



Founding Editor: Sir Edward D. Clarke 1887-1967

COORDINATION CHEMISTRY REVIEWS

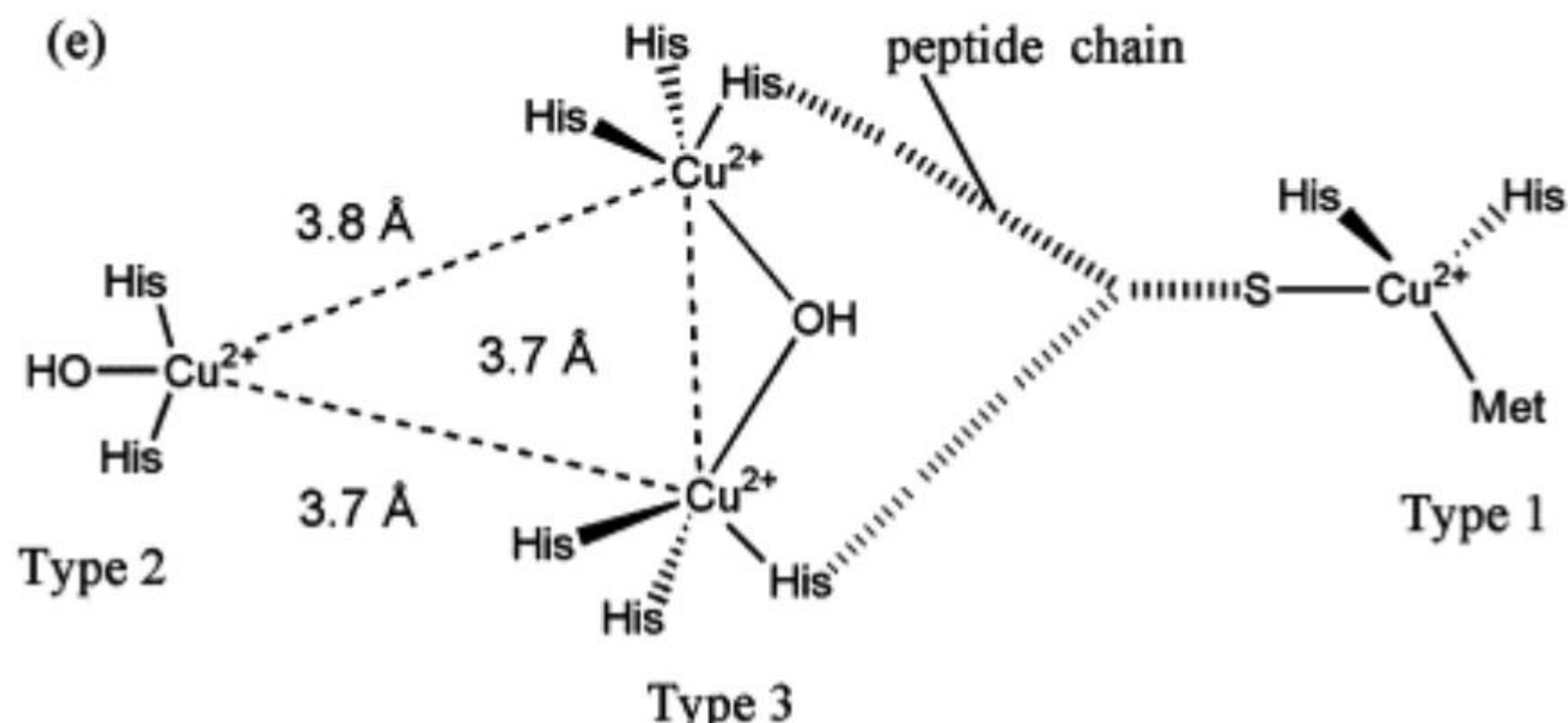
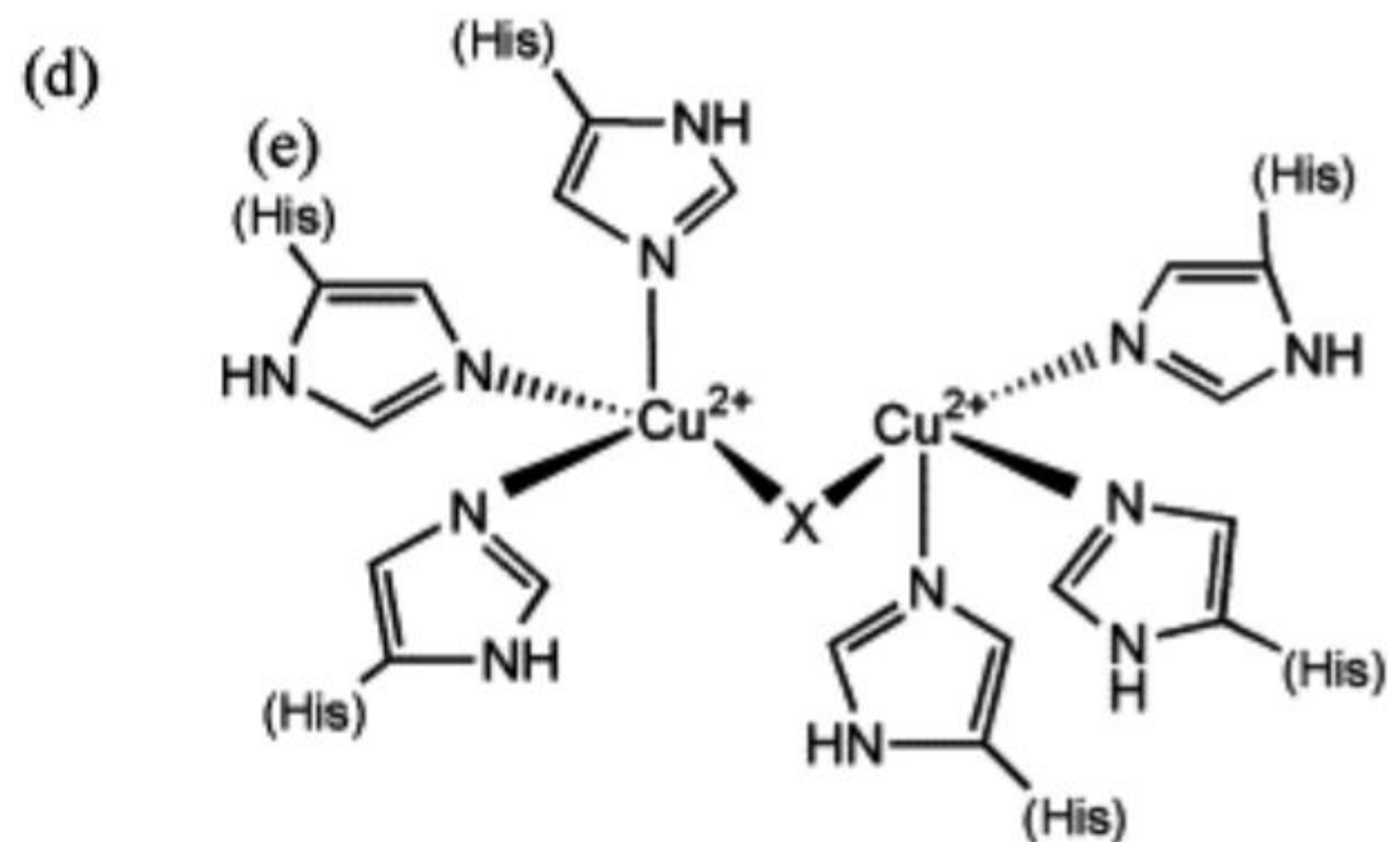
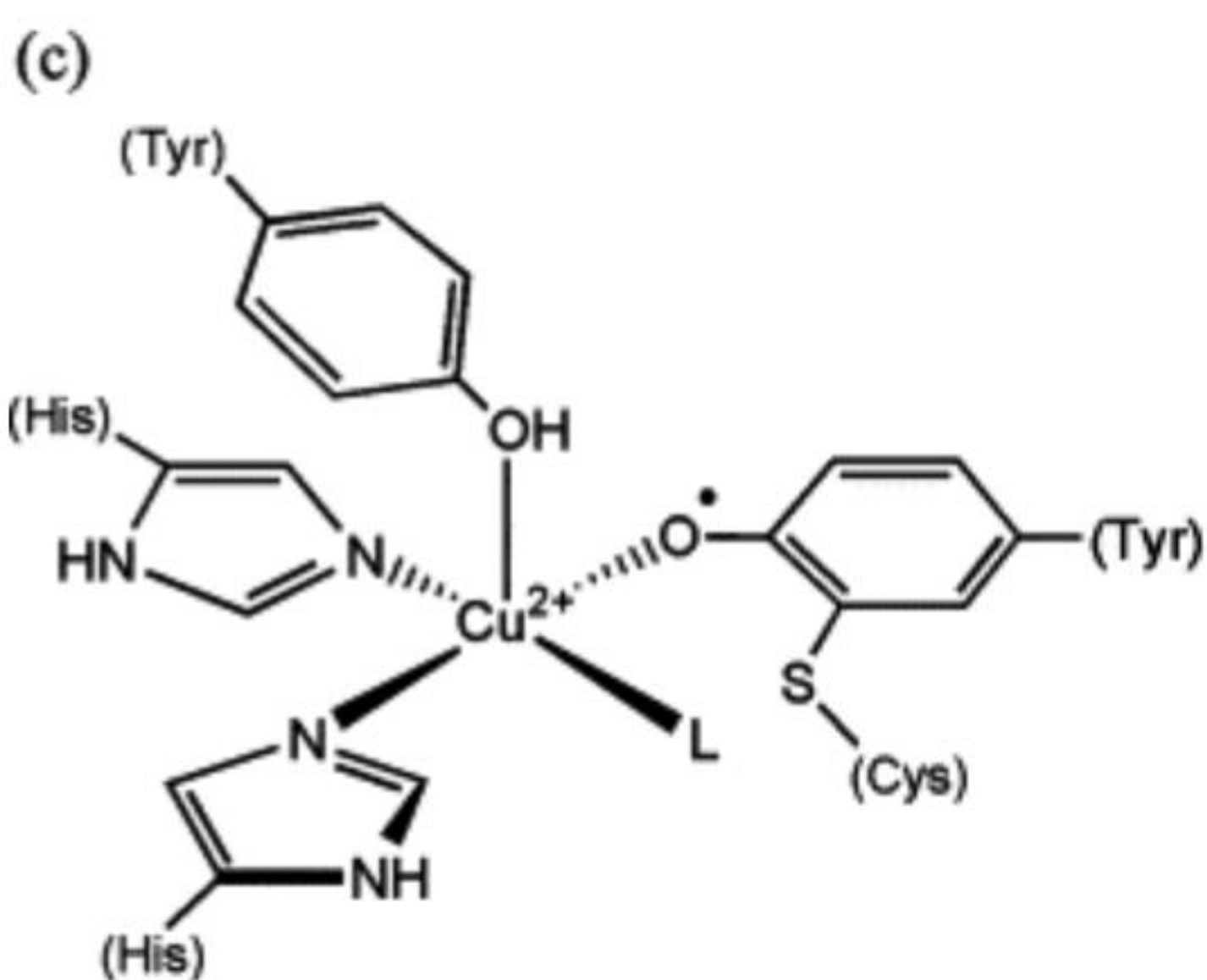
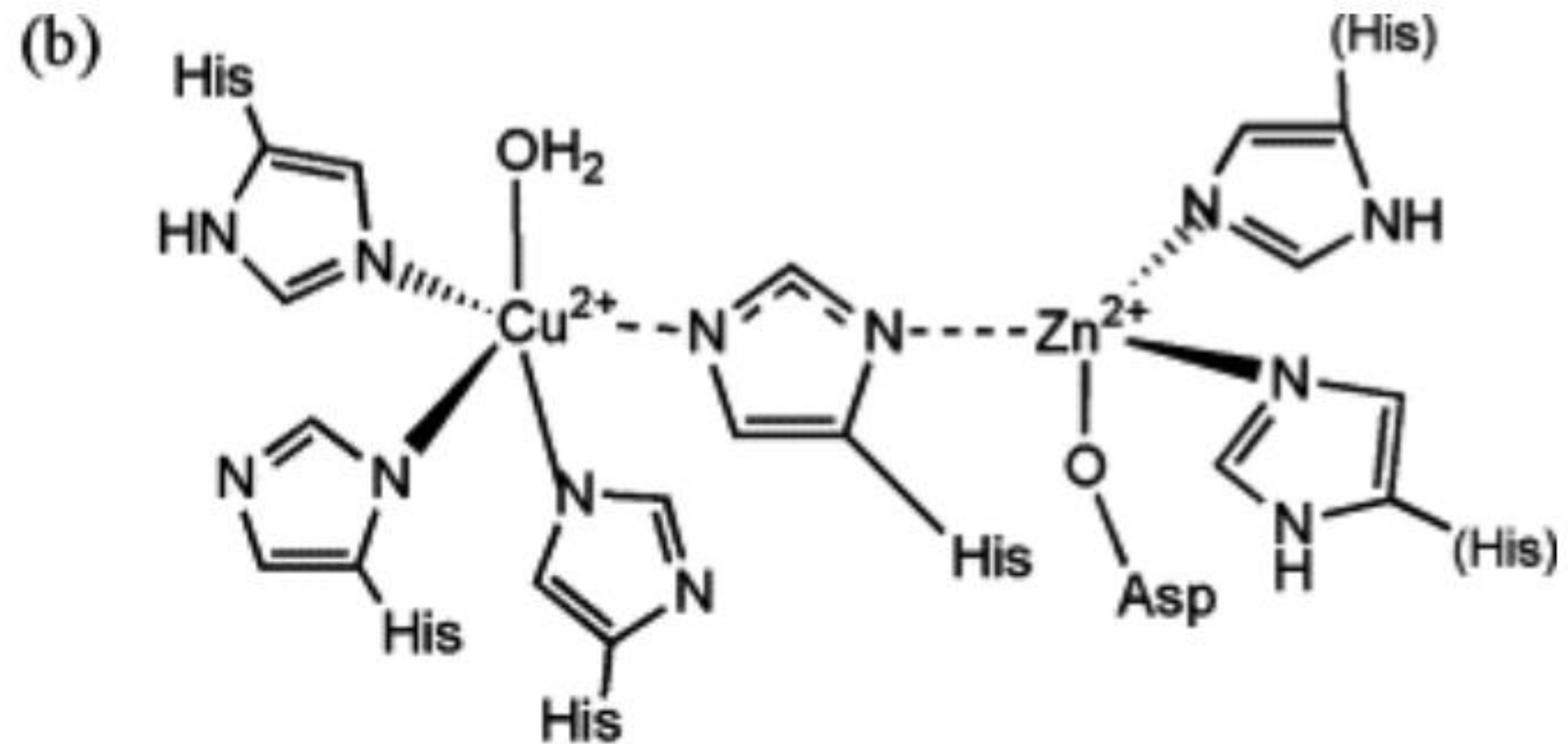
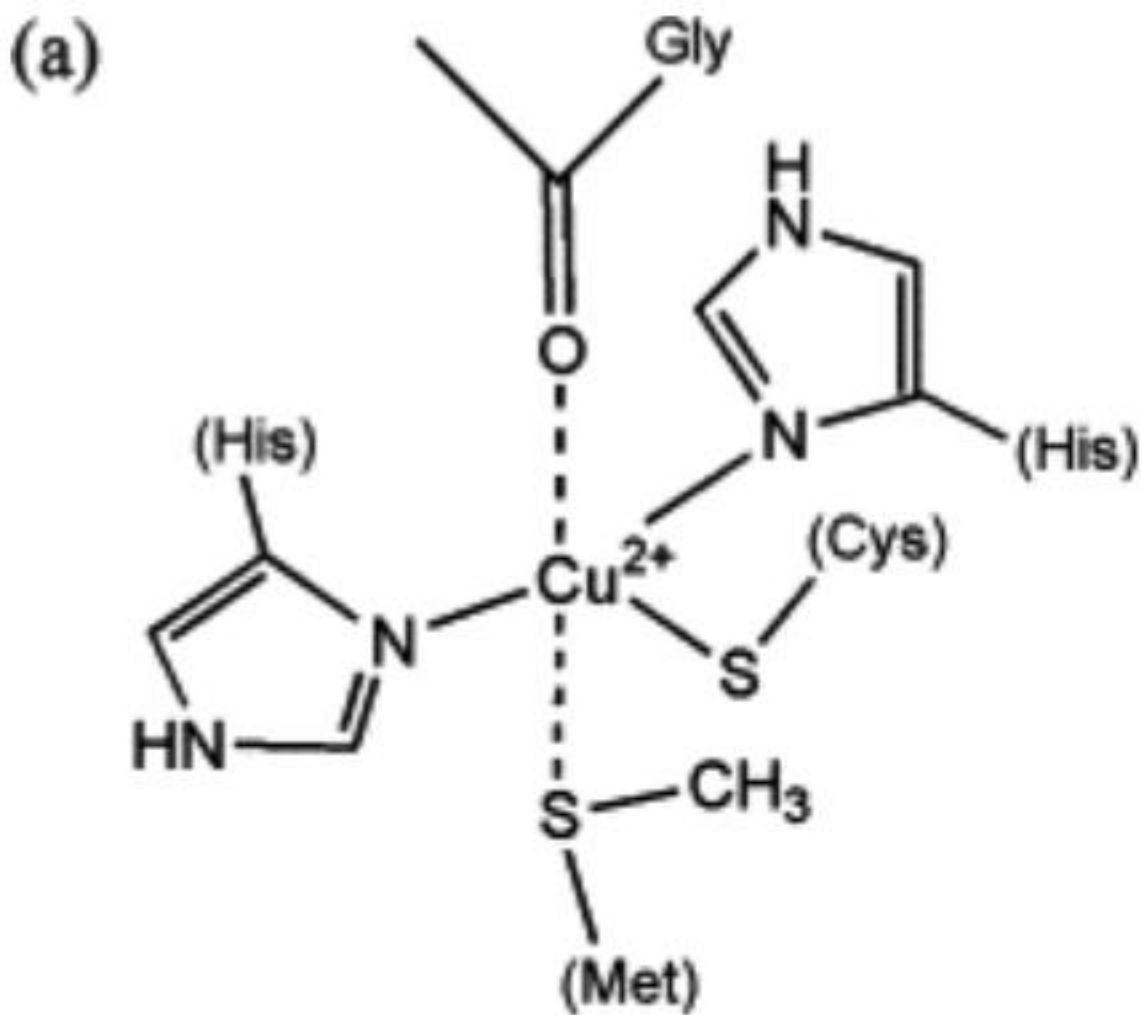
Editor: A.B.P. LEVER

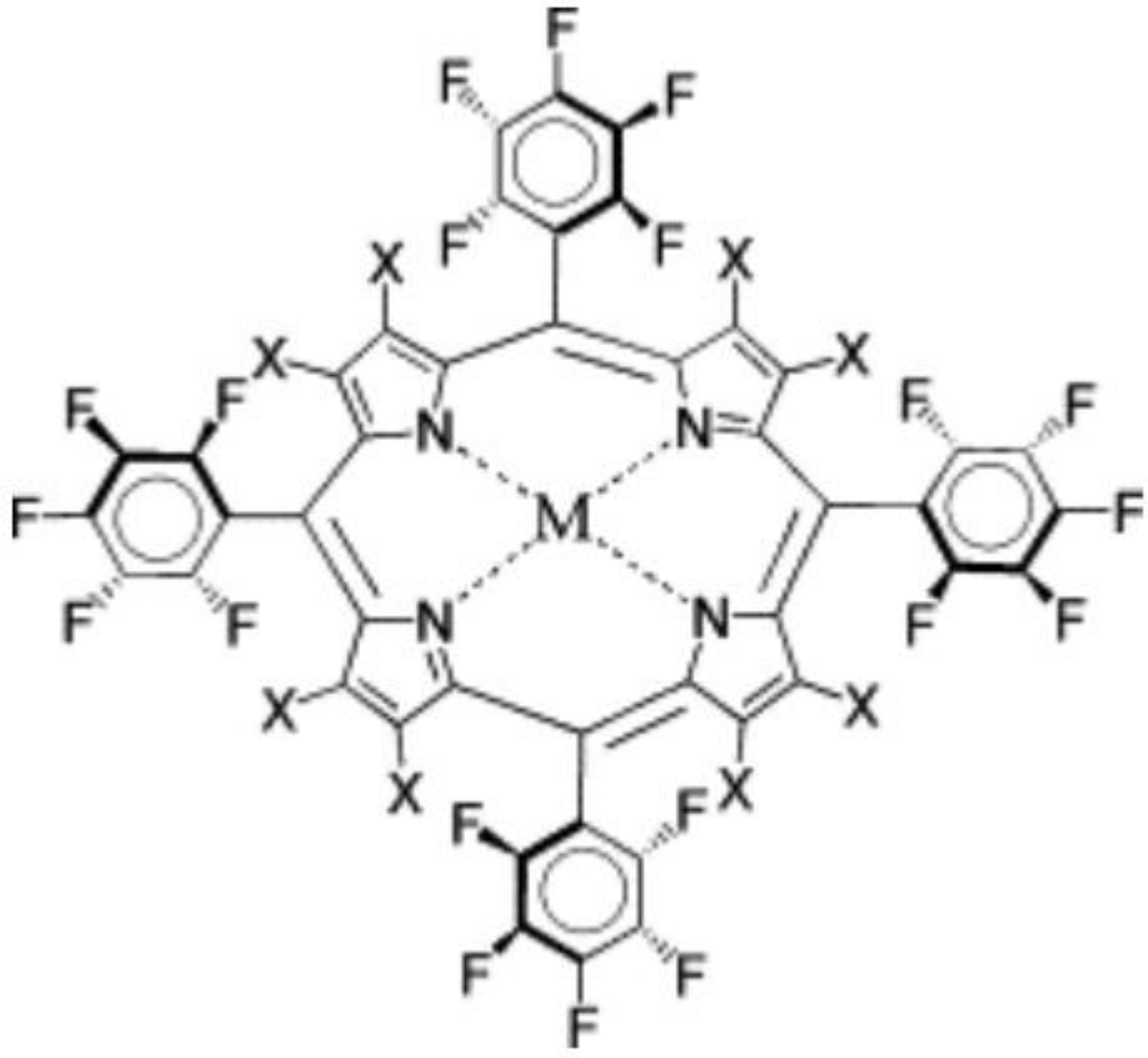
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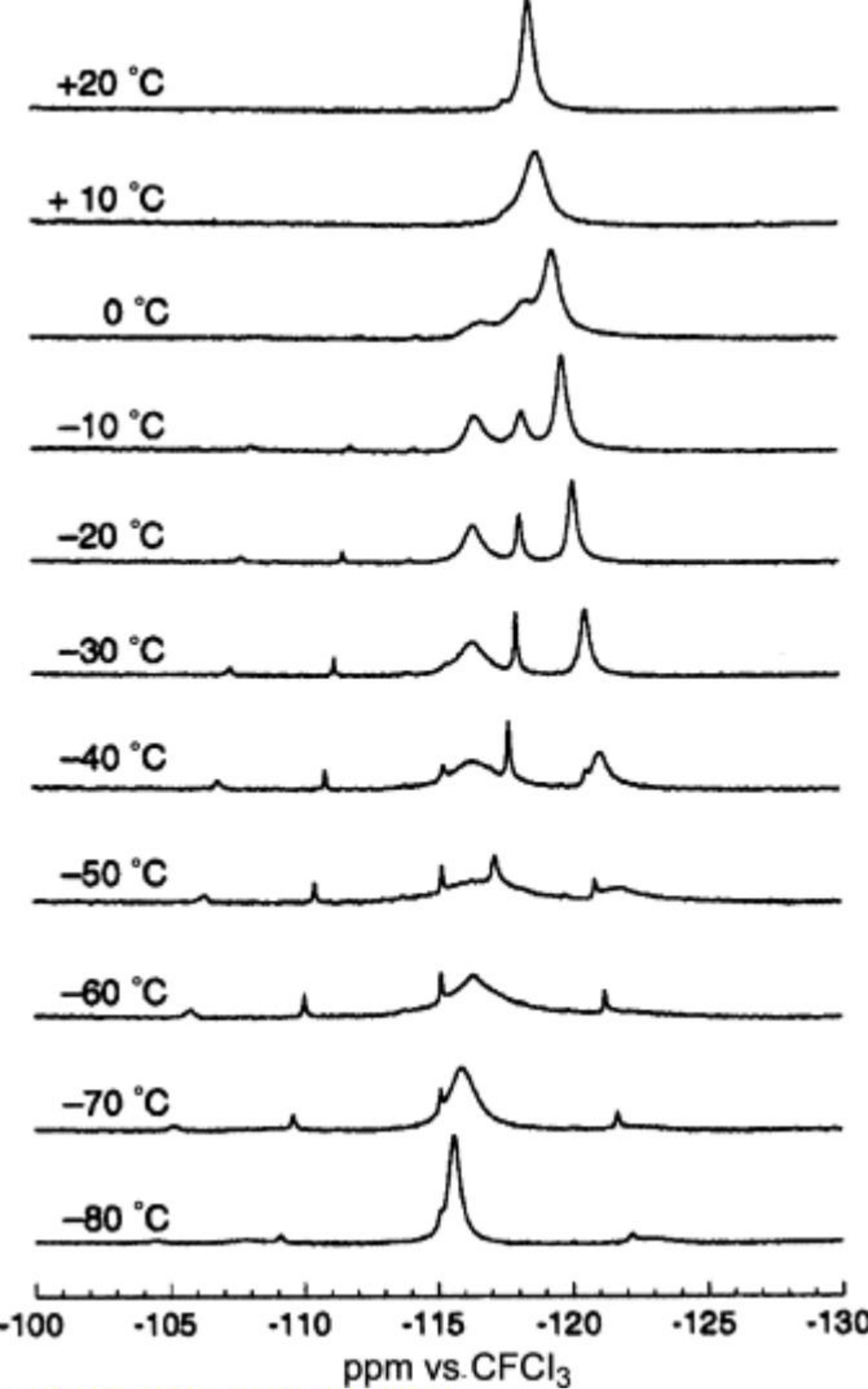
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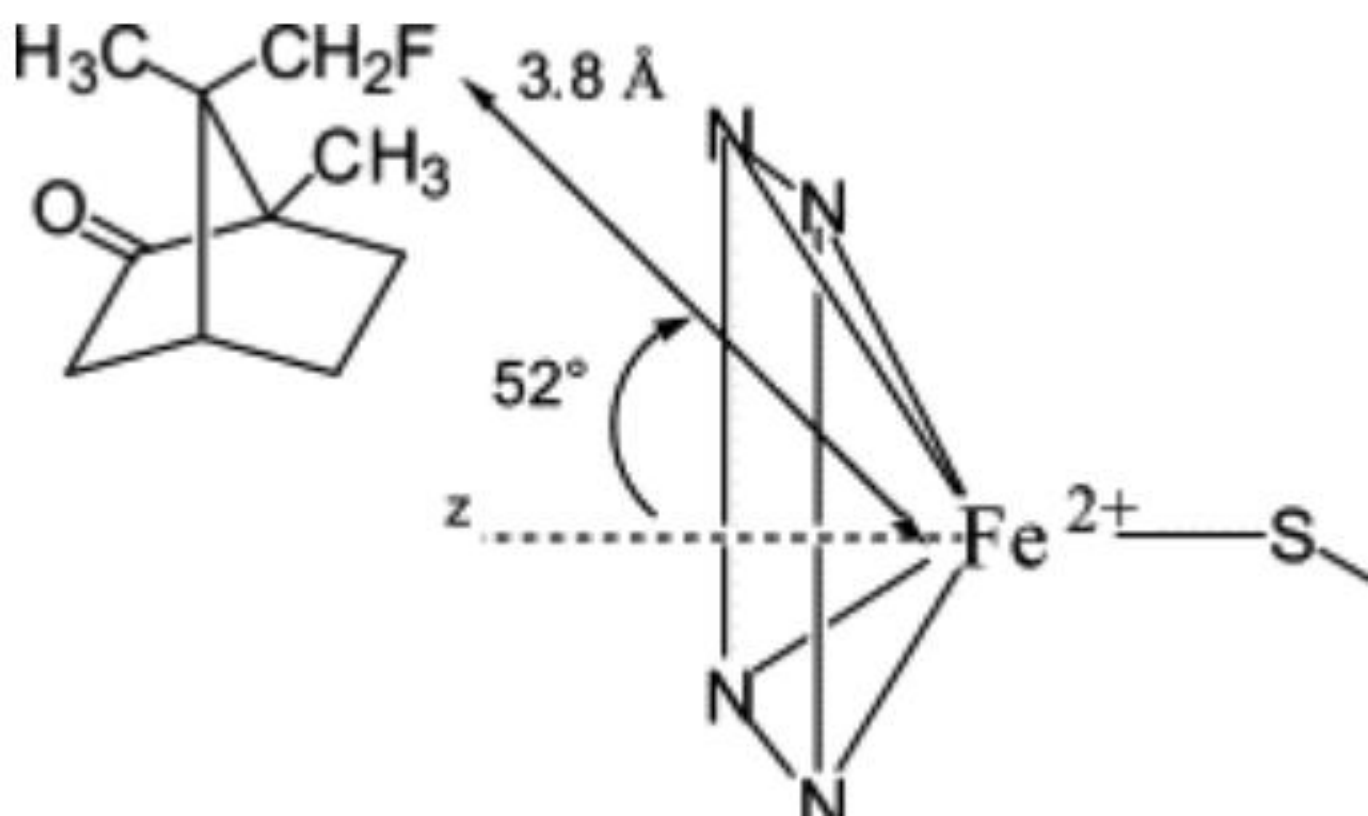


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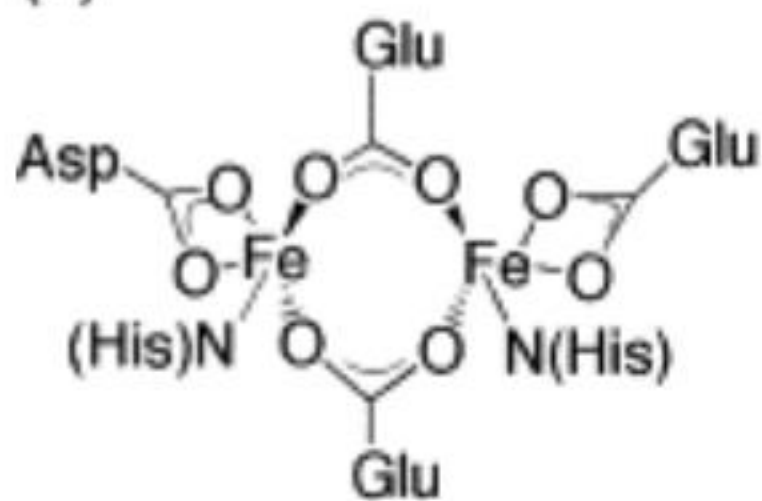




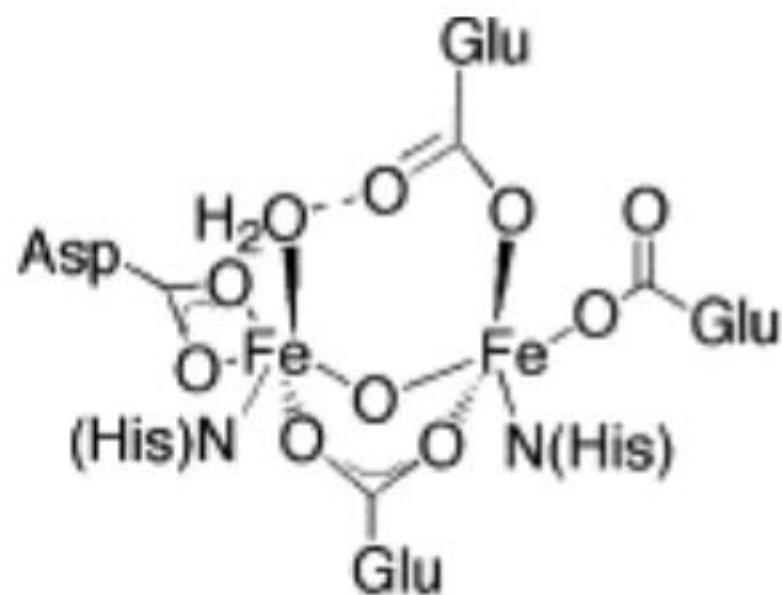




(a)

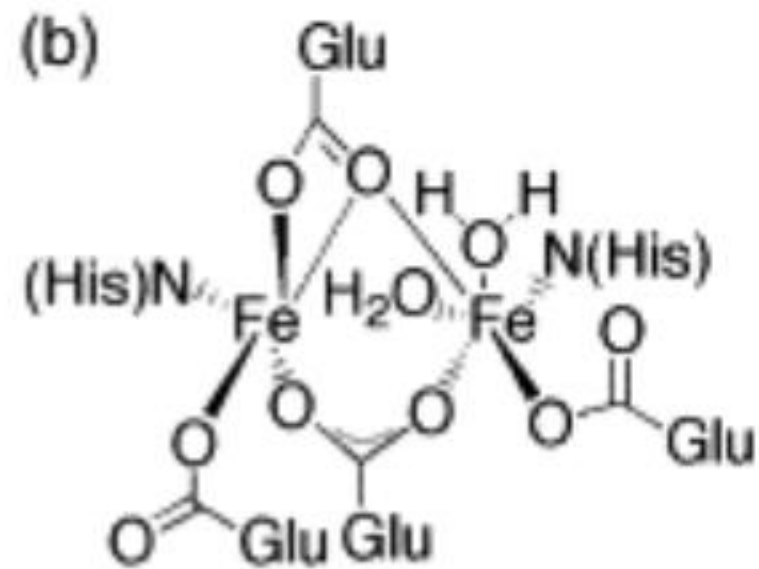


$R2_{red}$

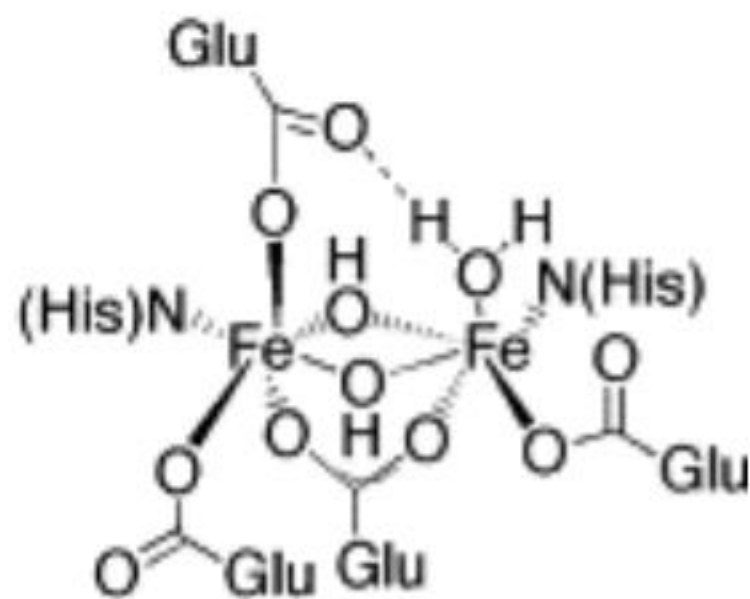


$R2_{ox}$

(b)



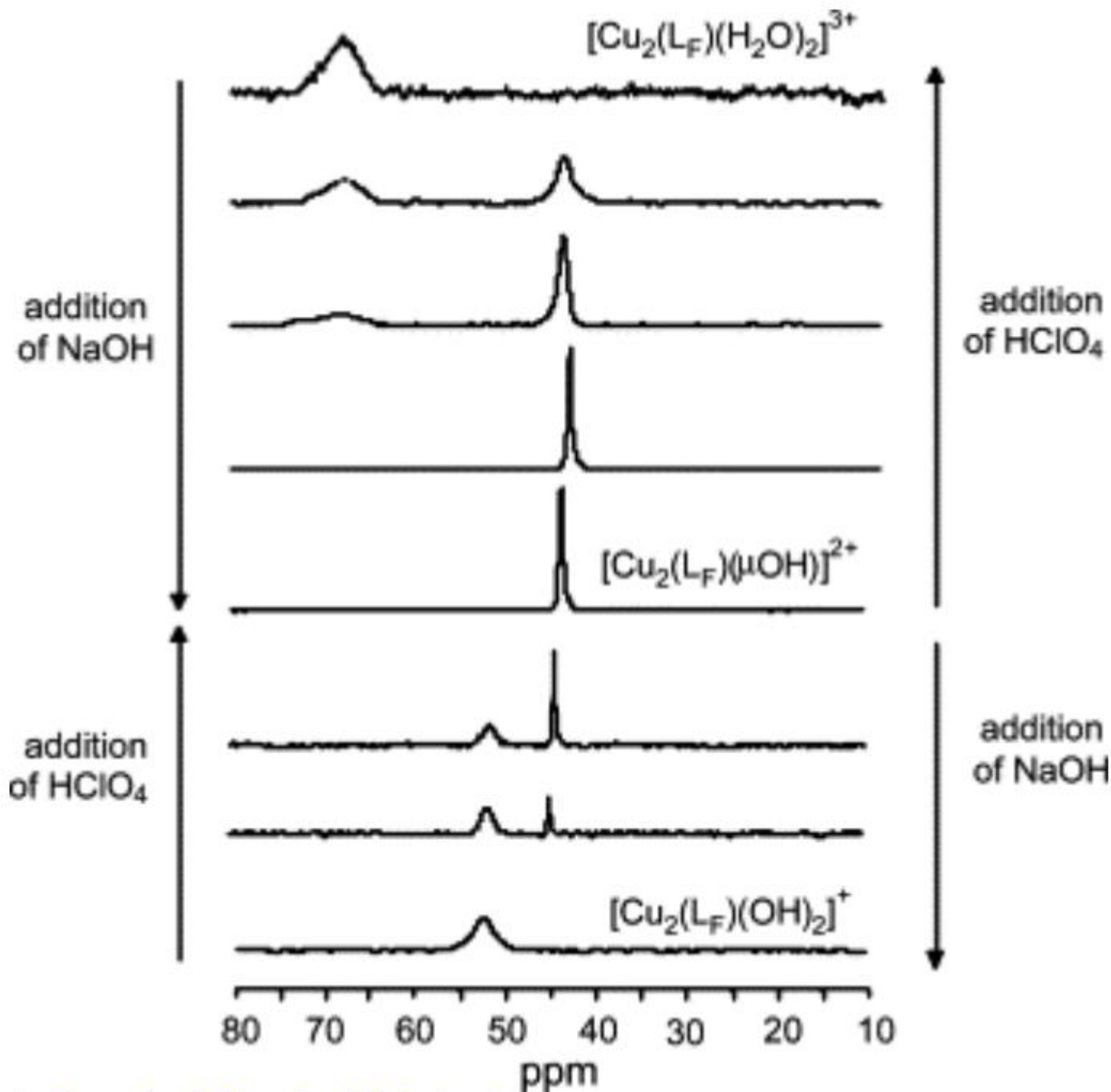
MMO_{red}

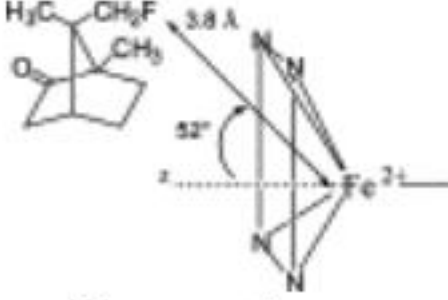
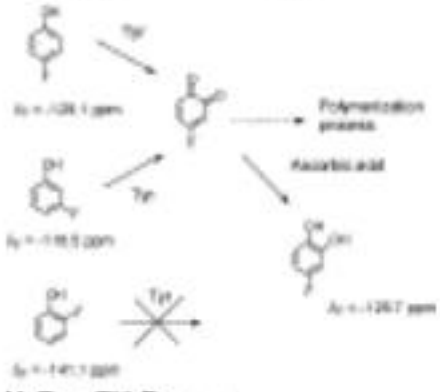
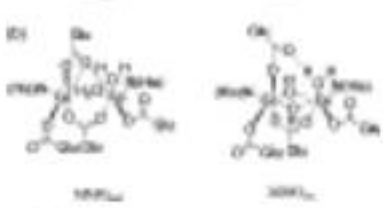
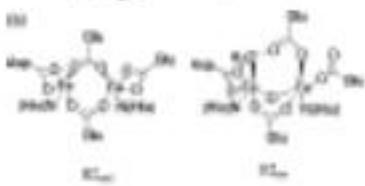
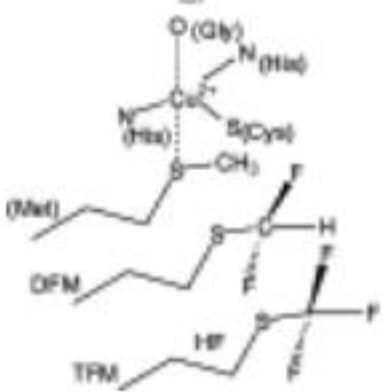
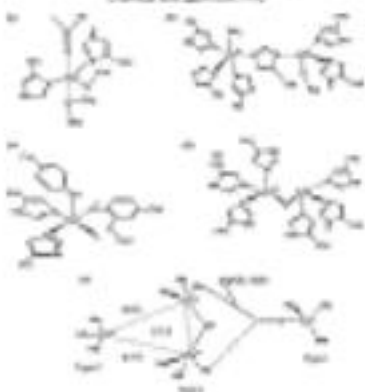
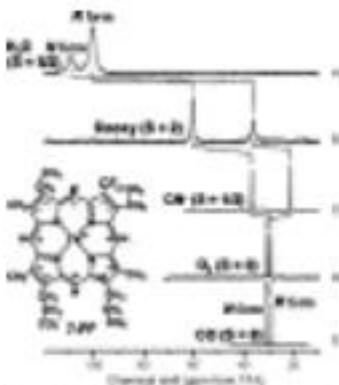


MMO_{ox}



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6. Show 9 more figures



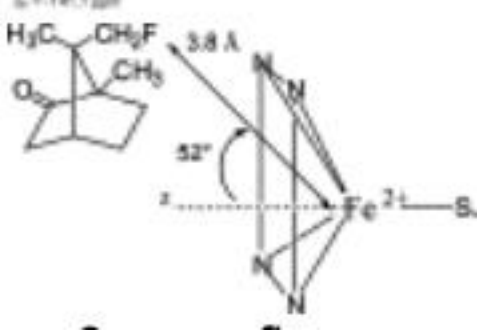
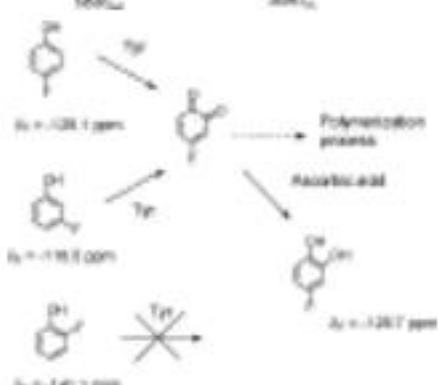
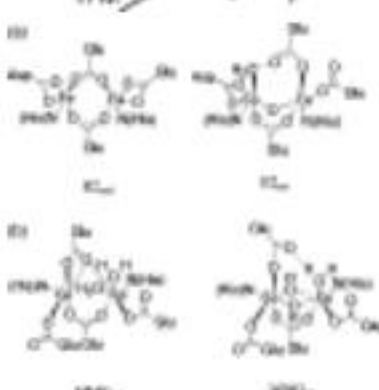
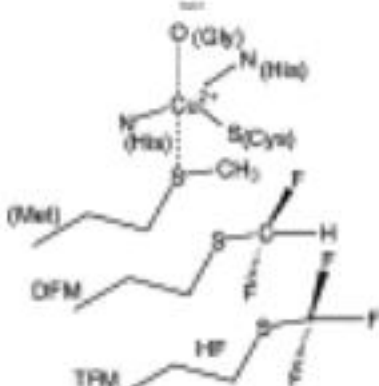
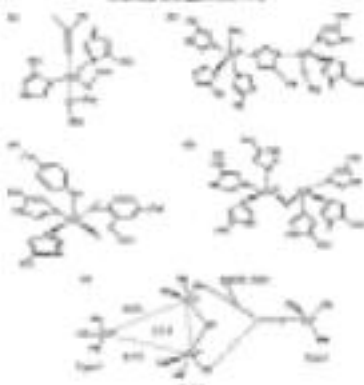
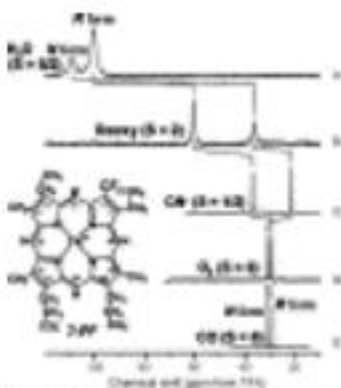
COORDINATION
CHEMISTRY REVIEWS

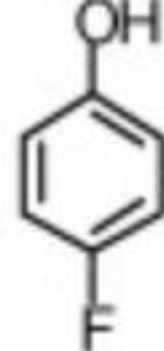
Editor: A. M. P. LEEVER

Keywords: child sexual abuse; disclosure; social support

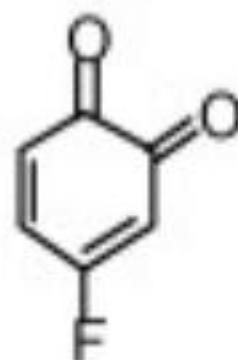
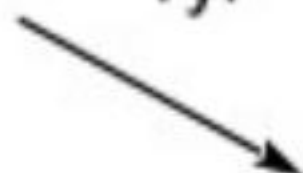
Submitted Thread

Further questions are raised about the





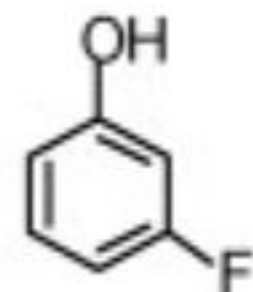
Tyr



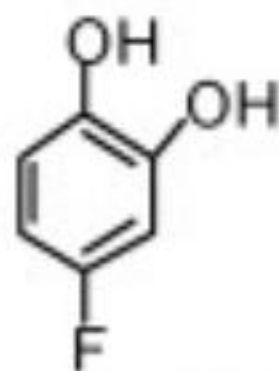
Polymerization
process



Ascorbic acid



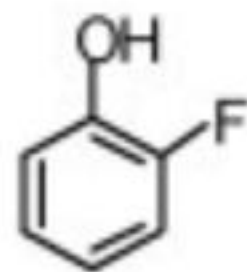
Tyr



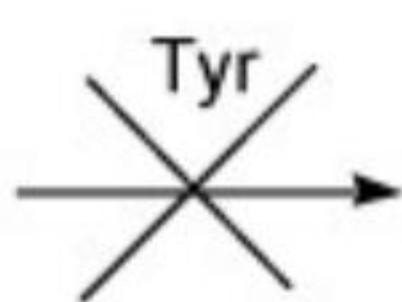
$\delta_F = -126.7$ ppm

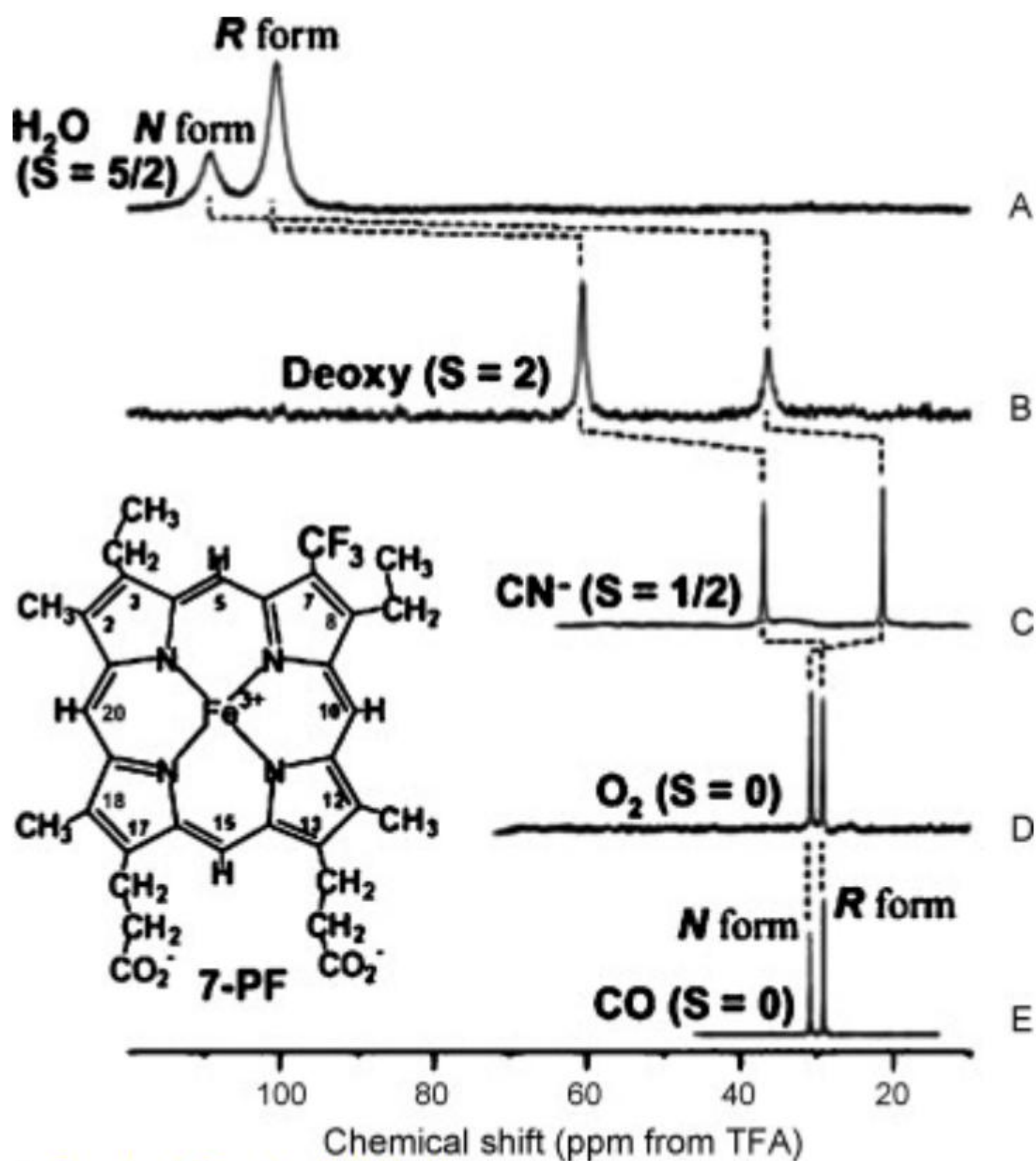
$\delta_F = -129.1$ ppm

$\delta_F = -116.5$ ppm



~~Tyr~~

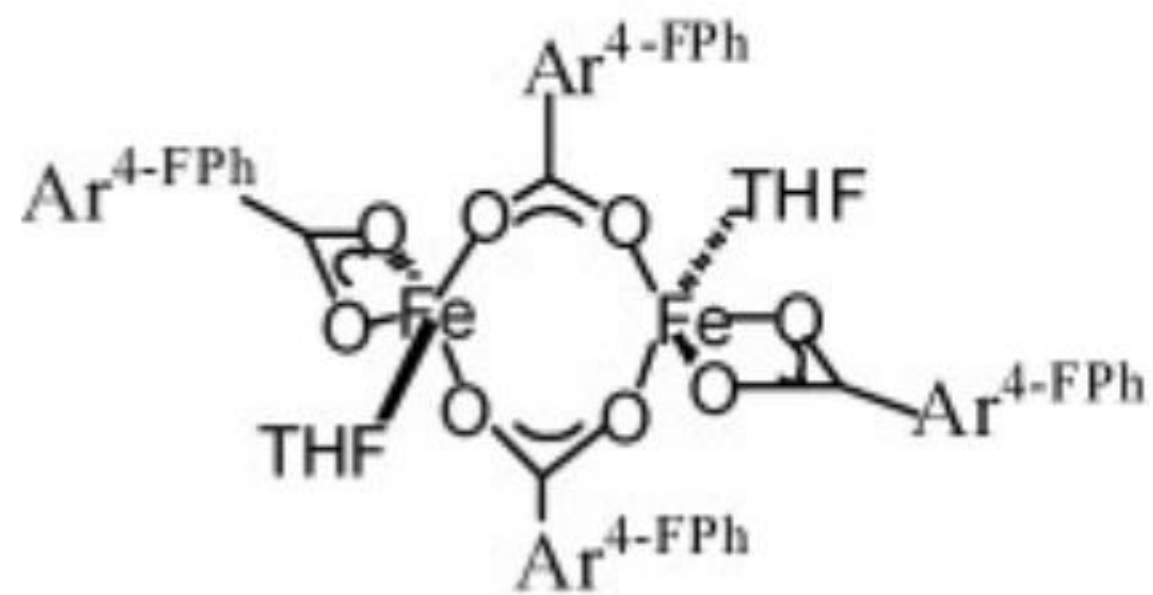
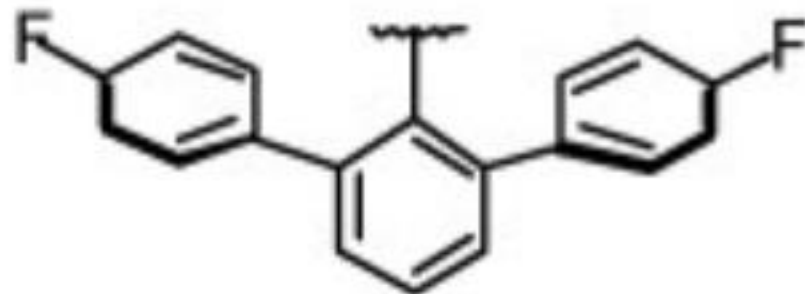




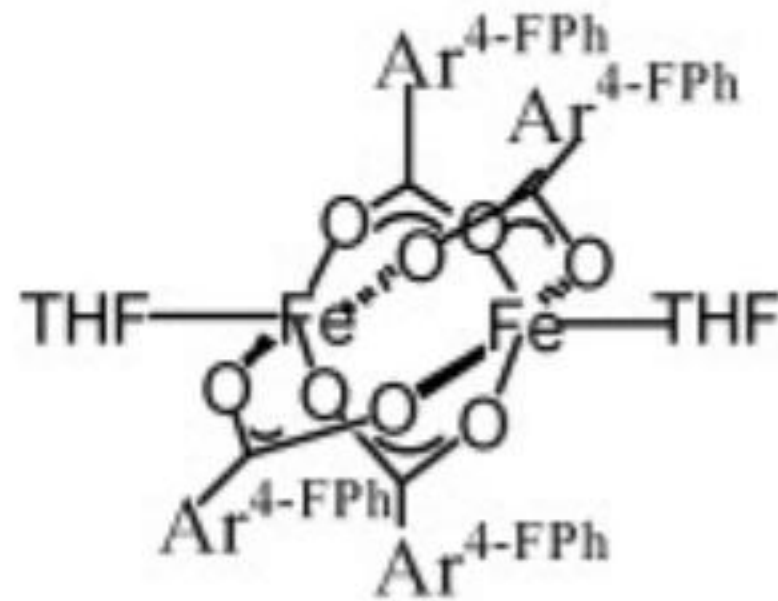


ET SEVIER

$\text{Ar}^{4\text{-FPh}}$

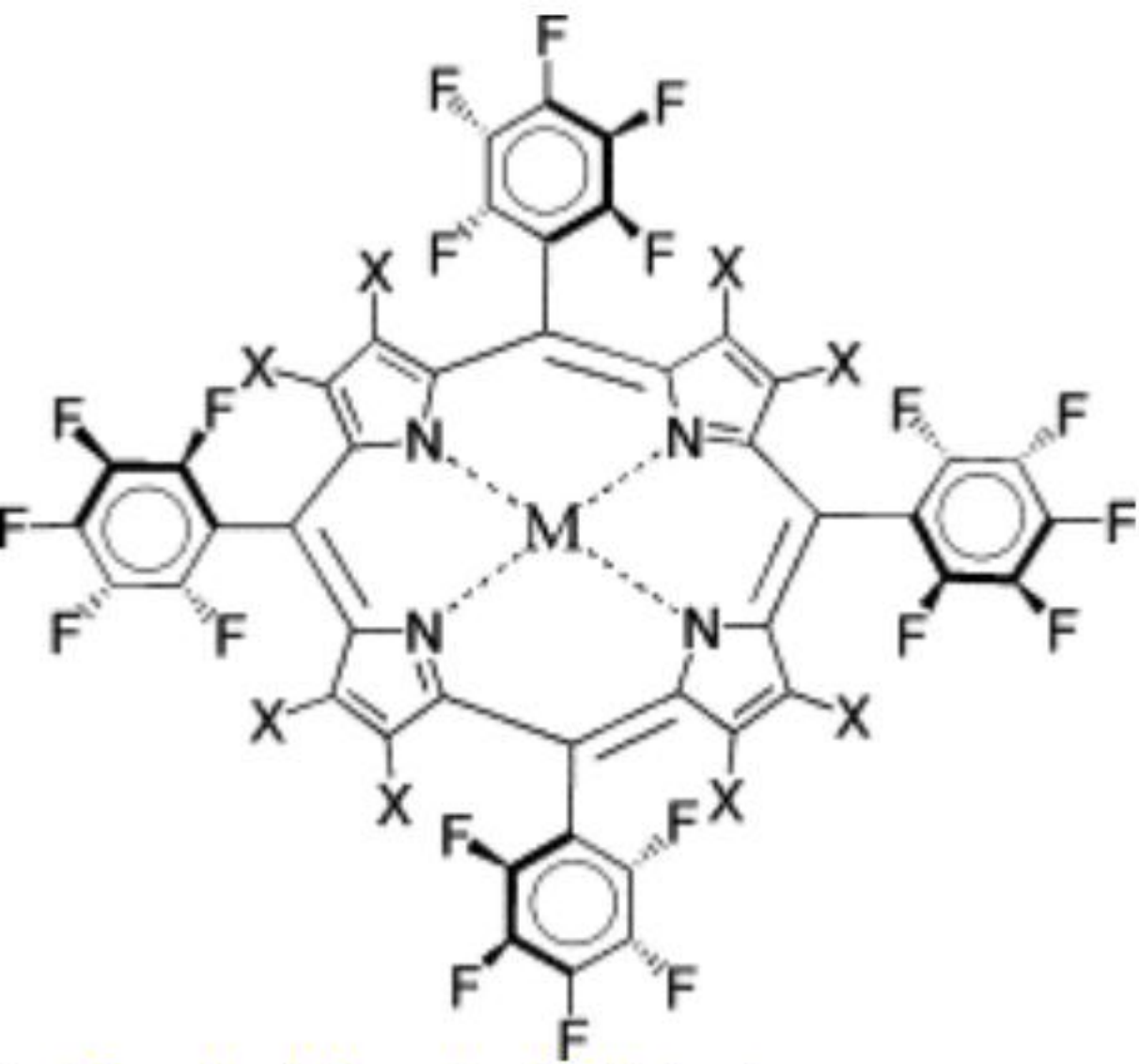


I



II





(a)

40.0

33.3

29.8

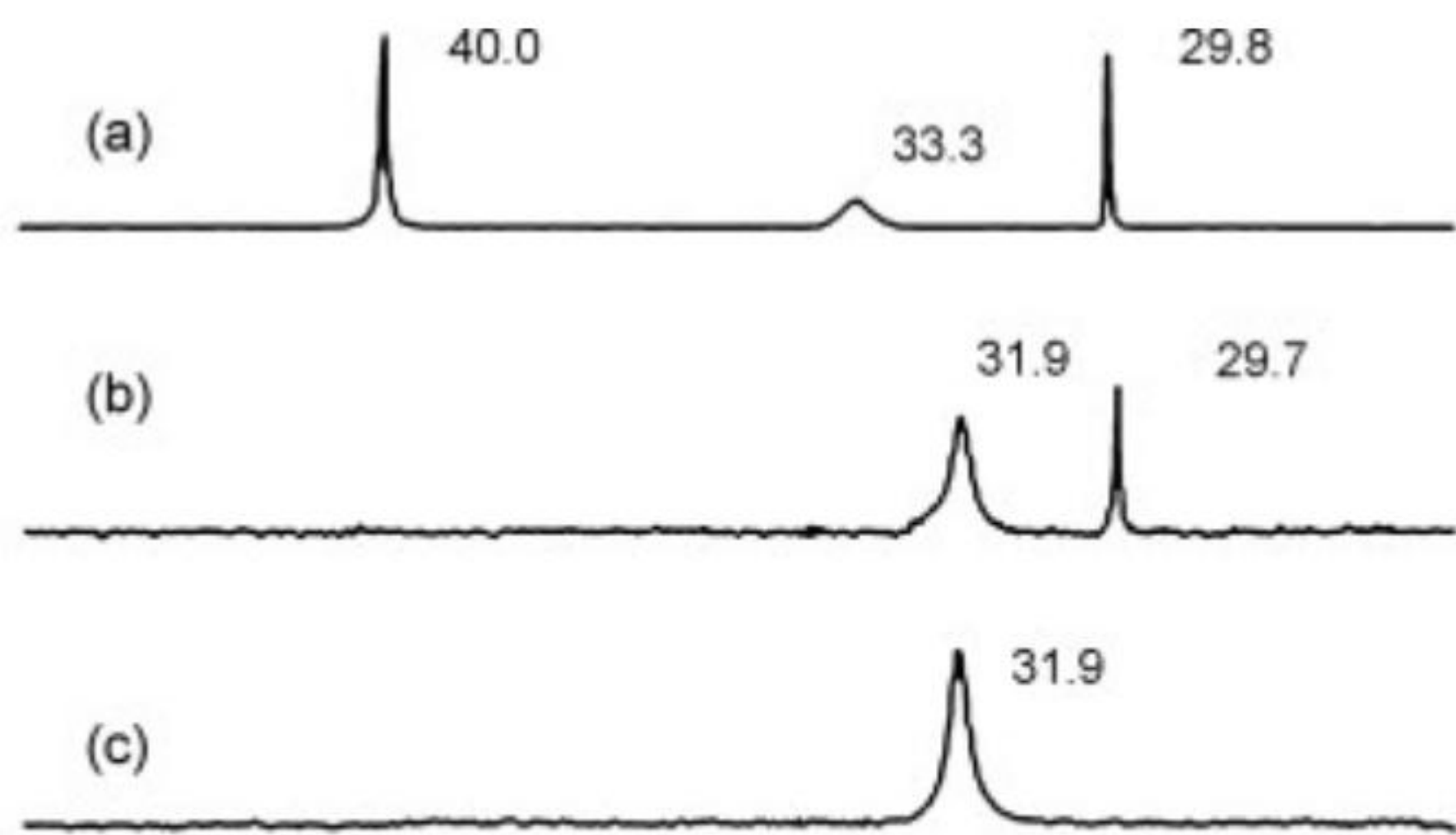
(b)

31.9

29.7

(c)

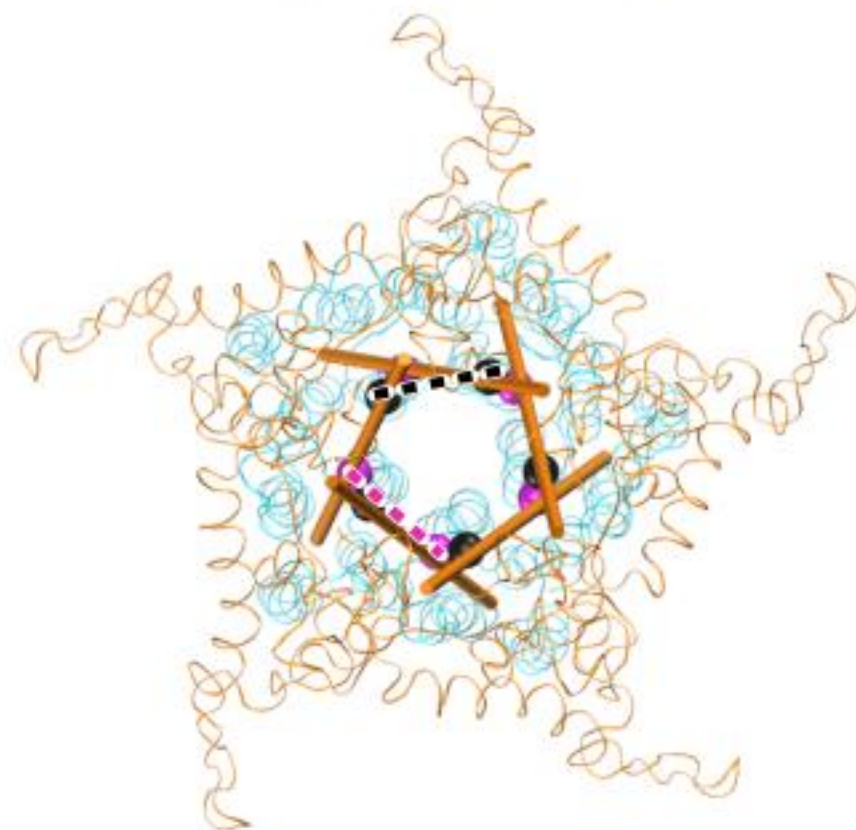
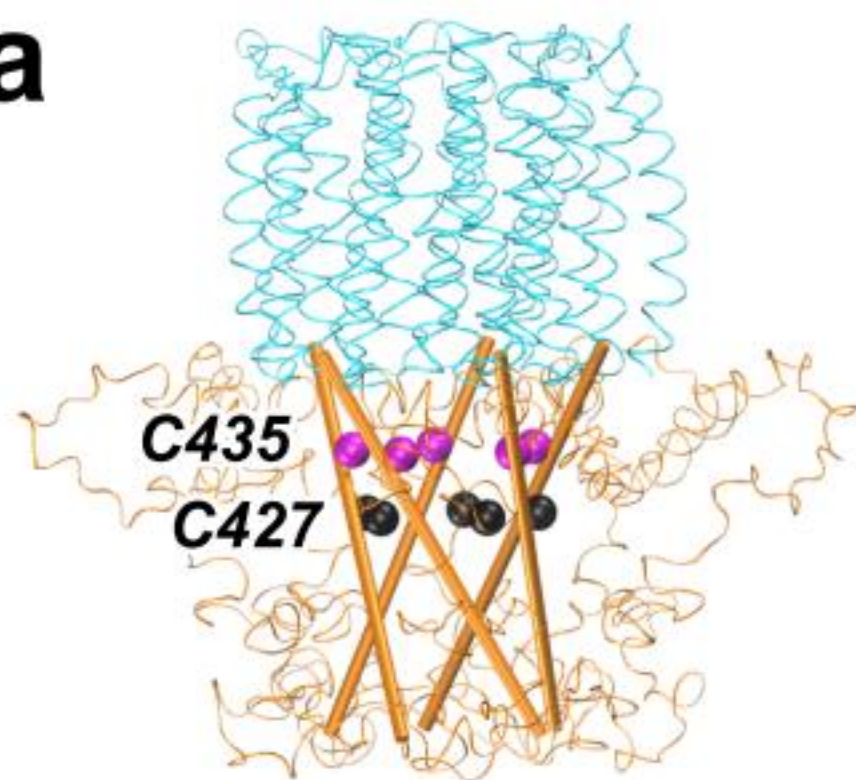
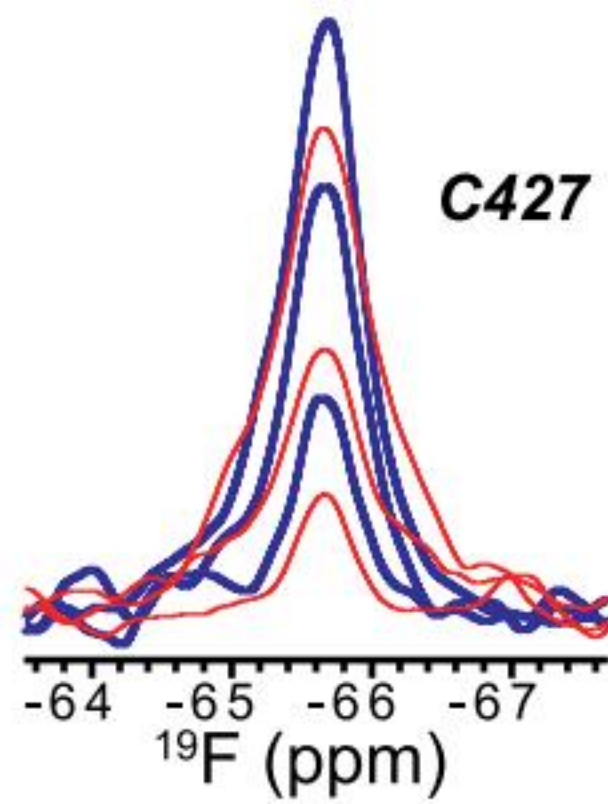
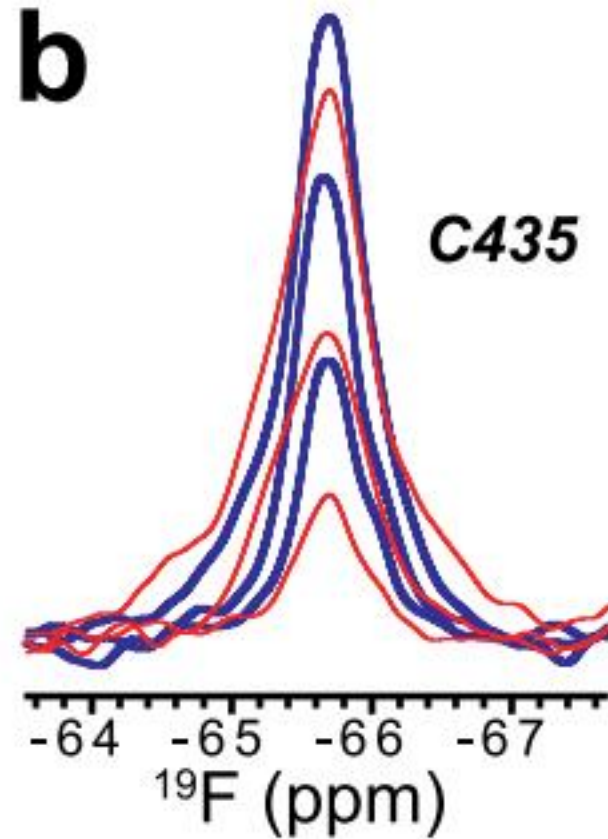
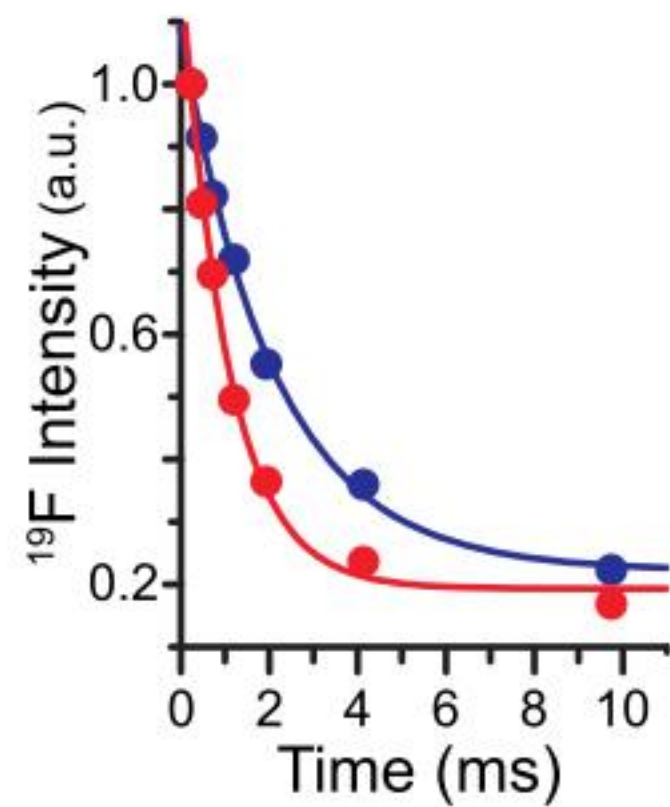
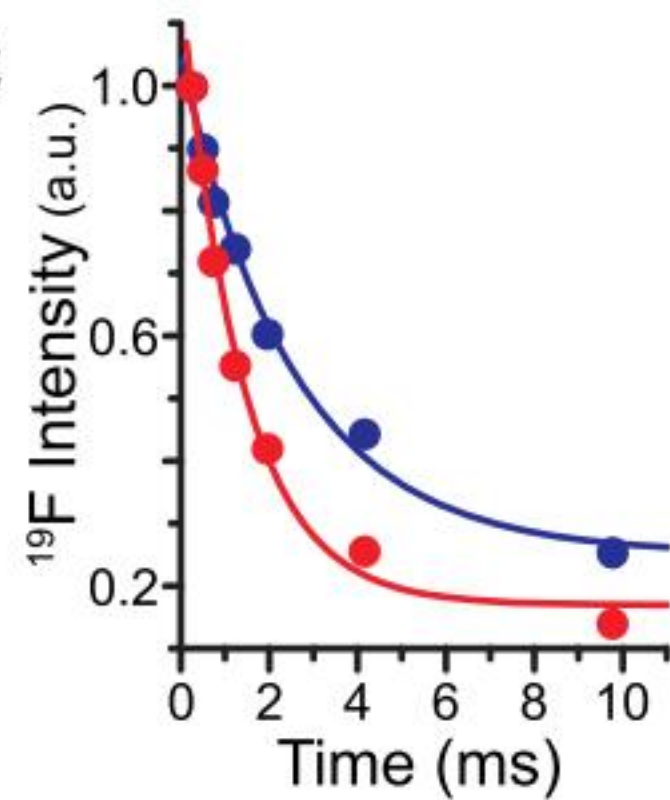
31.9

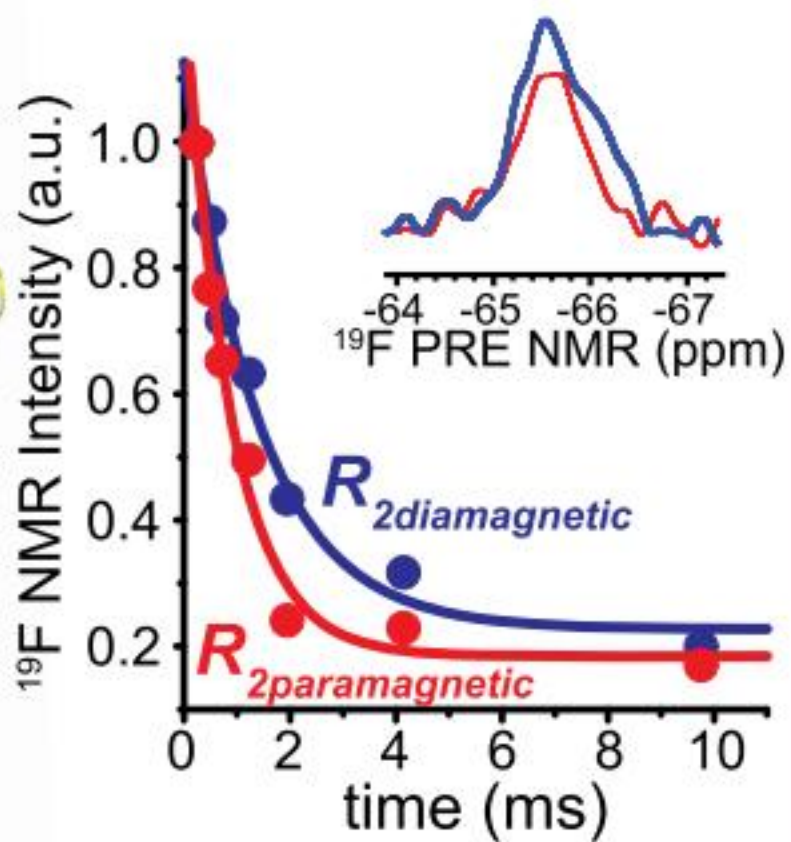
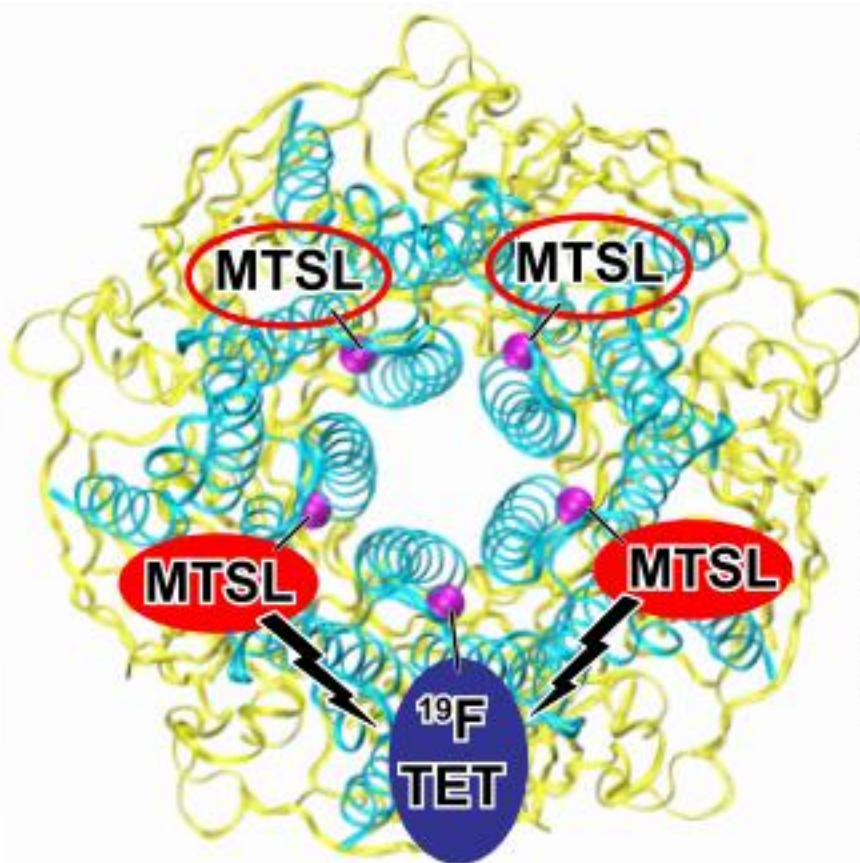


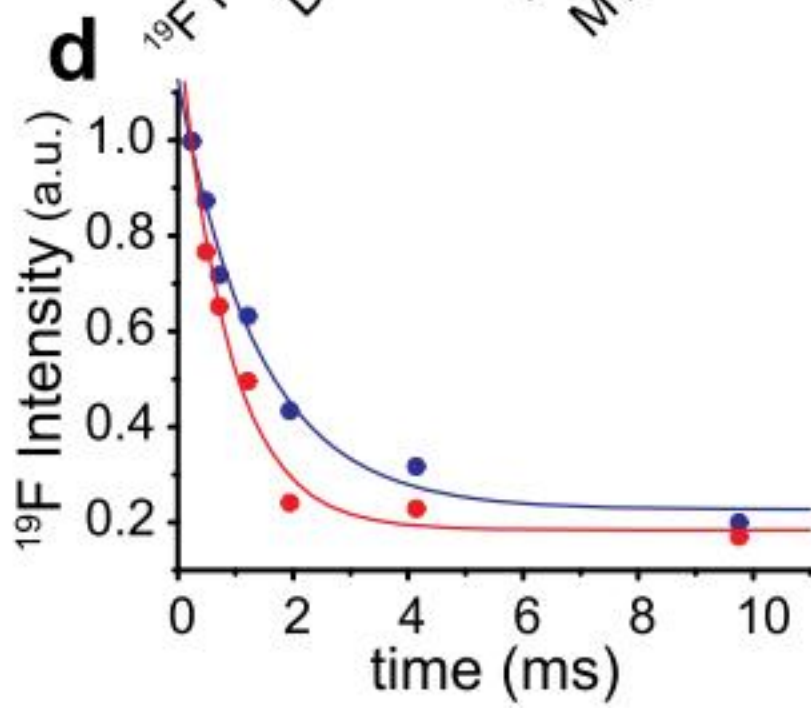
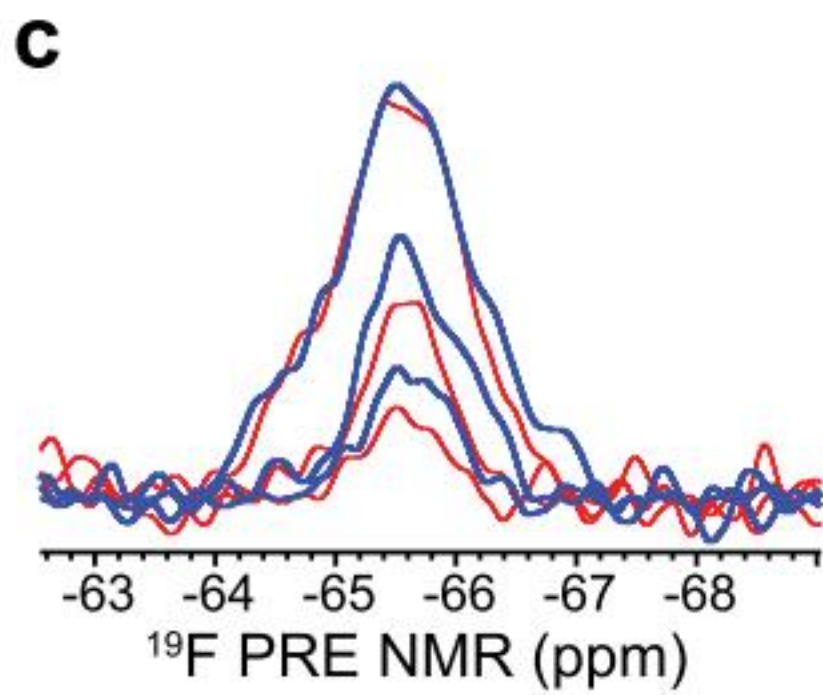
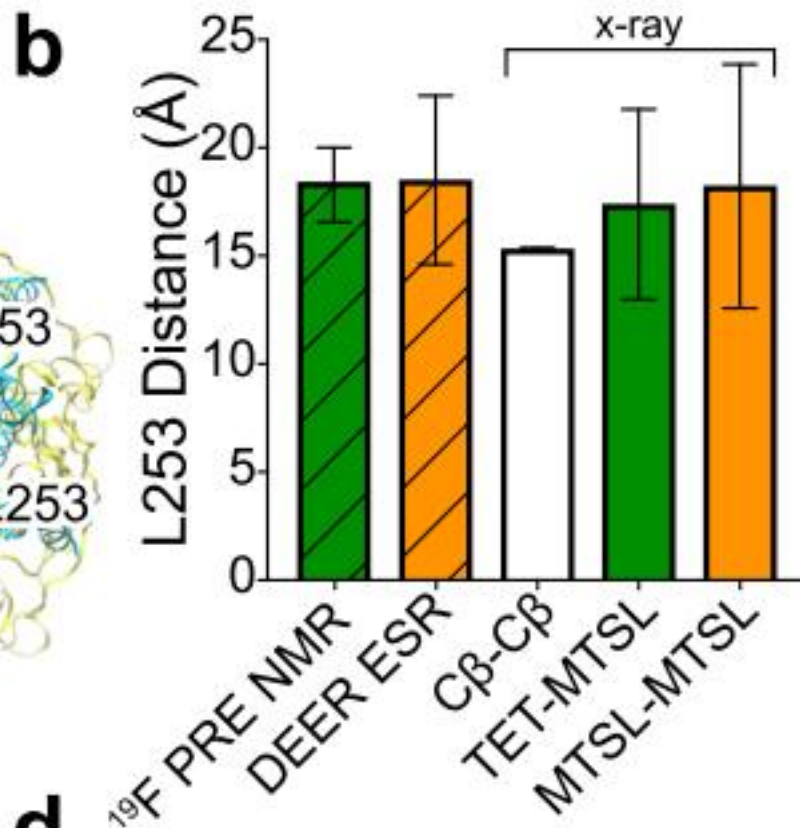
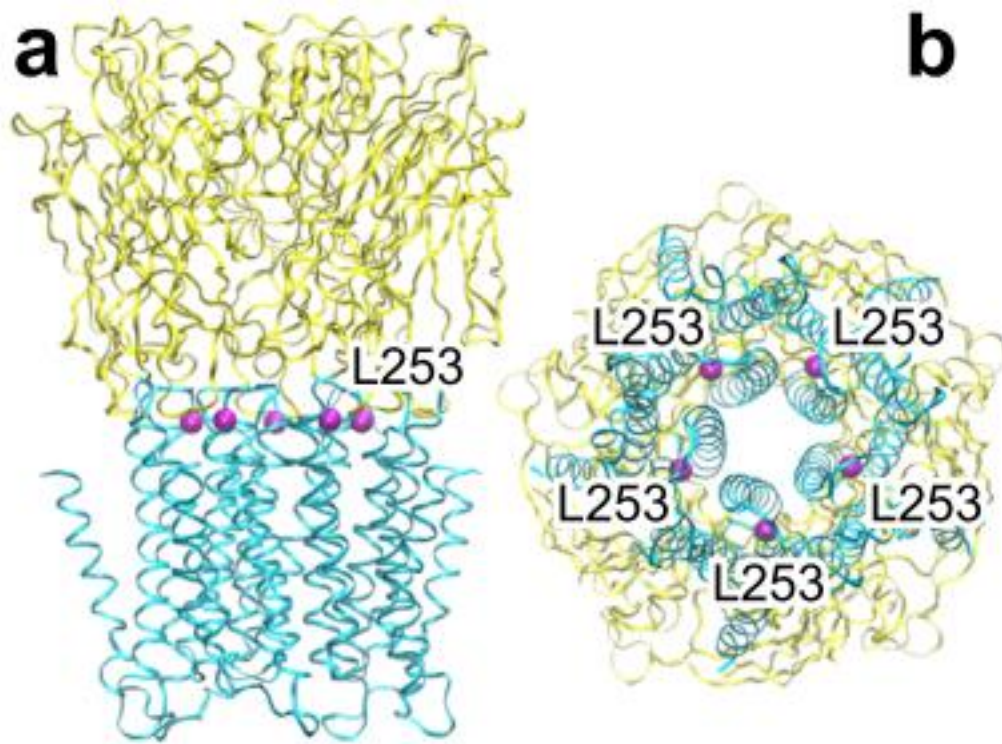


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a**b****c**



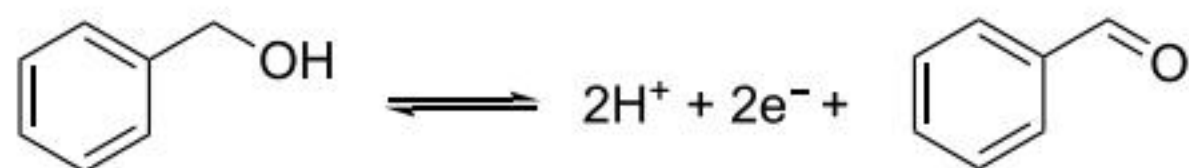




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(A) From Free Energy to Potential



ΔG°_f (kcal mol⁻¹): -5.01

ΔG°_f (kcal mol⁻¹): +1.59

$$\Delta G^\circ_{\text{rxn}} = +6.6 \text{ (kcal mol}^{-1}\text{)} \xrightarrow[\substack{n = 2 e^-, F = 96,485 \text{ C mol}^{-1}, \\ 1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}}]{\Delta G^\circ = -nF\Delta E^\circ} \Delta E^\circ_{\text{rxn}} \text{ (V): } -0.14$$

(C) Synthetically Relevant Oxidants ΔE° (V vs SHE)

SHE:	$2 \text{ H}^+ + 2 \text{ e}^- \rightleftharpoons \text{H}_2$	0.00
	$\text{O}_2 + 4 \text{ H}^+ + 4 \text{ e}^- \rightleftharpoons 2 \text{ H}_2\text{O}$	1.23
	$\text{O}_2 + 2 \text{ H}^+ + 2 \text{ e}^- \rightleftharpoons \text{H}_2\text{O}_2$	0.68
	$\text{H}_2\text{O}_2 + 2 \text{ H}^+ + 2 \text{ e}^- \rightleftharpoons 2 \text{ H}_2\text{O}$	1.78
1.	$\text{O}_3 + 2 \text{ H}^+ + 2 \text{ e}^- \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}$	2.08
2.	$\text{S}_2\text{O}_8^{2-} + 2 \text{ e}^- \rightleftharpoons 2 \text{ SO}_4^{2-}$	2.01
3.	$\text{TBHP} + 2 \text{ e}^- + 2 \text{ H}^+ \rightleftharpoons \text{tBuOH} + \text{H}_2\text{O}$	~1.7
4.	$\text{MnO}_4^- + 8 \text{ H}^+ + 5 \text{ e}^- \rightleftharpoons \text{Mn}^{2+} + 4 \text{ H}_2\text{O}$	1.51
5.	$\text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^+ + 6 \text{ e}^- \rightleftharpoons 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O}$	1.36
6.	$\text{Br}_{2(\text{aq})} + 2 \text{ e}^- \rightleftharpoons 2 \text{ Br}^-_{(\text{aq})}$	1.09
7.	$\text{NO}_2 + 2 \text{ H}^+ + 2 \text{ e}^- \rightleftharpoons \text{NO} + \text{H}_2\text{O}$	1.05
8.	$\text{TEMPO}^+ + 2 \text{ e}^- + 2 \text{ H}^+ \rightleftharpoons \text{TEMPOH}_2^+$	0.91 ^a
9.	$\text{DDQ} + 2 \text{ e}^- + 2 \text{ H}^+ \rightleftharpoons \text{DDH}_2\text{Q}$	0.89 ^a
10.	$\text{BQ} + 2 \text{ H}^+ + 2 \text{ e}^- \rightleftharpoons \text{H}_2\text{Q}$	0.64 ^a
11.	$\text{I}_{2(\text{aq})} + 2 \text{ e}^- \rightleftharpoons 2 \text{ I}^-_{(\text{aq})}$	0.54

(B) Organic Reaction Redox Potentials $-\Delta E^\circ$ (V vs SHE)

Alcohol Oxidation

a.	$\text{EtOH} \rightleftharpoons \text{acetaldehyde} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.28
b.	$\text{EtOH} + \text{H}_2\text{O} \rightleftharpoons \text{acetic acid} + 4 \text{ H}^+ + 4 \text{ e}^-$	0.06
c.	$\text{acetaldehyde} + \text{H}_2\text{O} \rightleftharpoons \text{acetic acid} + 2 \text{ H}^+ + 2 \text{ e}^-$	-0.16
d.	$\text{iPrOH} \rightleftharpoons \text{acetone} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.12
e.	$\text{BnOH} \rightleftharpoons \text{PhCHO} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.14

Alkene Oxidation

f.	$\text{propene} + \text{H}_2\text{O} \rightleftharpoons \text{acetone} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.09
g.	$\text{propene} + \text{H}_2\text{O} \rightleftharpoons \text{propanal} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.23
h.	$\text{ethylene} + \text{H}_2\text{O} \rightleftharpoons \text{acetaldehyde} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.26
i.	$\text{ethylene} + 2 \text{ H}_2\text{O} \rightleftharpoons \text{ethylene glycol} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.40
j.	$\text{propene} + \text{H}_2\text{O} \rightleftharpoons \text{propylene oxide} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.76

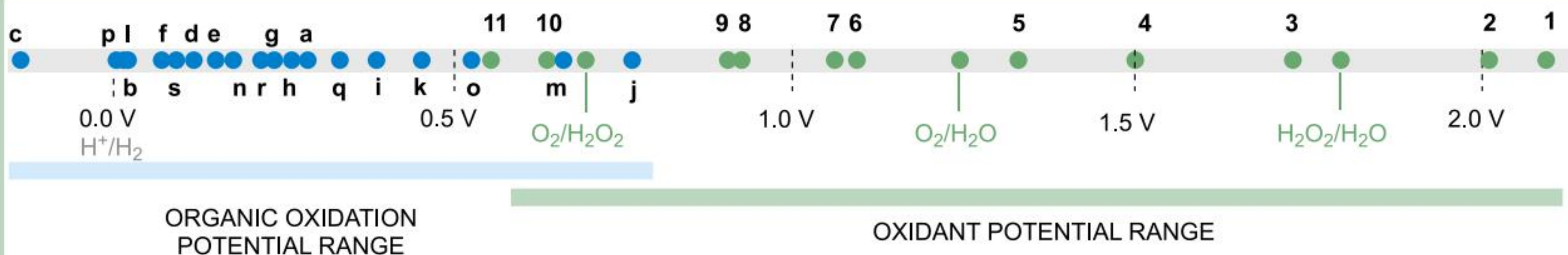
*sp*³ C–H Oxidation

k.	$\text{propane} \rightleftharpoons \text{propene} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.45
l.	$\text{pyrrolidine} + \text{H}_2\text{O} \rightleftharpoons \gamma\text{-lactam} + 4 \text{ H}^+ + 4 \text{ e}^-$	0.02
m.	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{methanol} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.63
n.	$\text{CH}_4 + 2 \text{ H}_2\text{O} \rightleftharpoons \text{CO}_2 + 8 \text{ H}^+ + 8 \text{ e}^-$	0.17
o.	$\text{toluene} + \text{H}_2\text{O} \rightleftharpoons \text{BnOH} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.53

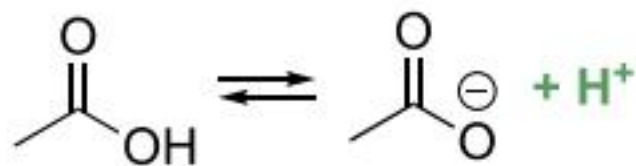
Arene C–H Oxidation

p.	$2 \text{ benzene} \rightleftharpoons \text{biphenyl} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.01
q.	$\text{benzene} + \text{H}_2\text{O} \rightleftharpoons \text{phenol} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.32
r.	$\text{benzene} + \text{NH}_3 \rightleftharpoons \text{aniline} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.21
s.	$\text{benzene} + \text{acetamide} \rightleftharpoons \text{acetanilide} + 2 \text{ H}^+ + 2 \text{ e}^-$	0.10

(D) Potentials for Organic Oxidations and Oxidants



Free Energy, pH, pK_a , Redox Potentials, and Equilibria

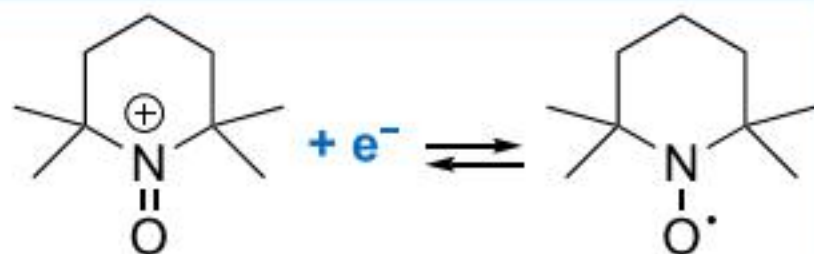
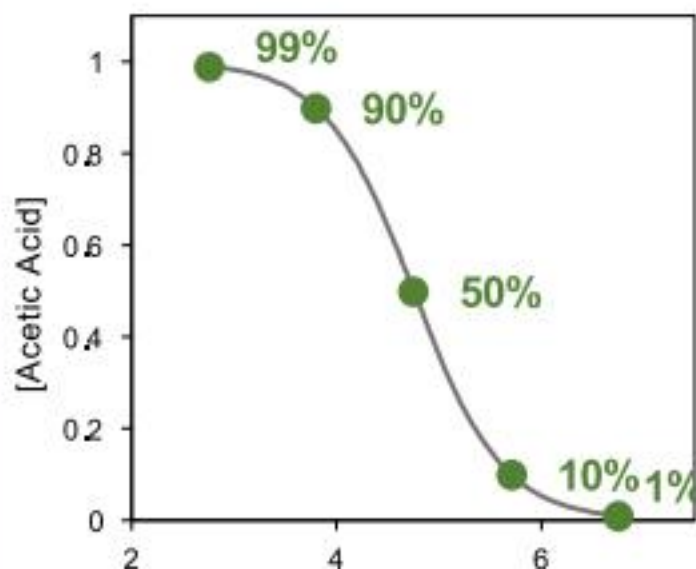


$$\text{pH} = \text{p}K_a + \log_{10}([\text{A}^-]/[\text{HA}])$$

$$\text{For } [\text{AcO}^-]/[\text{AcOH}] = 10$$

$$\Delta G = \Delta G^\circ + 2.3 RT \log_{10}(10)$$

$$\Delta G = \Delta G^\circ + 1.36 \text{ kcal mol}^{-1}$$

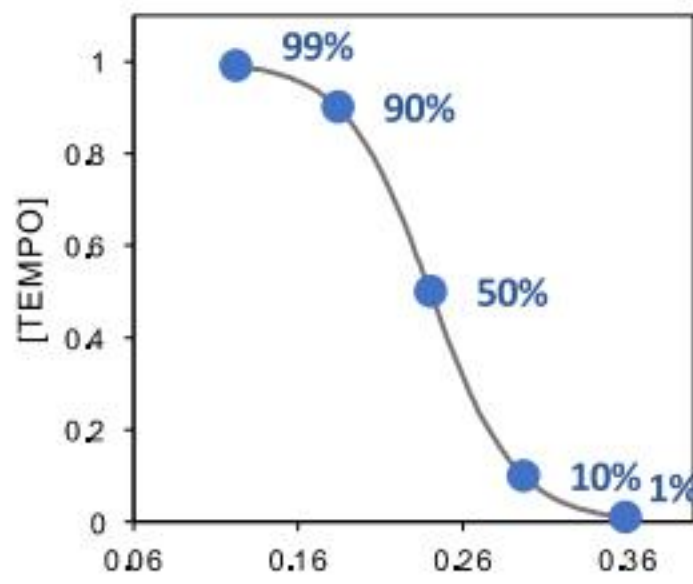


$$\Delta E = \Delta E^\circ - (RT/nF) \ln([T]/[T^+])$$

$$\text{for } [T]/[T^+] = 10$$

$$\Delta E = \Delta E^\circ - (2.3 RT/nF) \log_{10}(10)$$

$$\Delta E = \Delta E^\circ - 59 \text{ mV}/n$$







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needed to initiate single-electron transfer (SET), but these values are very different from the thermodynamic potentials for net two-electron redox reactions of interest to organic chemists.



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Supporting Information

ABSTRACT: Redox reactions are ubiquitous in organic synthesis and

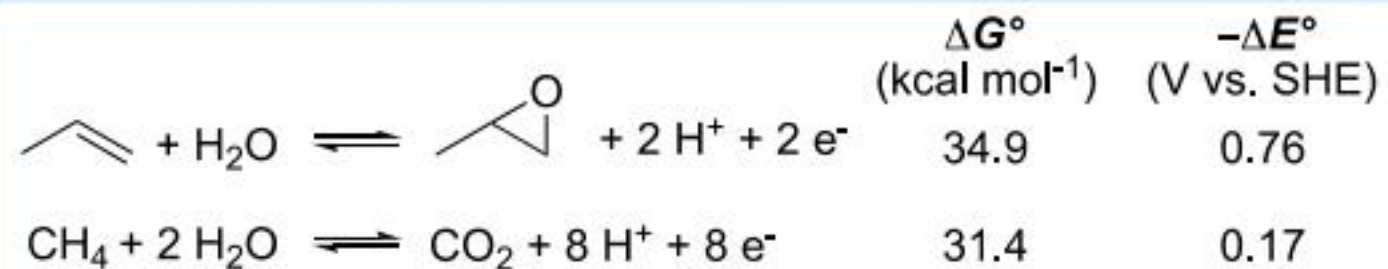


JOC

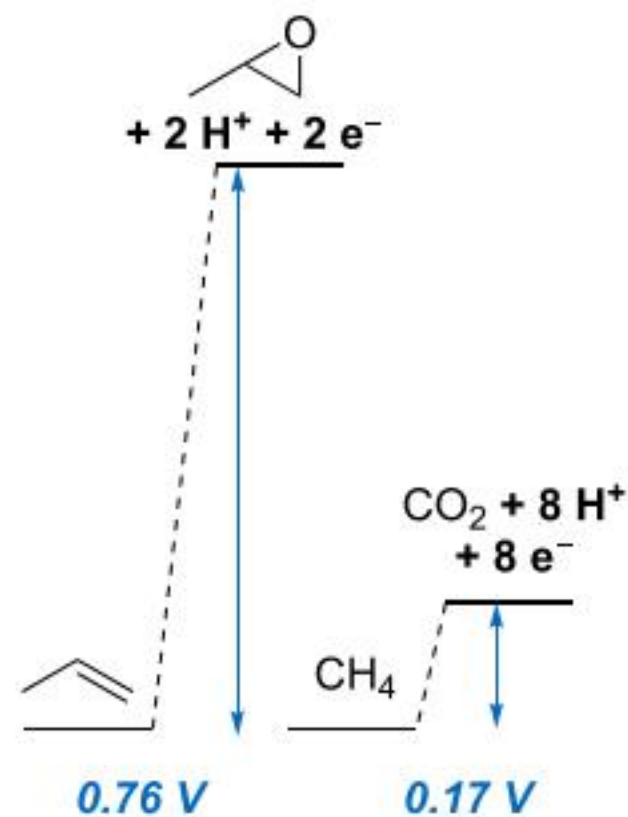
The Journal of Organic Chemistry
Volume 75, Number 1, January 2010



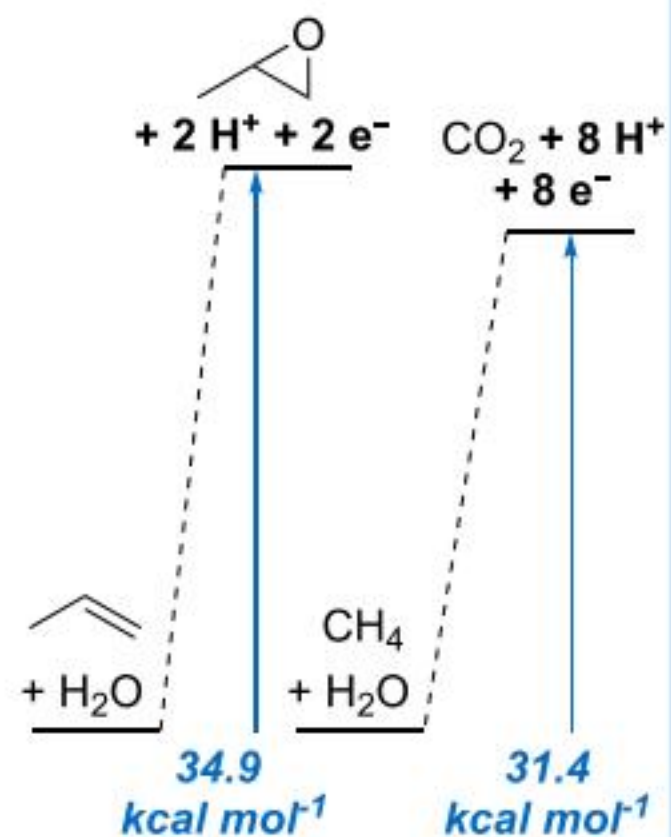
(A) Propylene Epoxidation vs. Methane Oxidation



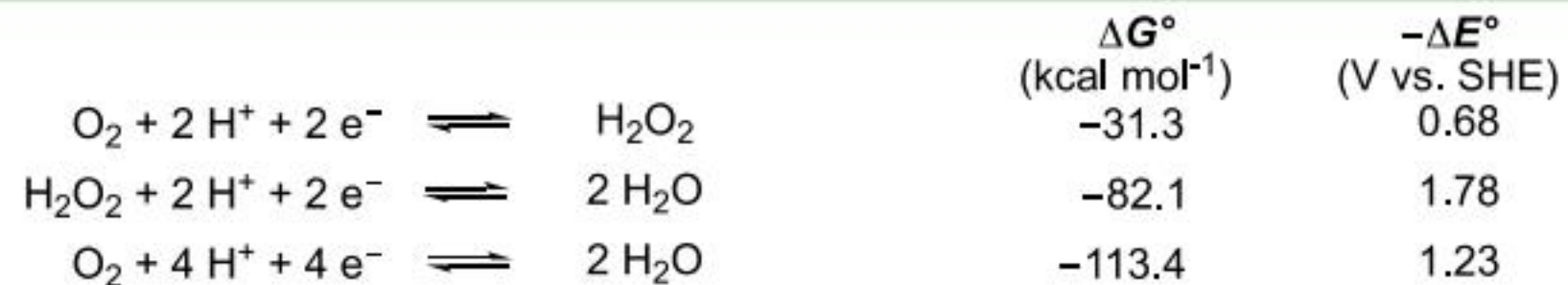
Standard Potential ΔE°



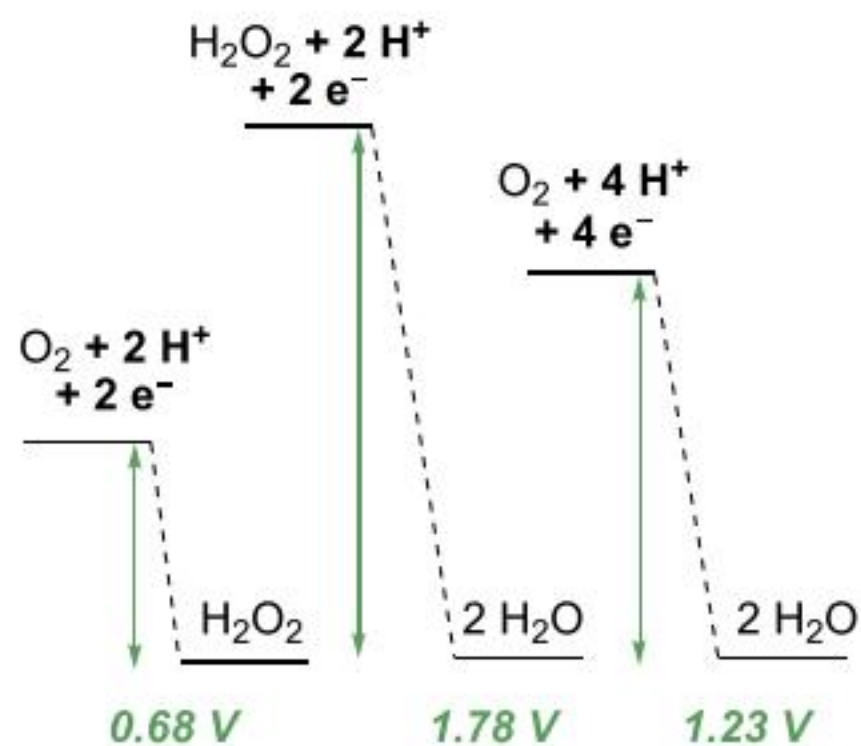
Free Energy ΔG°



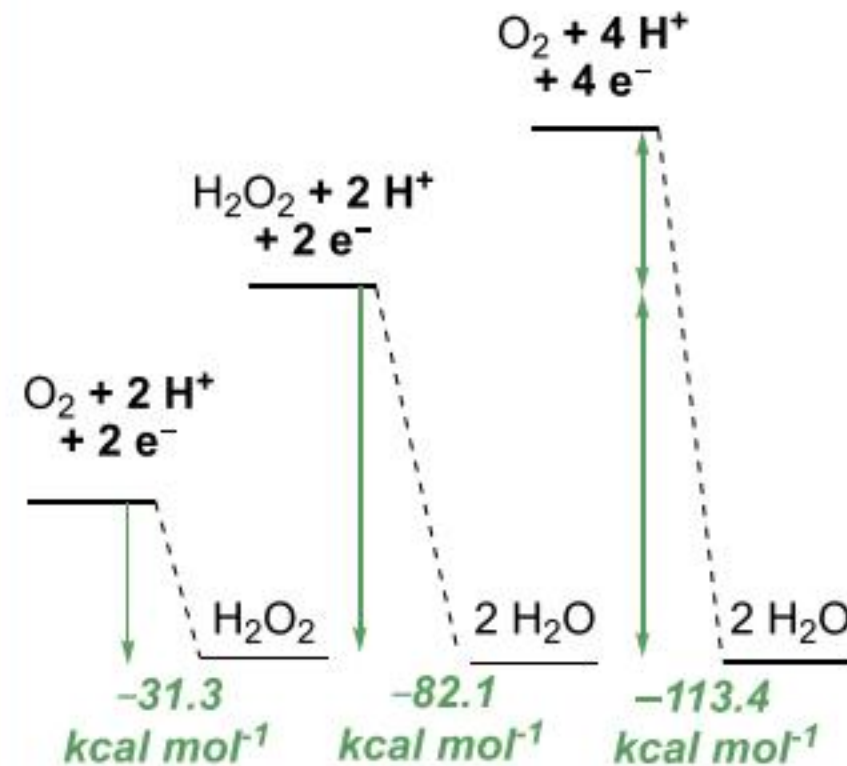
(B) O₂ and H₂O₂ Reduction



Standard Potential ΔE°

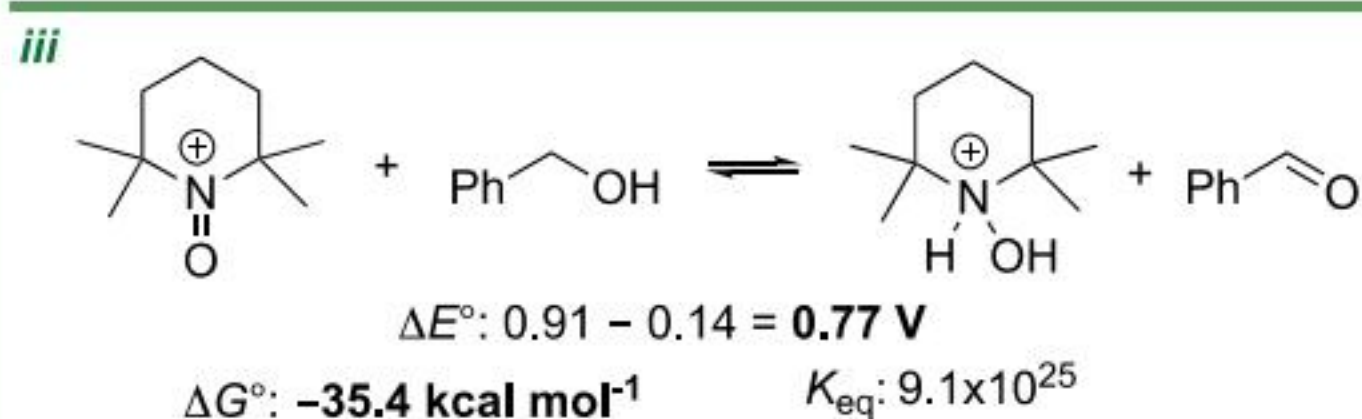
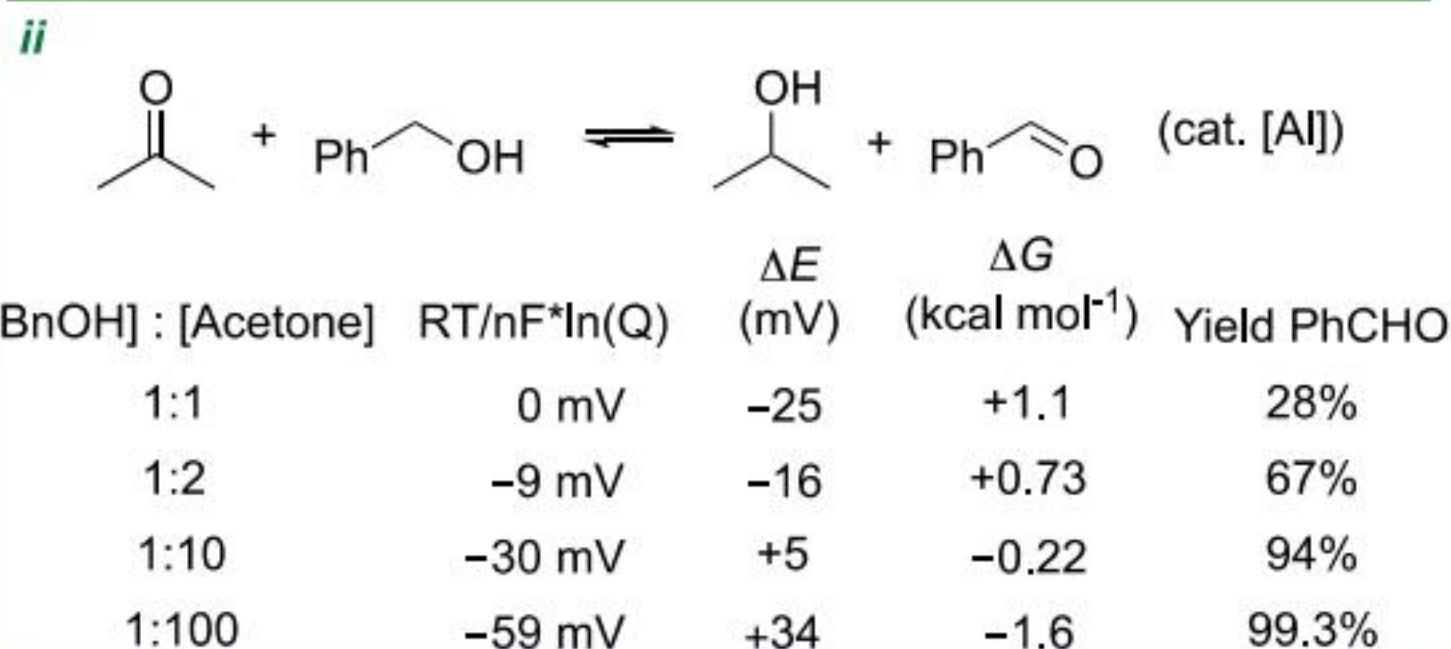
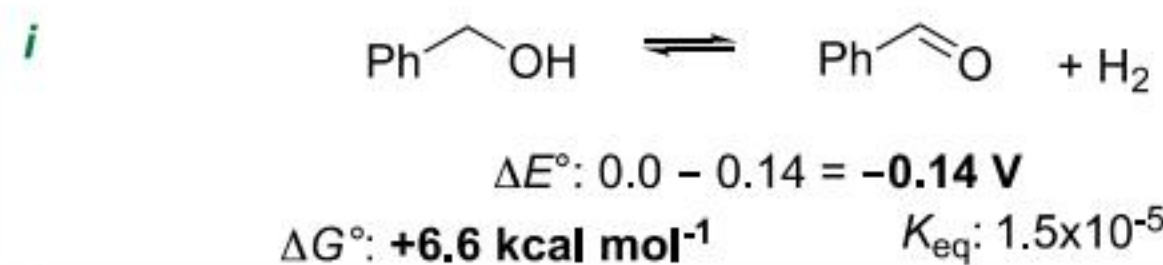


Free Energy ΔG°

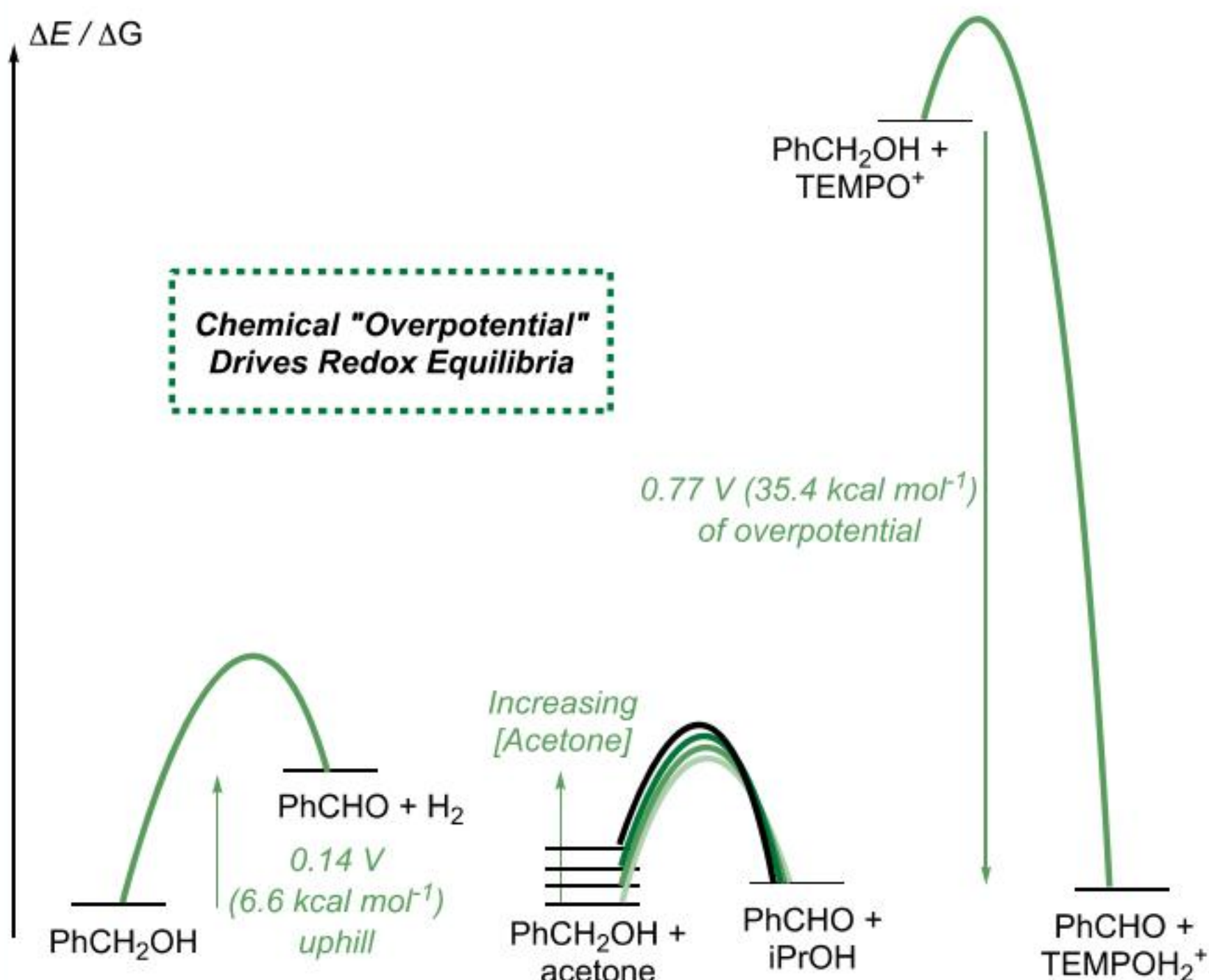


(A) Overpotential in Chemical Redox Reactions

Thermochemistry of Some Alcohol Oxidations

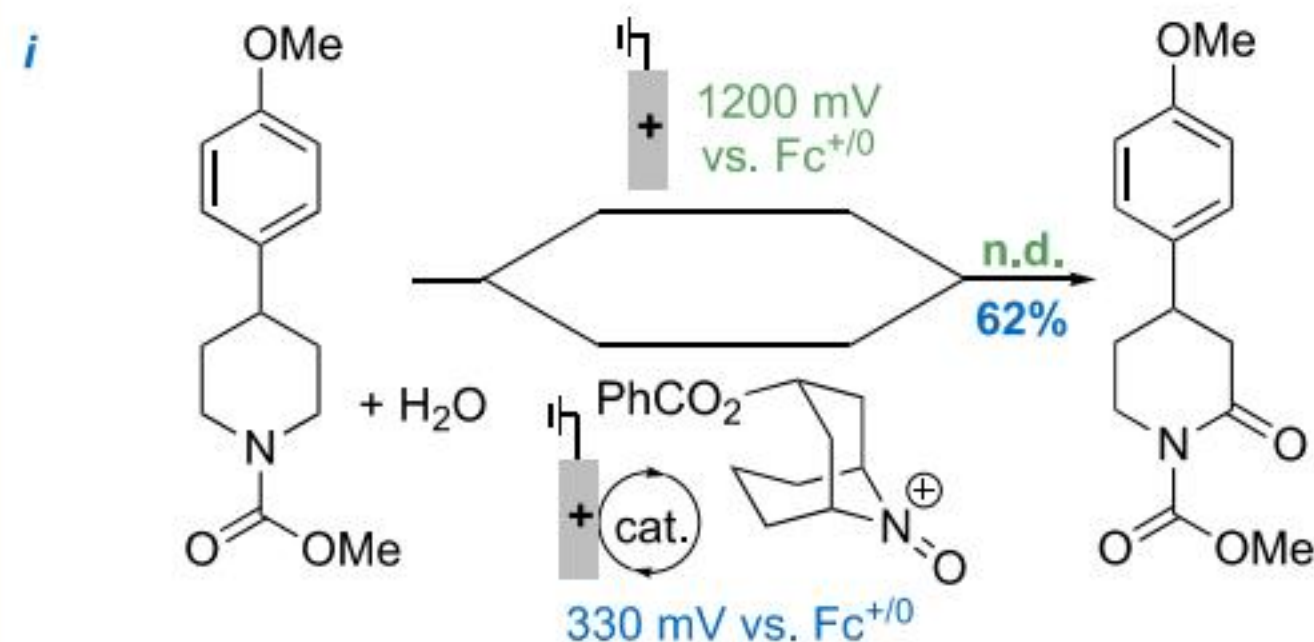


iv Overpotential and Reaction Coordinates

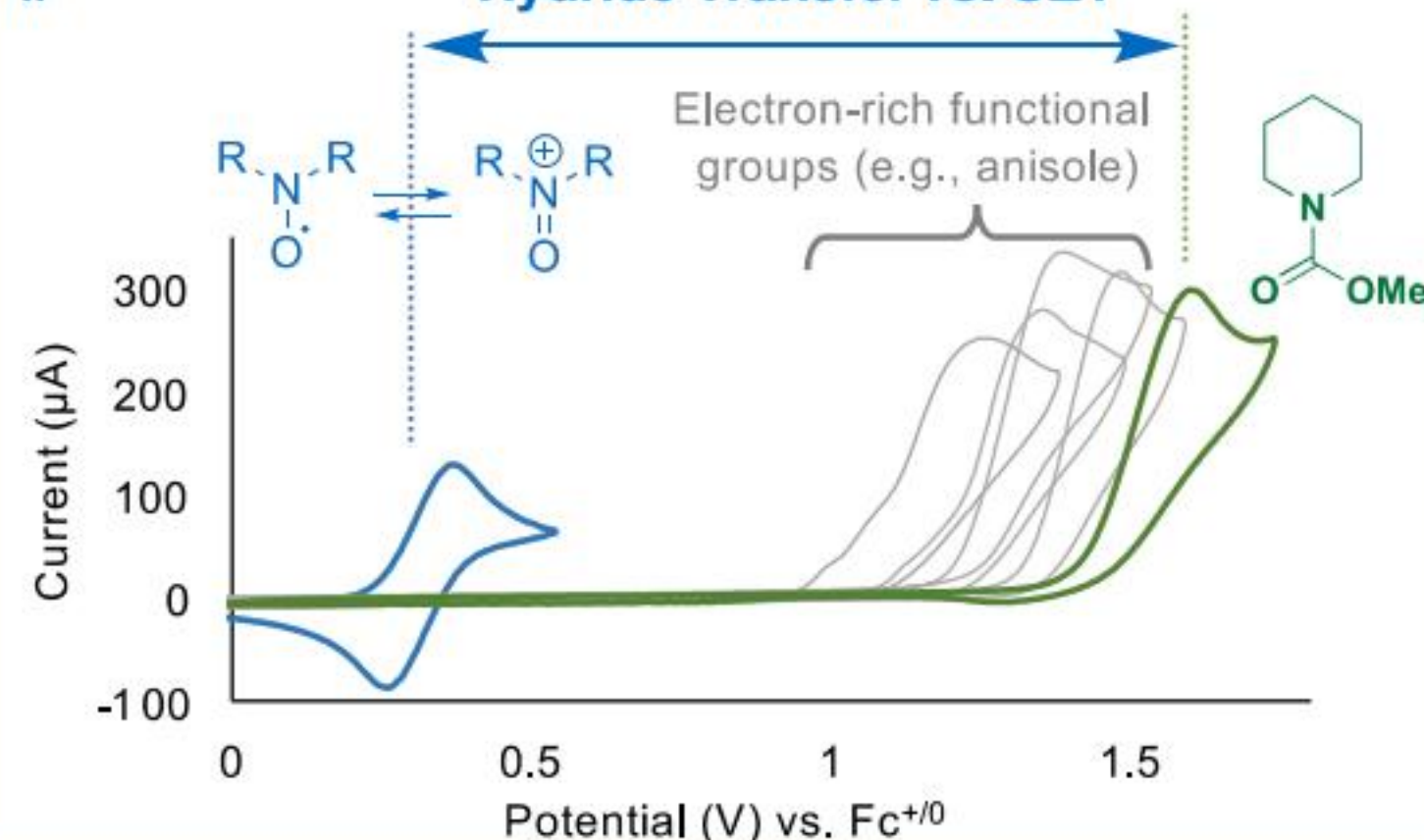


(B) Overpotential in Electrochemical Reactions

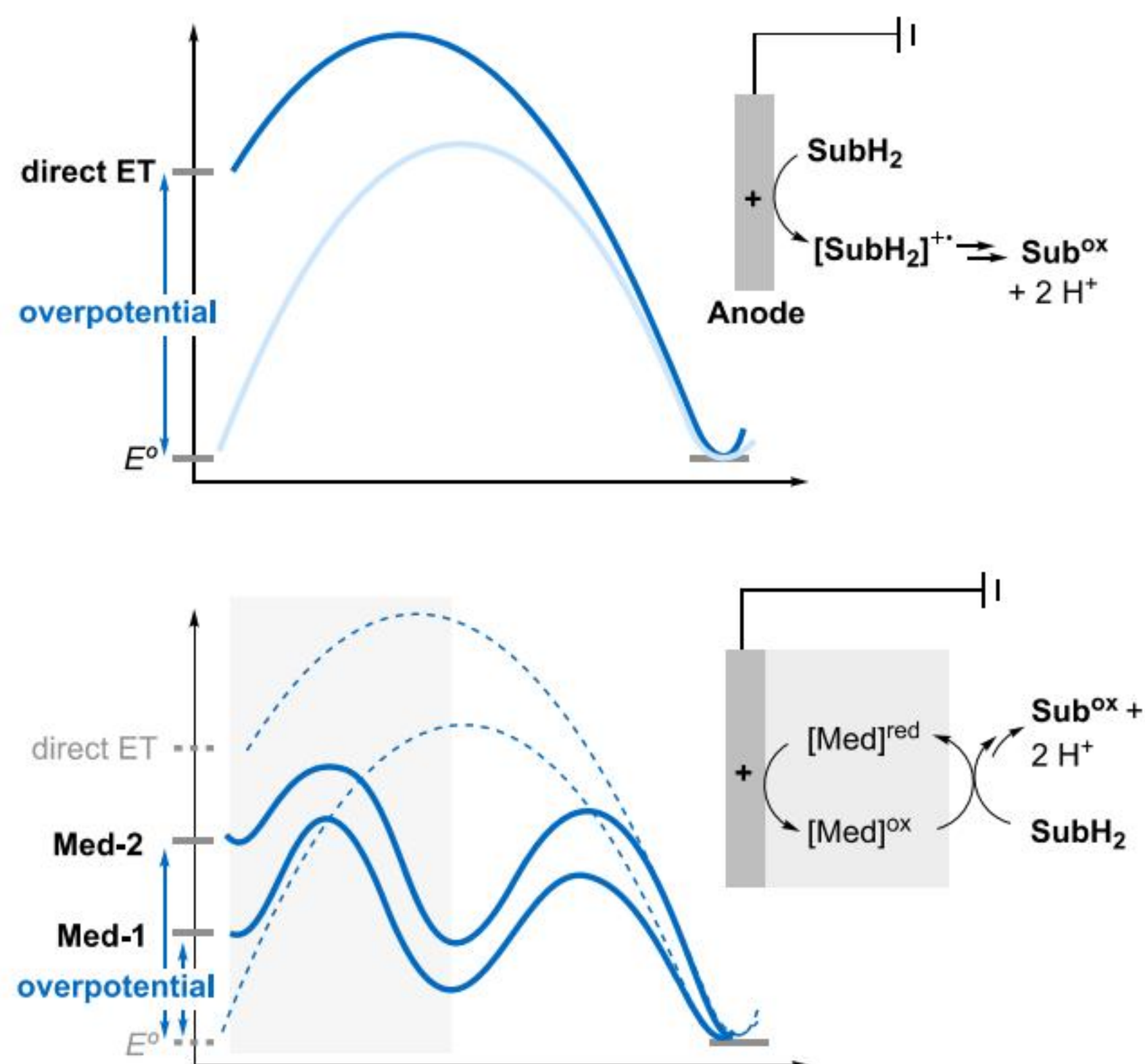
Shono-Type Carbamate Oxidation



ii Hydride Transfer vs. SET

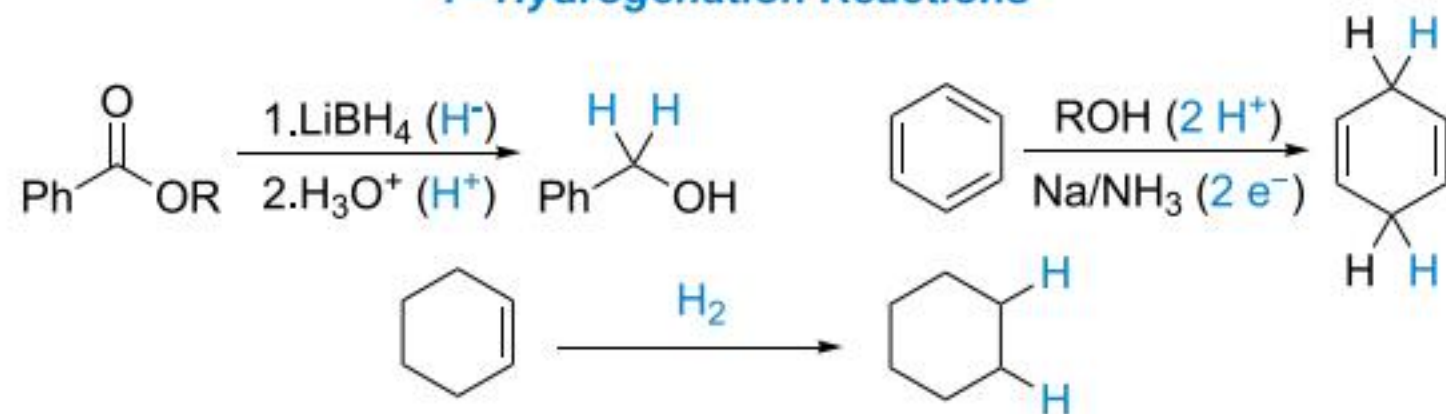


iii Reaction Coordinates for Electrochemical Redox Reactions

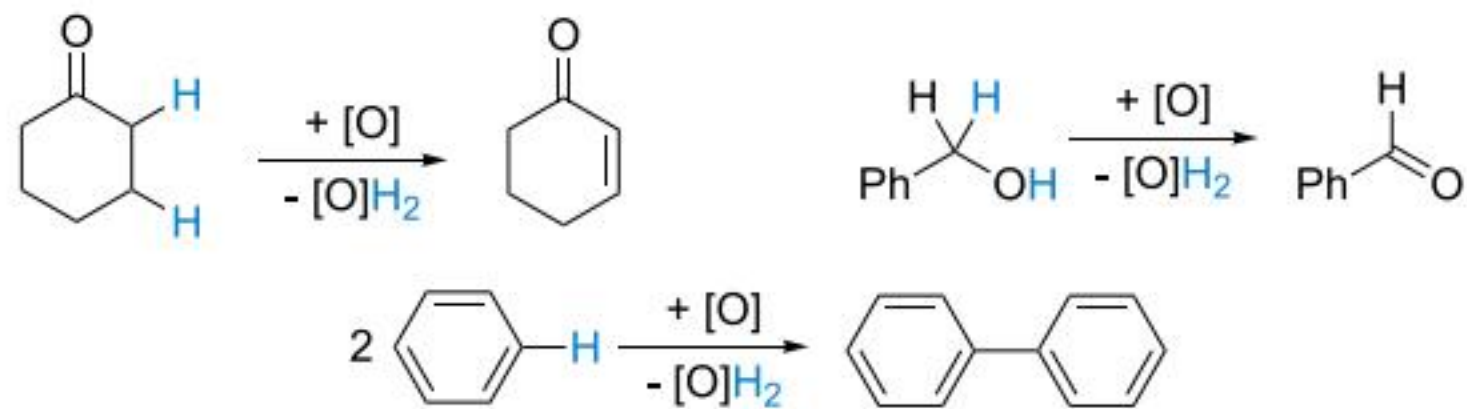


(A) Redox Reactions in Organic Chemistry

i - Hydrogenation Reactions

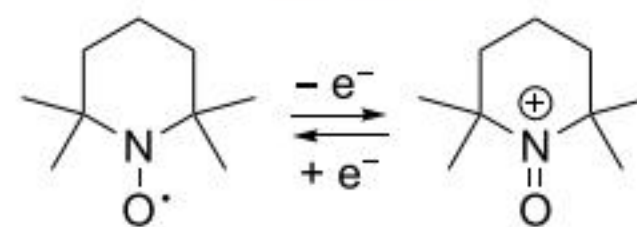


ii - Dehydrogenation Reactions

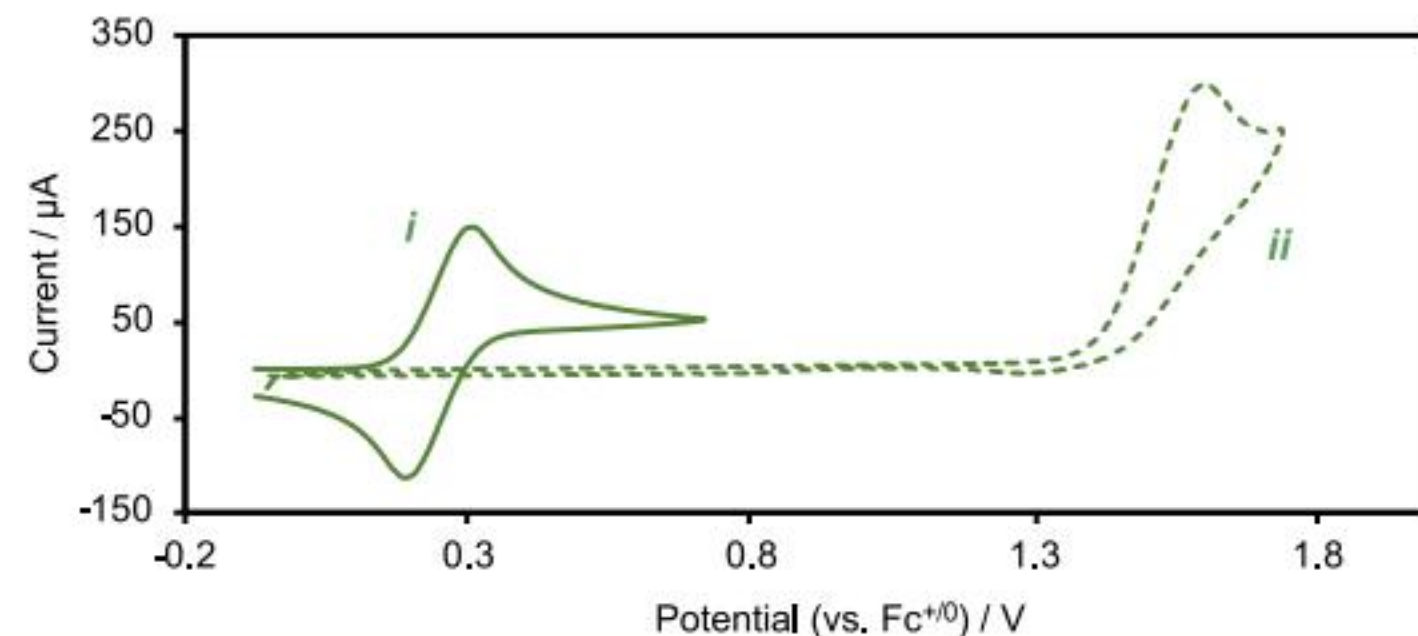
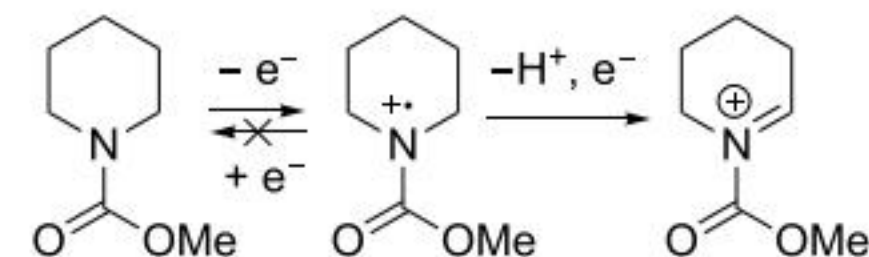


(B) Electron Transfer Reactions and Electrochemical Potentials

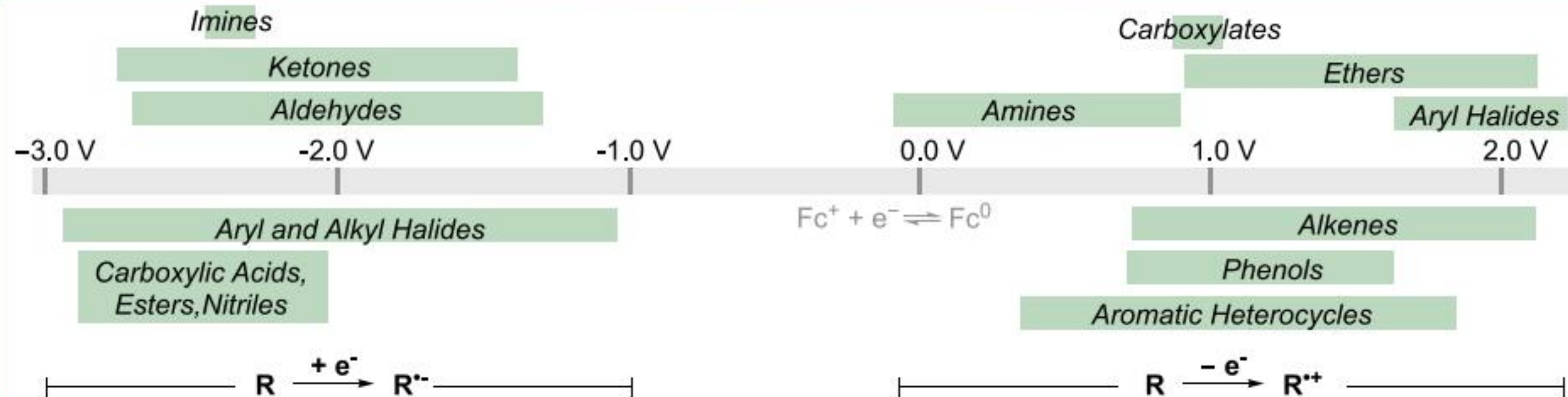
i - Reversible ET



ii - Irreversible ET



(C) Potentials Required for ET at an Electrode



(D) Reference Electrodes

Potential Conversions for Non-aqueous Reference Electrodes

