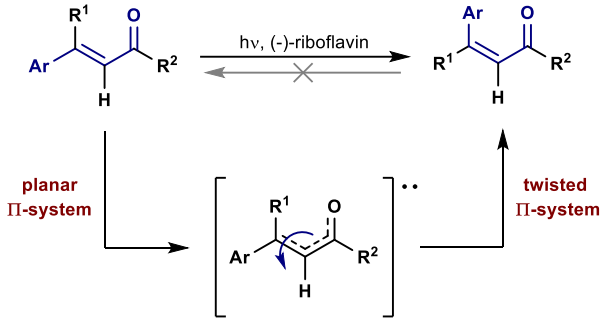
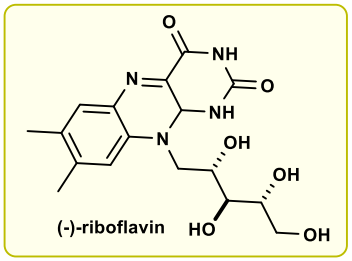
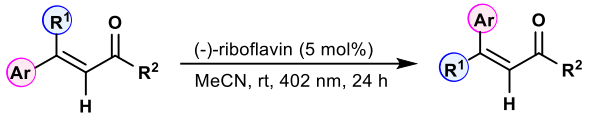
E → *Z* Isomerization of Polarized Olefins

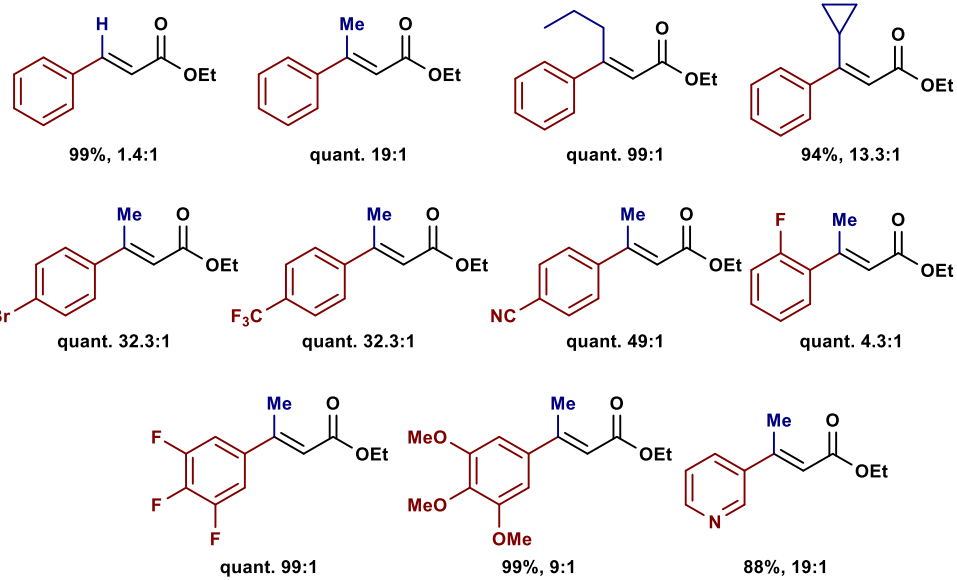
(-)-Riboflavin Isomerization of Activated Olefins:

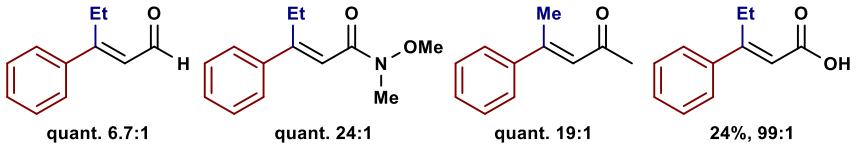






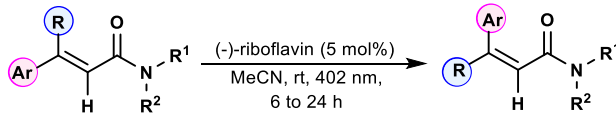
***Z:E* isomer ratios**



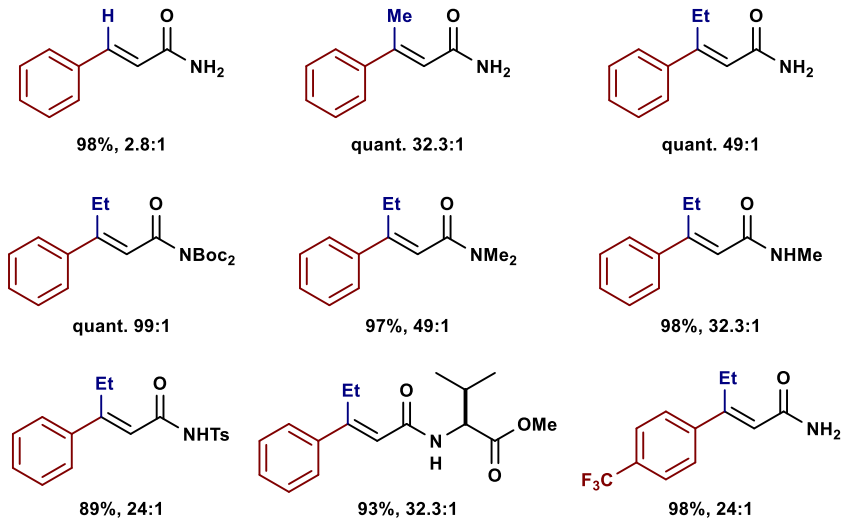


- General tolerance of deviation at R^1, R^2, and aryl
- Electronic modulation of aryl ring has negligible effect on stereoselectivity
  - Conjugation in substrate and deconjugation in product key to high levels of stereocontrol
- *Z/E* reatio increases with increasing α-radical stabilization of R^1
- Stern-Volmer consistent with triplet energy transfer mechanism
  - Photostationary state with constant Z/E ratio expected

Gilmour, R. *JACS.* **2015**, *137*, 11254. https://doi.org/10.1021/jacs.5b07136

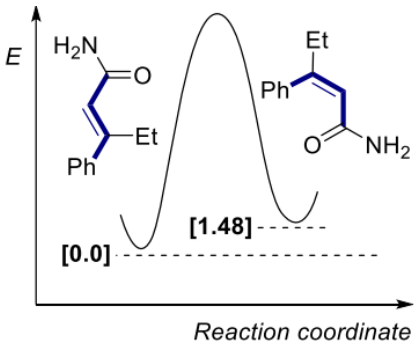


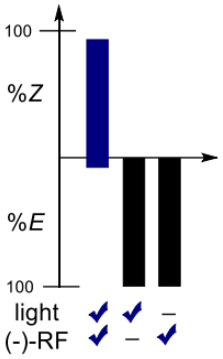
***Z:E* isomer ratios**



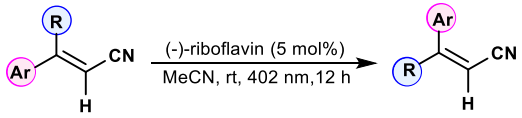
- Spin density concentrated in alkene fragment
- Allylic strain governs selectivity

E → *Z* Isomerization of Polarized Olefins

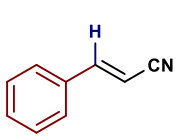




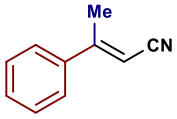
Gilmour, R. and Burley, G. A. Tetrahedron **2020**, 131198.
https://doi.org/10.1016/j.tet.2020.131198



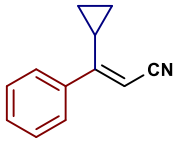
***Z*:*E* isomer ratios**



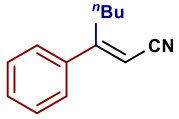
quant. 1.7:1



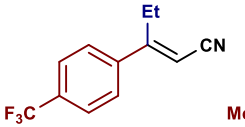
quant. 10.1:1



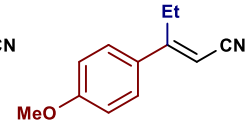
85%, 19:1



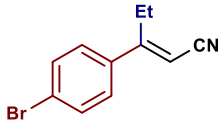
quant. 24:1



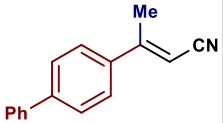
quant. 32.3:1



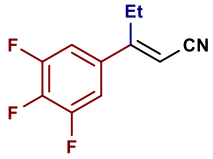
quant. 10.1:1



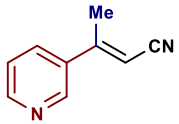
quant. 19:1



quant. 2.3:1



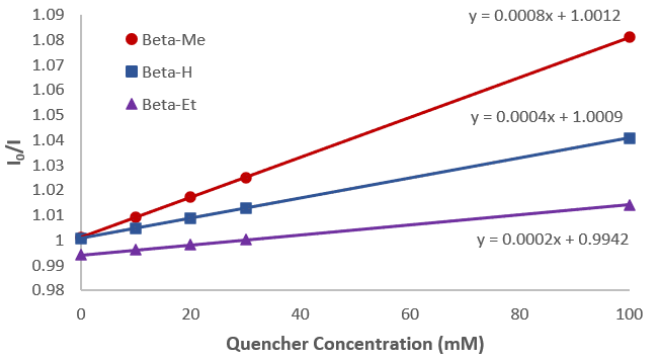
quant. 24:1



82%, 10.1:1

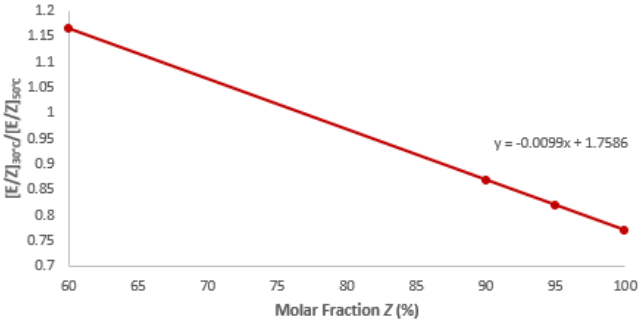
- **Augmenting strain in product enhances selectivity**

Stern-Volmer Fluorescence Quenching of (-)-RF



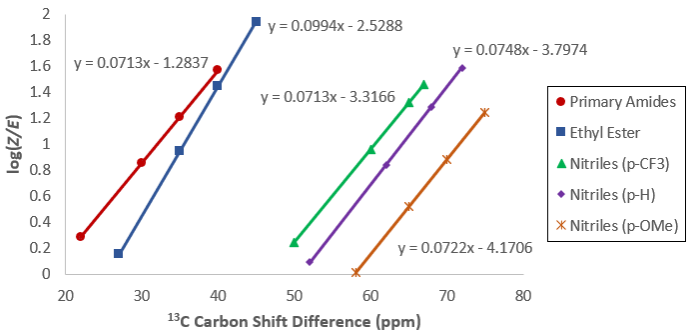
- **Selectivity does not correlate with quenching efficiency**
- **Viscosity effect in protic solvents in line with diffusion controlled, collisional singlet energy transfer mediation**
- **Reaction selectivity oxygen independent reinforcing Stern-Volmer notion of mechanistic dichotomy**

Correlation of Ratio of Photostationary State Composition at 30 and 50 °C



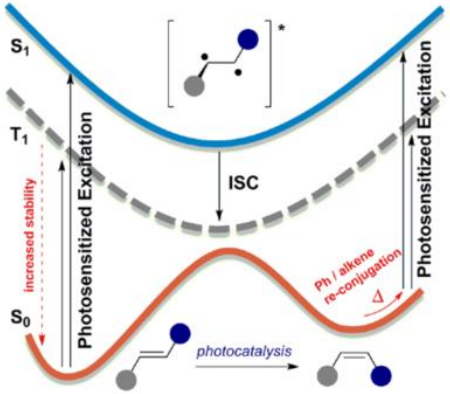
- **Linear correlation between Taft parameter and photostationary state Z-isomer molar fraction**
- **Ground state starting material influences photostaionary composition**
- **Longer excited state lifetimes and faster state and rotational transitions enhance reaction rate**

Correlation of ^{13}C β-α Carbon Shift Difference with Photostationary State *Z*/*E* Selectivity



- **Selectivity increases directly with electron deficiency of β-carbon**

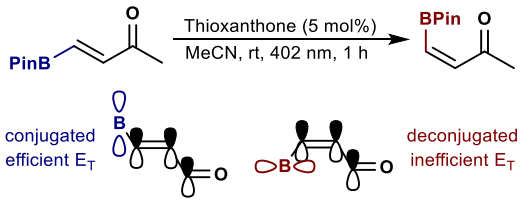
E → *Z* Isomerization of Polarized Olefins

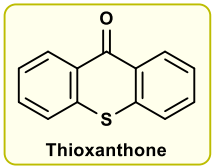


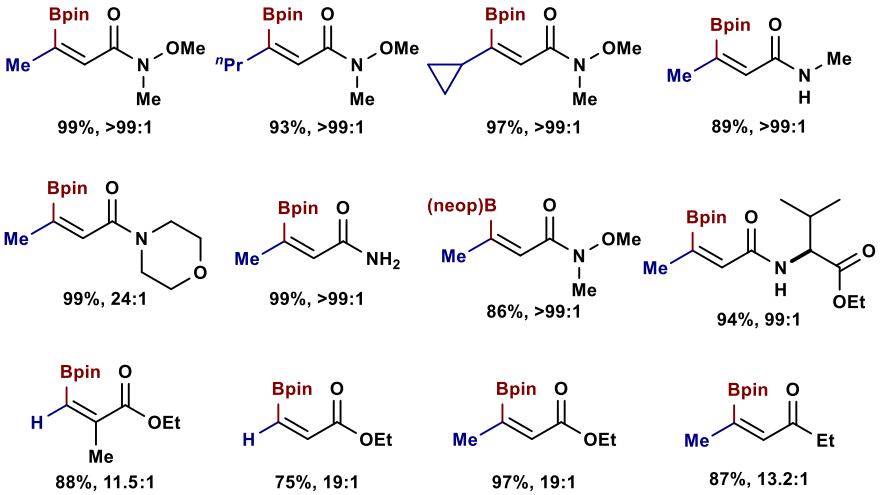
- **Substrate activation from polarized nature of alkene**
- **Electron withdrawing of carbonyl or nitril facilitates intersystem crossing**

Gilmour, R. *JOC* **2017**, *82*, 9955. https://doi.org/10.1021/acs.joc.7b01281

Thioxanthone Isomerization:







- **Undergoes energy transfer catalysis**
- **Inert atmosphere, light, and catalyst all required for reaction**
- **Boron p-orbital necessary for reaction to occur**
- **Provides useful precursor for further functionalization from boron**

Gilmour, R. *Science* **2020**, *369*, 302. https://doi.org/10.1126/science.abb7235

Examples of Photosensitized Alkene Isomerization: