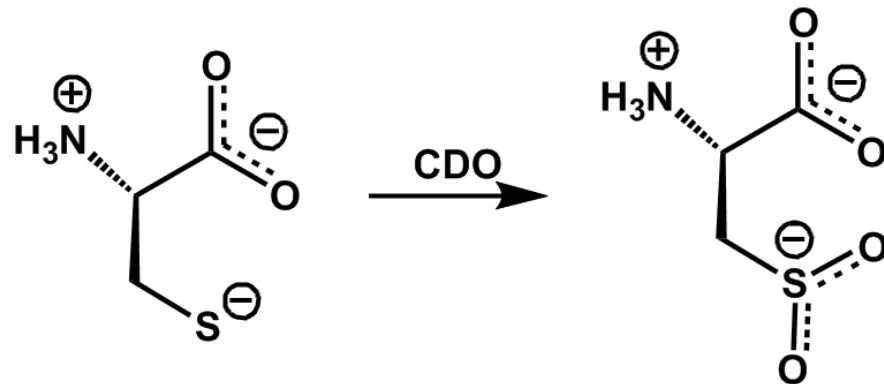


# Oxidative Desulfurization Using Functional Thiol Dioxygenase Models

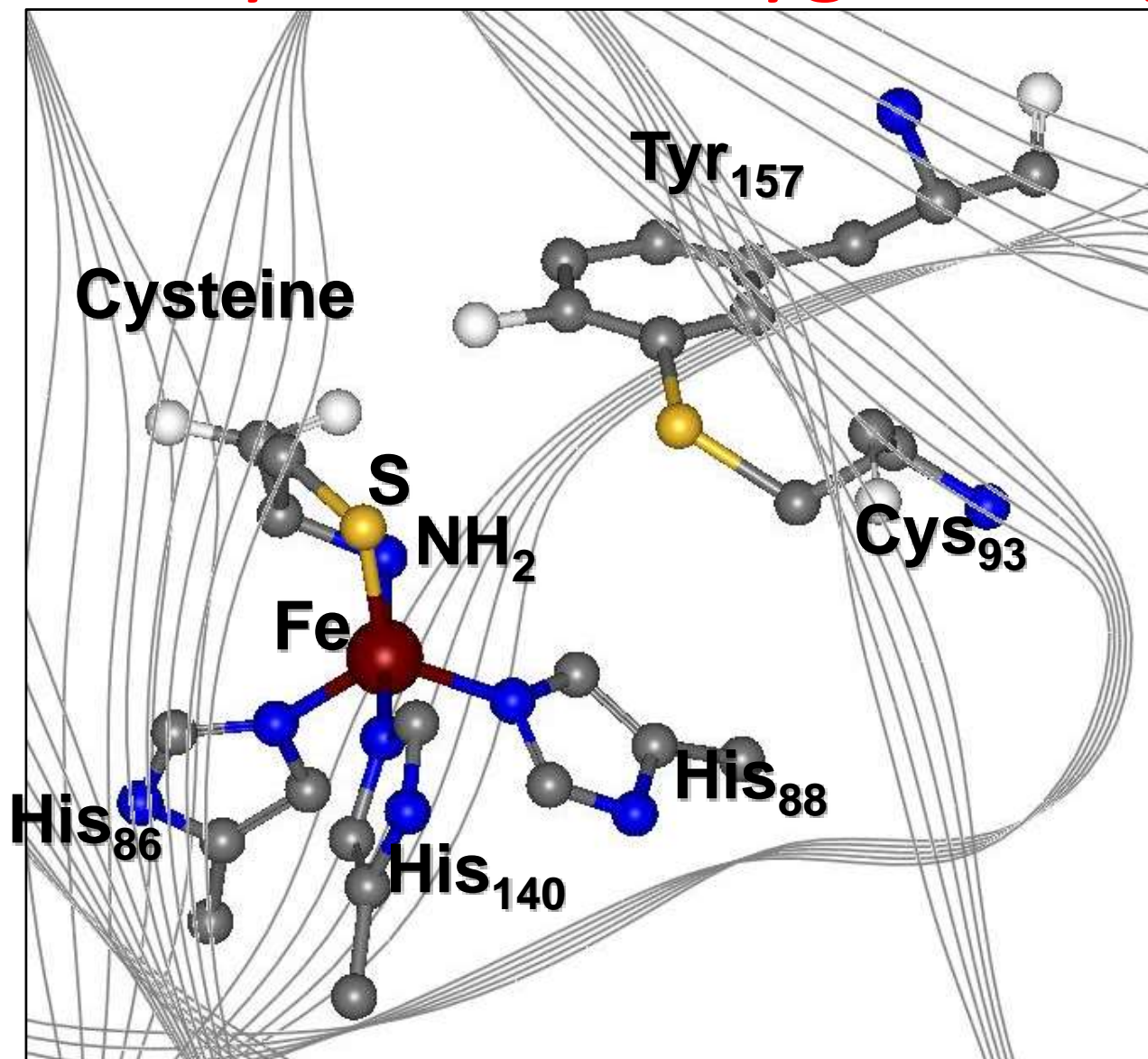
Pat Dilsaver

# Sulfur in Diesel Fuels

- Major Source of  $\text{SO}_2$ 
  - Greenhouse gas
- Difficult to remove
  - Many techniques are expensive, not universally effective
- Nature uses Thiol Dioxygenases
  - Iron center
  - Oxygen



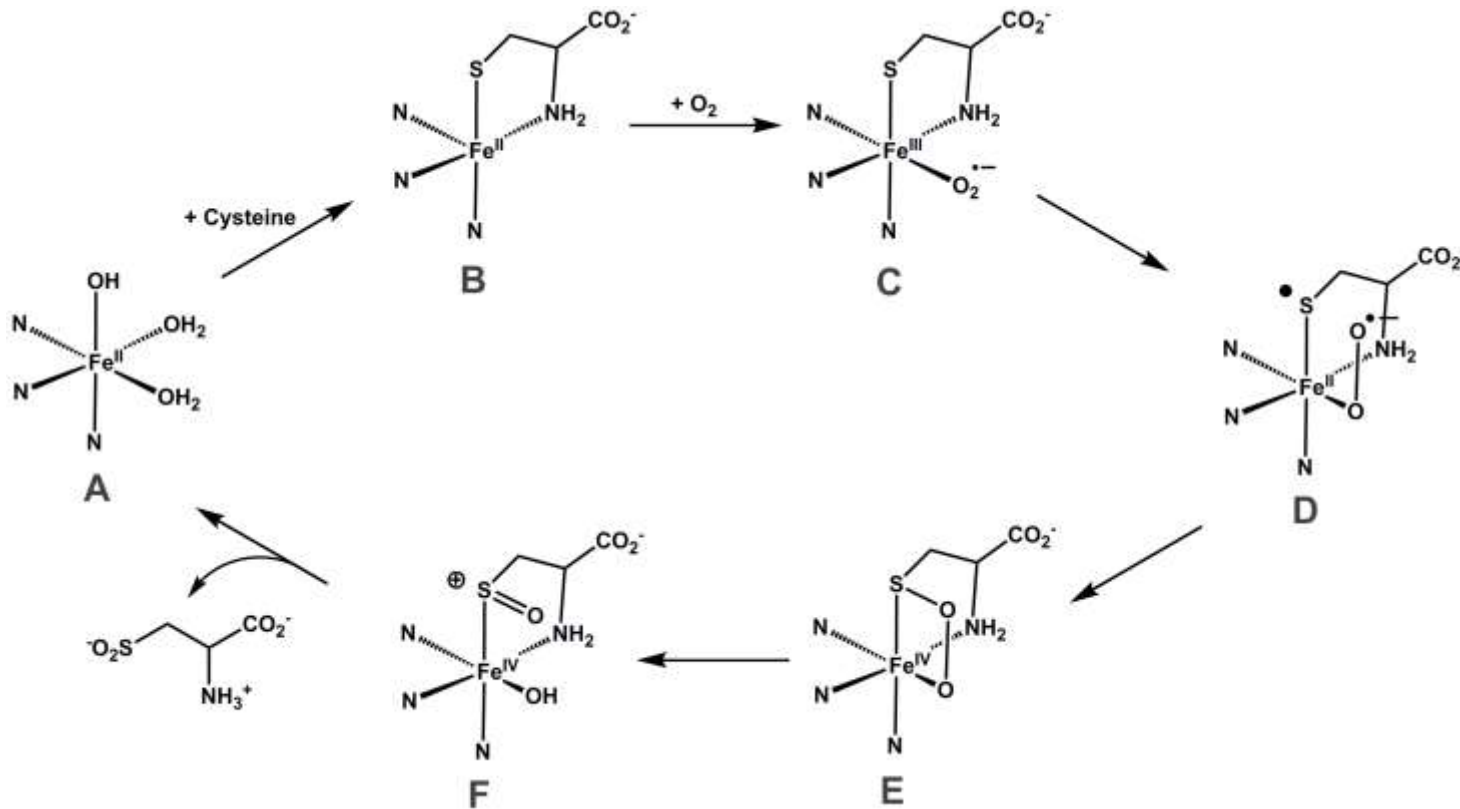
# Cysteine Dioxygenase (CDO)



- Three histidine residues anchor iron center in face-capping structure
- Cysteine bound in a bidentate fashion
- Open site adjacent to S

Ye, S; et al. J.Biol.Chem. 2007, 282, 3391-3402

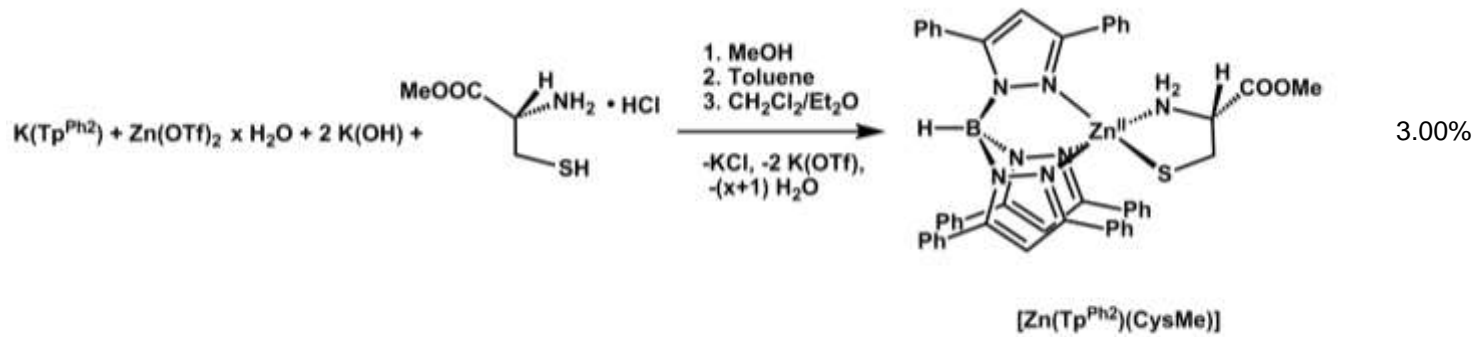
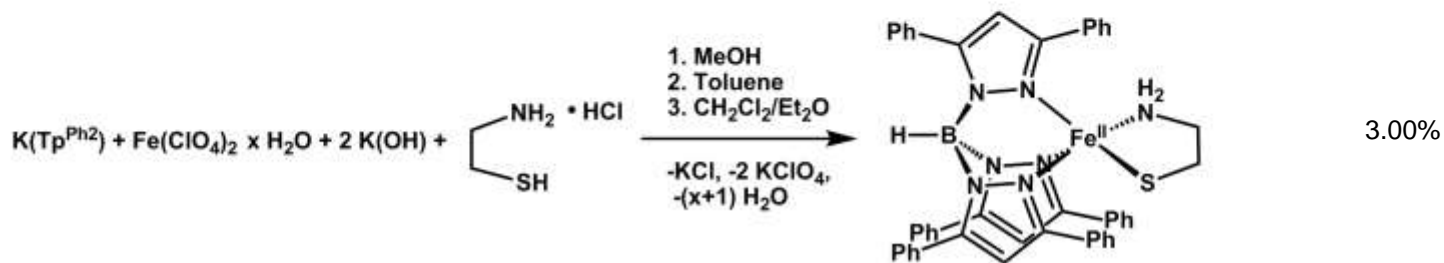
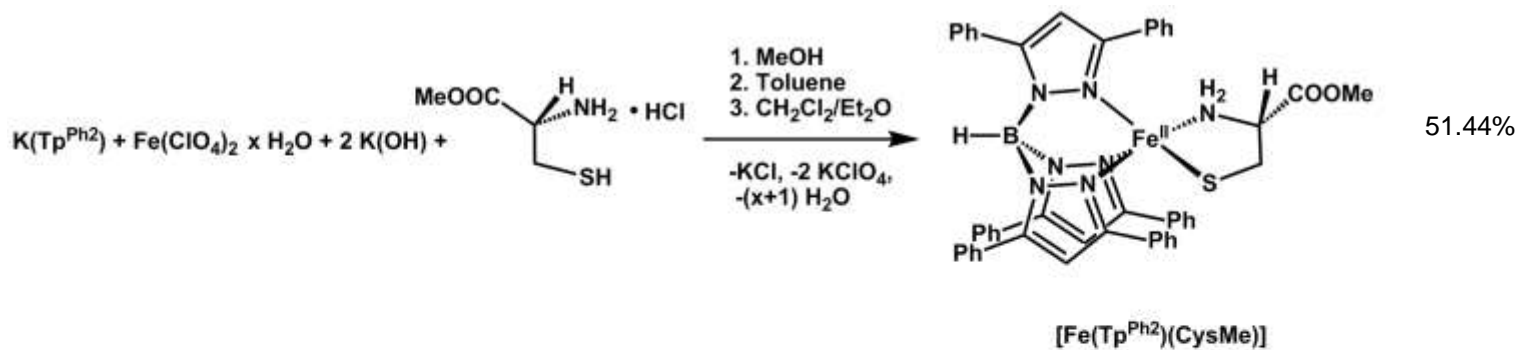
# Mechanism for CDO

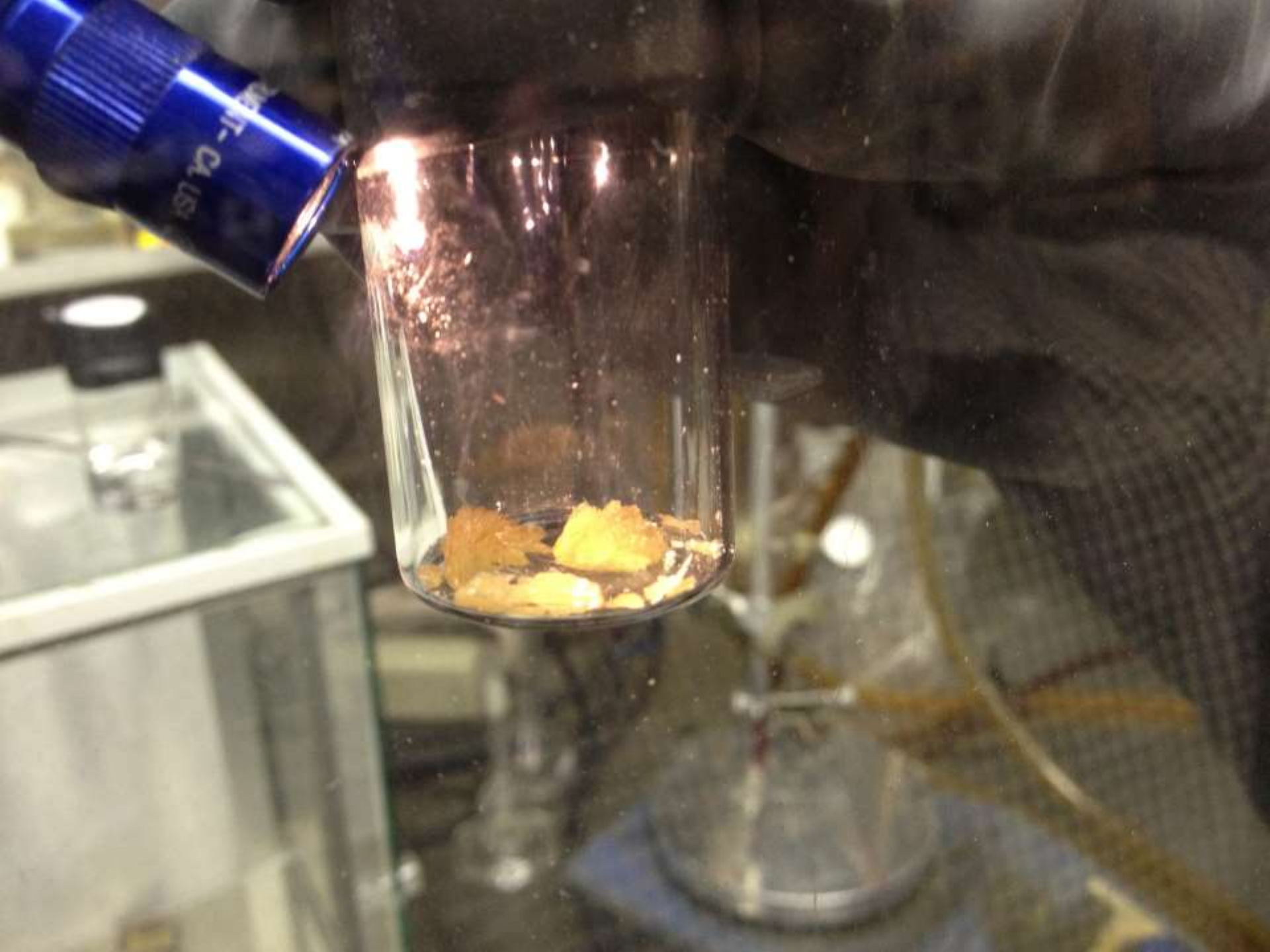


Gardner, J. D.; Pierce, B. S.; Fox, B. G.; Brunold, T. C. *Biochemistry* **2010**, *49*, 6033.

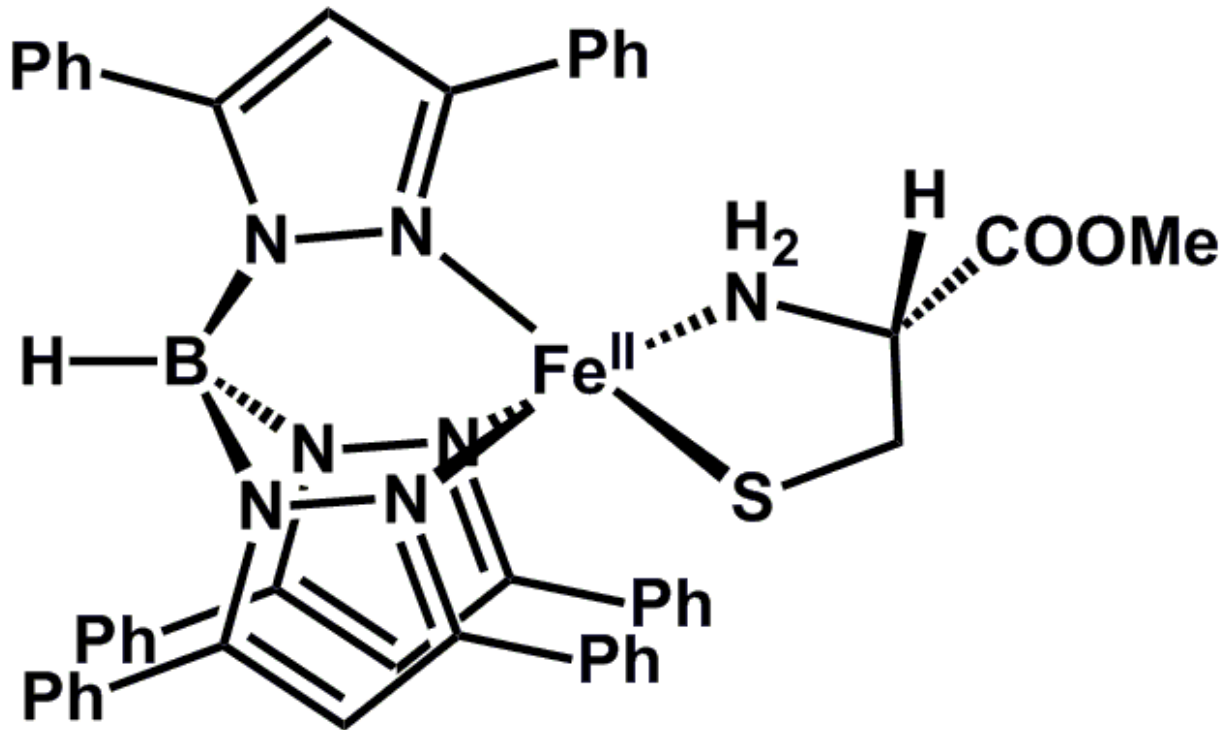
Pierce, B. S.; Gardner, J. D.; Bailey, L. J.; Brunold, T. C.; Fox, B. G. *Biochemistry* **2007**, *46*, 8569.

# Synthesis





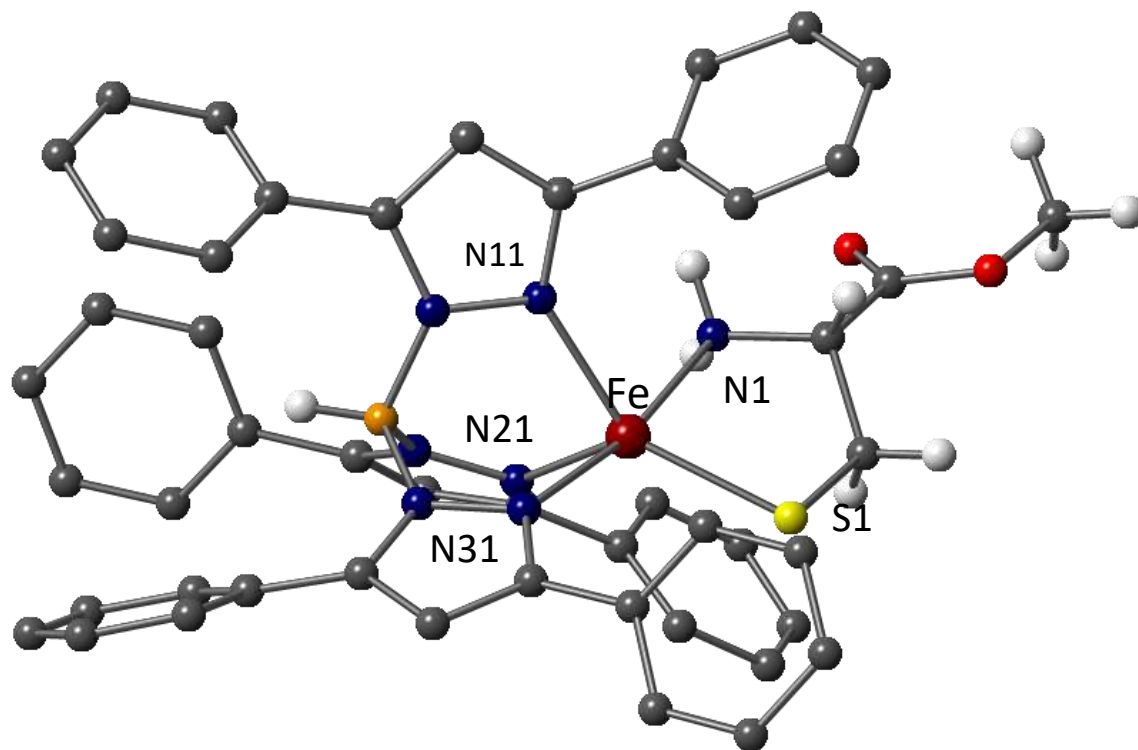
# Structural Mimic



- Mimics the three histidine, face capping structure of CDO
- Cysteine methyl ester also bound in a bidentate fashion
- Open site



# Crystal Structure of Iron complex

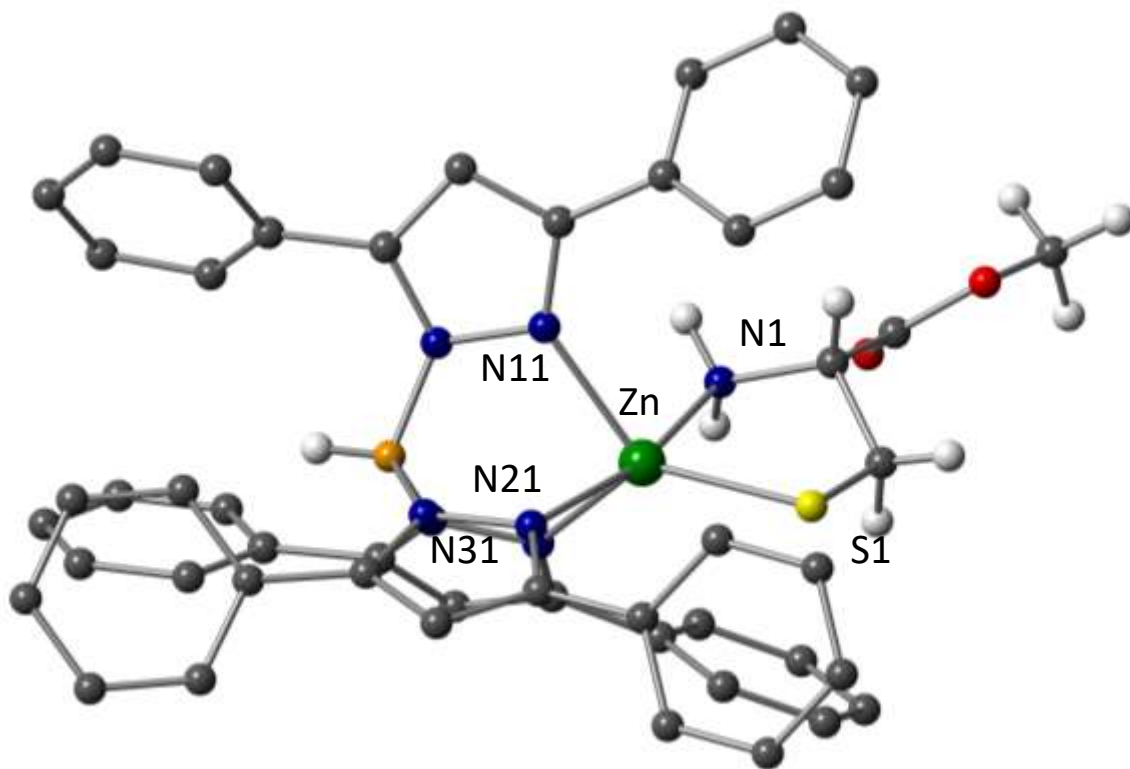


Selected Bond Lengths (Å) and Angles (°)

Fe-S1	2.3115(7)
Fe-N1	2.250(2)
Fe-N11	2.1232(19)
Fe-N21	2.1184(18)
Fe-N31	2.2096(19)
N1-Fe-S1	84.23(6)
N1-Fe-N11	87.14(8)
N1-Fe-N21	90.11(8)
N1-Fe-N31	169.43(8)
S1-Fe-N11	143.17(5)
S1-Fe-N21	123.32(6)
S1-Fe-N31	105.13(5)
N11-Fe-N21	92.34(7)
N11-Fe-N31	82.41(7)
N21-Fe-N31	88.75(7)
$\tau_5$ <sup>20</sup>	0.44



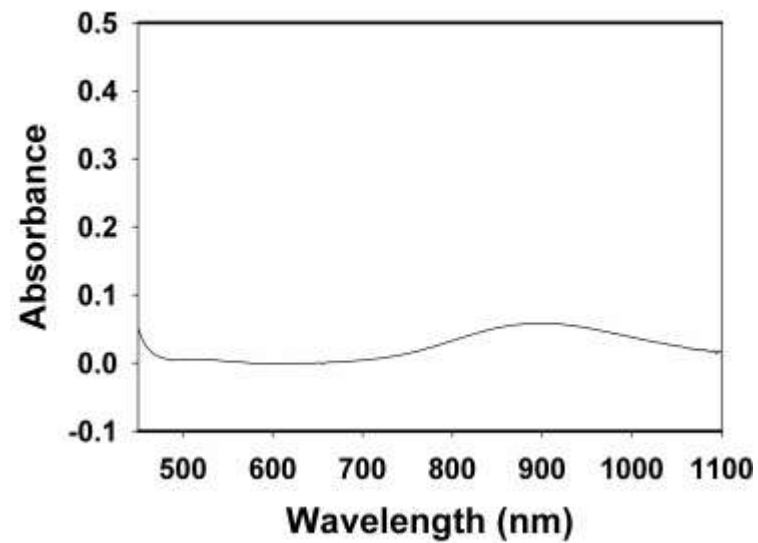
# Crystal structure of Zn complex



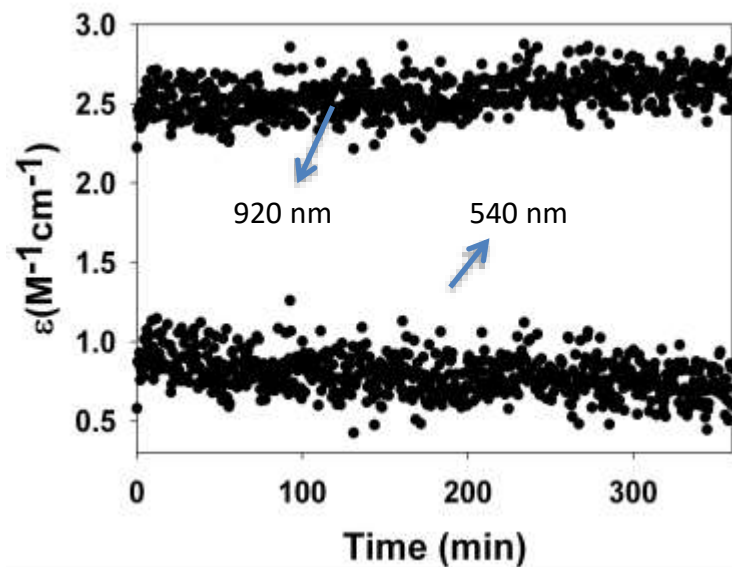
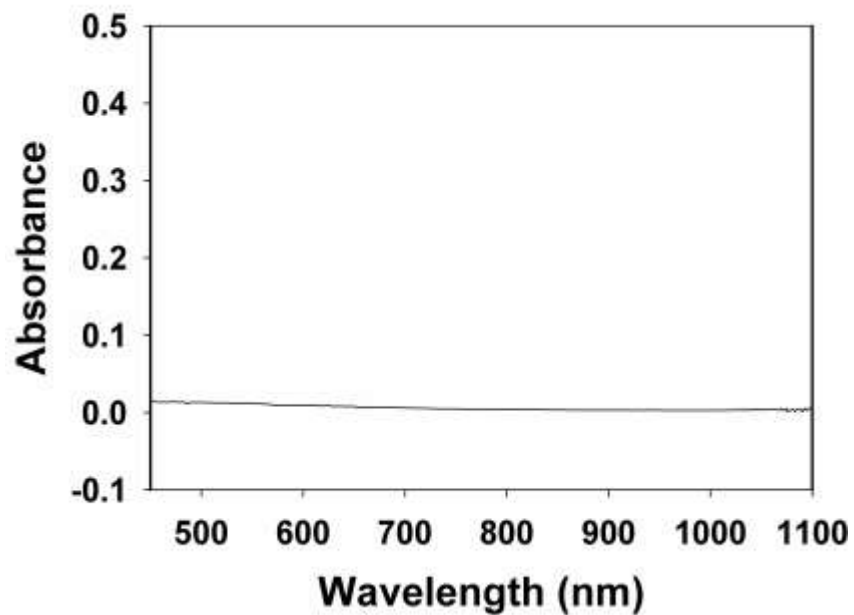
Selected Bond Lengths (Å) and Angles (°)

Zn(1)-N(21)	2.085
Zn(1)-N(31)	2.086
Zn(1)-N(11)	2.250
Zn(1)-S(1)	2.2630
Zn(1)-N(1)	2.335
N(21)-Zn(1)-N(31)	96.12
N(21)-Zn(1)-N(11)	82.15
N(31)-Zn(1)-N(11)	83.28
N(21)-Zn(1)-S(1)	131.62
N(31)-Zn(1)-S(1)	131.67
N(11)-Zn(1)-S(1)	107.07
N(21)-Zn(1)-N(1)	89.56
N(31)-Zn(1)-N(1)	88.69
N(11)-Zn(1)-N(1)	167.76
S(1)-Zn(1)-N(1)	85.17
$\tau_5$	.6015

# $\text{Fe}(\text{Tp}^{\text{Ph}_2})(\text{CysMe})$

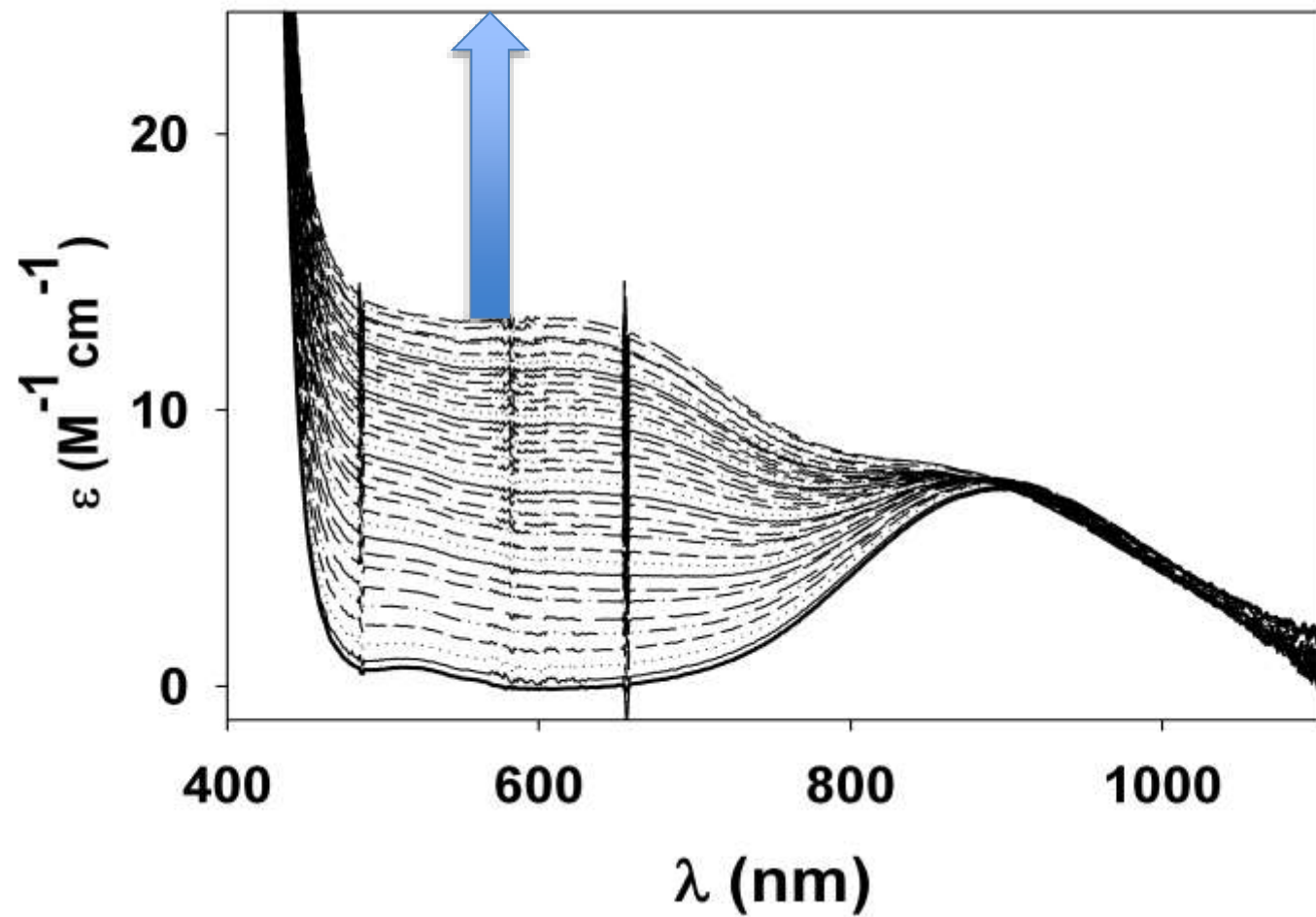


# Zn(Tp<sup>Ph</sup><sub>2</sub>)(CysMe), A control

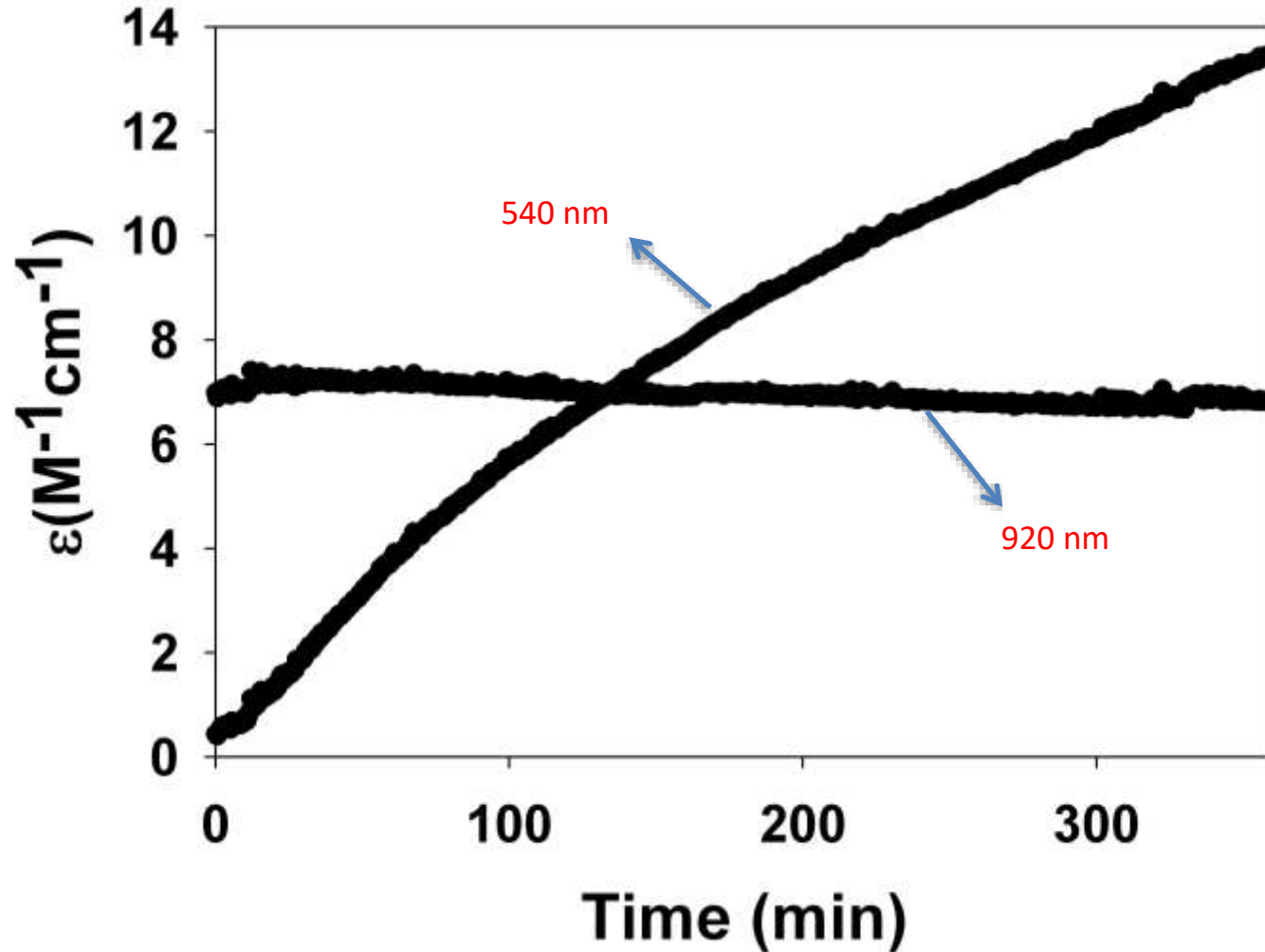




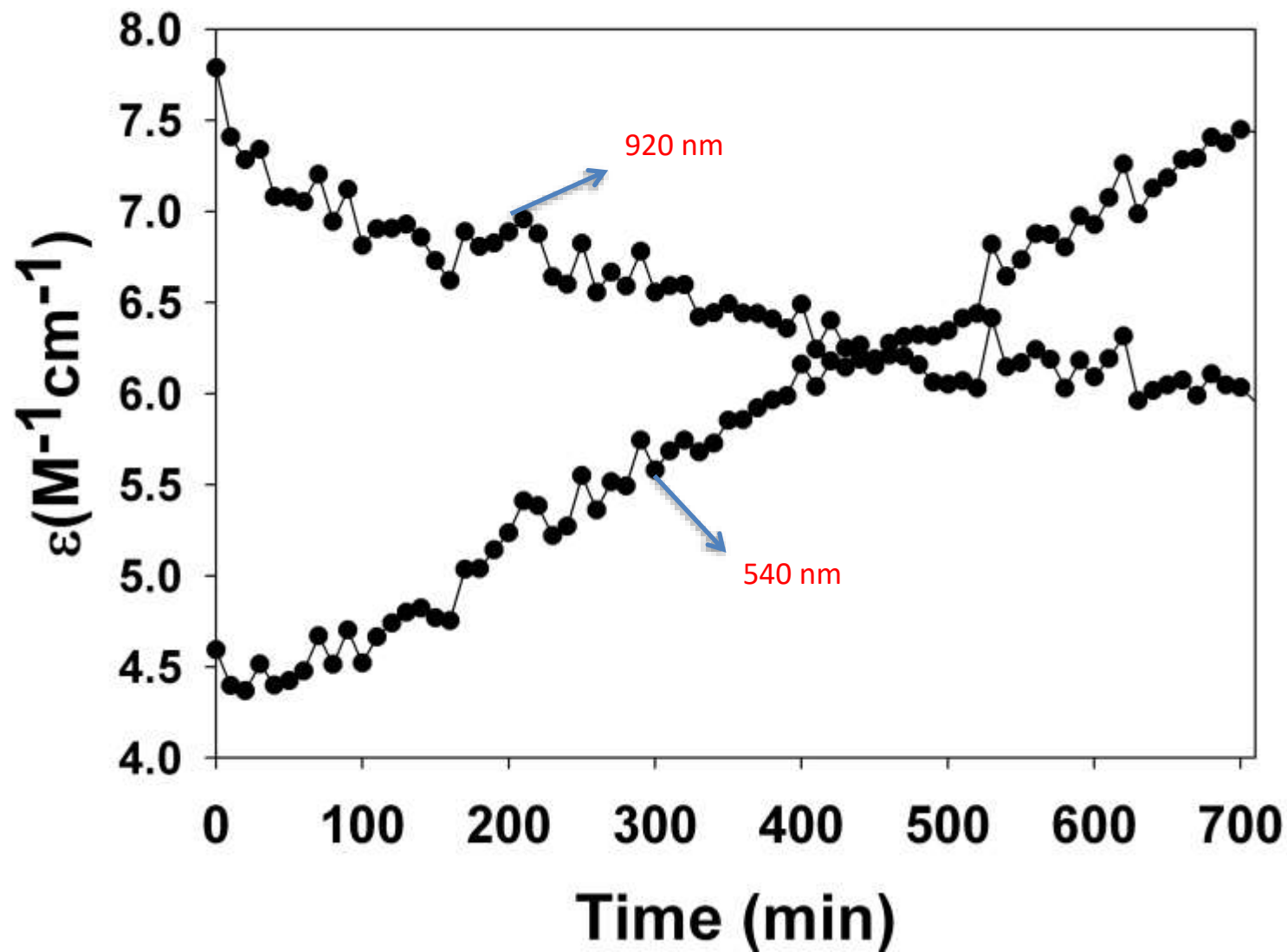
# Reactivity



# Benzene, 4 hours



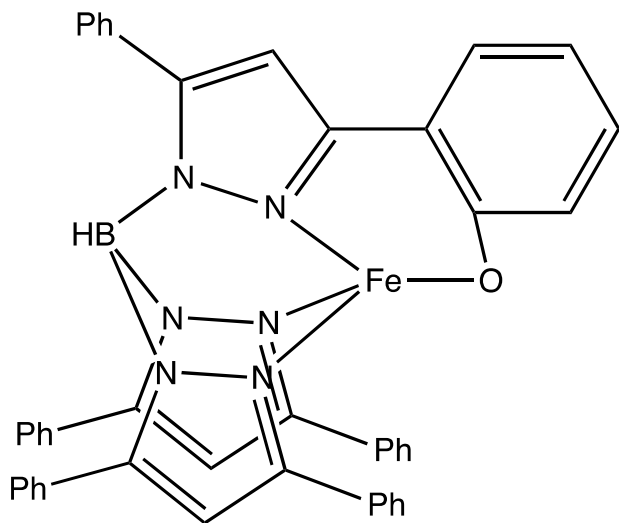
# Toluene, after 12 hours



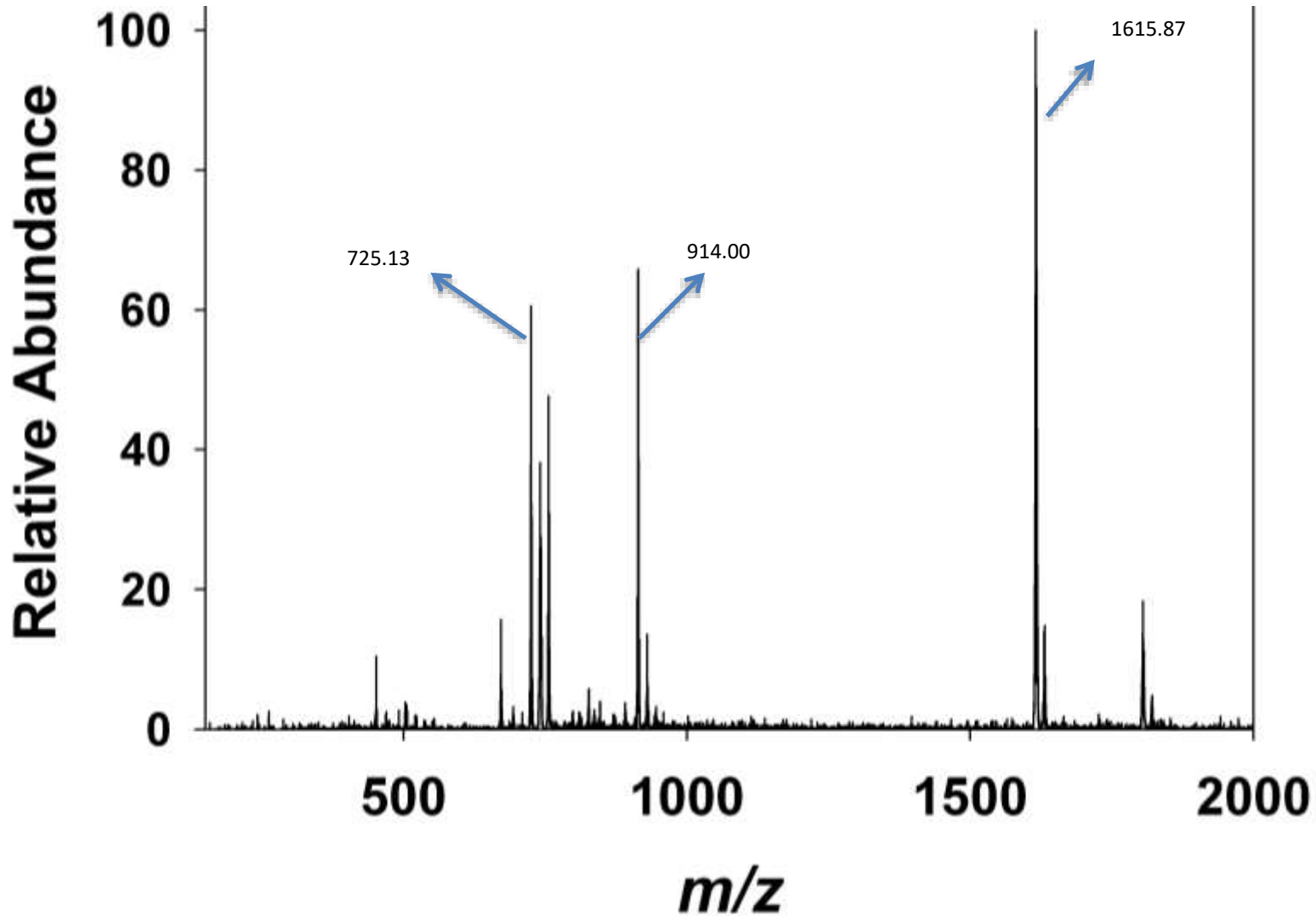


# What do these mean?

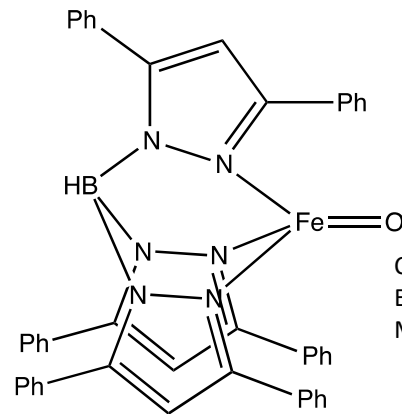
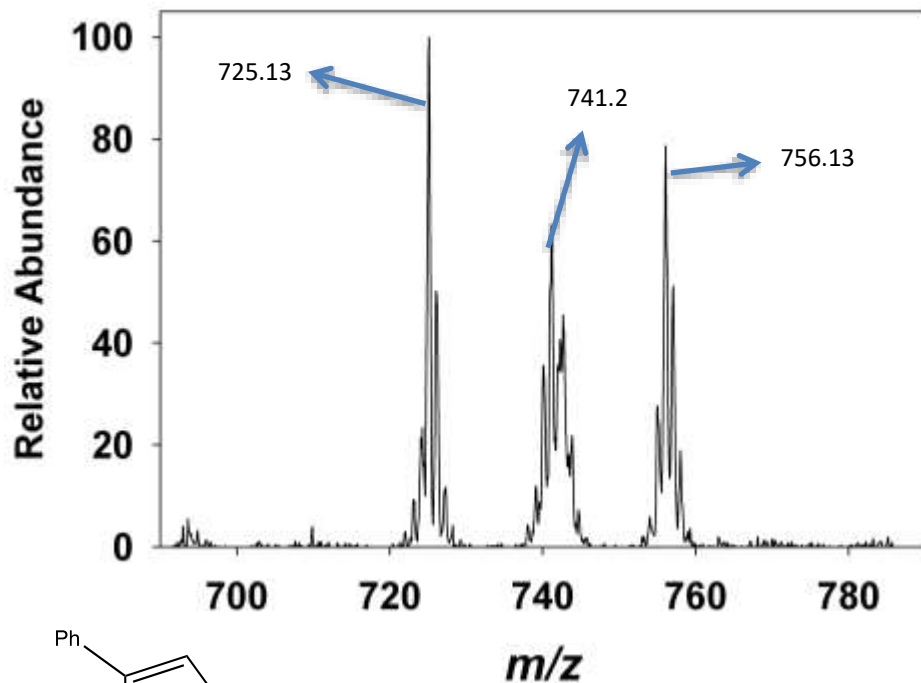
- $\text{Fe}^{\text{II}}$  - 920 nm
- Phenolate – 540 nm



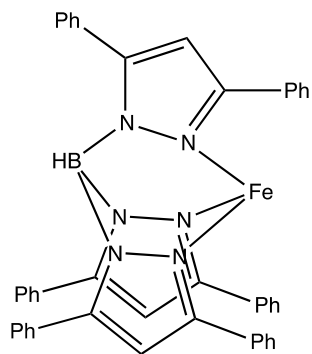
# Fe(Tp<sup>Ph2</sup>)(CysMe) Range



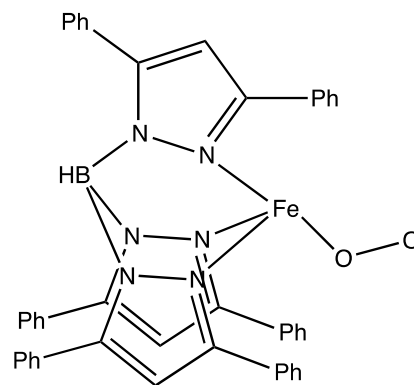
# Peaks around 700-800



Chemical Formula:  $C_{45}H_{34}BFeN_6O$   
Exact Mass: 741.22  
Molecular Weight: 741.45

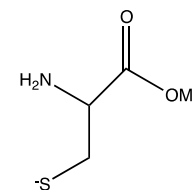
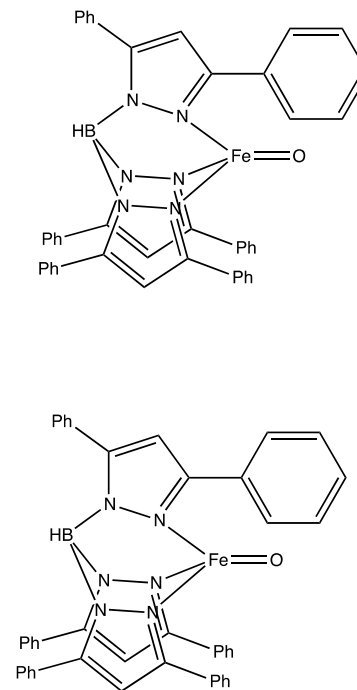
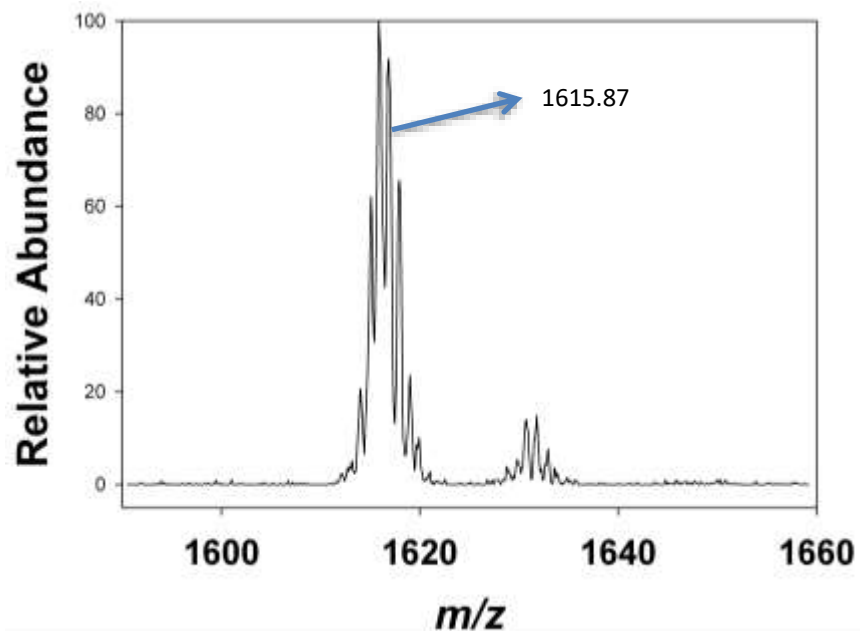


Chemical Formula:  
 $C_{45}H_{34}BFeN_6$   
Exact Mass: 725.23  
Molecular Weight: 725.45



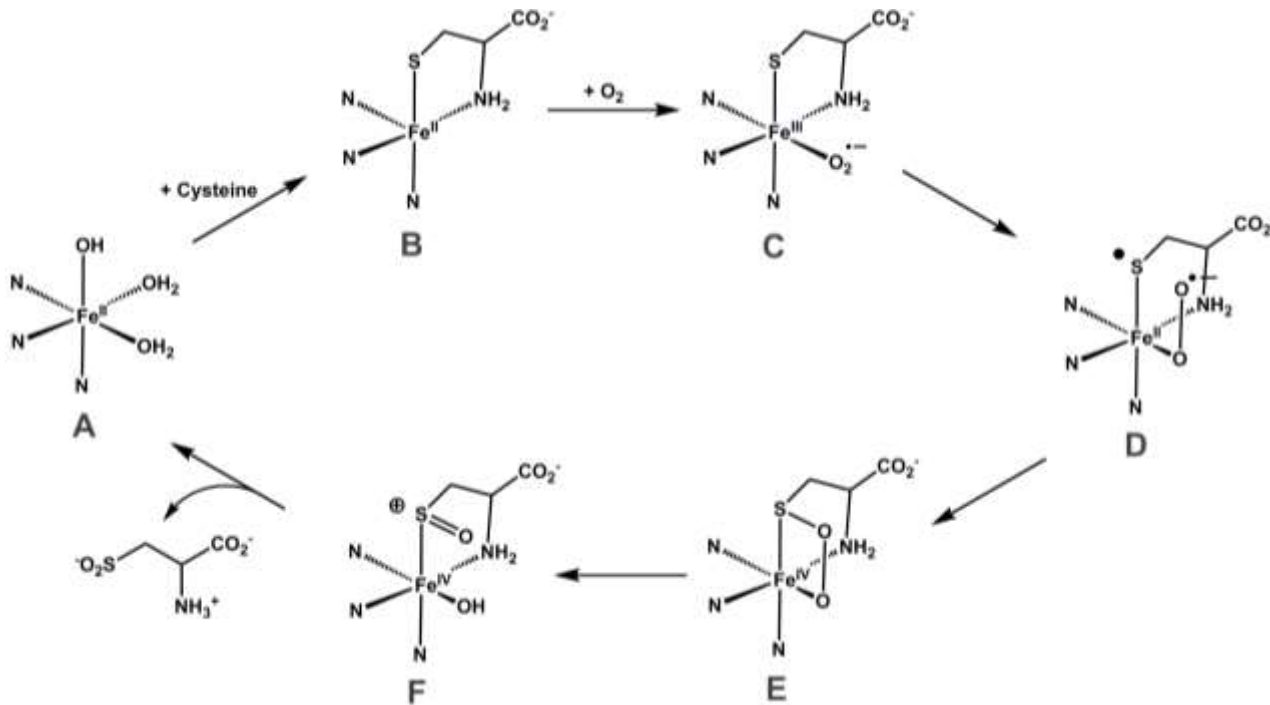
Chemical Formula:  $C_{45}H_{34}BFeN_6O_2^-$   
Exact Mass: 757.22  
Molecular Weight: 757.45

# Peaks around 1600



Chemical Formula:  $C_{94}H_{76}B_2Fe_2N_{13}O_4S^-$   
Exact Mass: 1616.48  
Molecular Weight: 1617.07

# Back to the Mechanism



- Work on capturing intermediates
- Probe the mechanism further

# Acknowledgments

- Torrey Mullin and Mackenzie Norlin for (Tp<sup>Ph2</sup>)
- Navamoney Arulsamy for Crystal XRD structures
- Mark Mehn for support and direction when I felt lost

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