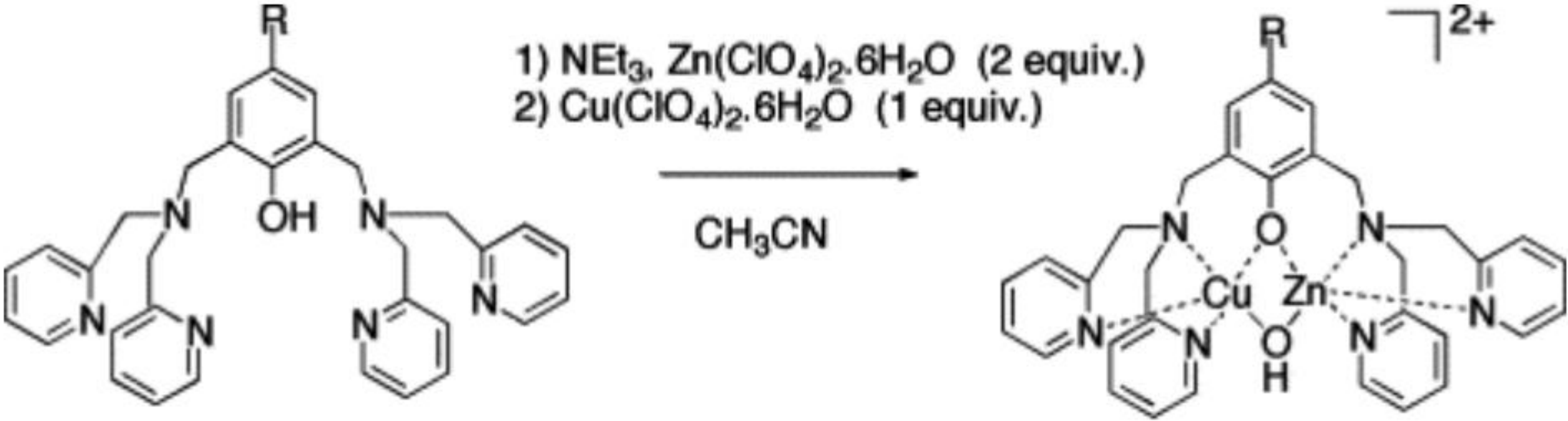
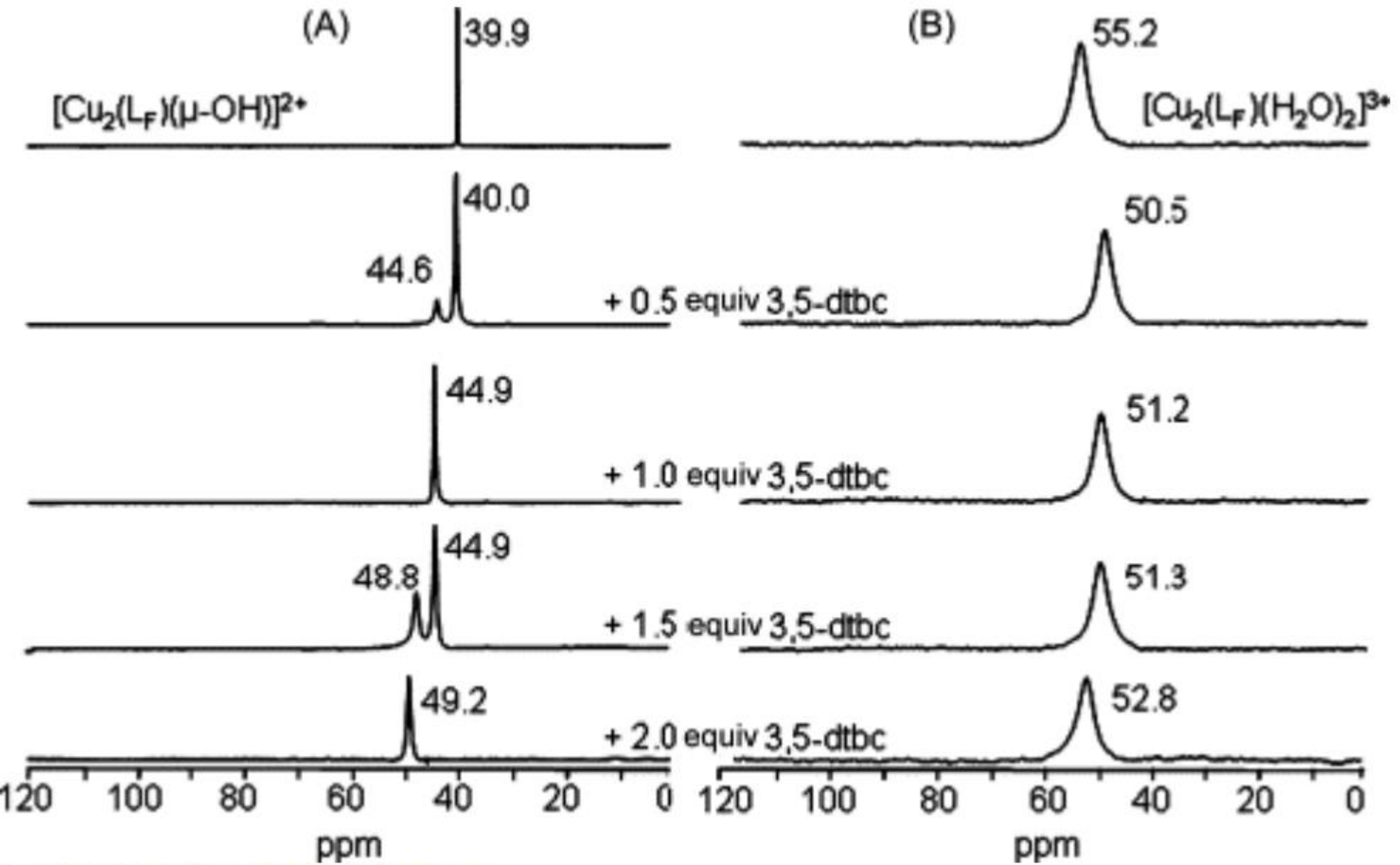


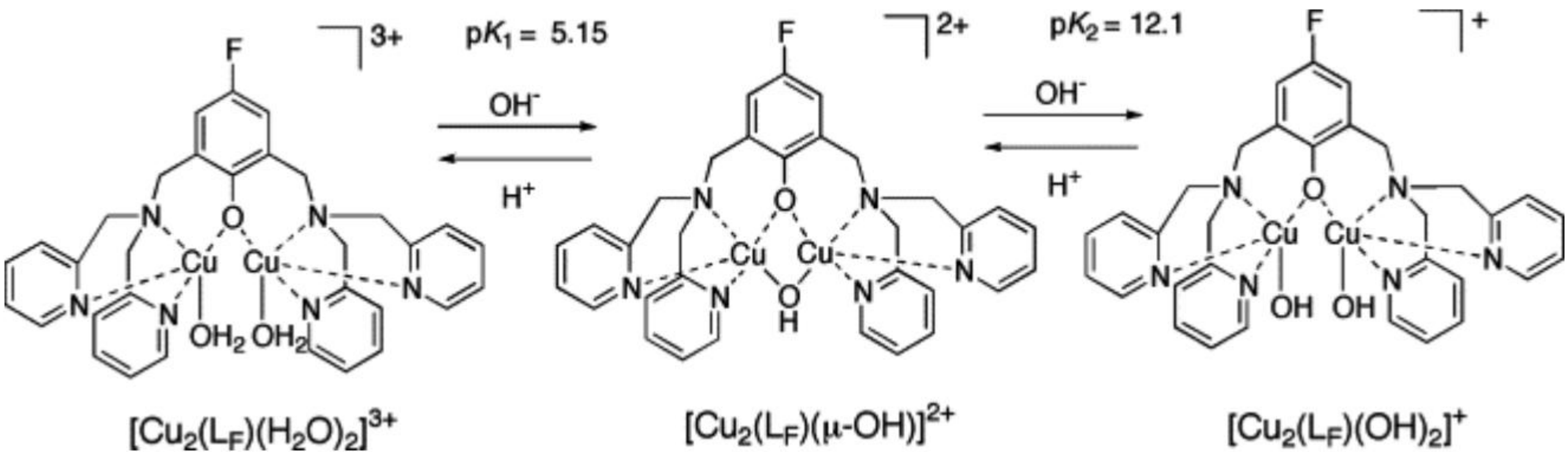
$H\text{-}L_F$ (R = F)
H-L (R = CH_3)

$(Cu\text{-}ZnL_F(\mu OH))^{2+}$ (R = F)
$(Cu\text{-}ZnL(\mu OH))^{2+}$ (R = CH_3)

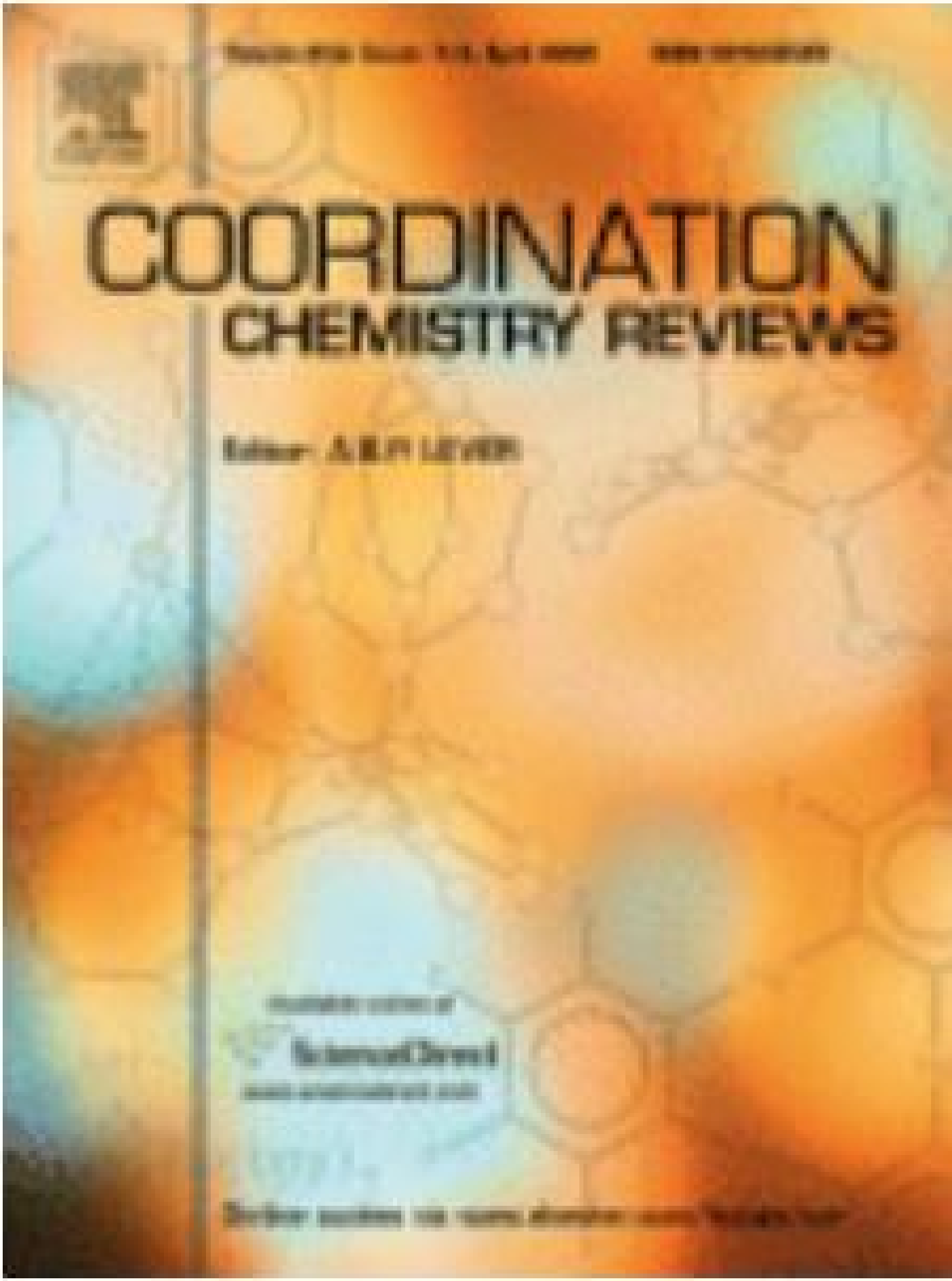
1. Download: Download full-size image



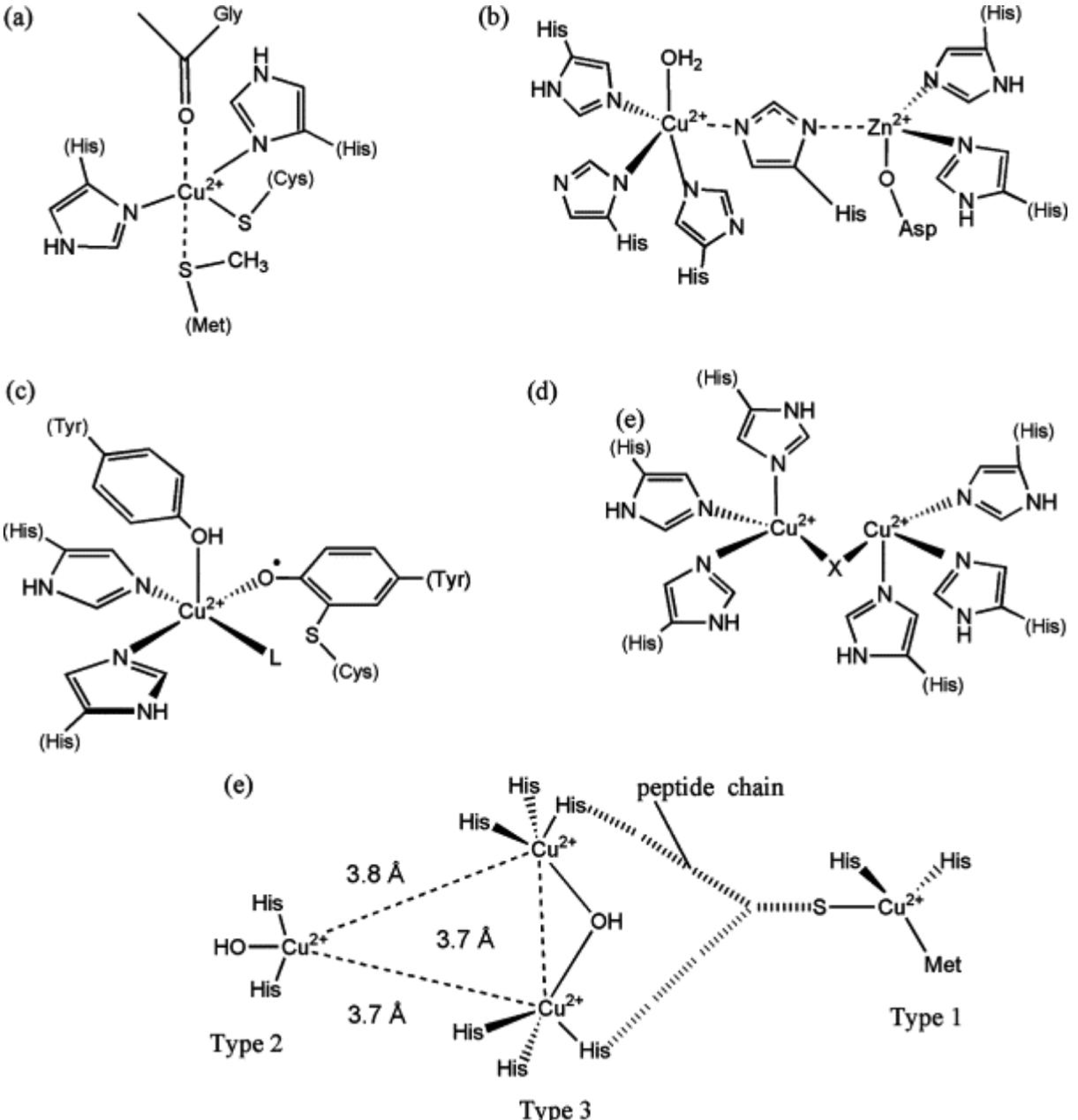
1. Download: Download full-size image

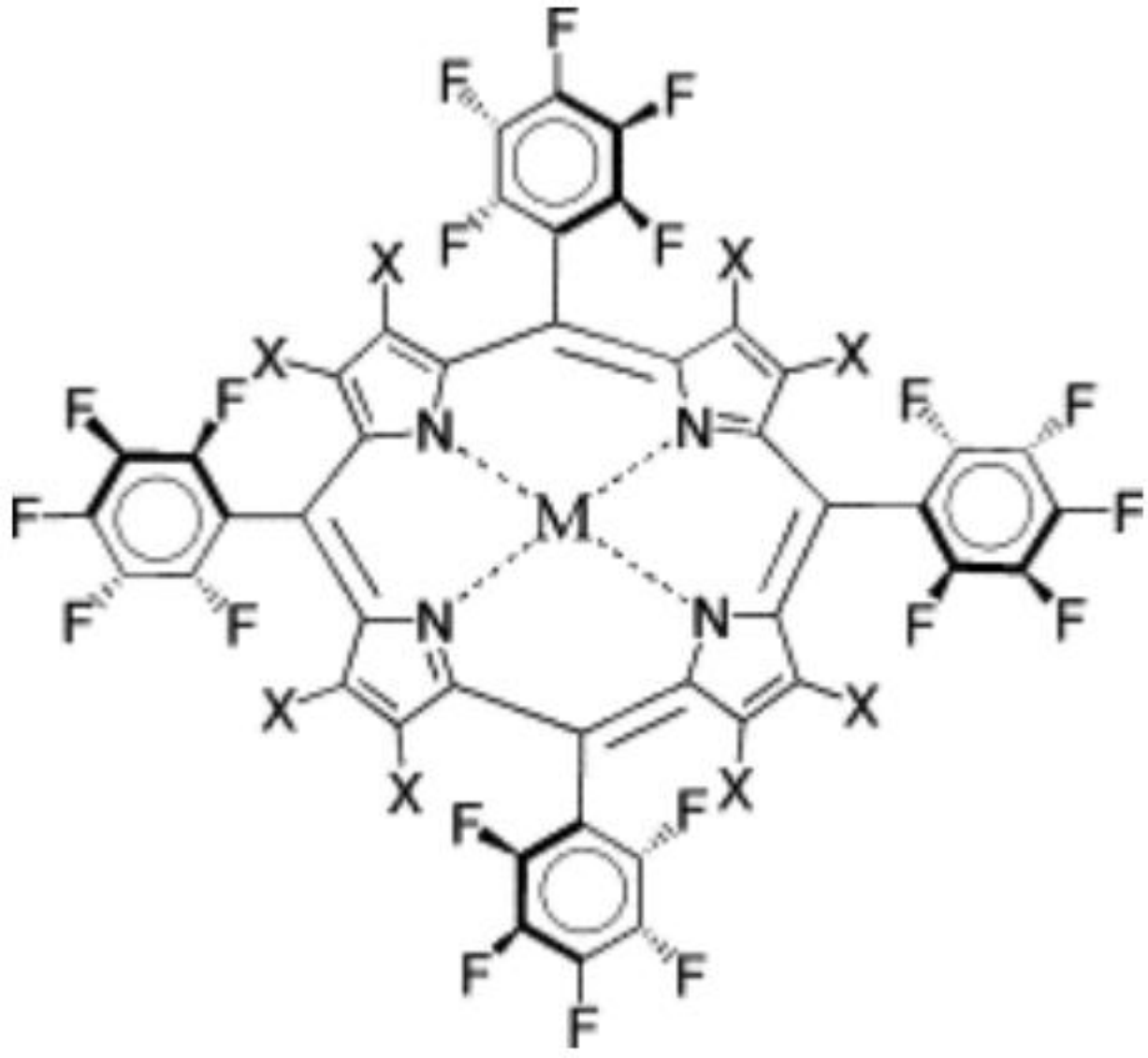


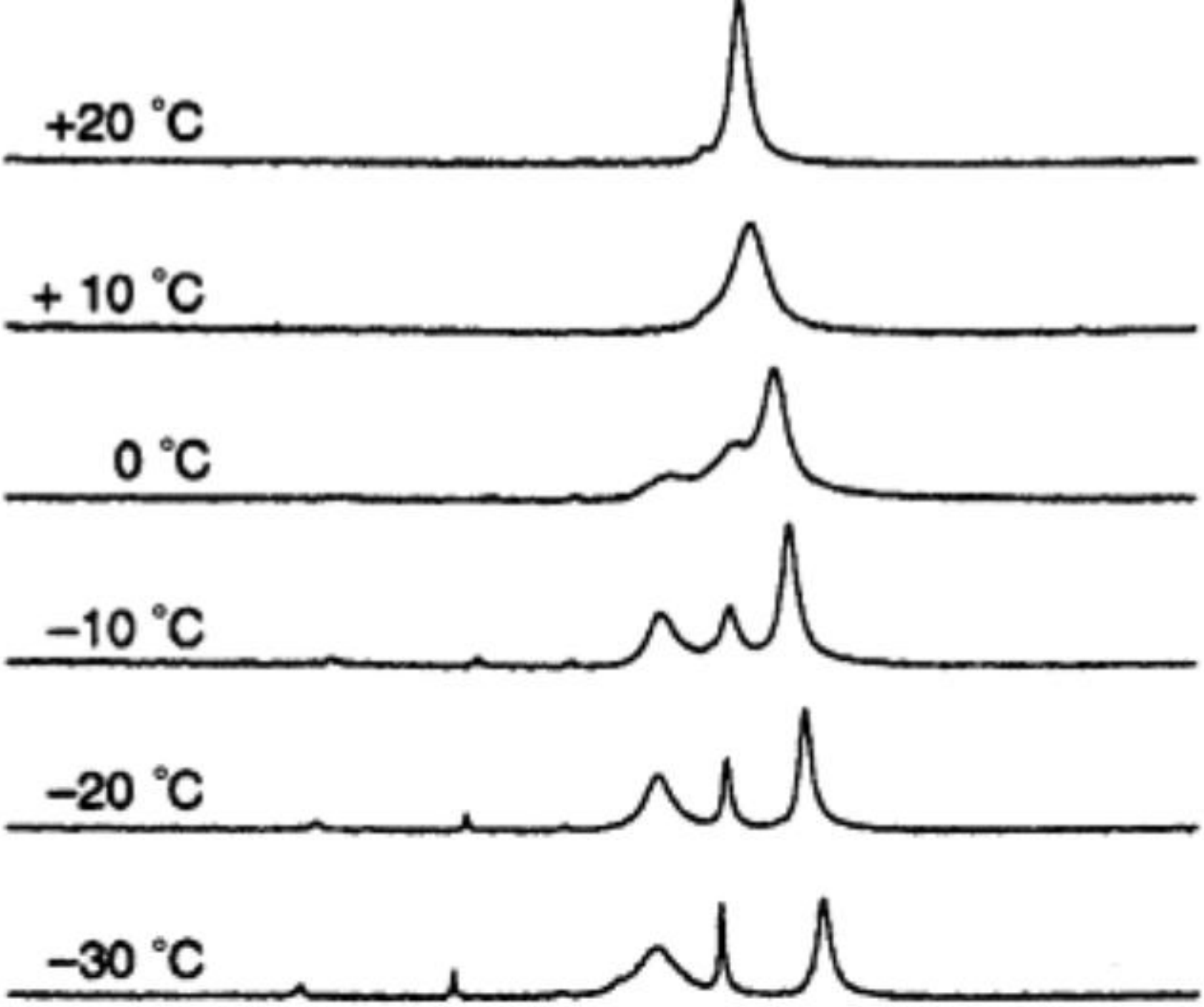
1. Download: Download full-size image


COORDINATION
CHEMISTRY REVIEWS

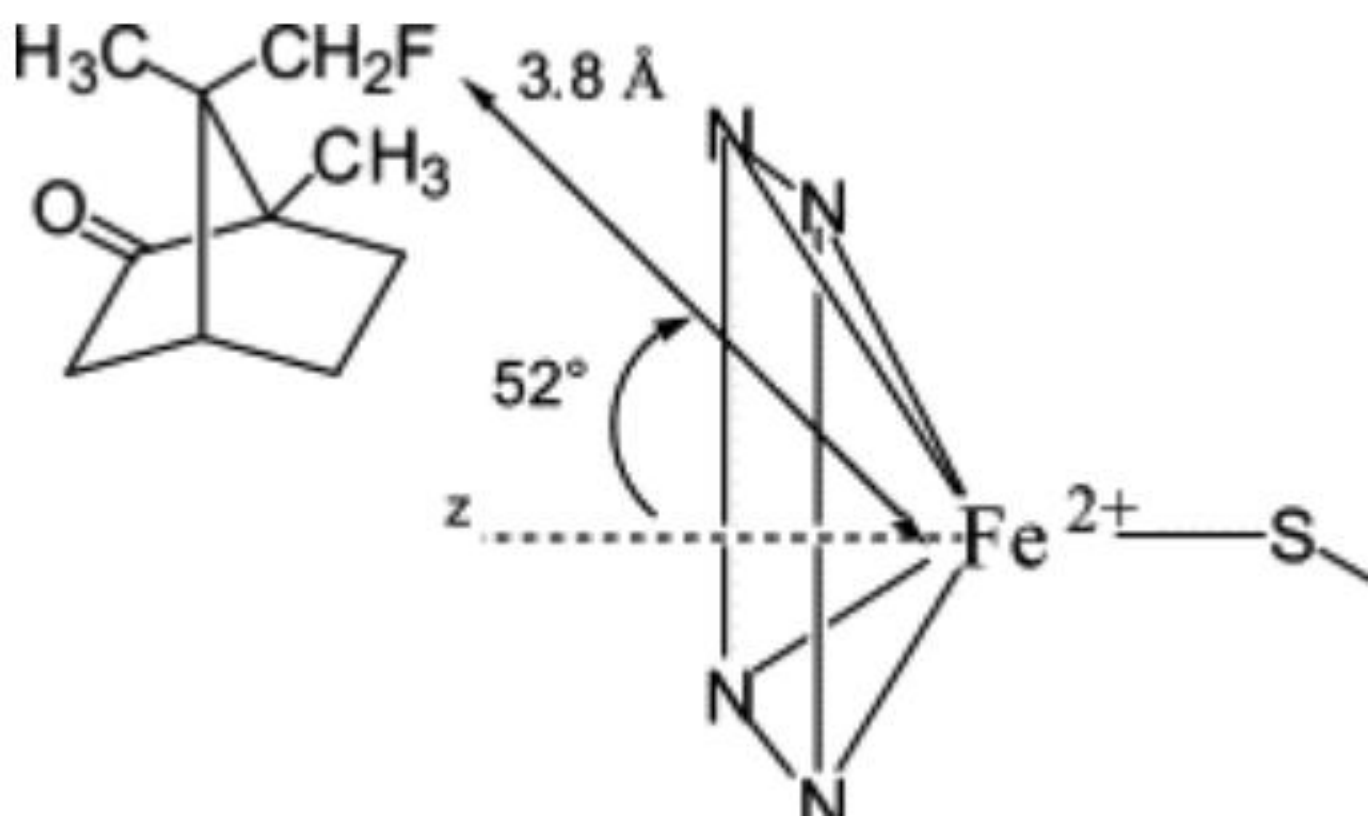
View details


(a)
Gly
(His)
(His)
(Cys)
Cu^{2+}
S
CH_3
(Met)
(b)
His
OH_2
Cu^{2+}
Zn^{2+}
(His)
Asp
(c)
(Tyr)
(His)
OH
Cu^{2+}
(Tyr)
L
(Cys)
(d)
(e)
(His)
Cu^{2+}
X
(e)
peptide chain
3.8 Å
3.7 Å
3.7 Å
HO
OH
S
Met
Type 1
Type 2
Type 3

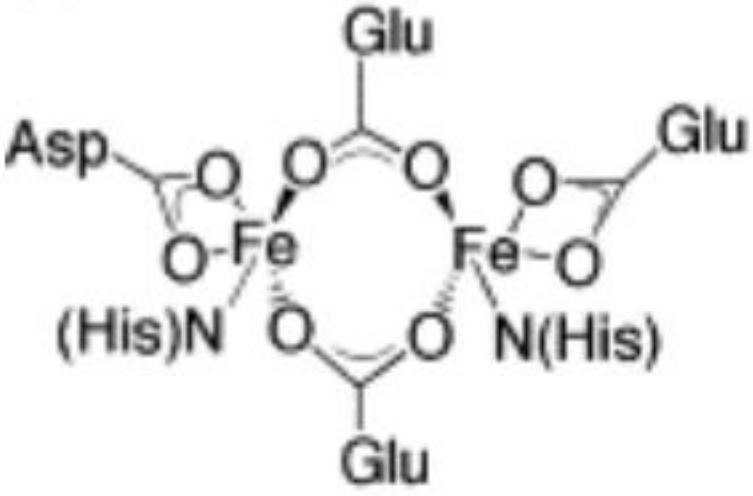

F
F
F
F
F
F
X
X
X
X
F
F
F
F
F
F
F
F
N
N
M
N
N
X
X
X
X
F
F
F
F
F
F
F
F
F
F



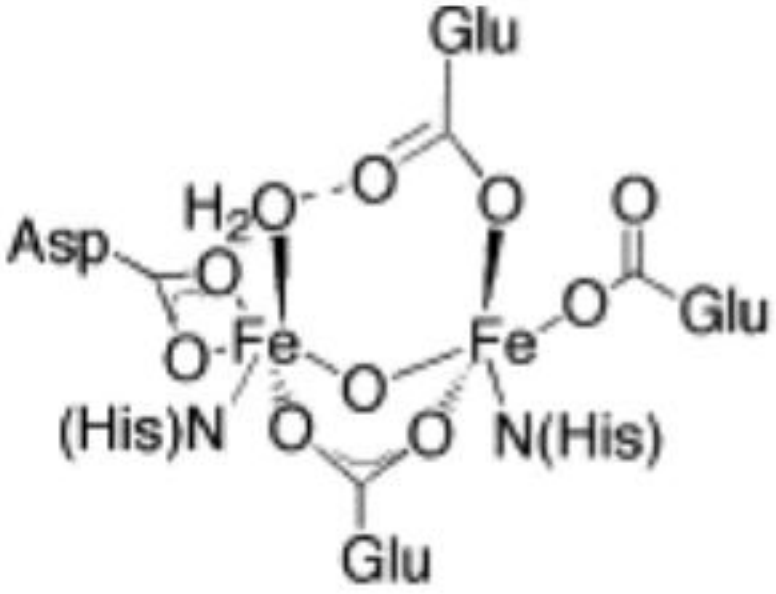
1. Download: Download full-size image


H3C
CH2F
CH3
O
3.8 Å
52°
z
N
N
N
N
Fe 2+
S

(a)

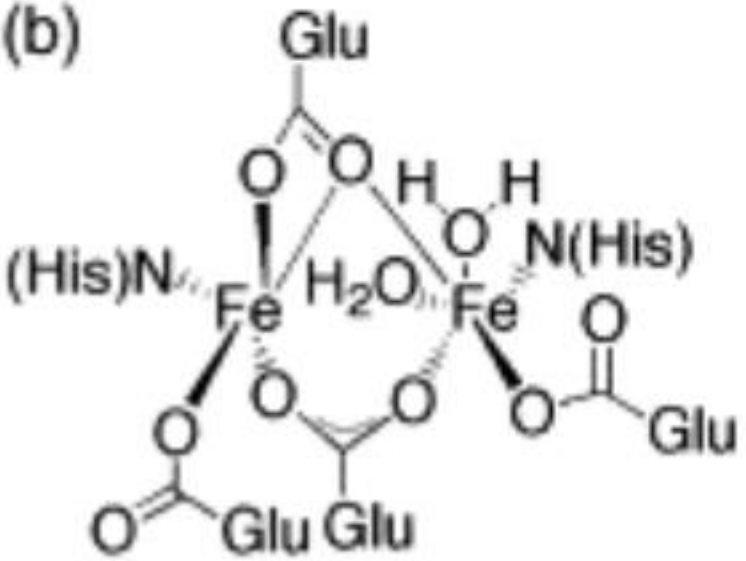


$R2_{red}$

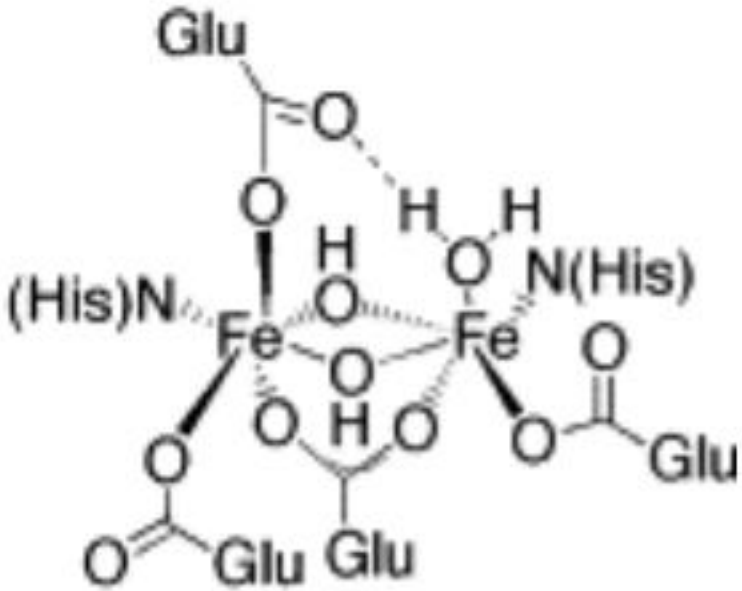


$R2_{ox}$

(b)

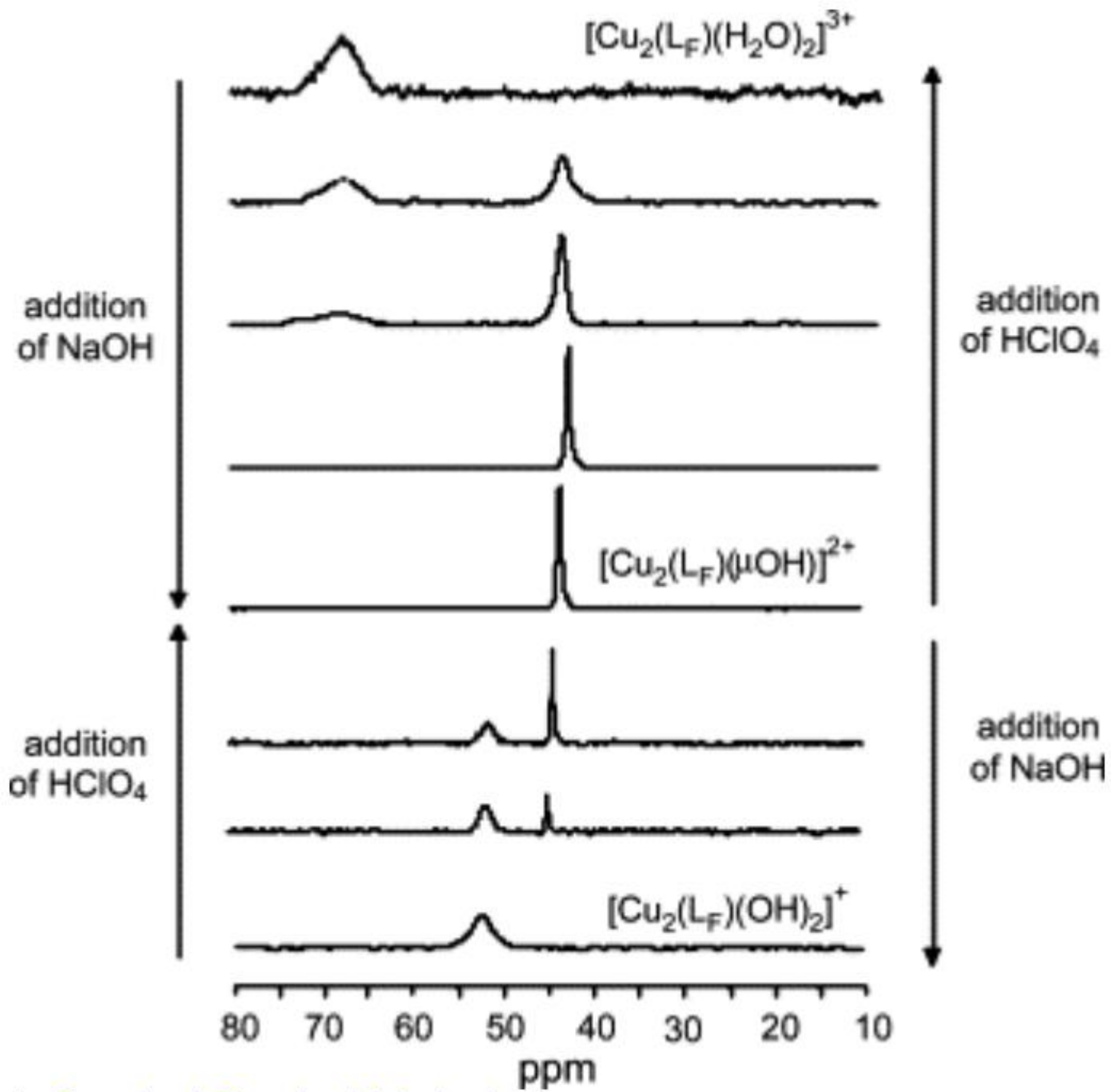


MMO_{red}



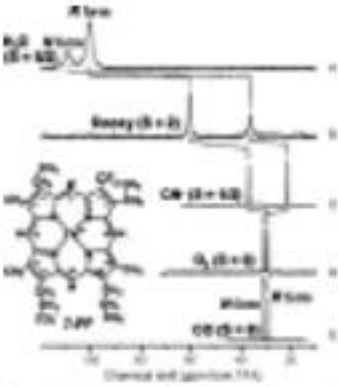
MMO_{ox}

View details



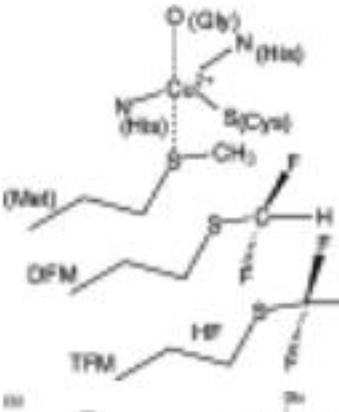
1. Download: Download full-size image

1.

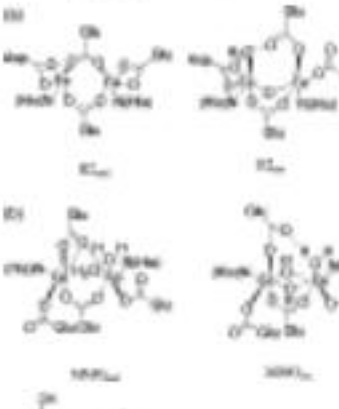


2.

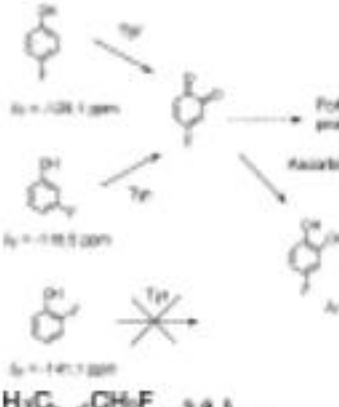
3.



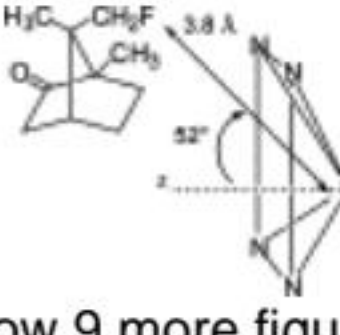
4.



5.

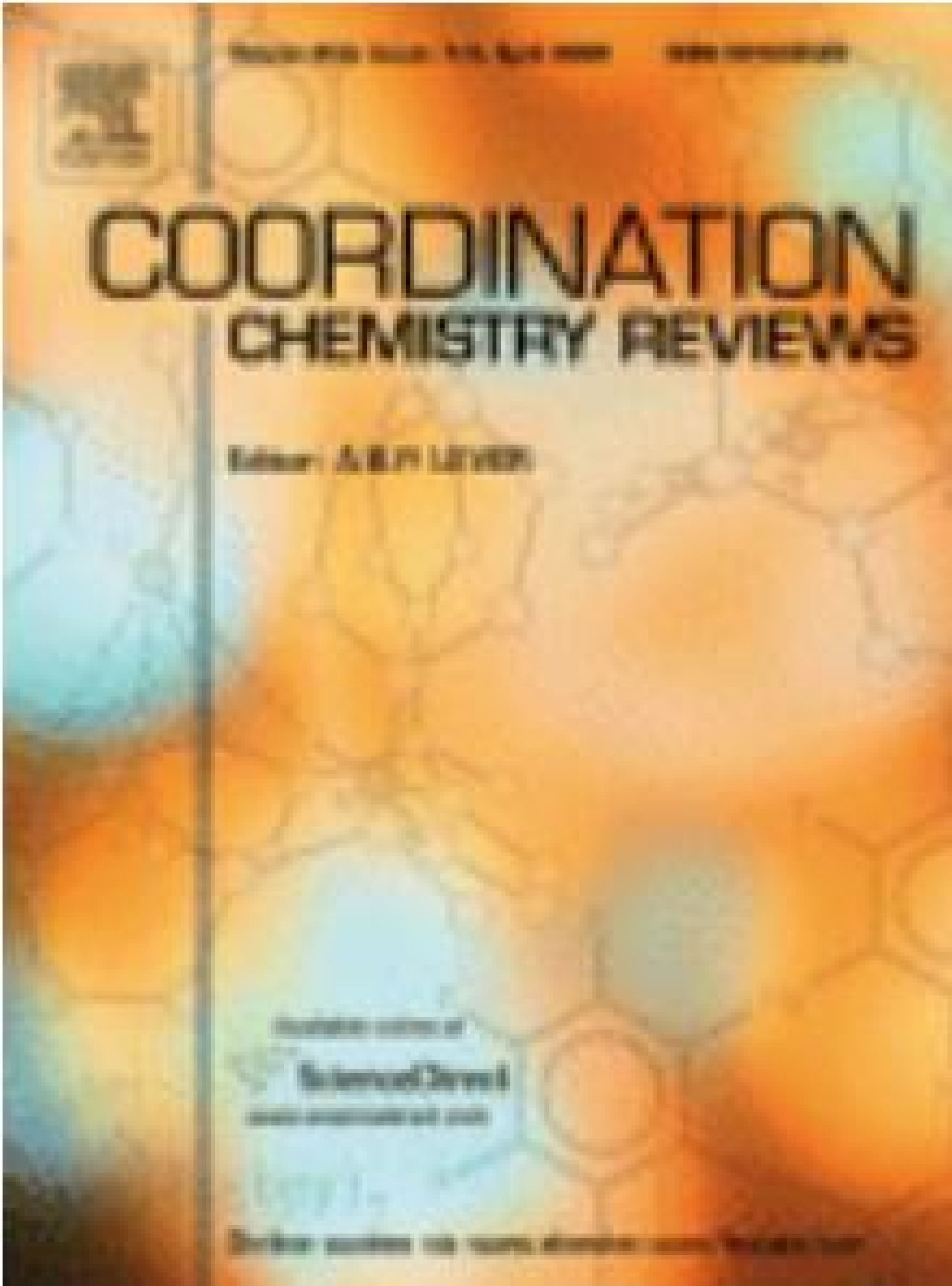


6.

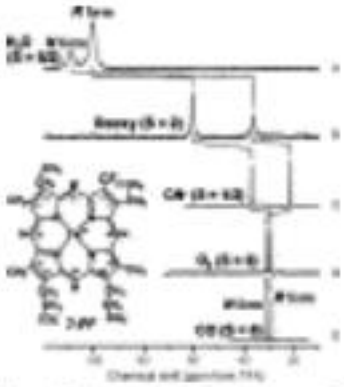


Show 9 more figures


(NON SOLUS

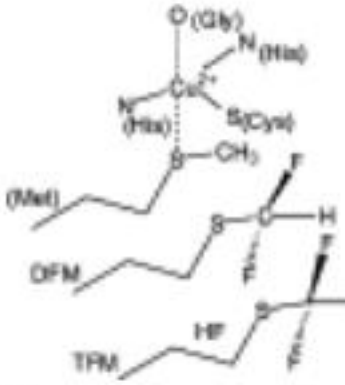

COORDINATION
CHEMISTRY REVIEWS

1.

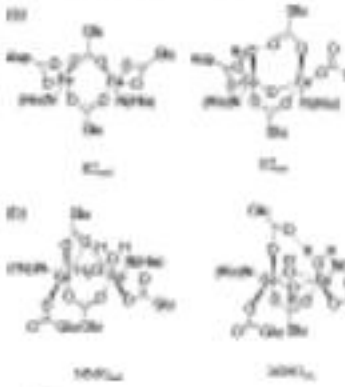


2.

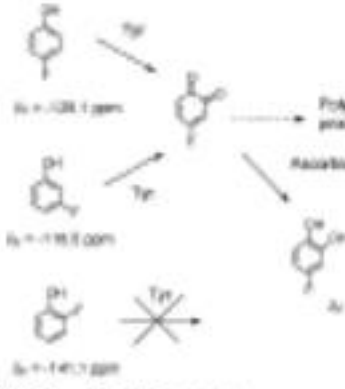
3.


O (Gly)
N (His)
Cu2+
N (His)
S(Cys)
S
CH3
(Met)
S
C
H
F
F
F
OFM
HF
F
TRM

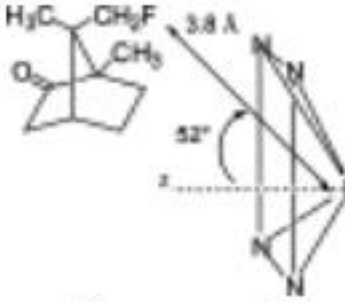
4.

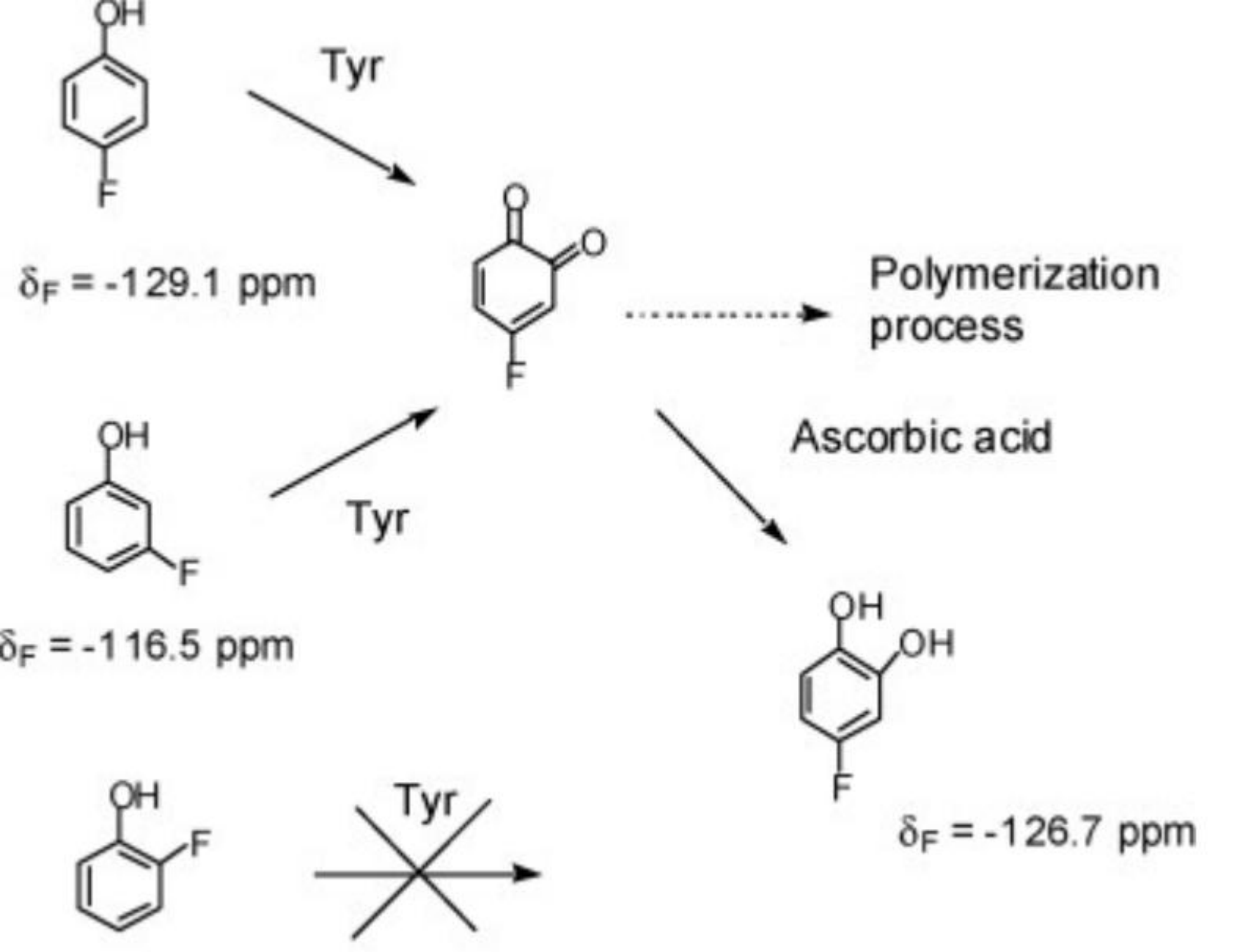


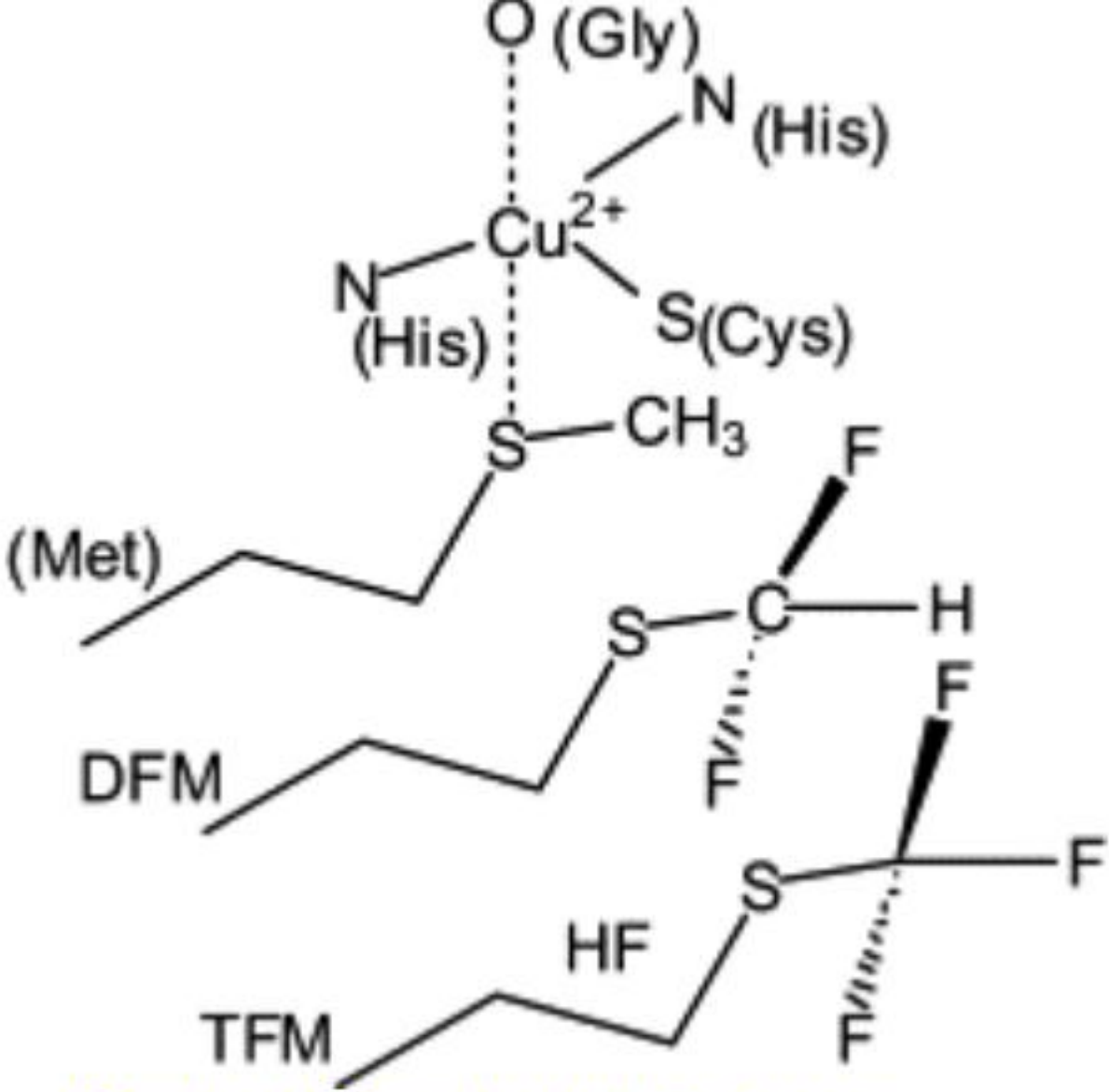
5.


Polymerization process
Ascorbic acid

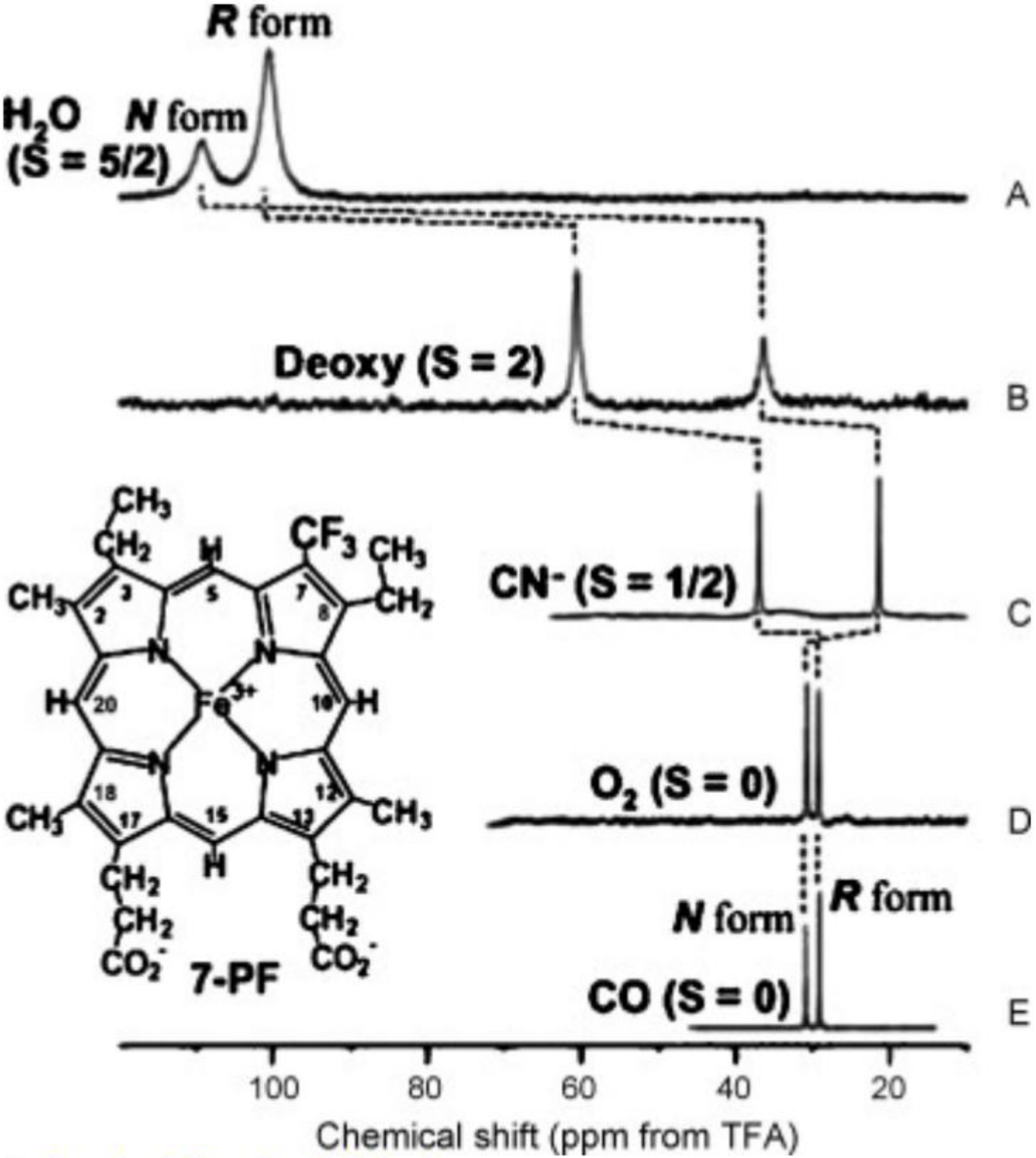
6.


H3C
CH2F
CH3
O
3.8 Å
N
N
52°
z
Fe2+
S
N
N

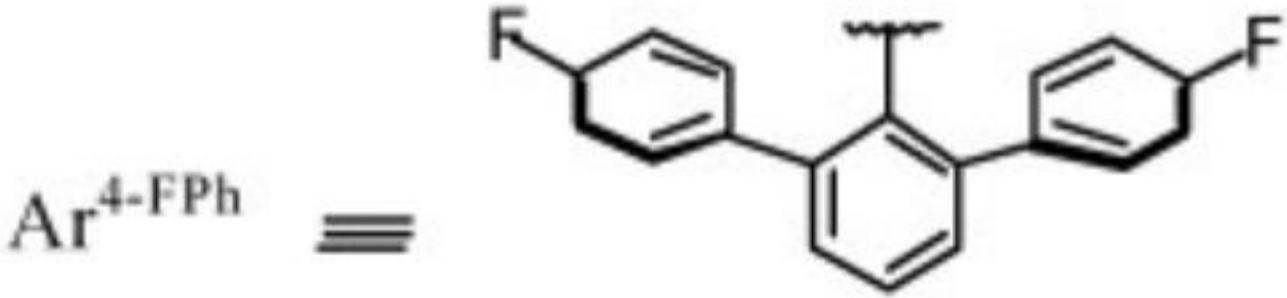

OH
F
Tyr
δ_F = -129.1 ppm
O
O
F
Polymerization process
OH
F
Tyr
Ascorbic acid
δ_F = -116.5 ppm
OH
OH
F
δ_F = -126.7 ppm
OH
F
Tyr

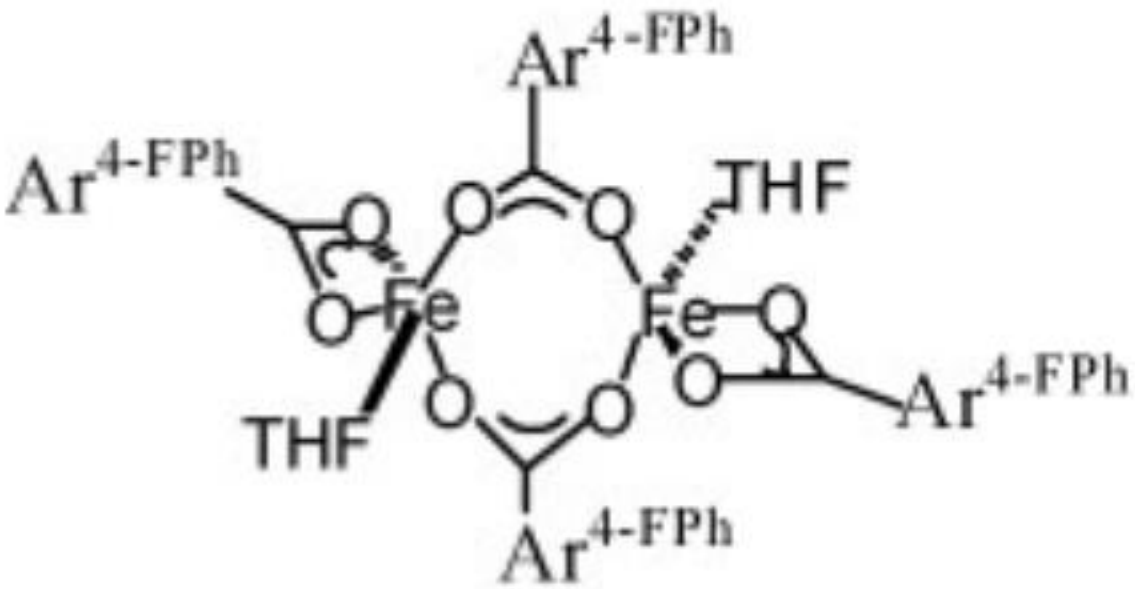


1. Download: Download full-size image

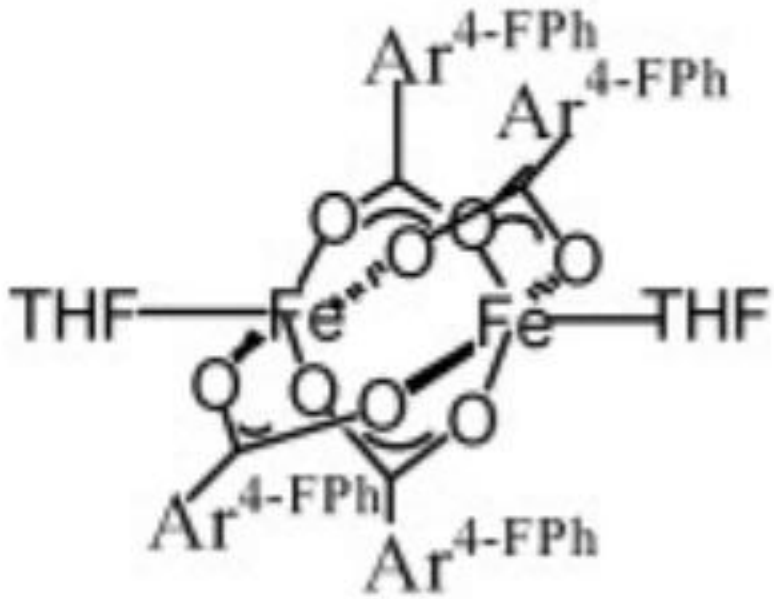

R form
H2O
N form
(S = 5/2)
A
Deoxy (S = 2)
B
CN- (S = 1/2)
C
O2 (S = 0)
D
N form
R form
CO (S = 0)
E
7-PF
100
80
60
40
20
Chemical shift (ppm from TFA)

ELSEVIER

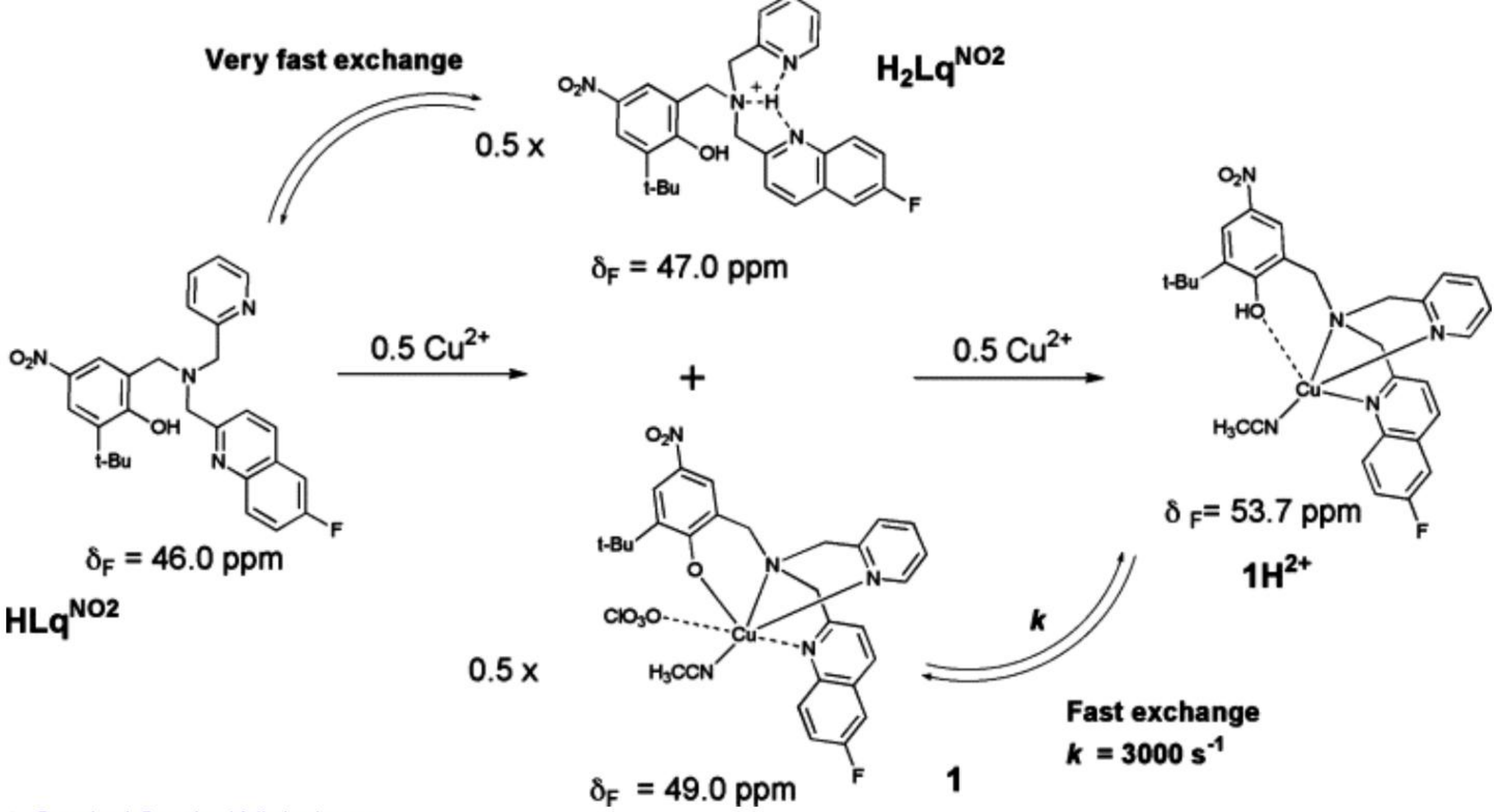

Ar4-FPh
F
F


Ar4-FPh
Ar4-FPh
THF
Fe
Fe
THF
Ar4-FPh
Ar4-FPh

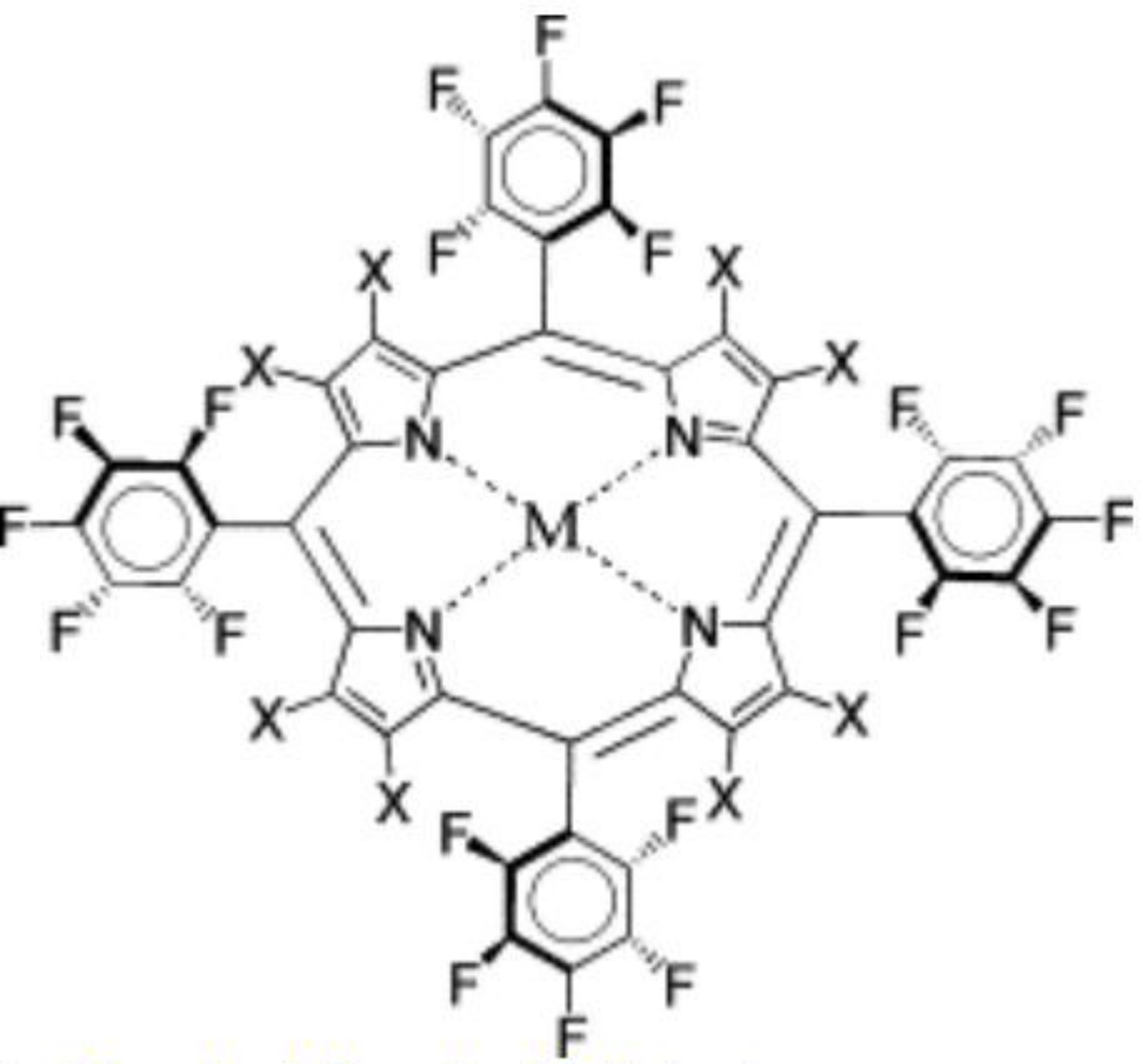
I


Ar4-FPh
Ar4-FPh
THF
Fe
Fe
THF
Ar4-FPh
Ar4-FPh

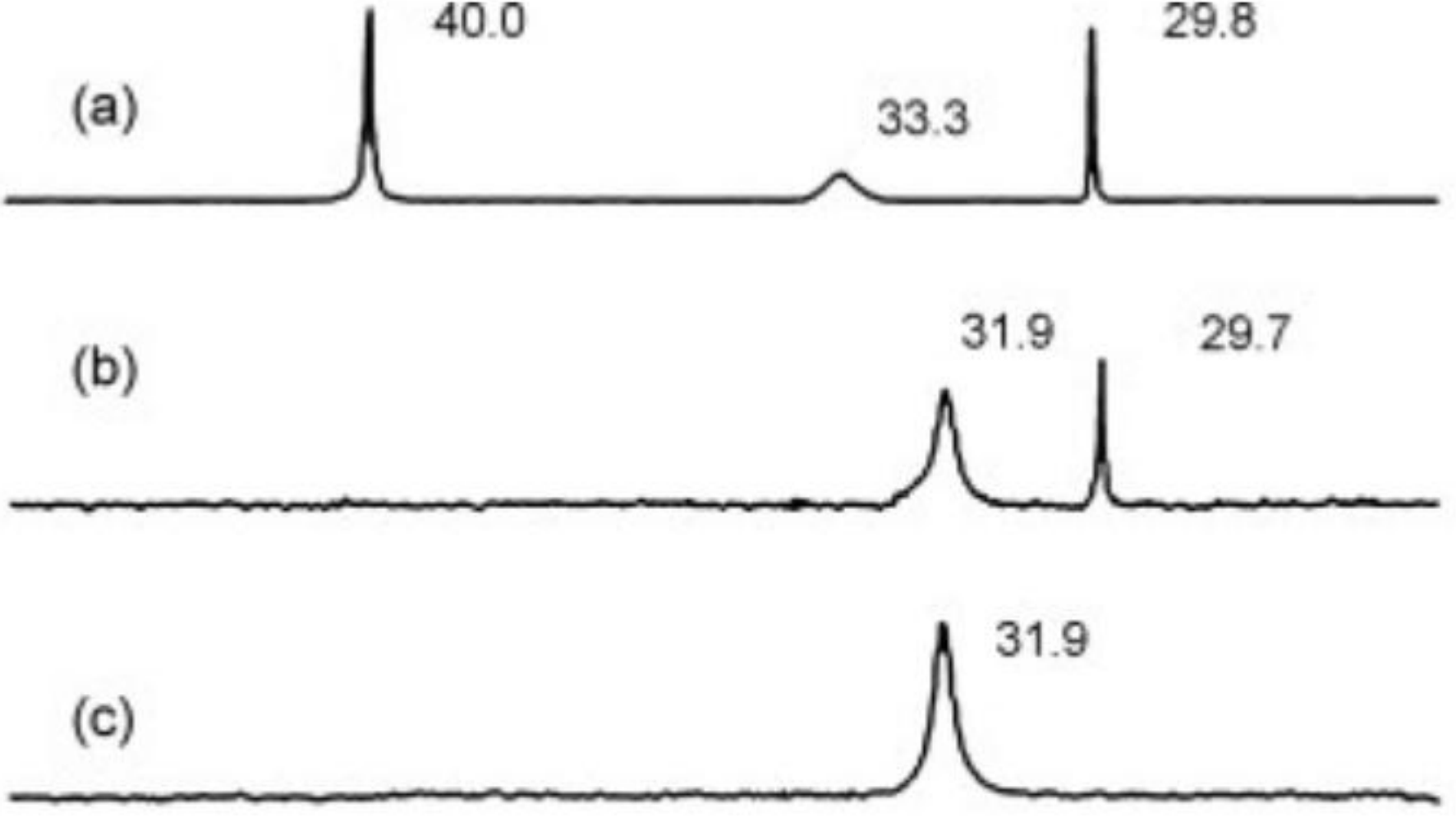
II



1 Download: Download full-size image

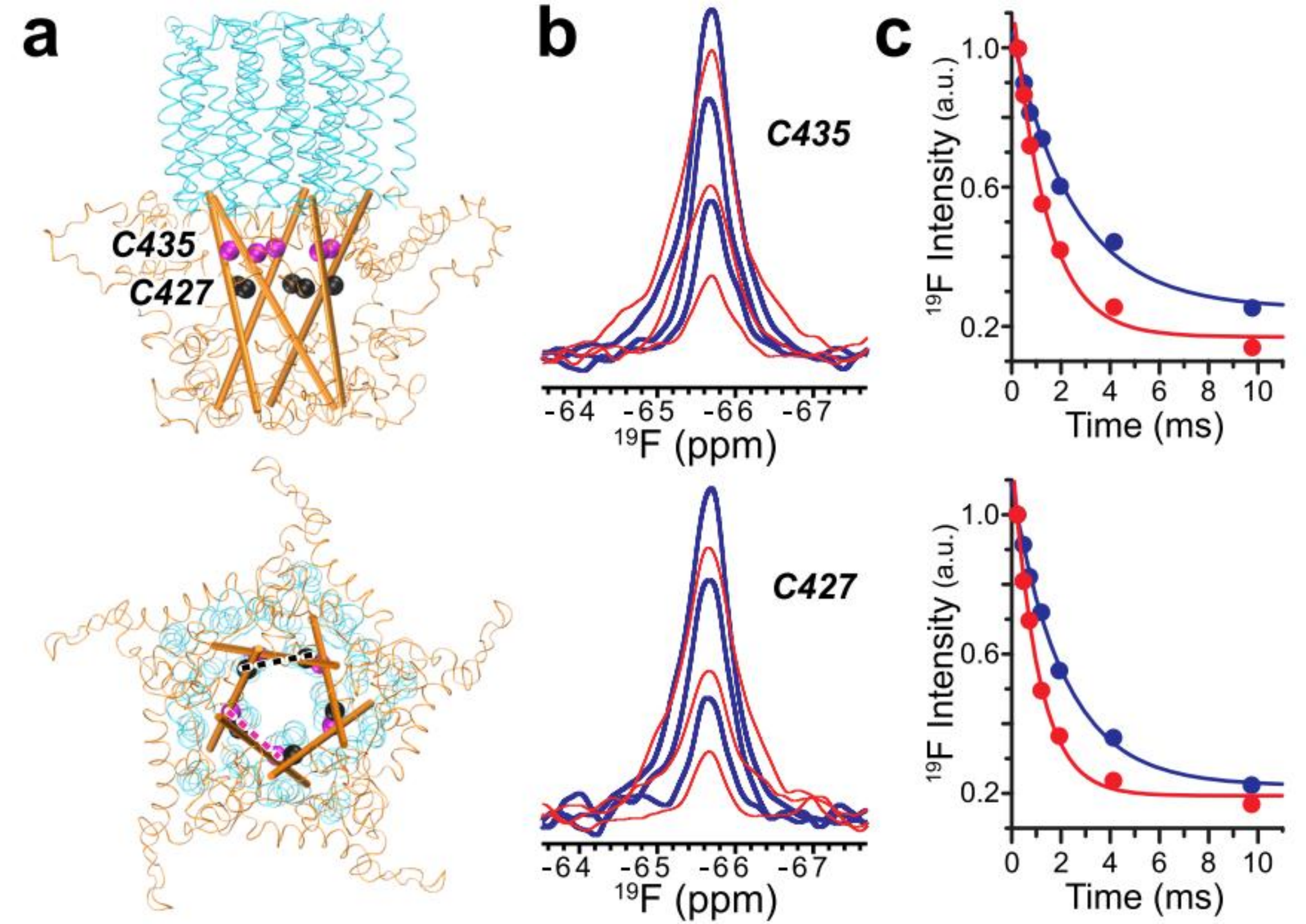


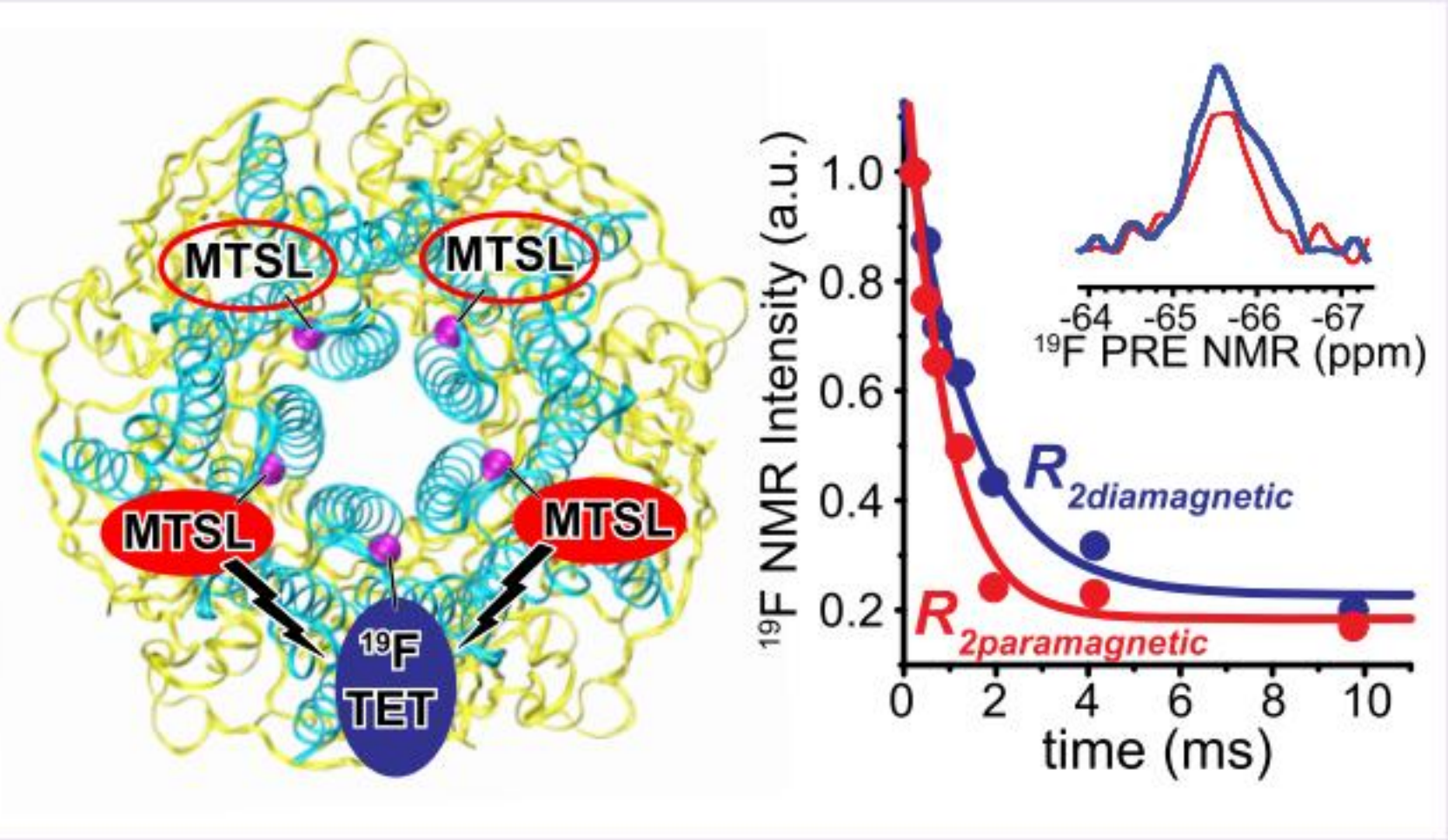
1 Download: Download full-size image


40.0
29.8
(a)
33.3
31.9
29.7
(b)
31.9
(c)

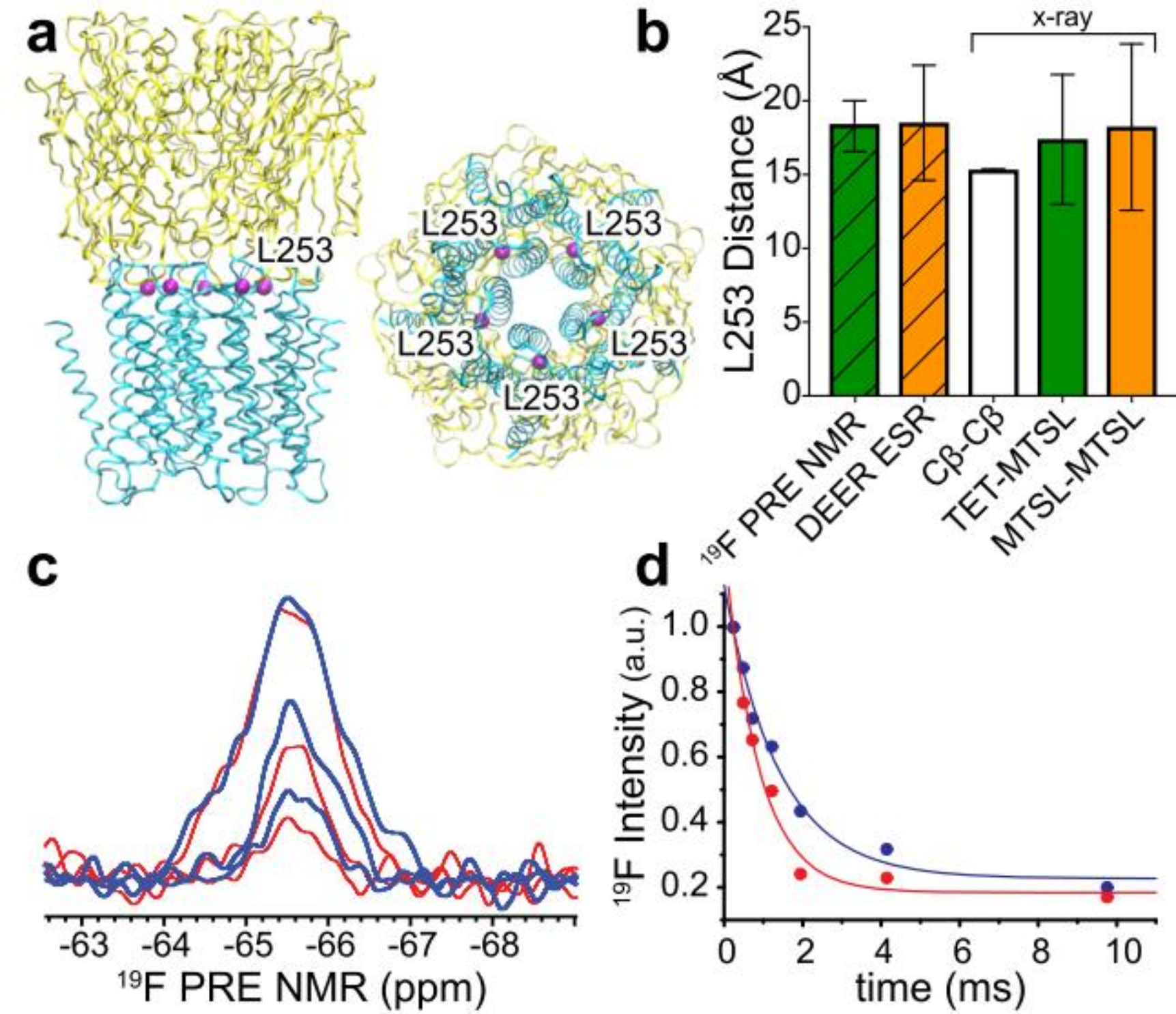

A
C


ACS
chemical
biology


a
C435
C427
b
C435
-64
-65
-66
-67
19F (ppm)
C427
-64
-65
-66
-67
19F (ppm)
c
19F Intensity (a.u.)
1.0
0.6
0.2
0
2
4
6
8
10
Time (ms)
19F Intensity (a.u.)
1.0
0.6
0.2
0
2
4
6
8
10
Time (ms)

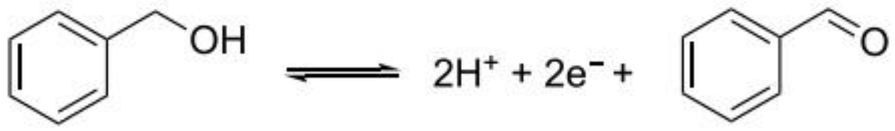


ory structures


a
L253
L253
L253
L253
L253
L253
b
x-ray
L253 Distance (Å)
25
20
15
10
5
0
^{19}F PRE NMR
DEER ESR
Cβ-Cβ
TET-MTSL
MTSL-MTSL
c
-63
-64
-65
-66
-67
-68
^{19}F PRE NMR (ppm)
d
^{19}F Intensity (a.u.)
1.0
0.8
0.6
0.4
0.2
0
2
4
6
8
10
time (ms)

ACS Publications

(A) From Free Energy to Potential



$\Delta G°_f$ (kcal mol^{-1}): −5.01 $\Delta G°_f$ (kcal mol^{-1}): +1.59

$\Delta G°_{rxn}$ = +6.6 (kcal mol^{-1}) → $\Delta G° = -nF\Delta E°$ → $\Delta E°_{rxn}$ (V): −0.14

n = 2 e$^-$, *F* = 96,485 C mol^{-1}, 1 kcal mol^{-1} = 4.184 kJ mol^{-1}

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

Alcohol Oxidation

a.	EtOH ⇌ acetaldehyde + 2 H$^+$ + 2 e$^-$	0.28
b.	EtOH + H_2O ⇌ acetic acid + 4 H$^+$ + 4 e$^-$	0.06
c.	acetaldehyde + H_2O ⇌ acetic acid + 2 H$^+$ + 2 e$^-$	−0.16
d.	iPrOH ⇌ acetone + 2 H$^+$ + 2 e$^-$	0.12
e.	BnOH ⇌ PhCHO + 2 H$^+$ + 2 e$^-$	0.14

Alkene Oxidation

f.	propene + H_2O ⇌ acetone + 2 H$^+$ + 2 e$^-$	0.09
g.	propene + H_2O ⇌ propanal + 2 H$^+$ + 2 e$^-$	0.23
h.	ethylene + H_2O ⇌ acetaldehyde + 2 H$^+$ + 2 e$^-$	0.26
i.	ethylene + 2 H_2O ⇌ ethylene glycol + 2 H$^+$ + 2 e$^-$	0.40
j.	propene + H_2O ⇌ propylene oxide + 2 H$^+$ + 2 e$^-$	0.76

sp^3 C–H Oxidation

k.	propane ⇌ propene + 2 H$^+$ + 2 e$^-$	0.45
l.	pyrrolidine + H_2O ⇌ γ-lactam + 4 H$^+$ + 4 e$^-$	0.02
m.	CH_4 + H_2O ⇌ methanol + 2 H$^+$ + 2 e$^-$	0.63
n.	CH_4 + 2 H_2O ⇌ CO_2 + 8 H$^+$ + 8 e$^-$	0.17
o.	toluene + H_2O ⇌ BnOH + 2 H$^+$ + 2 e$^-$	0.53

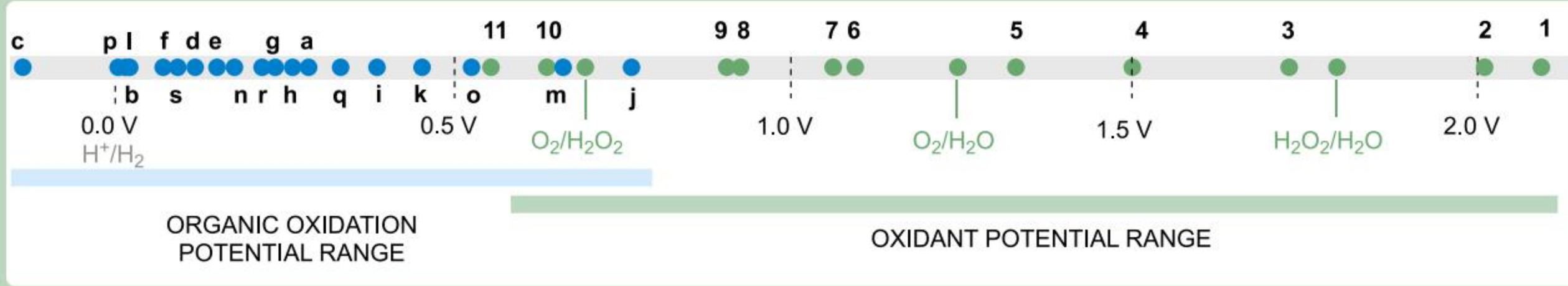
Arene C–H Oxidation

p.	2 benzene ⇌ biphenyl + 2 H$^+$ + 2 e$^-$	0.01
q.	benzene + H_2O ⇌ phenol + 2 H$^+$ + 2 e$^-$	0.32
r.	benzene + NH_3 ⇌ aniline + 2 H$^+$ + 2 e$^-$	0.21
s.	benzene + acetamide ⇌ acetanilide + 2 H$^+$ + 2 e$^-$	0.10

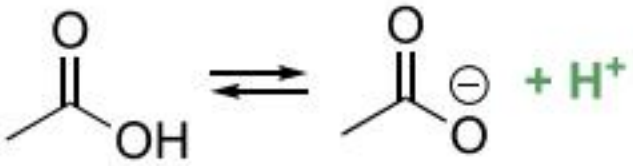
(C) Synthetically Relevant Oxidants $\Delta E°$ (V vs SHE)

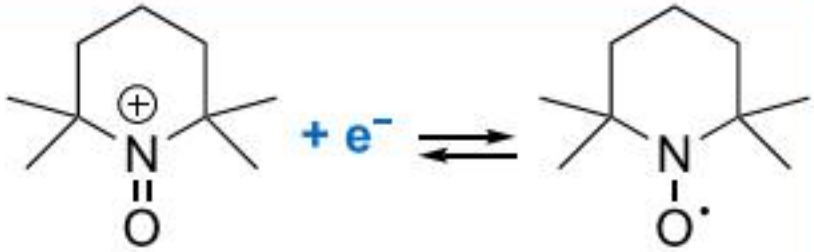
SHE:	2 H$^+$ + 2 e$^-$ ⇌ H_2	0.00
	O_2 + 4 H$^+$ + 4 e$^-$ ⇌ 2 H_2O	1.23
	O_2 + 2 H$^+$ + 2 e$^-$ ⇌ H_2O_2	0.68
	H_2O_2 + 2 H$^+$ + 2 e$^-$ ⇌ 2 H_2O	1.78
1.	O_3 + 2 H$^+$ + 2 e$^-$ ⇌ O_2 + H_2O	2.08
2.	$S_2O_8^{2-}$ + 2 e$^-$ ⇌ 2 SO_4^{2-}	2.01
3.	TBHP + 2 e$^-$ + 2 H$^+$ ⇌ ^{t}BuOH + H_2O	~1.7
4.	MnO_4^- + 8 H$^+$ + 5 e$^-$ ⇌ Mn^{2+} + 4 H_2O	1.51
5.	$Cr_2O_7^{2-}$ + 14 H$^+$ + 6 e$^-$ ⇌ 2 Cr^{3+} + 7 H_2O	1.36
6.	$Br_{2(aq)}$ + 2 e$^-$ ⇌ 2 $Br^-_{(aq)}$	1.09
7.	NO_2 + 2 H$^+$ + 2 e$^-$ ⇌ NO + H_2O	1.05
8.	TEMPO$^+$ + 2 e$^-$ + 2 H$^+$ ⇌ $TEMPOH_2^+$	0.91[a]
9.	DDQ + 2 e$^-$ + 2 H$^+$ ⇌ DDH_2Q	0.89[a]
10.	BQ + 2 H$^+$ + 2 e$^-$ ⇌ H_2Q	0.64[a]
11.	$I_{2(aq)}$ + 2e$^-$ ⇌ 2 $I^-_{(aq)}$	0.54

(D) Potentials for Organic Oxidations and Oxidants



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





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

For $[AcO^-]/[AcOH] = 10$

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

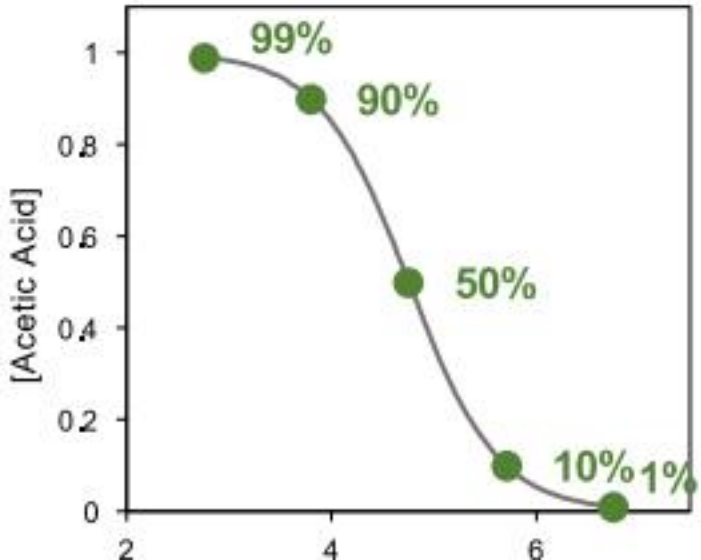
$$\Delta G = \Delta G^\circ + 1.36\ kcal\ mol^{-1}$$

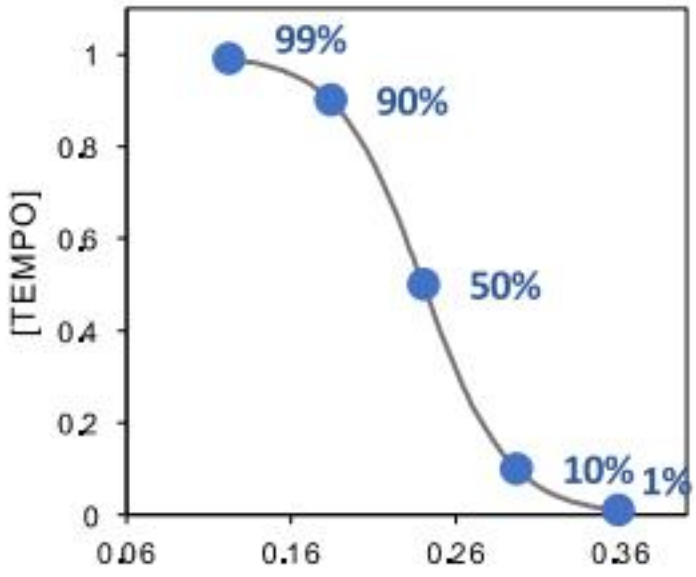
$$\Delta E = \Delta E^\circ - (RT/nF)\ \ln([T]/[T+])$$

for $[T]/[T+] = 10$

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

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



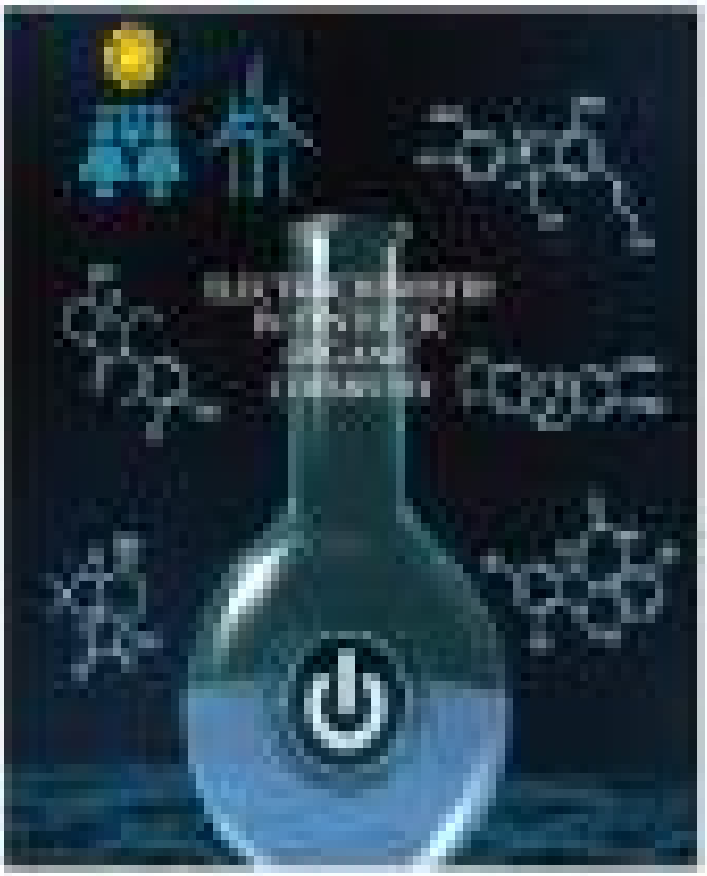


Read Online

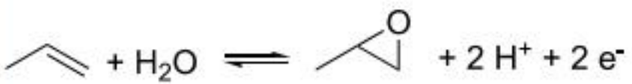
needed to initiate single-electron transfer (SET), but these values are very different from the thermodynamic potentials for net two-electron redox reactions of interest to organic chemists.

ABSTRACT: Redox reactions are ubiquitous in organic synthesis and

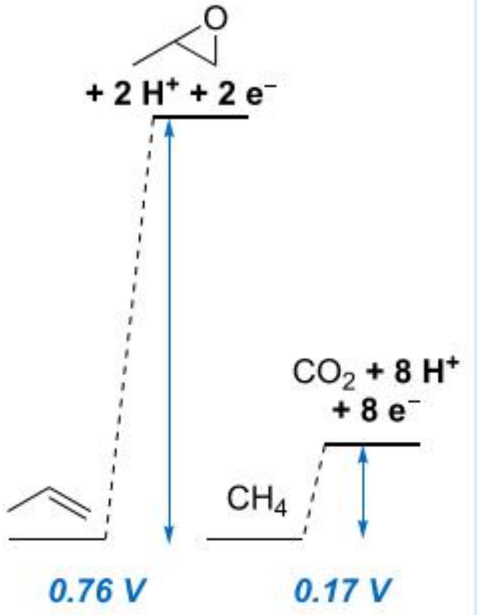
JOC
The Journal of Organic Chemistry



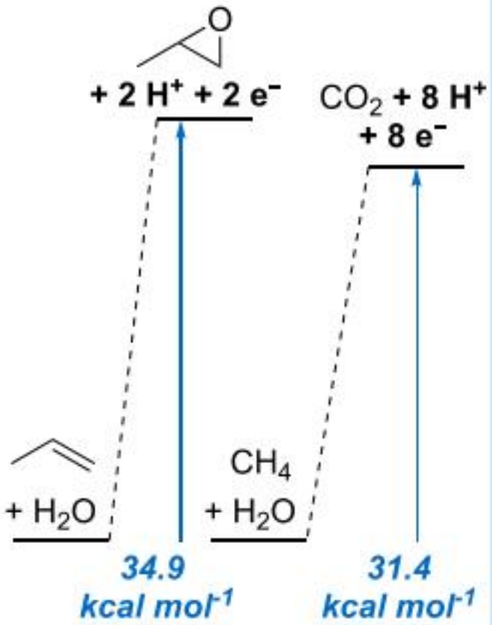
(A) Proplyene Epoxidation vs. Methane Oxidation

	$\Delta G°$ (kcal mol^{-1})	$-\Delta E°$ (V vs. SHE)
	34.9	0.76
$CH_4 + 2\ H_2O \rightleftharpoons CO_2 + 8\ H^+ + 8\ e^-$	31.4	0.17

Standard Potential $\Delta E°$



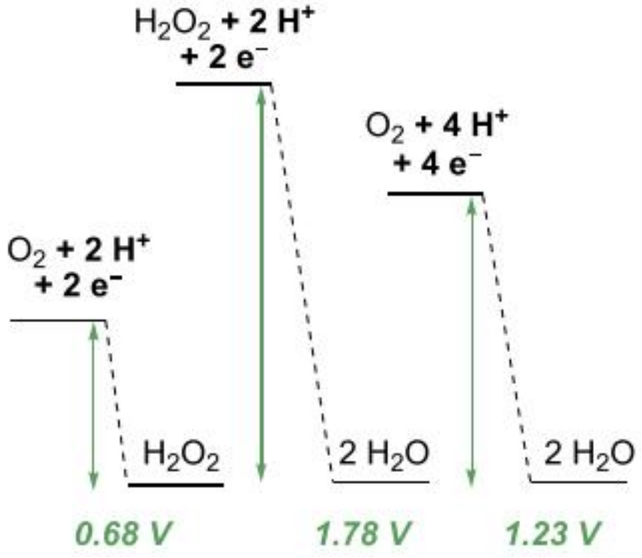
Free Energy $\Delta G°$



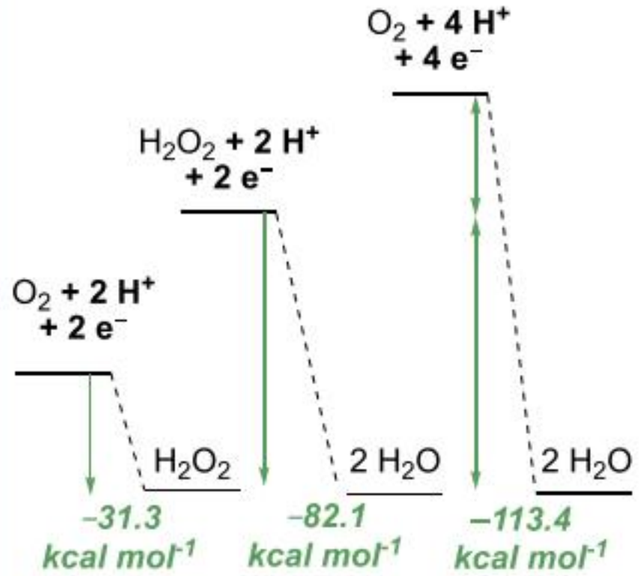
(B) O_2 and H_2O_2 Reduction

	$\Delta G°$ (kcal mol^{-1})	$-\Delta E°$ (V vs. SHE)
$O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons H_2O_2$	−31.3	0.68
$H_2O_2 + 2\ H^+ + 2\ e^- \rightleftharpoons 2\ H_2O$	−82.1	1.78
$O_2 + 4\ H^+ + 4\ e^- \rightleftharpoons 2\ H_2O$	−113.4	1.23

Standard Potential $\Delta E°$



Free Energy $\Delta G°$



(A) Overpotential in Chemical Redox Reactions

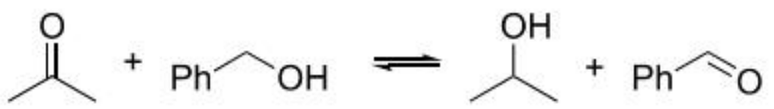
Thermochemistry of Some Alcohol Oxidations

i

$\Delta E°$: 0.0 − 0.14 = **−0.14 V**

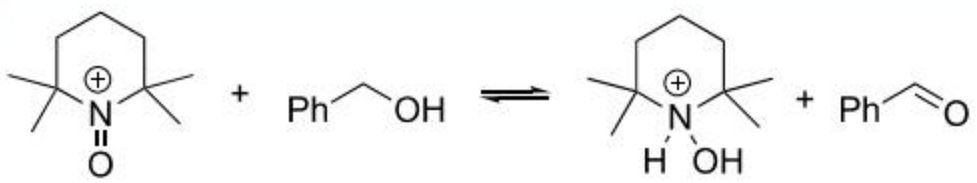
$\Delta G°$: **+6.6 kcal mol^{-1}** K_{eq}: 1.5x10^{-5}

ii



[BnOH] : [Acetone]	RT/nF*ln(Q)	ΔE (mV)	ΔG (kcal mol^{-1})	Yield PhCHO
1:1	0 mV	−25	+1.1	28%
1:2	−9 mV	−16	+0.73	67%
1:10	−30 mV	+5	−0.22	94%
1:100	−59 mV	+34	−1.6	99.3%

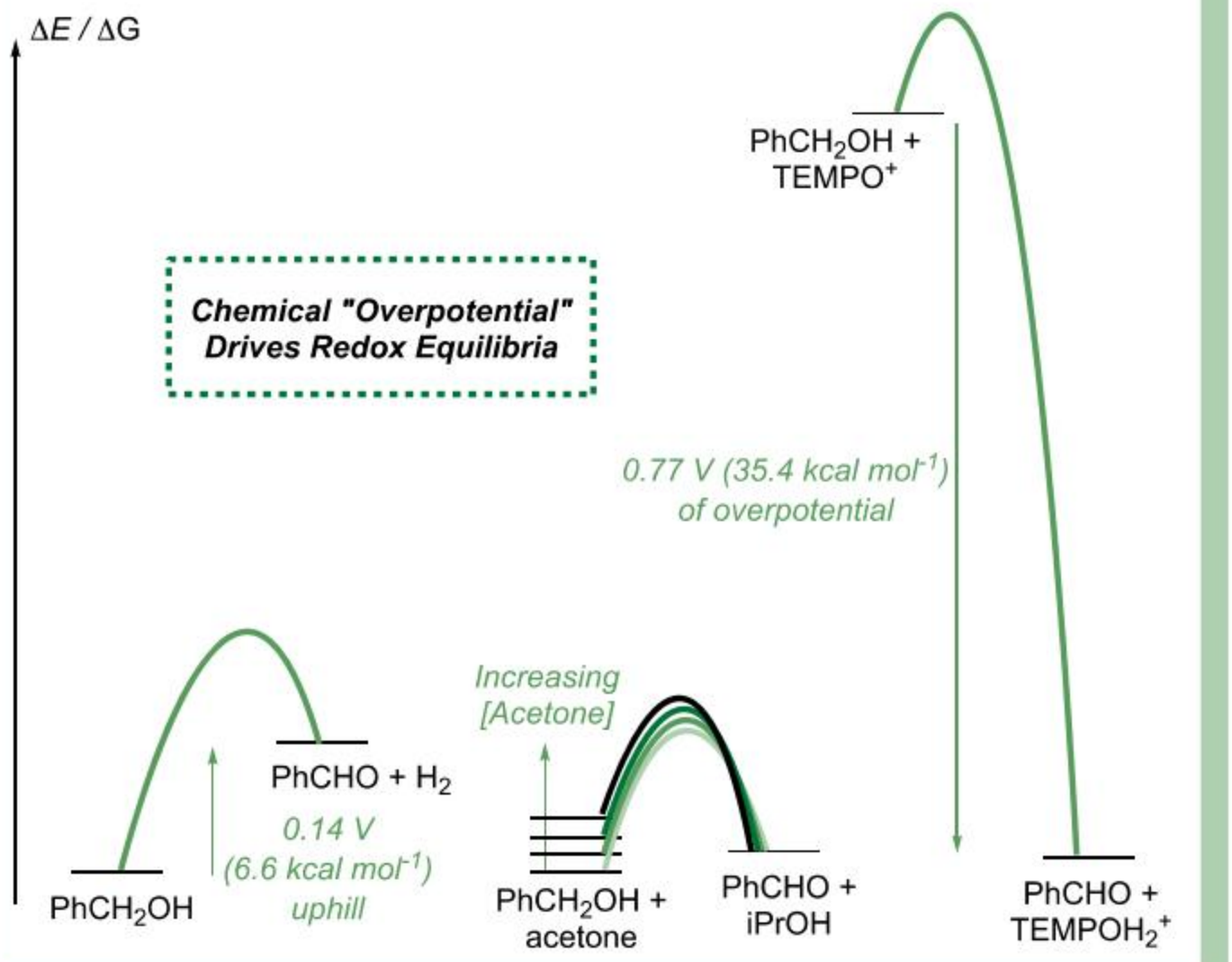
iii



$\Delta E°$: 0.91 − 0.14 = **0.77 V**

$\Delta G°$: **−35.4 kcal mol^{-1}** K_{eq}: 9.1x10^{25}

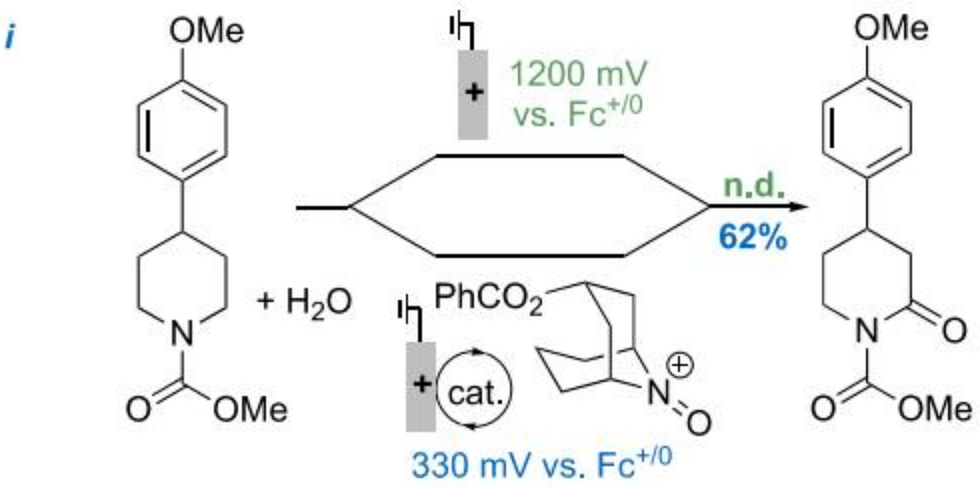
iv *Overpotential and Reaction Coordinates*



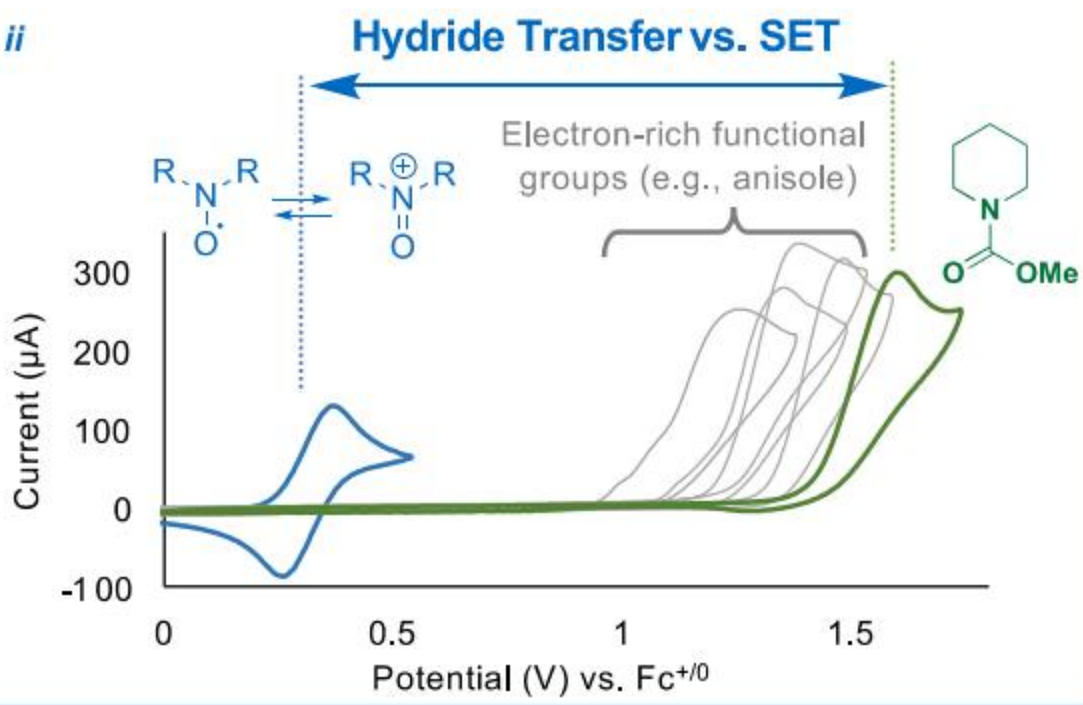
(B) Overpotential in Electrochemical Reactions

Shono-Type Carbamate Oxidation

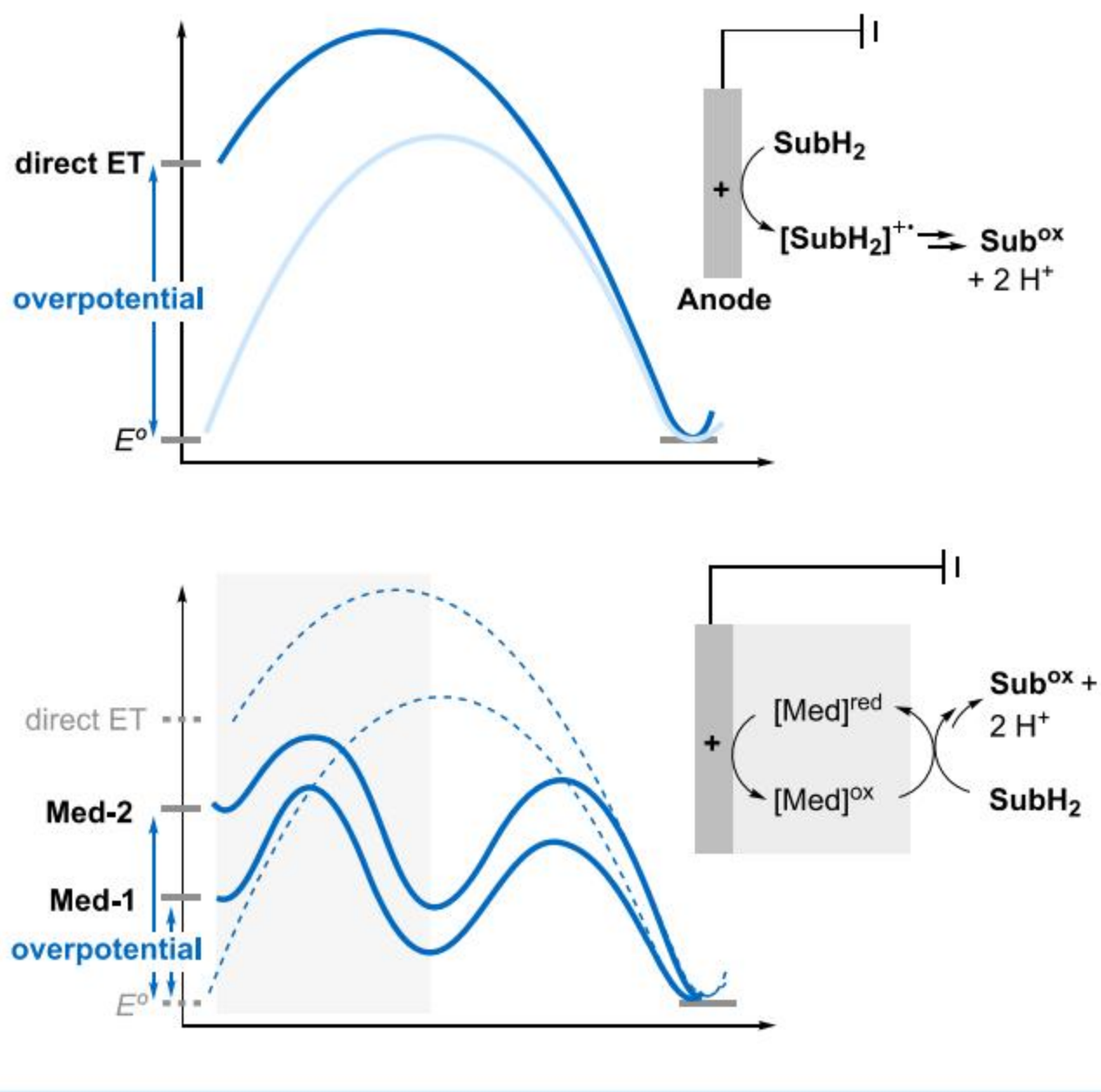
i



ii

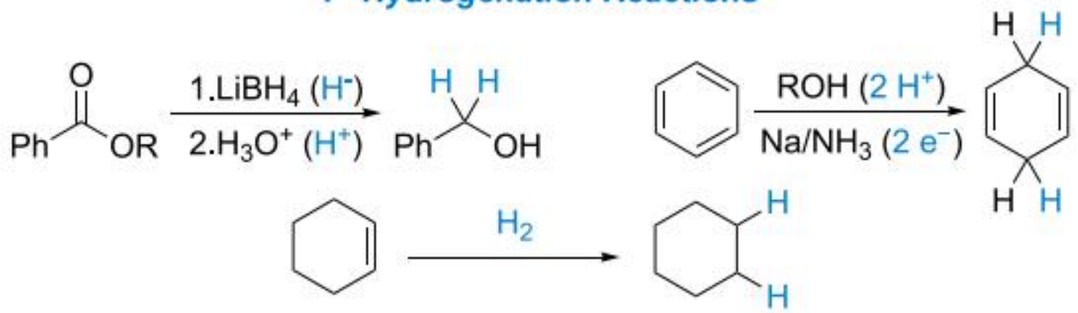


iii *Reaction Coordinates for Electrochemical Redox Reactions*

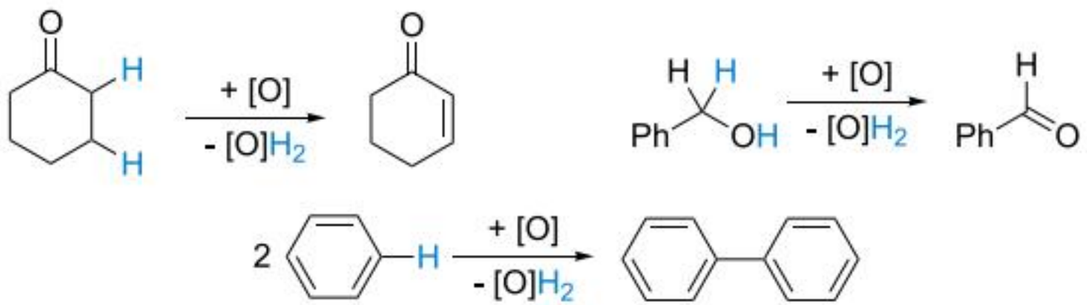


(A) Redox Reactions in Organic Chemistry

i - Hydrogenation Reactions

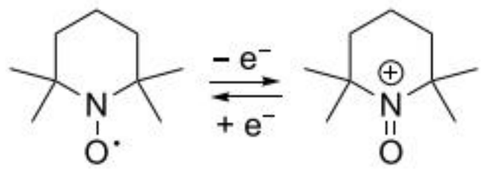


ii - Dehydrogenation Reactions

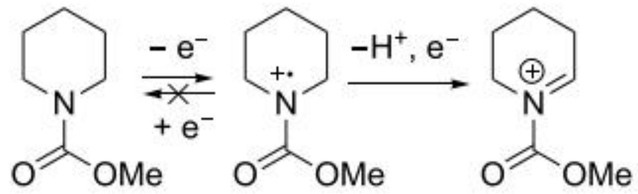


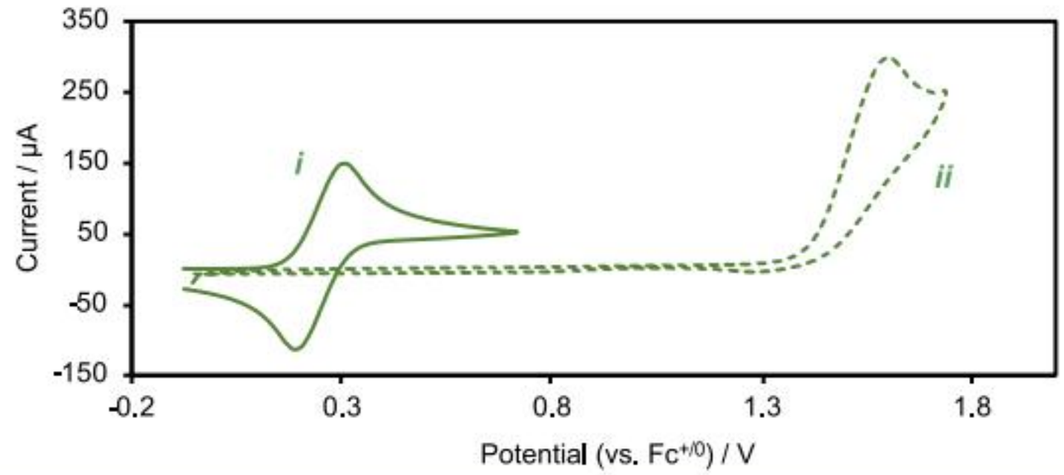
(B) Electron Transfer Reactions and Electrochemical Potentials

i - Reversible ET

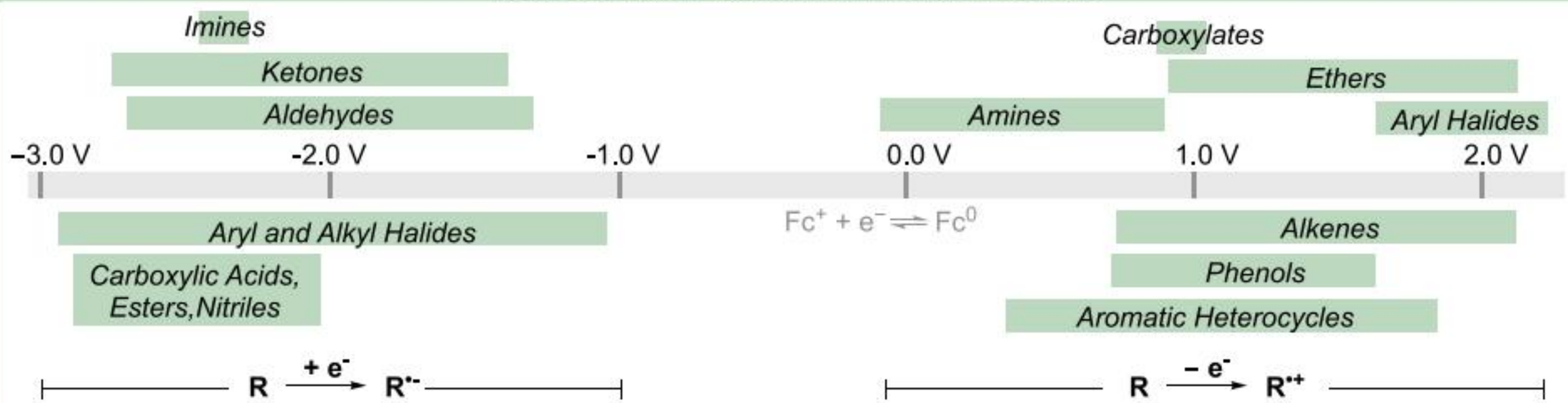


ii - Irreversible ET





(C) Potentials Required for ET at an Electrode



(D) Reference Electrodes

Potential Conversions for Non-aqueous Reference Electrodes