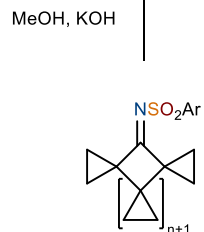


n = 1

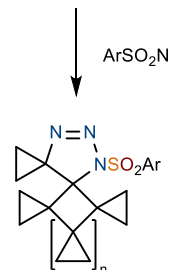


n = 2

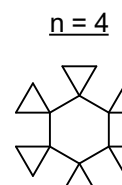
**Iterative synthesis of [n]rotanes**



if (n < desired):



n = 3

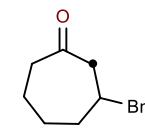
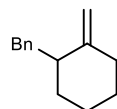
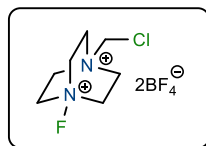


n = 4

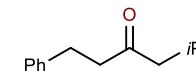
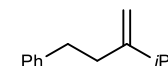
Fitjer, L. *Angew. Chem. Int. Ed.* **1976**, *15*, 7663. <https://doi.org/10.1002/anie.197607631>

## Modern conditions

10 mol% Pd(MeCN)<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub>  
1.2 eq. Selectfluor  
MeCN/H<sub>2</sub>O, RT



63%, rr = 6.5 : 1



59%, rr = 1.4 : 1

Zhu J. *Science*. **2023**, *379*, 1363. <https://doi.org/10.1126/science.adg3182>