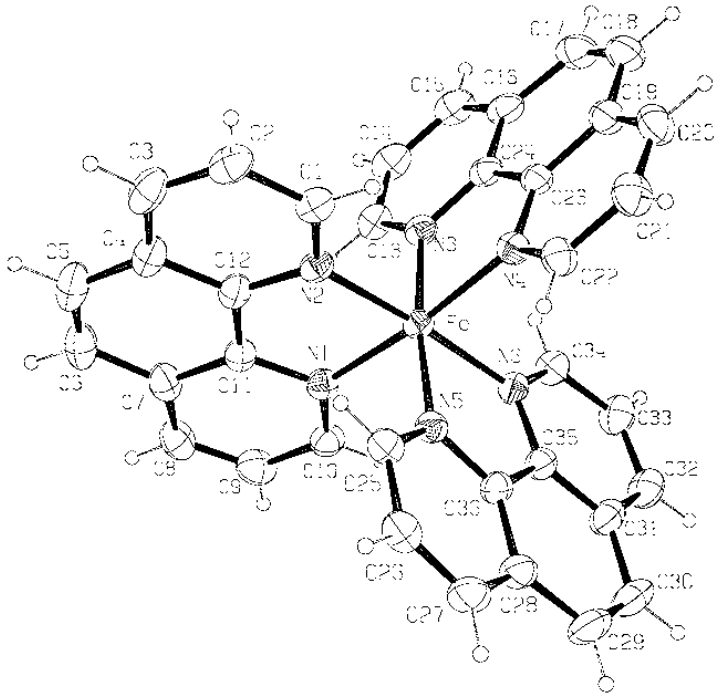
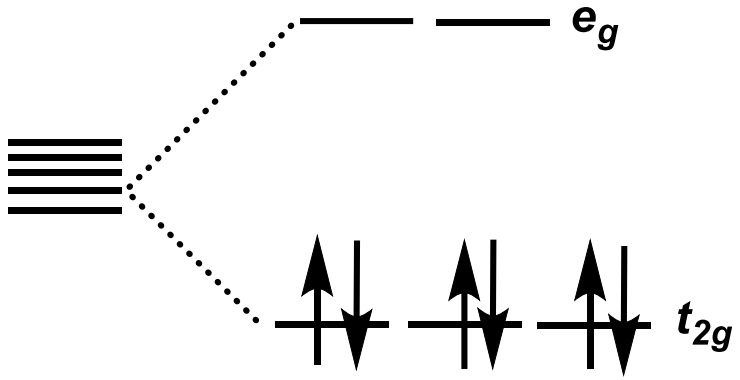
ESPERIENZA 5

Sintesi di complessi ottaedrici omolettici di ferro con leganti bidentati a base di 1,10-fenantrolina



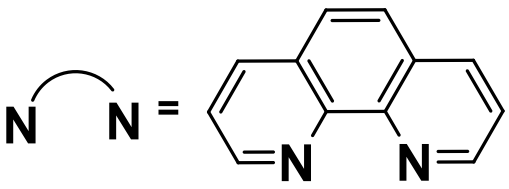
$Fe^{II}(phen)_3]^{2+}$

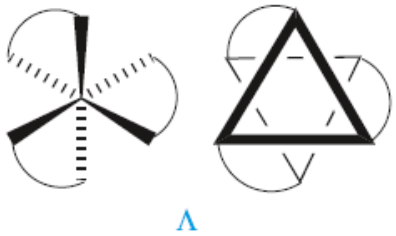


d^6, diamagnetico
basso spin

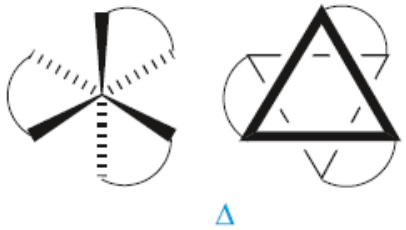
Geometria ottaedrica

Isomeria ottica in complessi ottaedrici

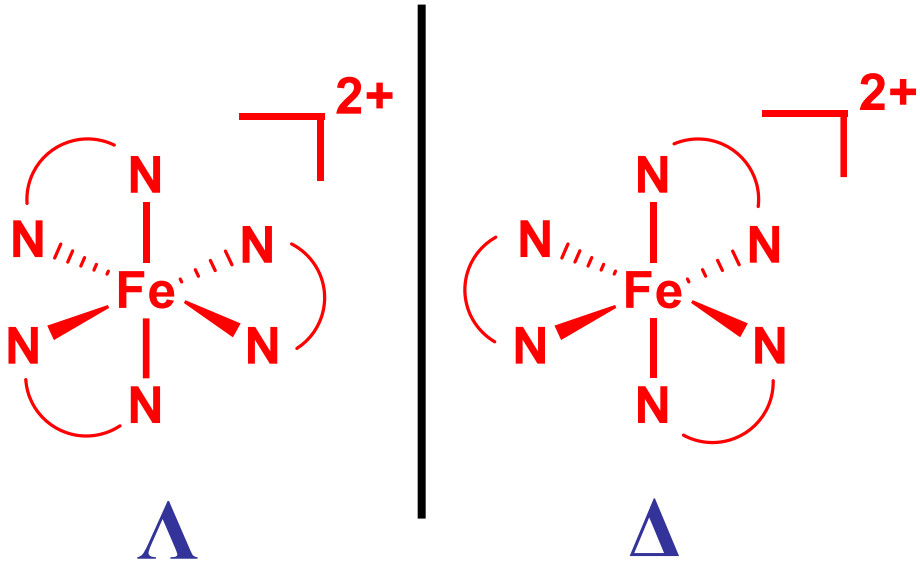




Λ



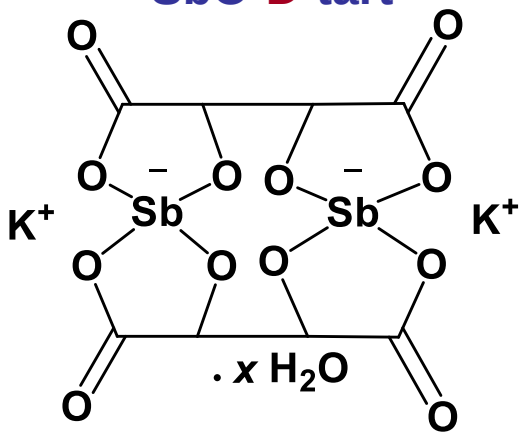
Δ



Λ Δ

Risoluzione della miscela racemica $[Fe(phen)_3]^{2+}$ nei suoi due enantiomeri può essere ottenuta attraverso uno scambio di controione utilizzando un sale enantiomericamente puro (es. SbO-D-tart)

SbO-D-tart

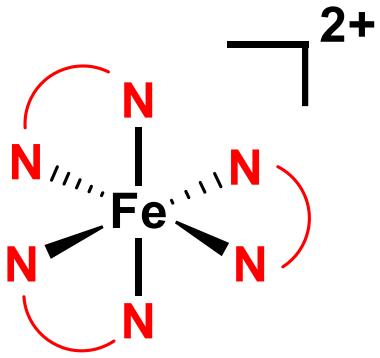


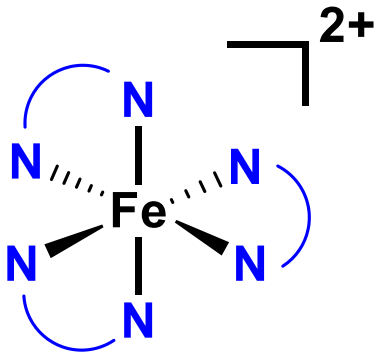
Tecniche di caratterizzazione

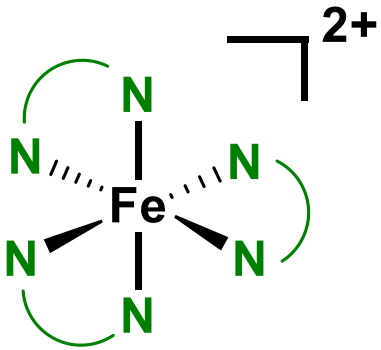
- **Spettroscopia NMR, confronto degli spettri della serie di complessi di Fe (^{1}H, ^{13}C)**

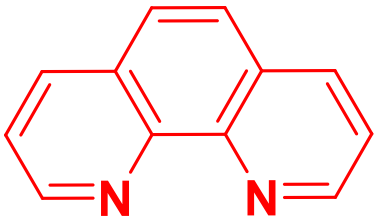
- **Voltammetria ciclica (CV), per lo studio dell'effetto elettronico dei sostituenti della 1,10-fenantrolina sul potenziale redox $Fe^{III/II}$**

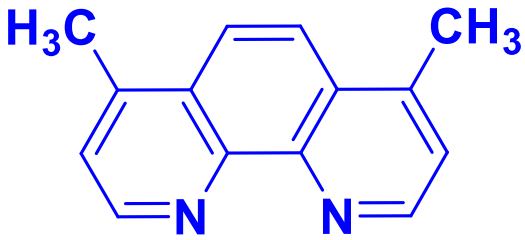
EFFETTO ELETTRONICO dei sostituenti sul legante

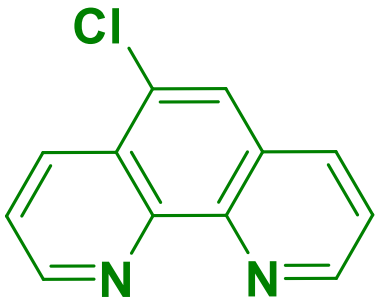








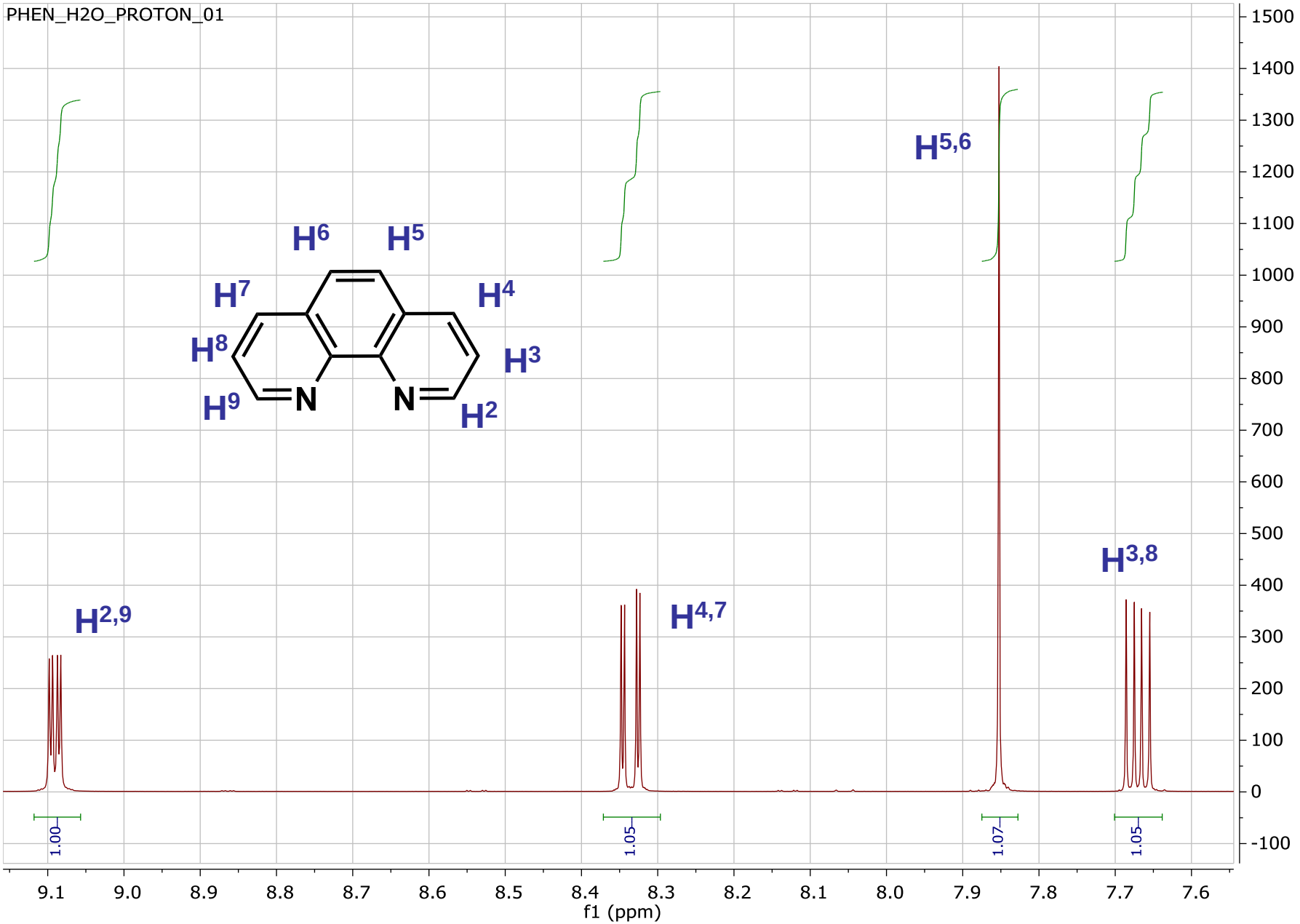




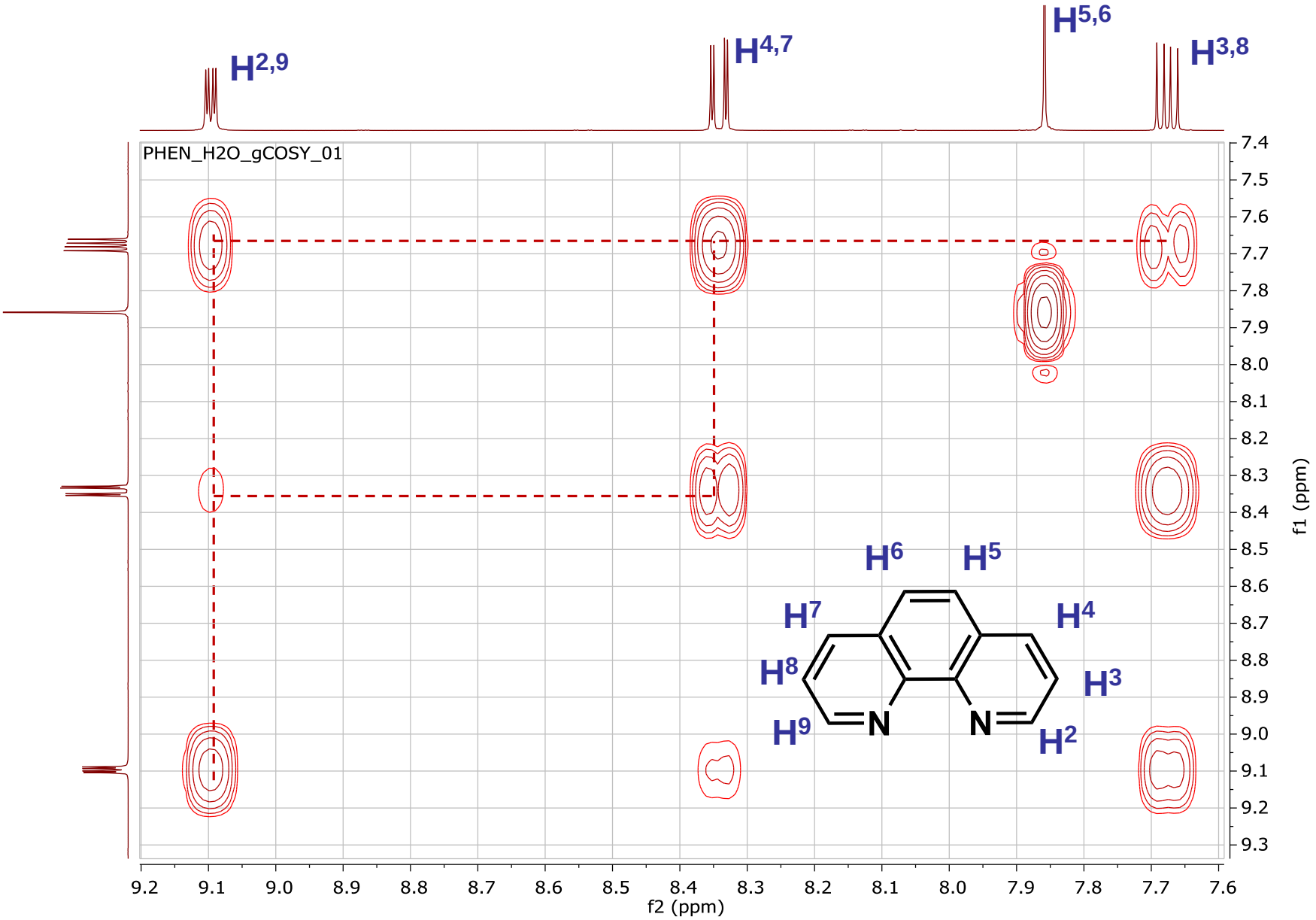
Sostituente elettron-donatore (EDG)

Sostituente elettron-accettore (EWG)

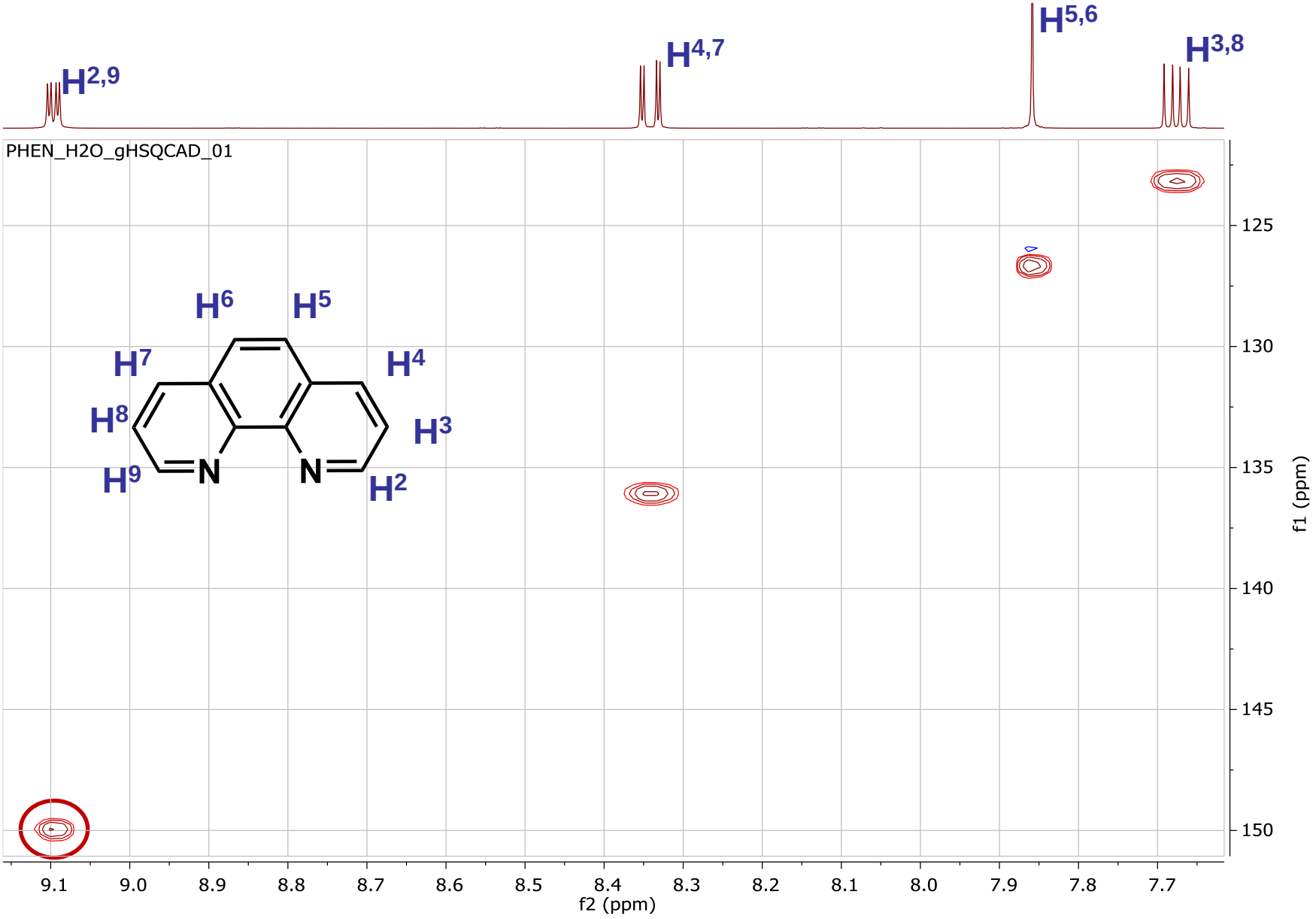
Spettro ^{1}H-NMR della 1,10-fenantrolina in CD_3CN



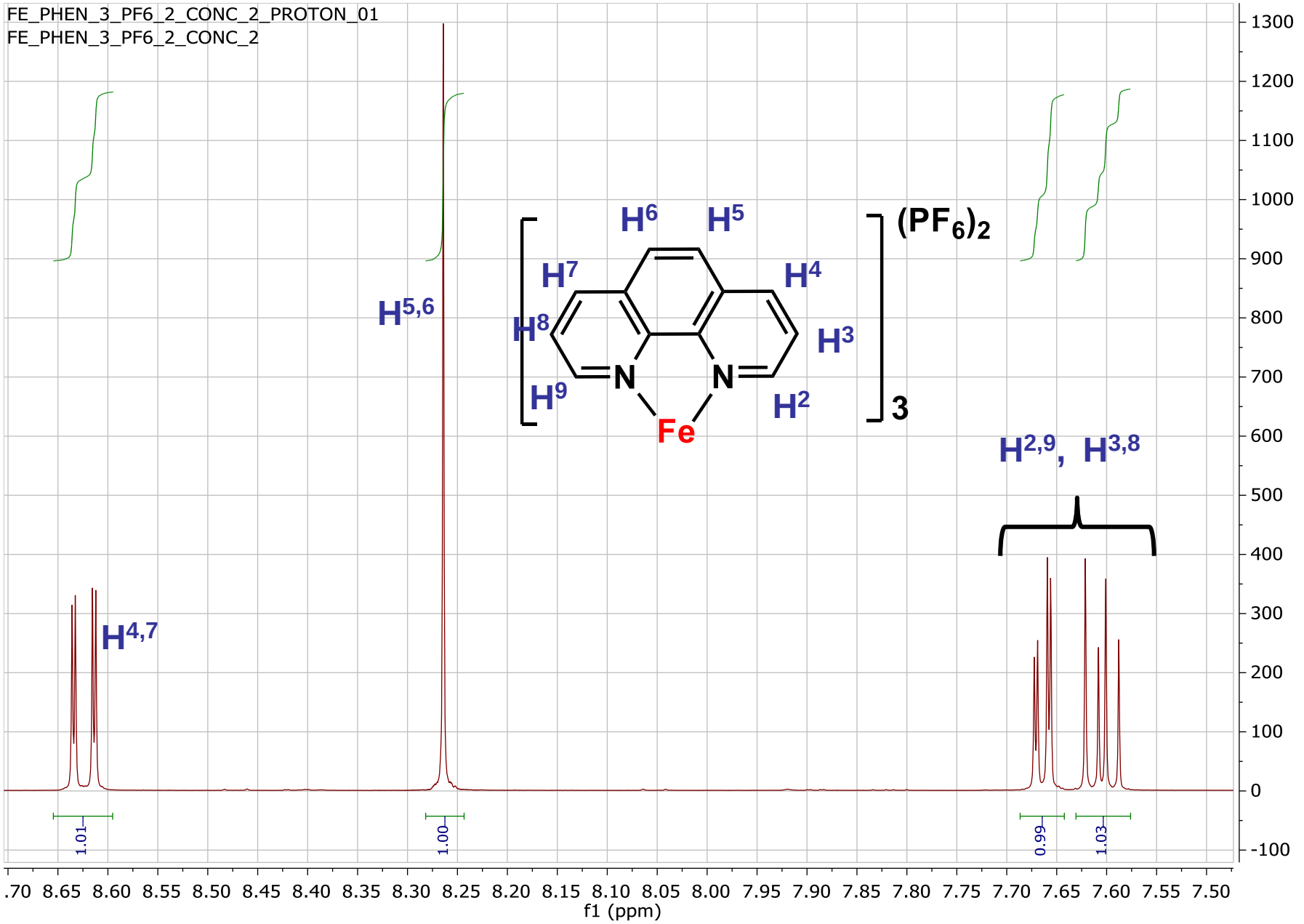
Spettro $^{1}H,^{1}H$-COSY della 1,10-fenantrolina in CD_3CN



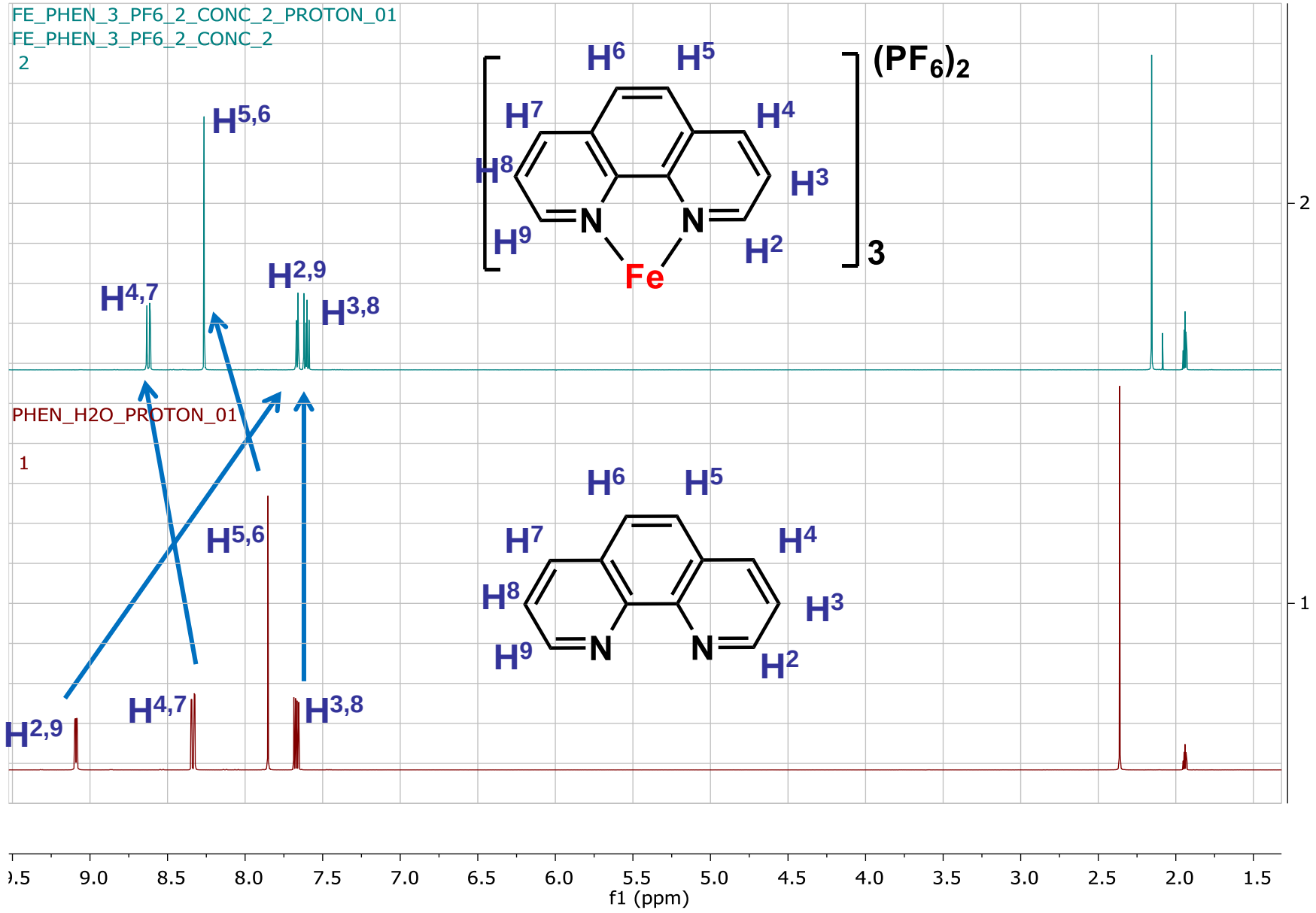
Spettro $^{1}H,^{13}C$-HSQC della 1,10-fenantrolina in CD_3CN



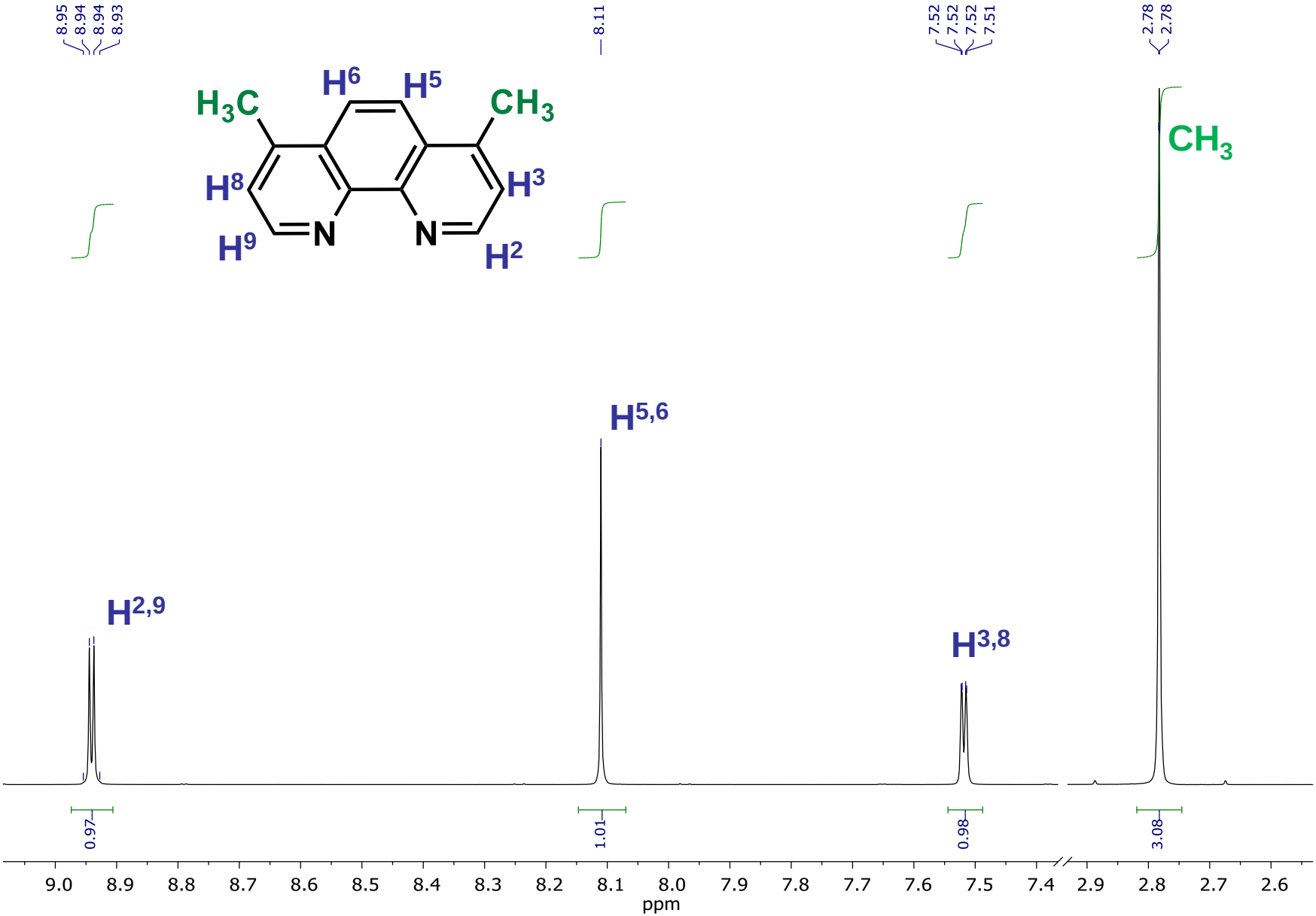
Spettro ^{1}H-NMR del complesso $[Fe(phen)_3](PF_6)_2$ in CD_3CN

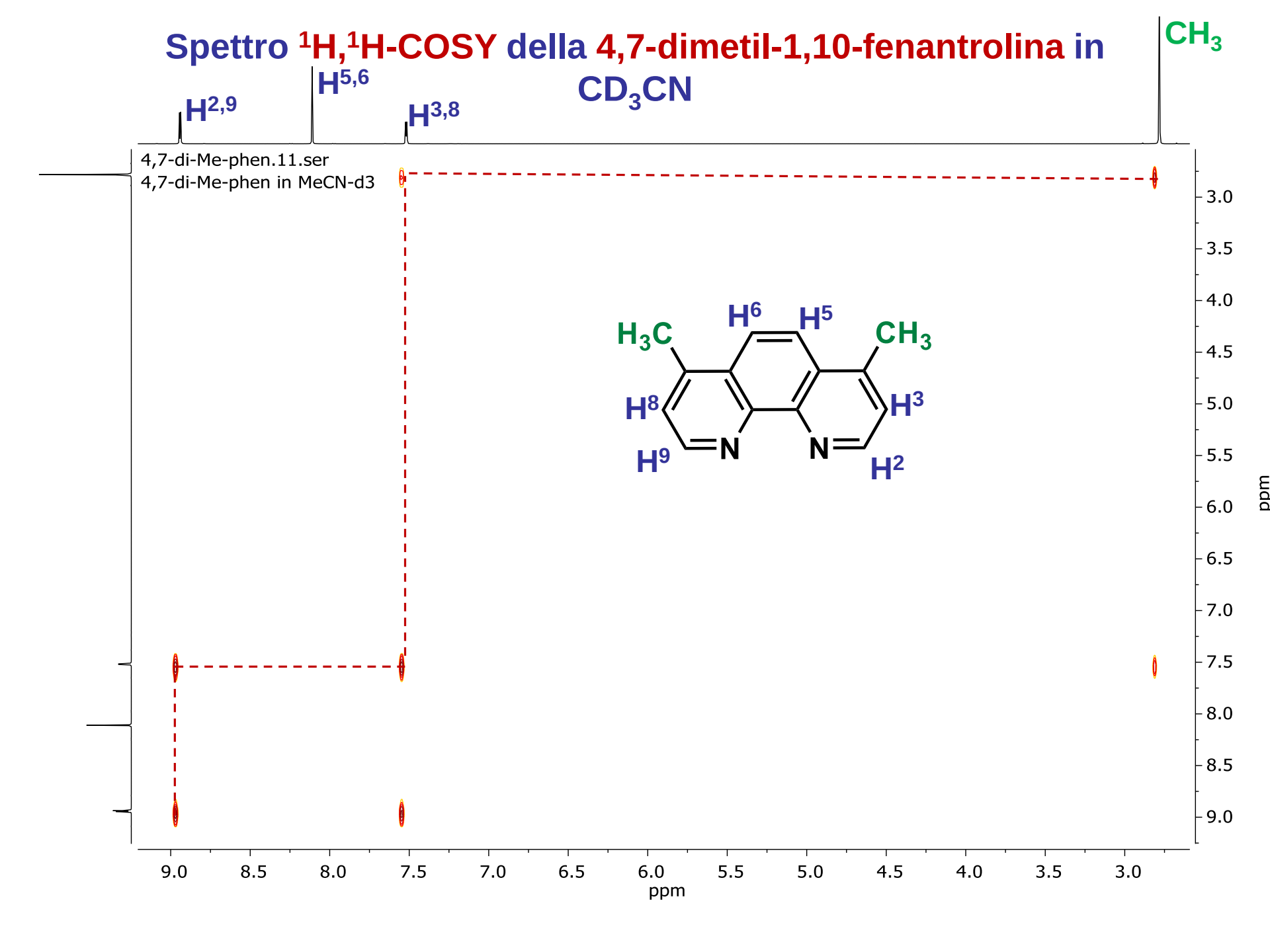


Confronto spettri ^{1}H-NMR del legante e del complesso di Fe

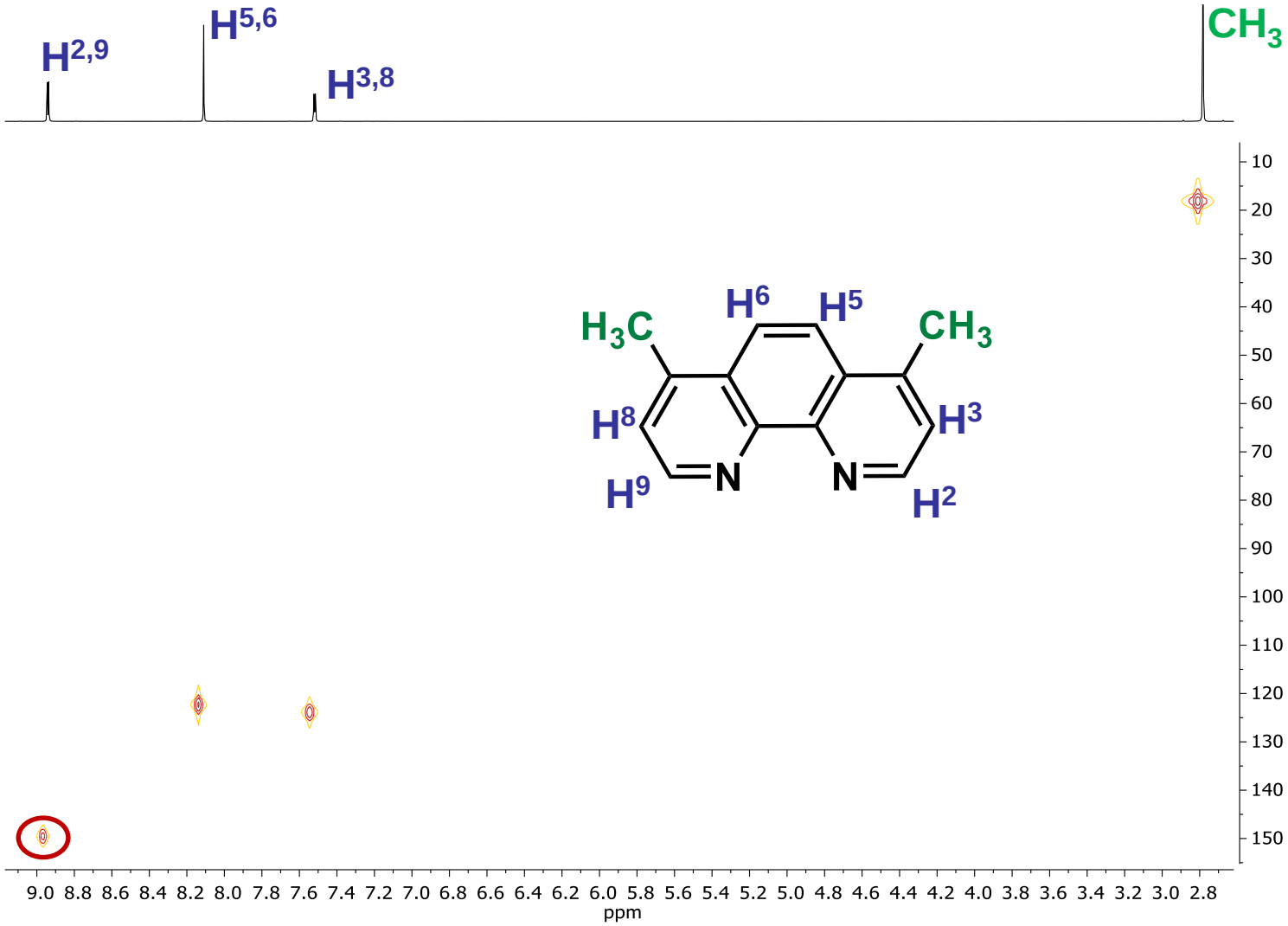


Spettro ^{1}H-NMR della 4,7-dimetil-1,10-fenantrolina in CD_3CN

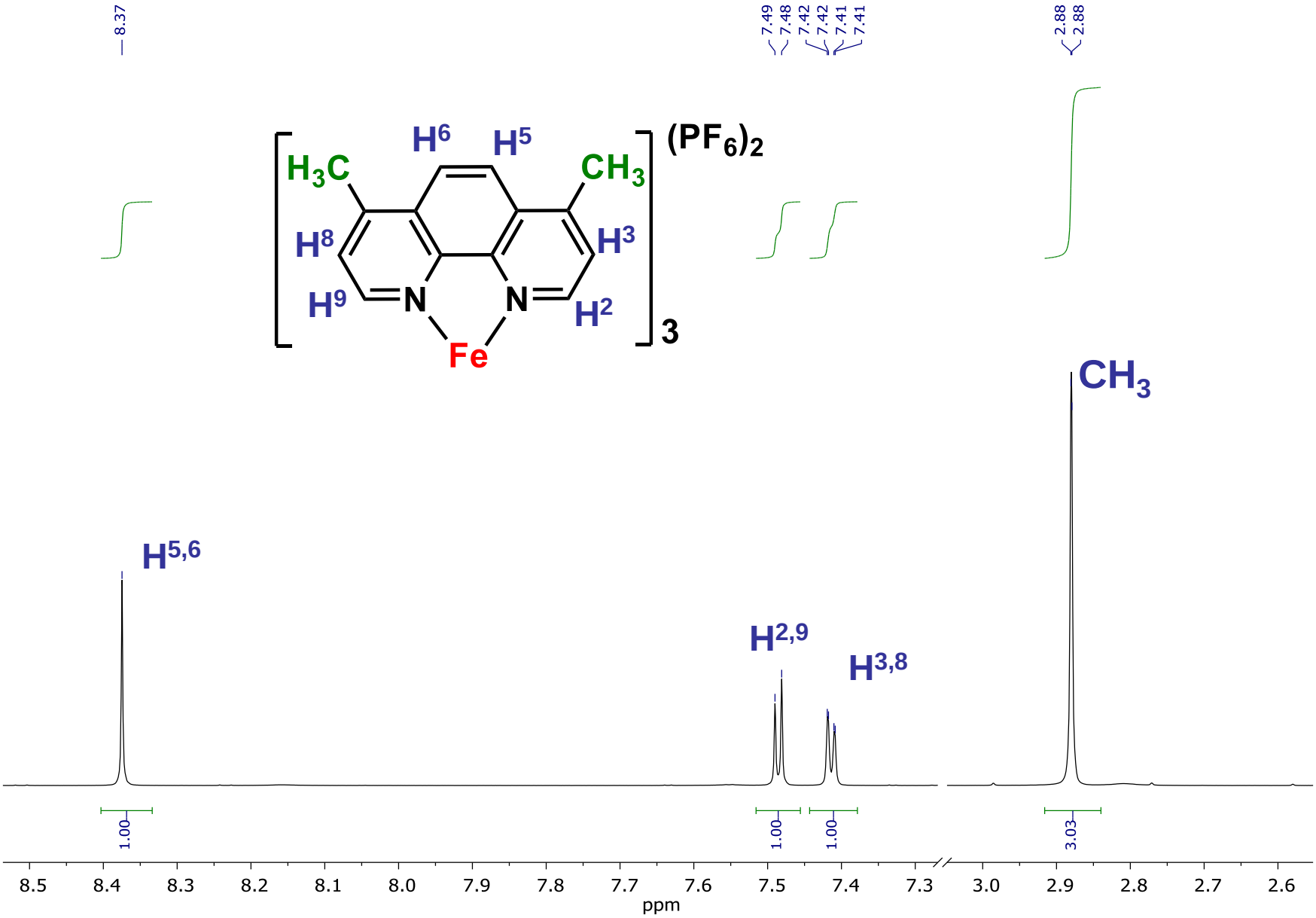



Spettro ^{1}H,^{1}H-COSY della 4,7-dimetil-1,10-fenantrolina in CD_3CN
H2,9
H5,6
H3,8
CH3
4,7-di-Me-phen.11.ser
4,7-di-Me-phen in MeCN-d3
H3C
H6
H5
CH3
H8
H3
H9
N
N
H2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm

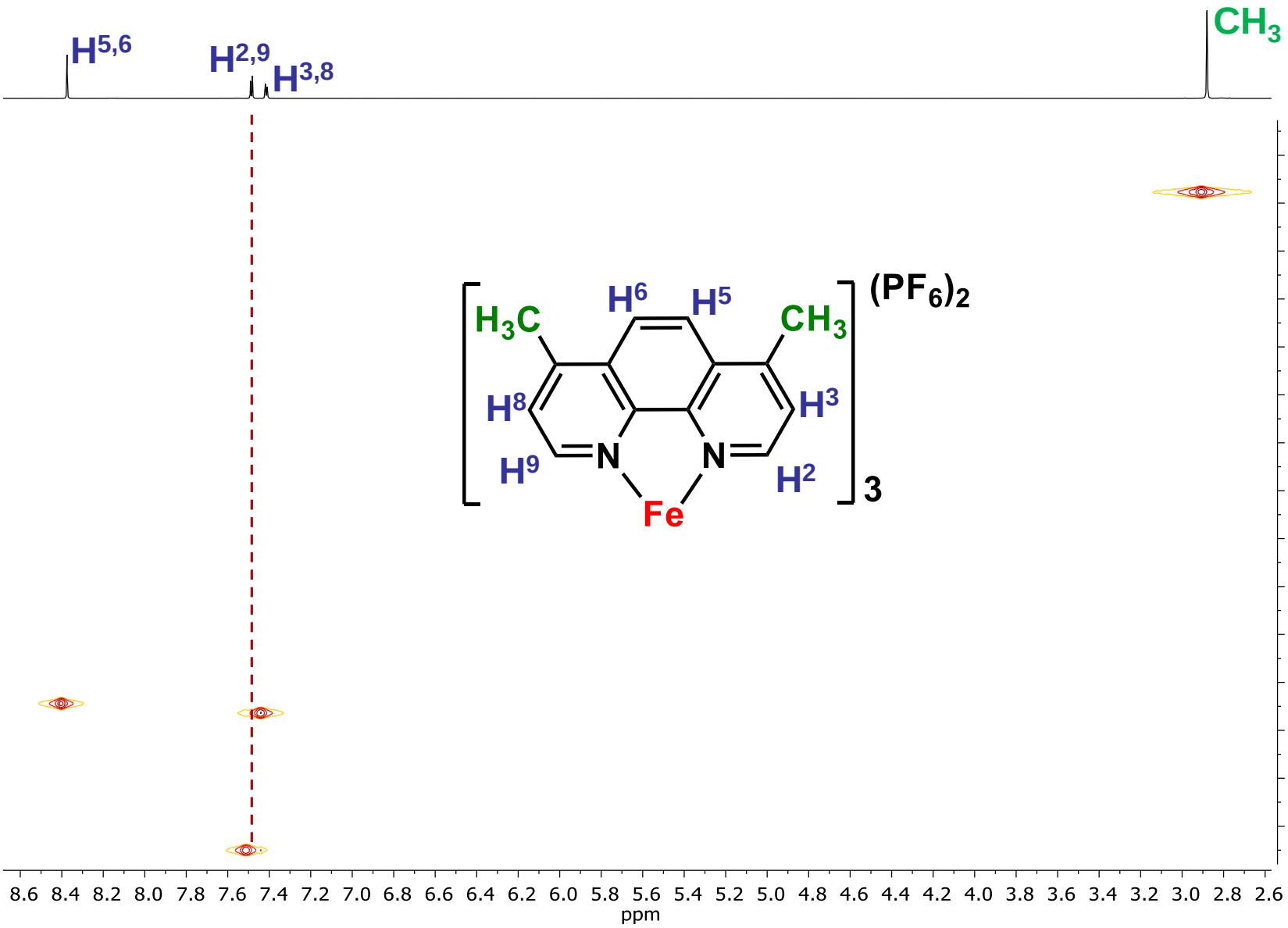
Spettro $^{1}H,^{13}C$-HSQC della 4,7-dimetil-1,10-fenantrolina in CD_3CN



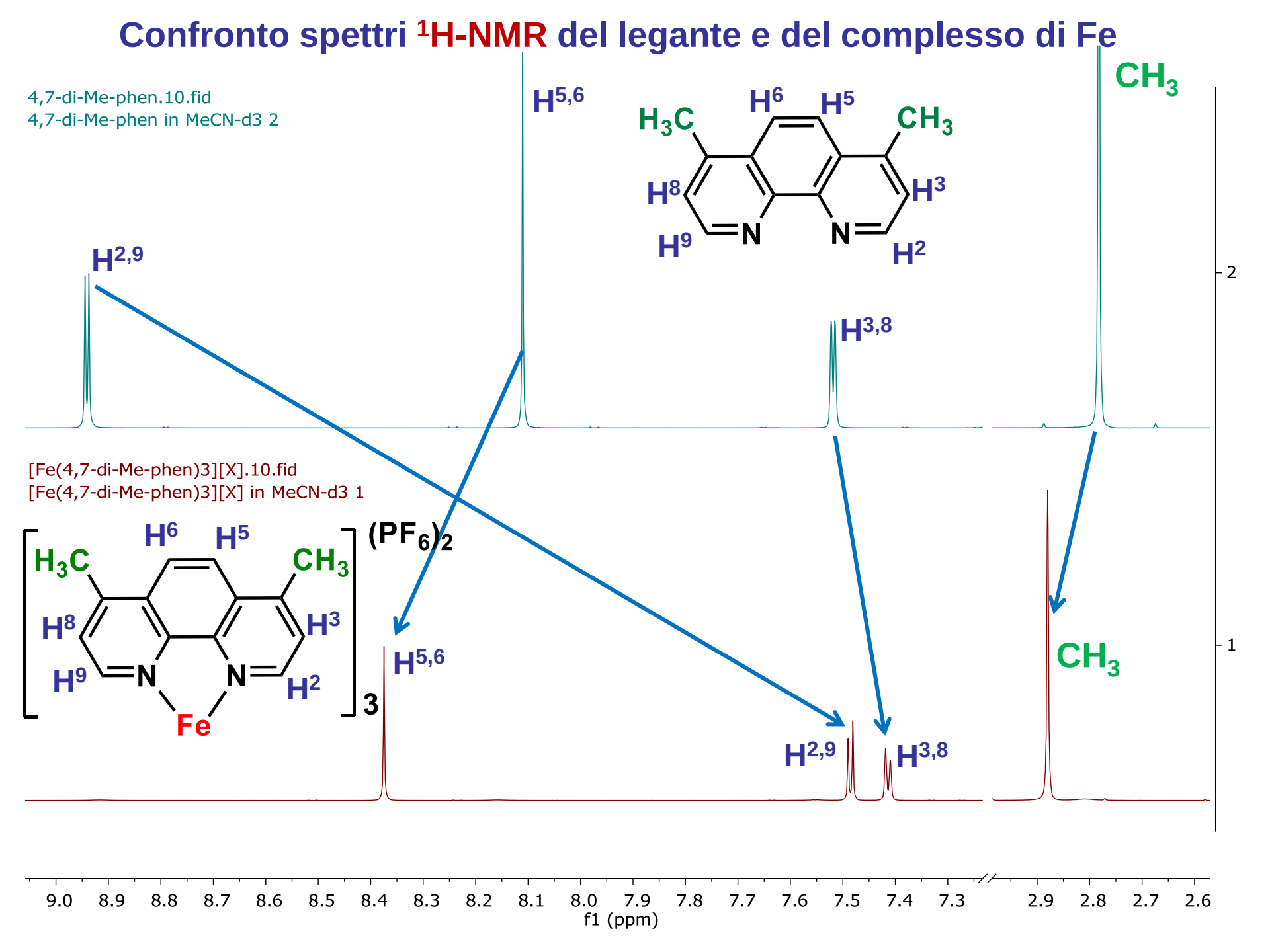
Spettro ^{1}H-NMR del complesso $[Fe((CH_3)_2\text{-phen})_3](PF_6)_2$ in CD_3CN



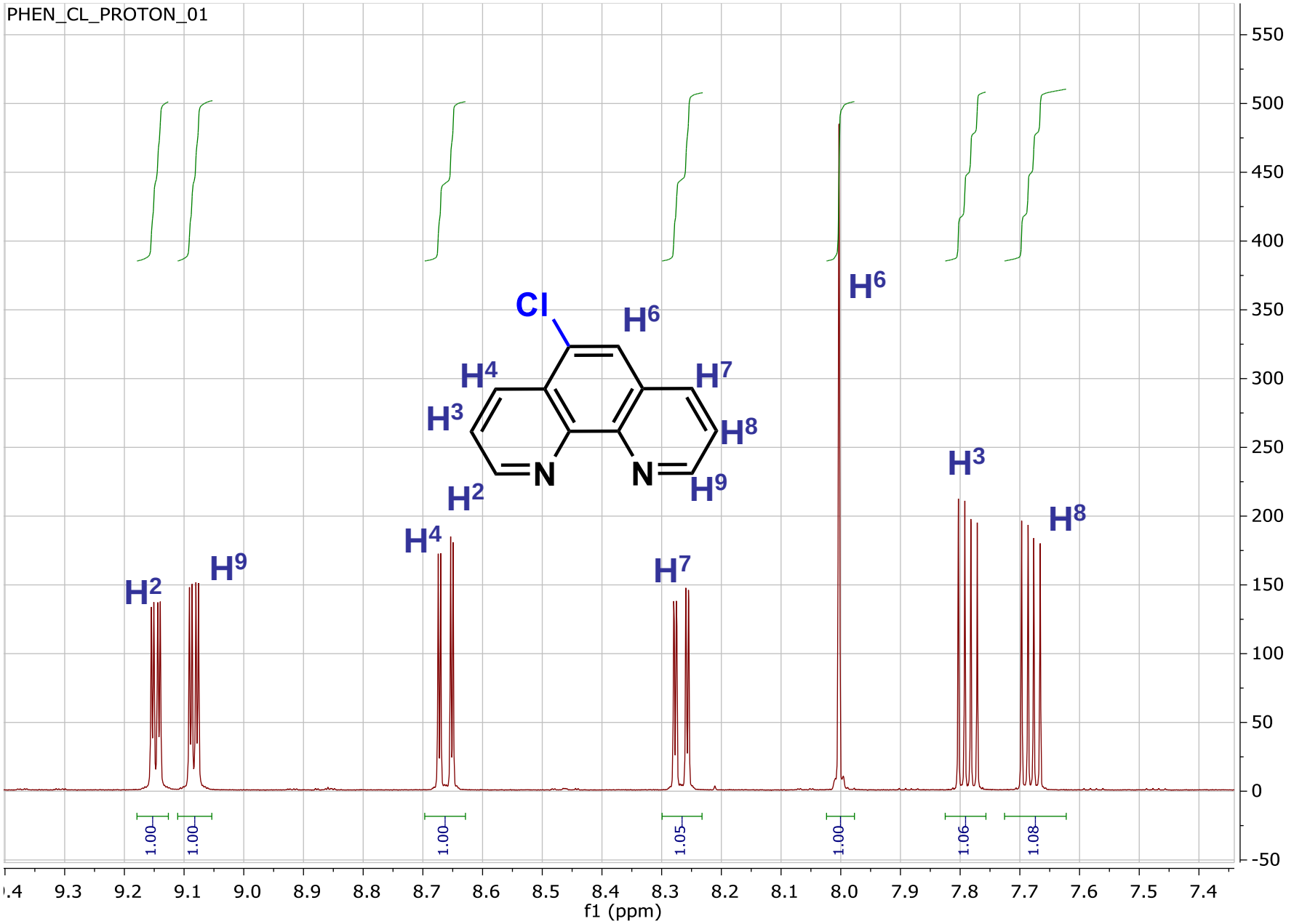
Spettro $^{1}H,^{13}C$-HSQC del complesso $[Fe((CH_3)_2\text{-phen})_3](PF_6)_2$ in CD_3CN



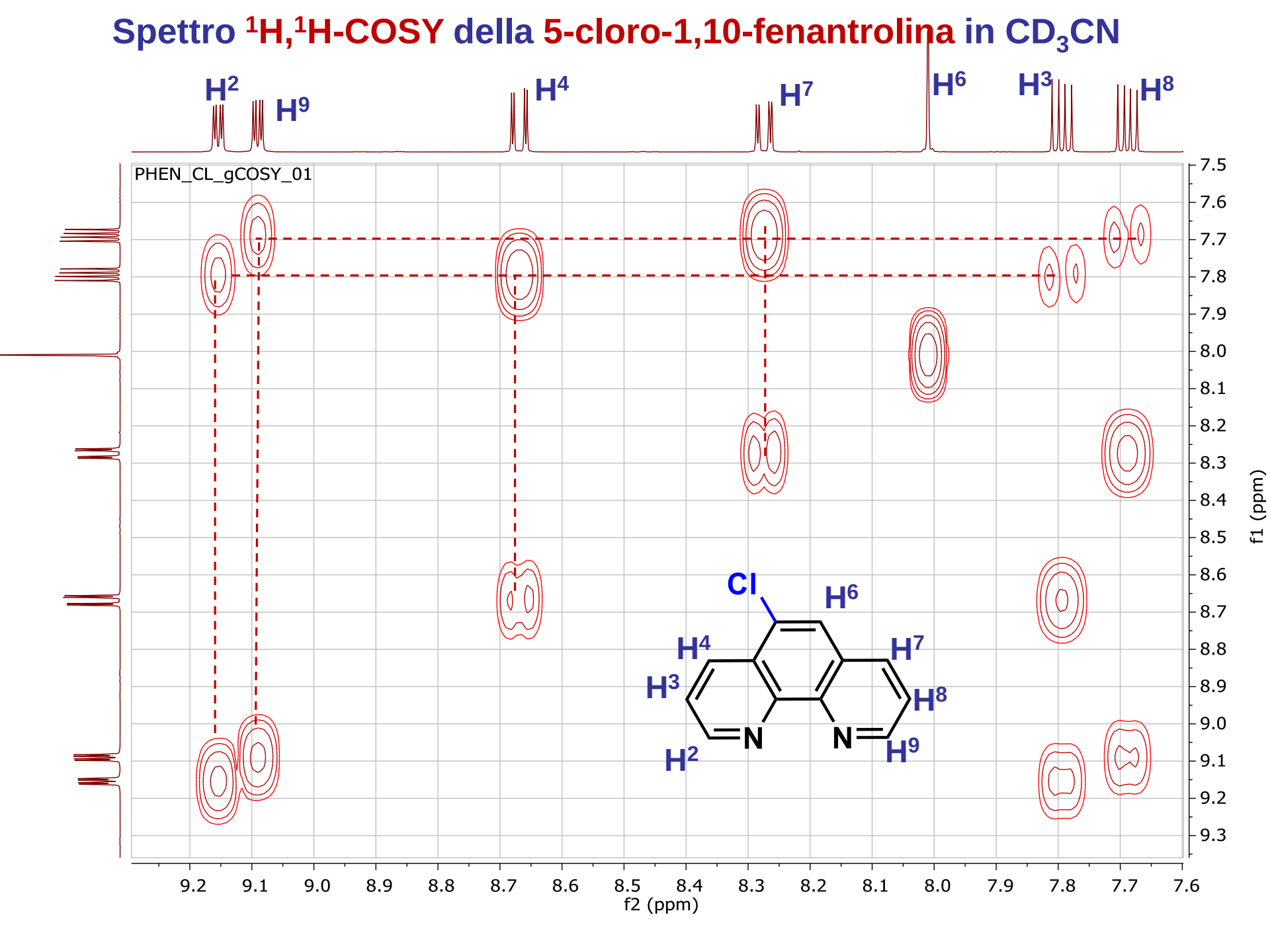
Confronto spettri ^{1}H-NMR del legante e del complesso di Fe



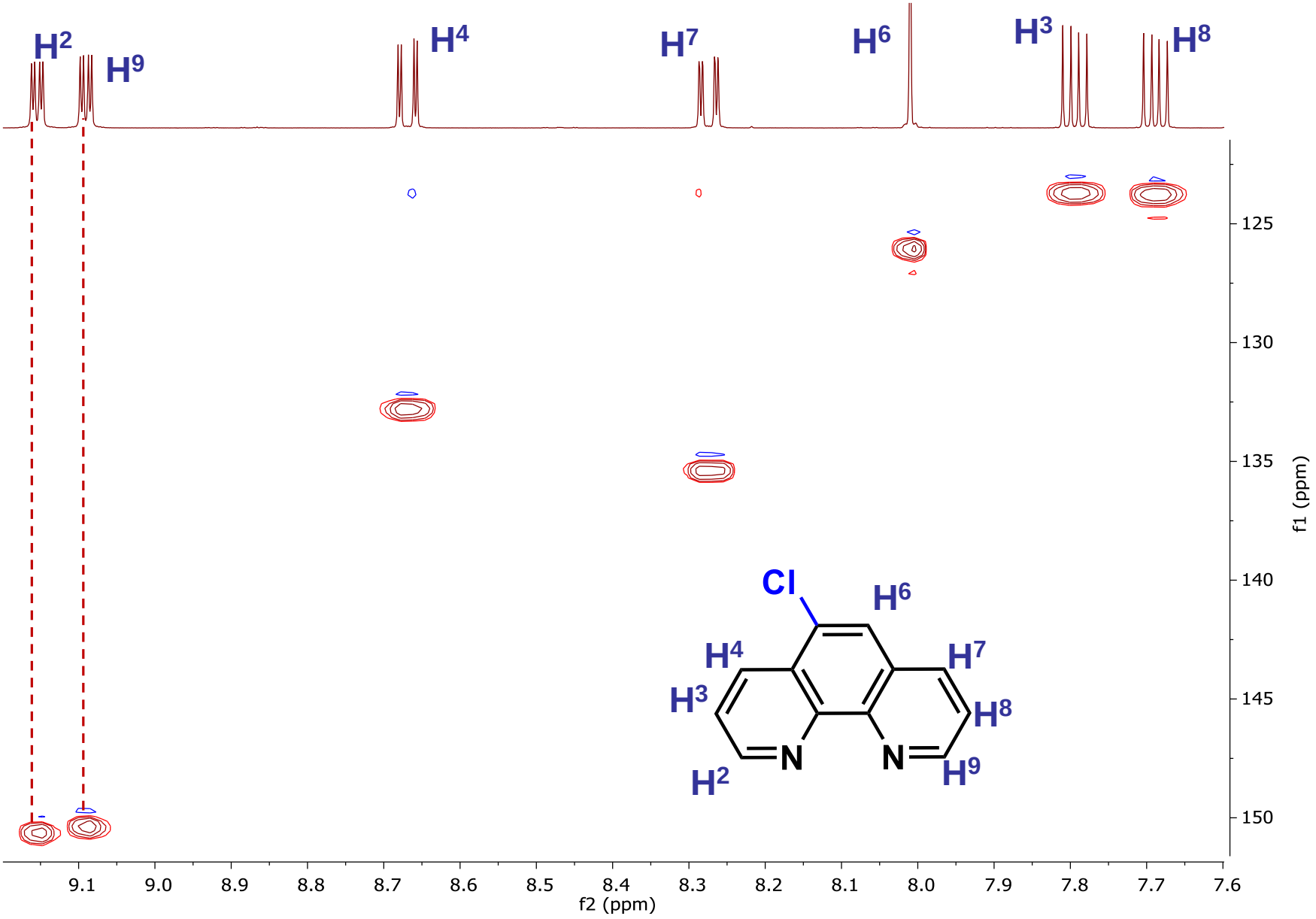
Spettro ^{1}H-NMR della 5-cloro-1,10-fenantrolina in CD_3CN



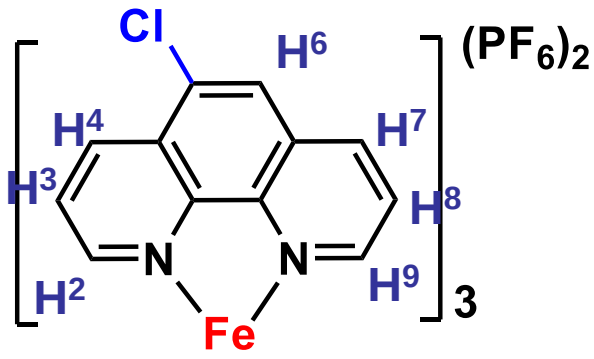
Spettro $^{1}H,^{1}H$-COSY della 5-cloro-1,10-fenantrolina in CD_3CN



Spettro $^{1}H,^{13}C$-HSQC della 5-Cl-1,10-fenantrolina in CD_3CN



Spettro ^{1}H-NMR del complesso $[Fe(Cl\text{-}phen)_3](PF_6)_2$ in CD_3CN



Isomeri *mer* e *fac*

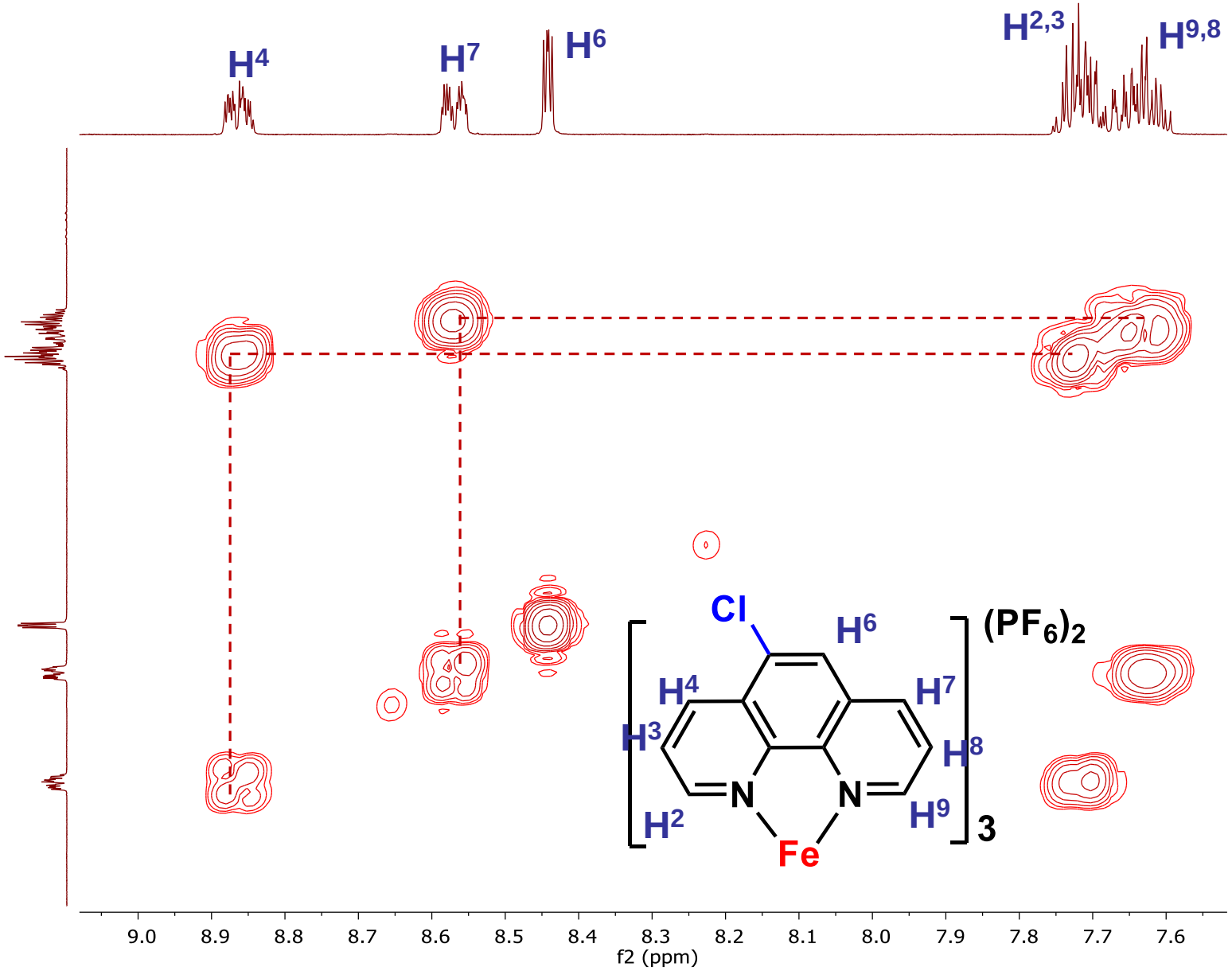
H4
H7
H6
H2,3
H9,8

8.90 8.85 8.80 8.75 8.70 8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55

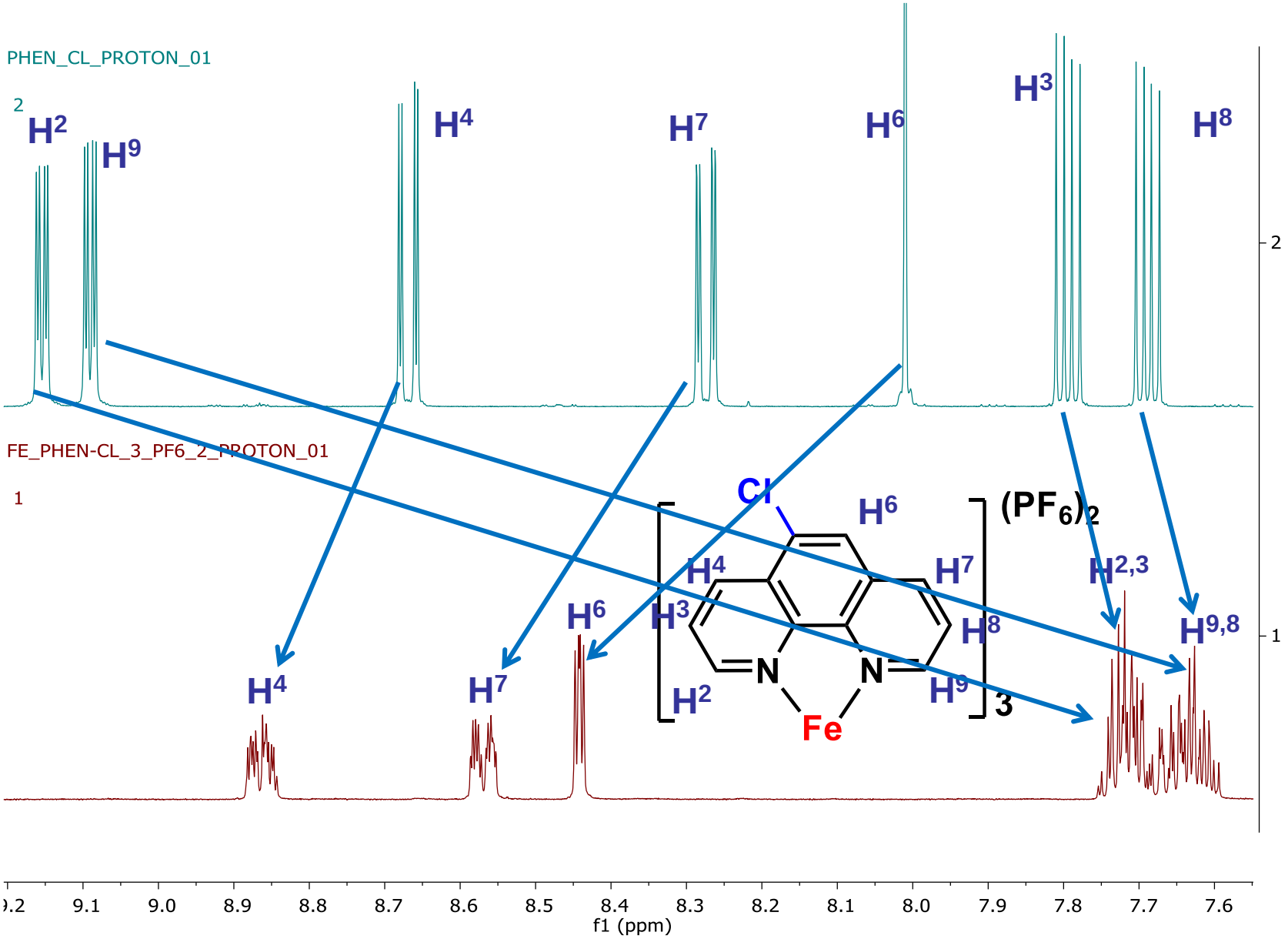
f1 (ppm)

130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Spettro $^{1}H,^{1}H$-COSY della 5-Cl-1,10-fenantrolina in CD_3CN



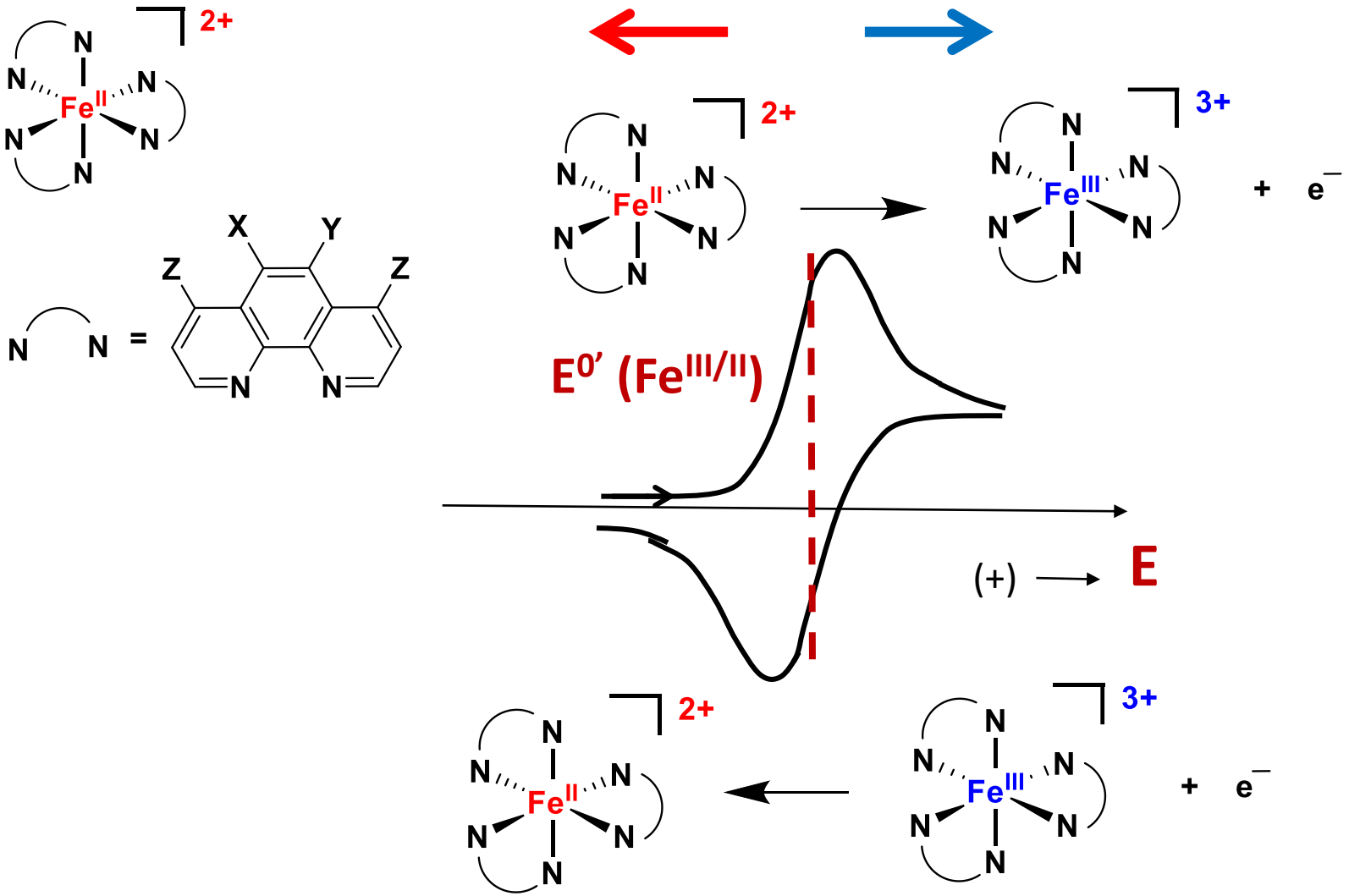
Confronto spettri ^{1}H-NMR del legante e del complesso di Fe



EFFETTO ELETTRONICO DEI SOSTITUENTI SUL POTENZIALE REDOX

Sostituenti elettron-repulsori (EDG)

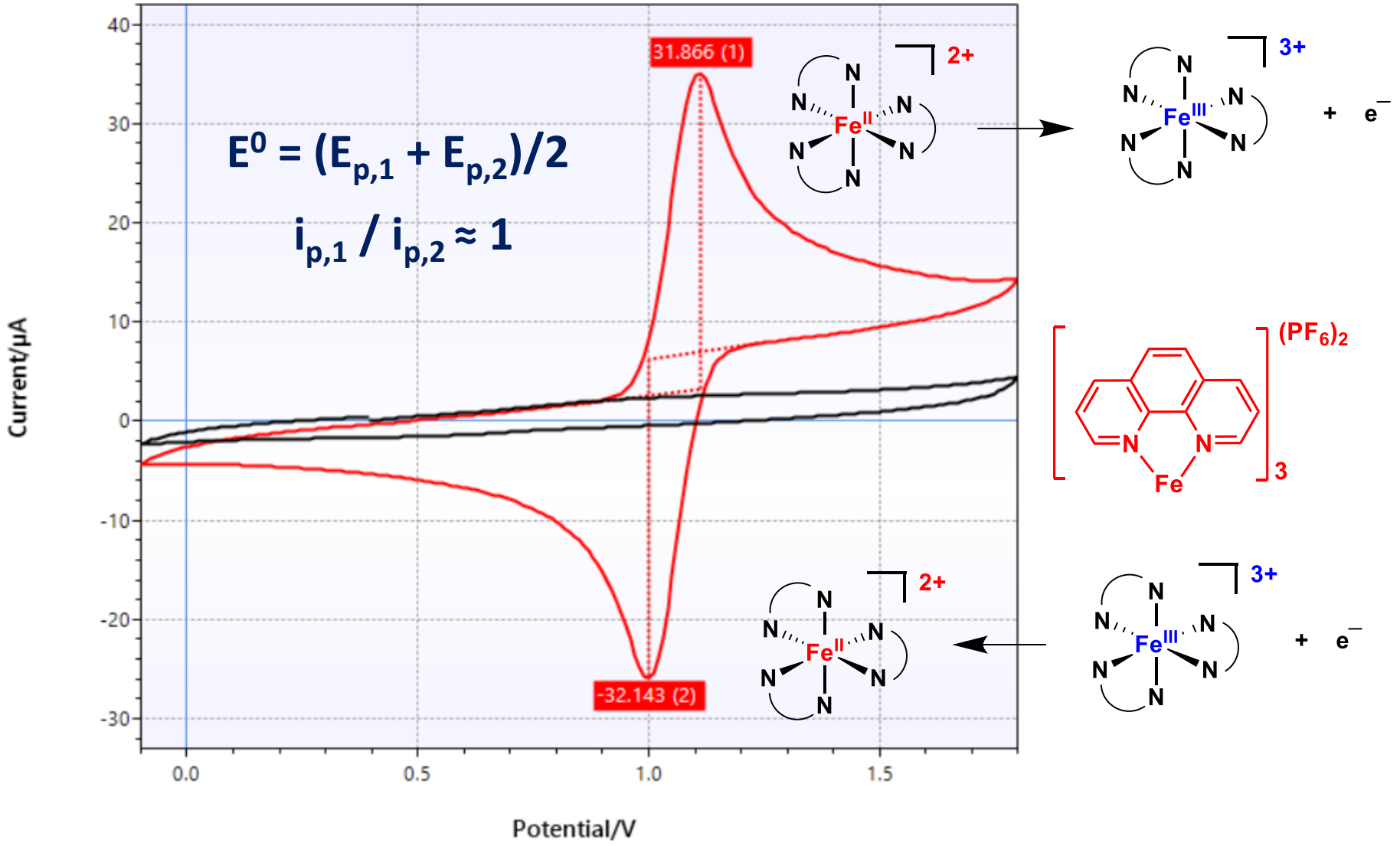
Sostituenti elettron-accettori (EWG)



Voltammetria ciclica dei complessi di Fe(II)

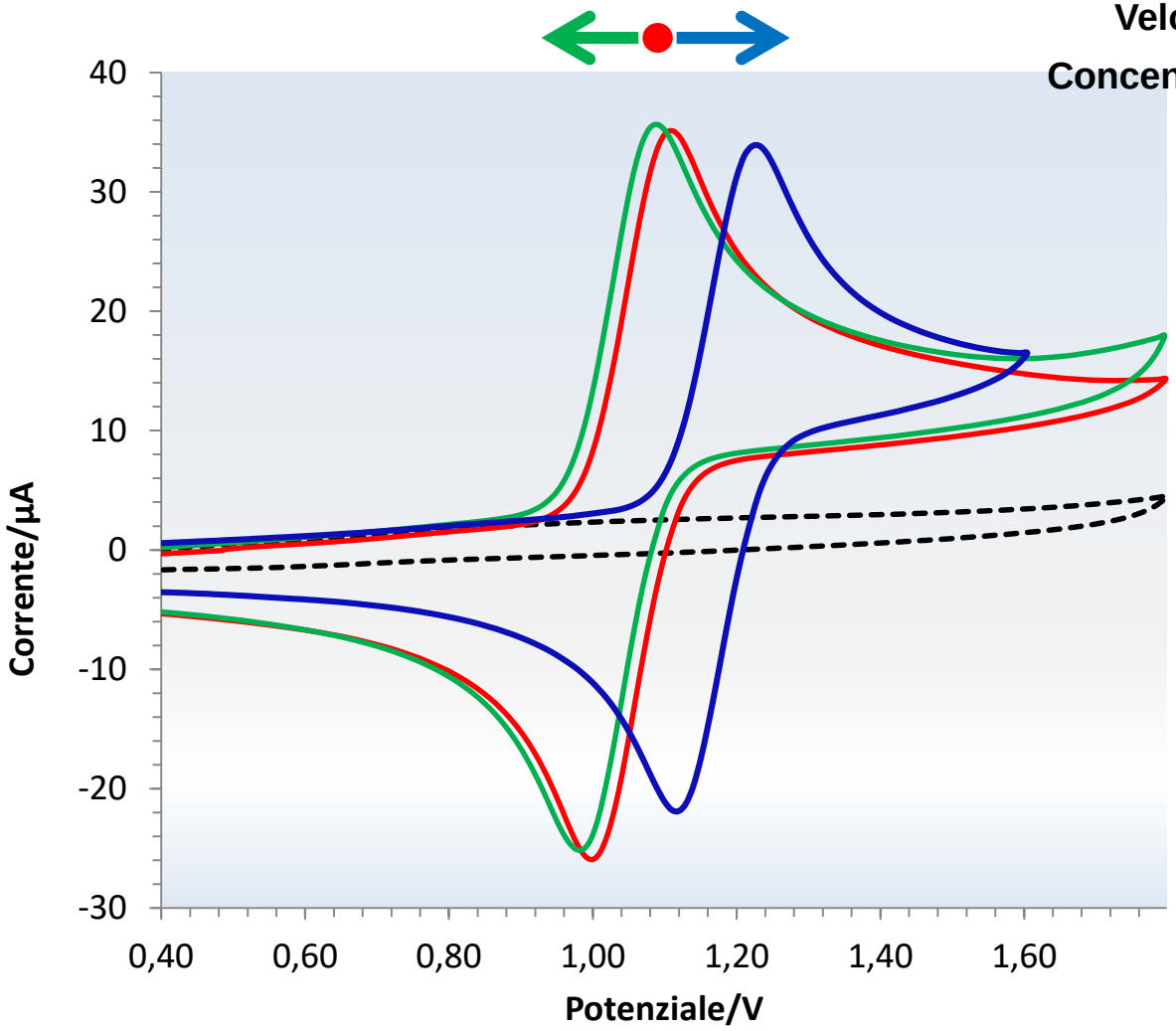
Processo reversibile

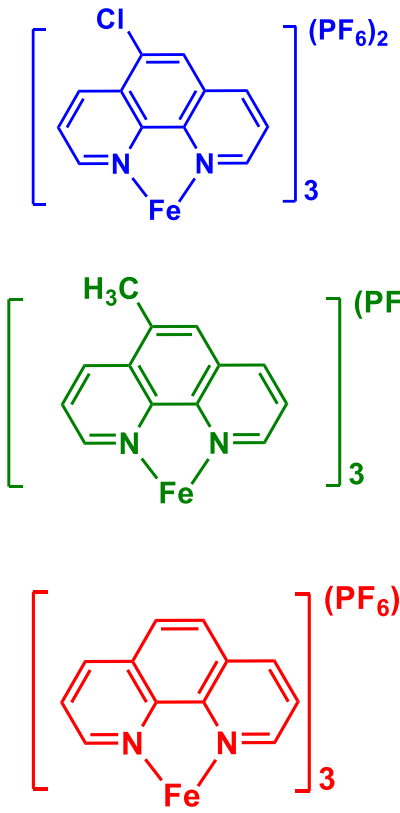
$Fe^{III/II}$



EFFETTO ELETTRONICO dei sostituenti del legante sul potenziale redox $Fe^{III/II}$

Elettrolita: 0.1 M $TBAPF_6$ in acetonitrile
Velocità di scansione: 0.1 V/s
Concentrazione complesso Fe: 2 mM





Complesso	E_{p1}, E_{p2} (V vs Ag/AgCl)	E^0 (V vs. Ag/AgCl)	E^0 (V vs. $Fc^{+/0}$) [a]	E^0 (V vs. $Fc^{+/0}$) **Letteratura** [b]
CH_3-phen	1.09 0.98	**1.03**	**0.69**	0.67
phen	1.11 1.00	**1.06**	**0.72**	0.70
Cl-phen	1.23 1.12	**1.18**	**0.84**	0.80

[a] *E^0 $Fc^{+/0}$ (vs. Ag/AgCl) = 0.34 V*

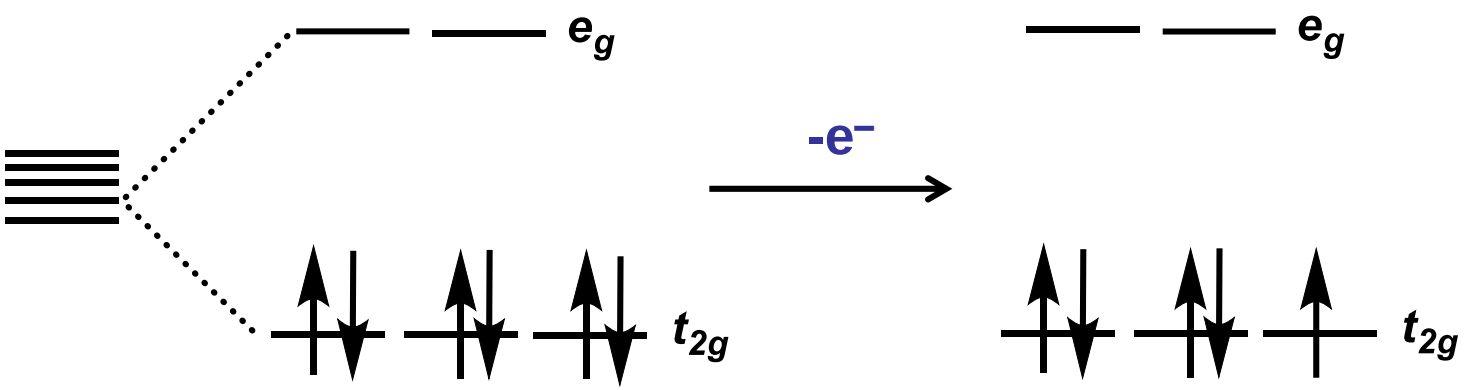
[b] *H. Ferreira et al. , Electroch. Acta 216 (**2016**) 339–346*

E^0 ($Fe^{III/II}$): CH_3-phen < phen < Cl-phen

1,10-fenantrolina = legante a campo forte

Geometria ottaedrica

$[Fe^{II}(phen)_3]^{2+}$ $[Fe^{III}(phen)_3]^{3+}$



d^6, diamagnetico
basso spin

d^5, paramagnetico
basso spin

Trasferimento elettronico molto veloce

Fe-N ($Fe^{II}(phen)_3]^{2+}$) ≈ Fe-N ($Fe^{III}(phen)_3]^{3+}$) ≈ 1.97 Å