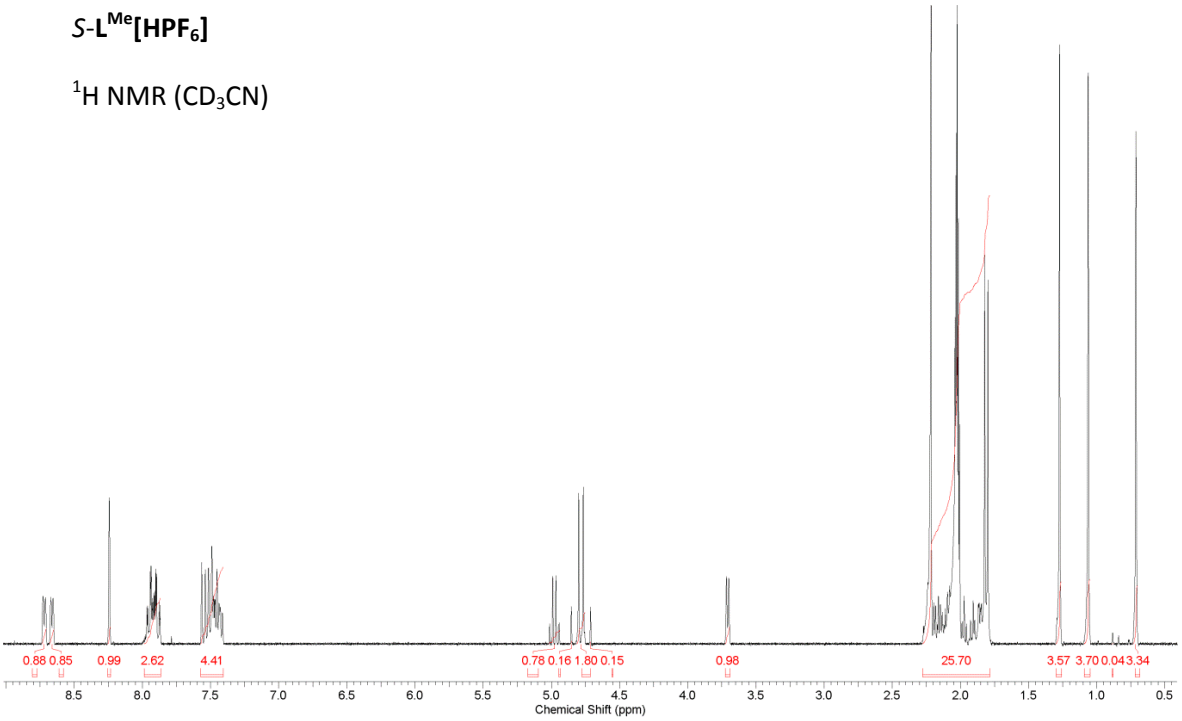
Selected NMR spectra:

13/09/2013 12:42:48

S-**L^{Me}[HPF$_6$]**

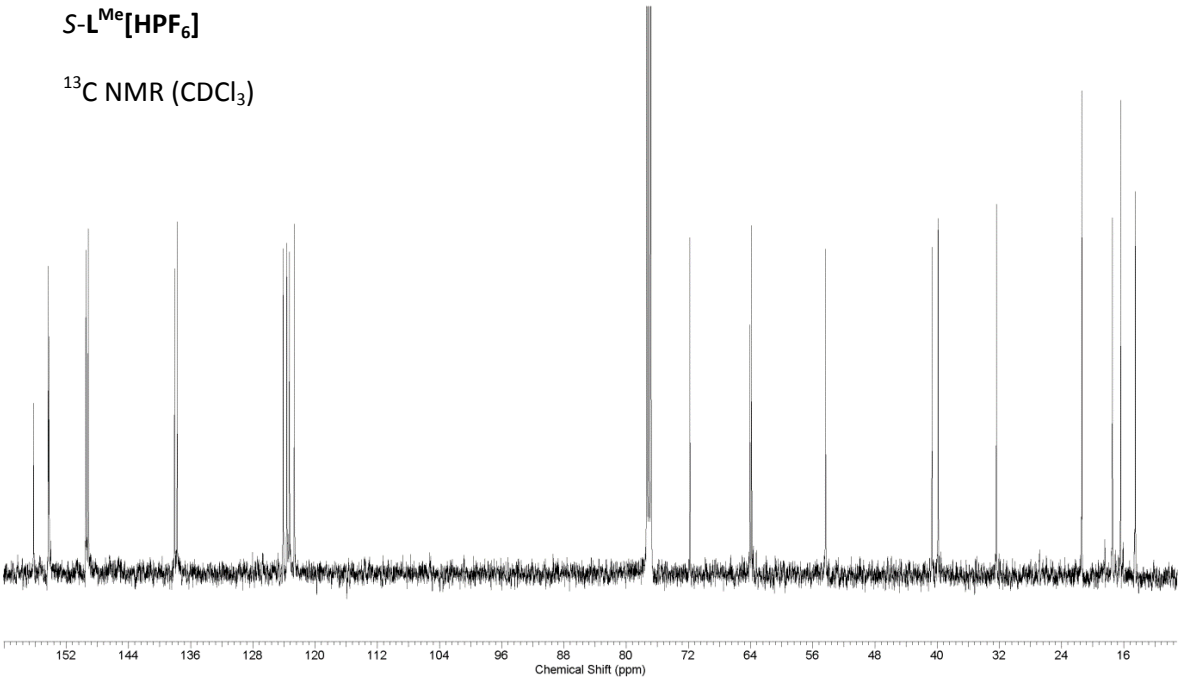
^{1}H NMR (CD_3CN)



13/09/2013 15:36:11

S-**L^{Me}[HPF$_6$]**

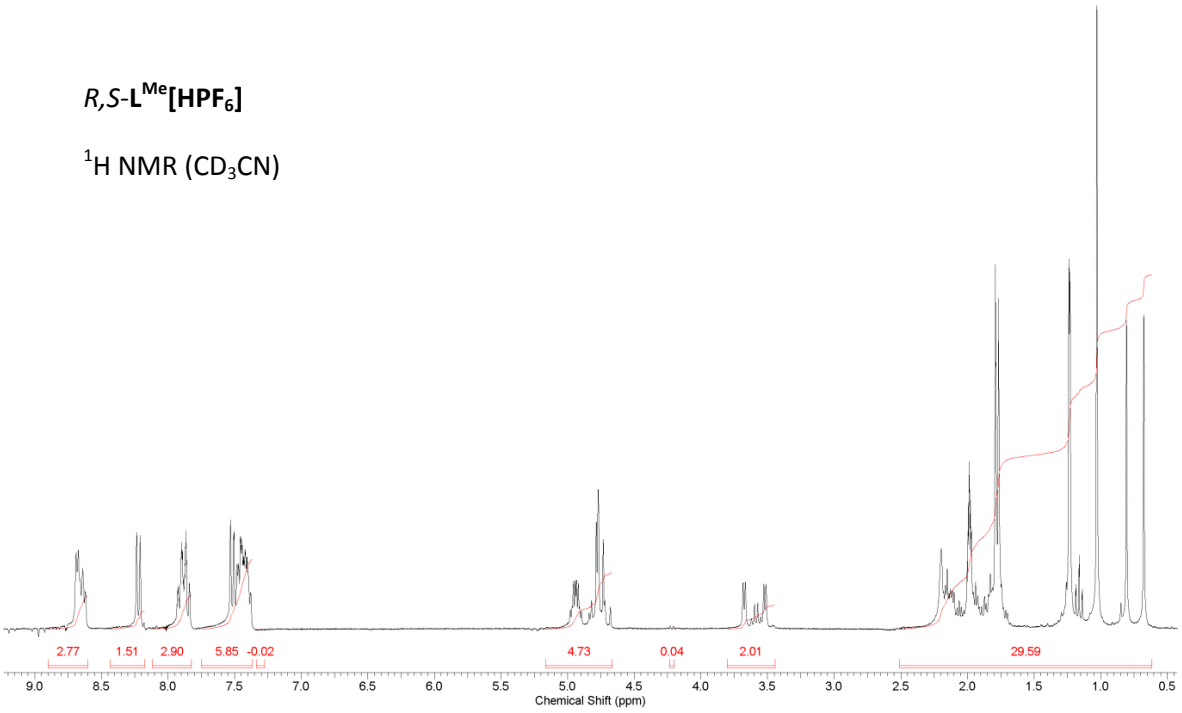
^{13}C NMR ($CDCl_3$)



13/09/2013 13:02:03

R,S-**L^{Me}[HPF$_6$]**

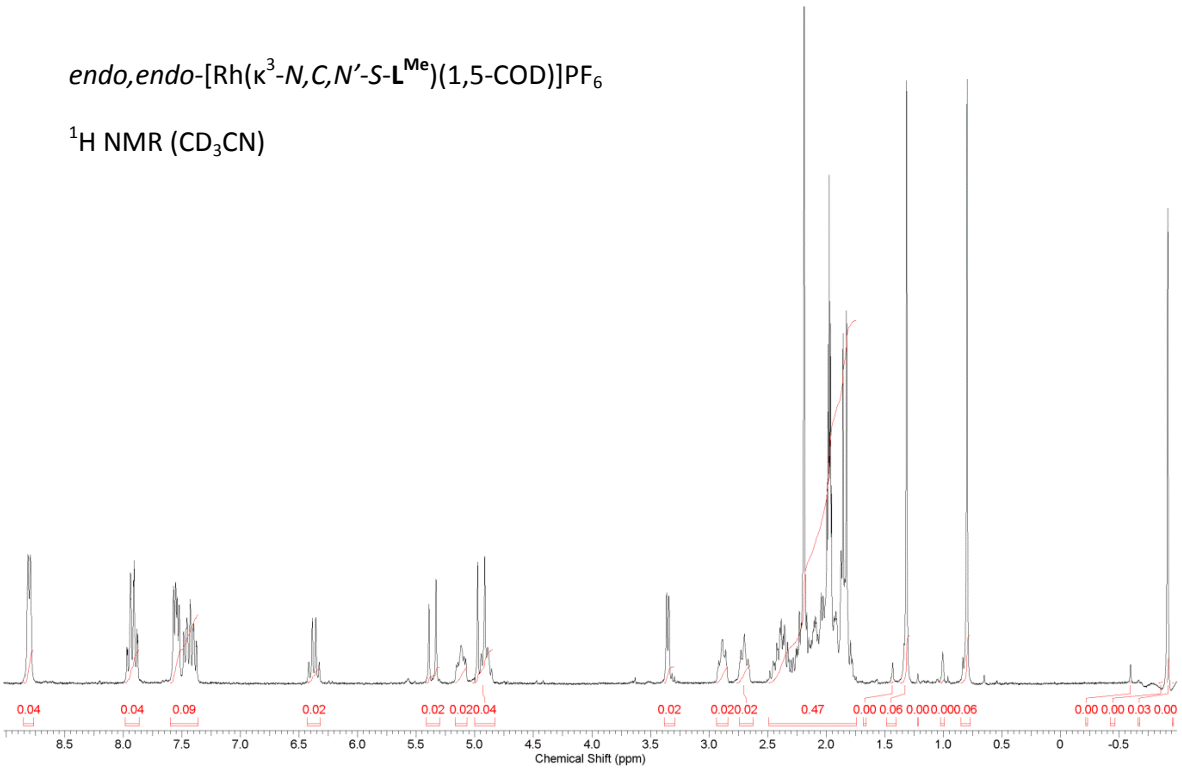
^{1}H NMR (CD_3CN)



13/09/2013 13:20:20

endo,endo-[Rh(κ^3-*N,C,N'-S*-**L^{Me}**)(1,5-COD)]PF_6

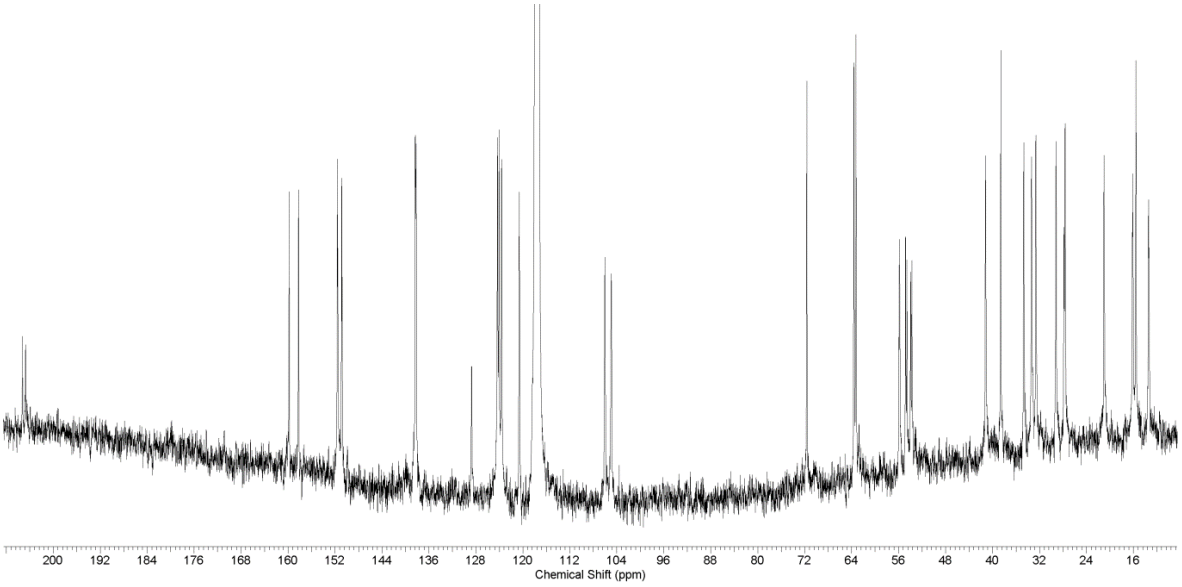
^{1}H NMR (CD_3CN)



13/09/2013 15:24:55

endo,endo-[Rh(κ^3-*N,C,N'-S*-**L**$^{\mathbf{Me}}$)(1,5-COD)]PF_6

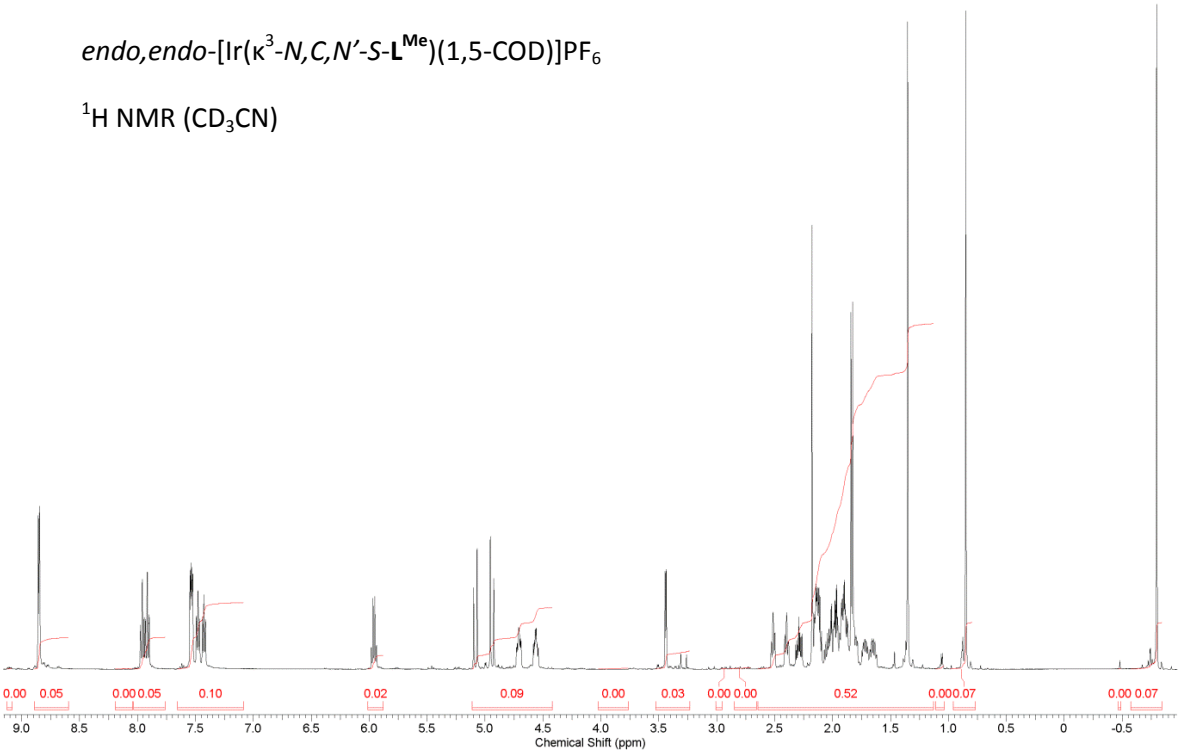
$^{13}C\{^1H\}$ NMR (CD_3CN)



13/09/2013 12:22:24

endo,endo-[Ir(κ^3-*N,C,N'-S*-**L**$^{\mathbf{Me}}$)(1,5-COD)]PF_6

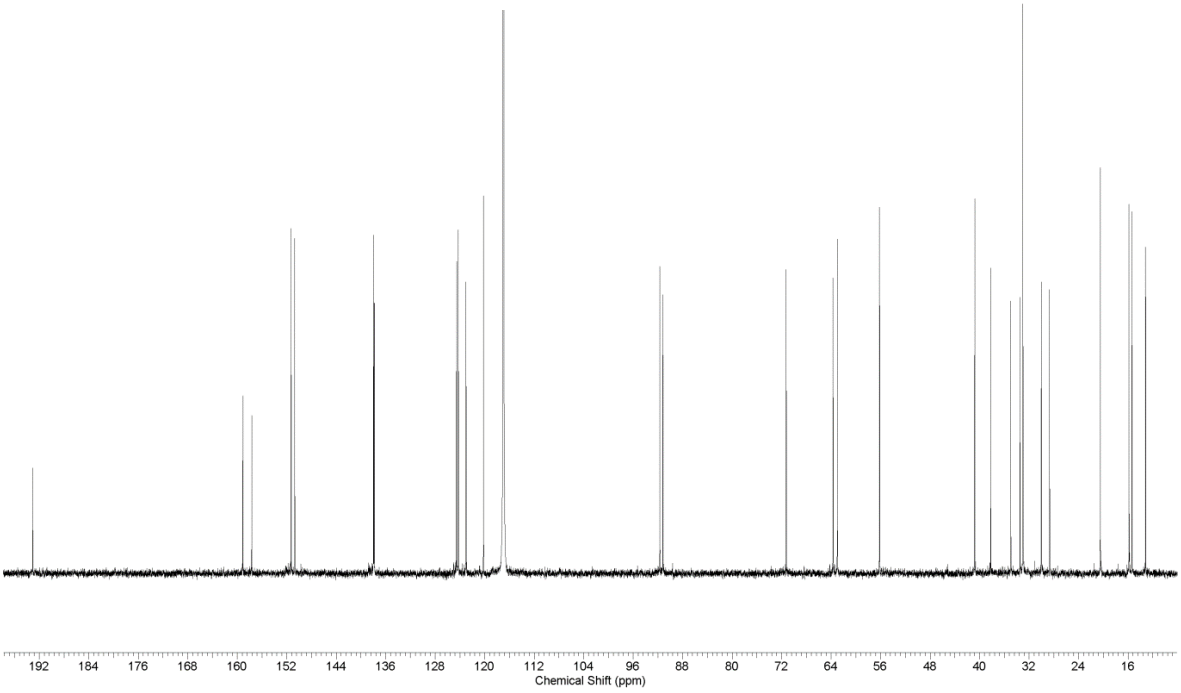
^1H NMR (CD_3CN)



endo,endo-[Ir(κ^3-*N,C,N'-S*-**L^{Me}**)(1,5-COD)]PF_6

13/09/2013 13:24:35

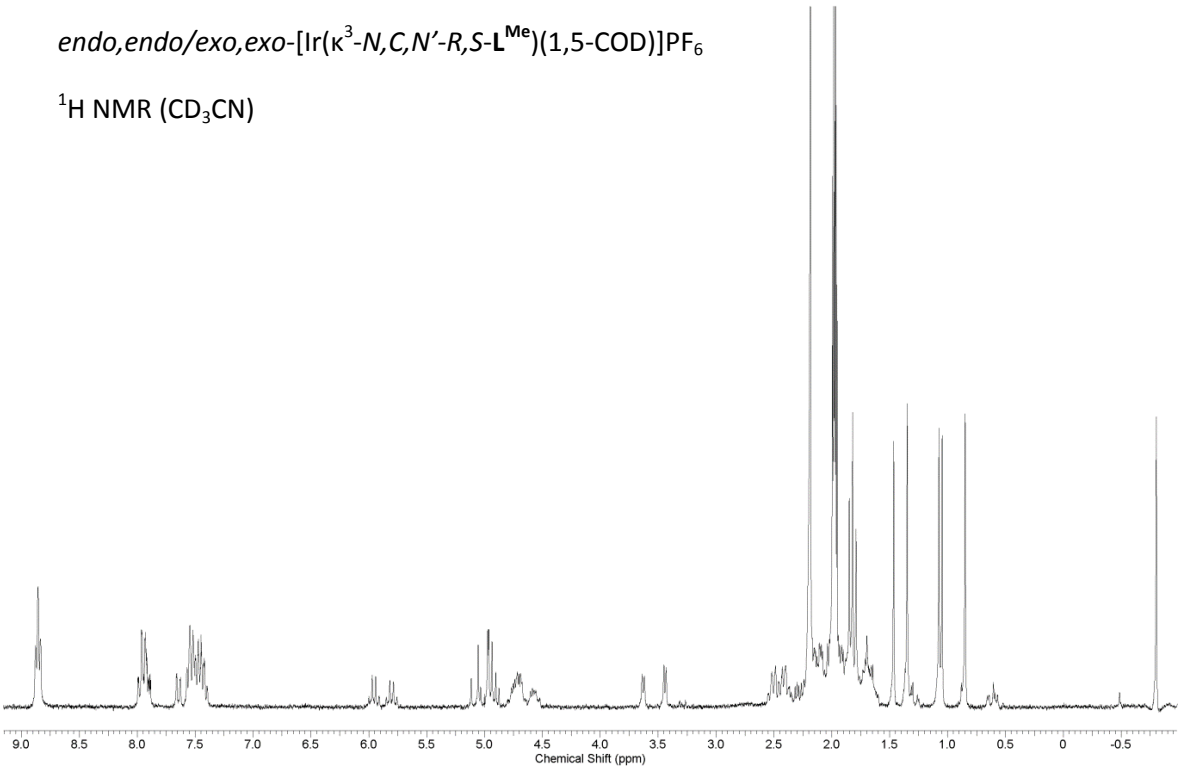
$^{13}C\{^1H\}$ NMR (CD_3CN)



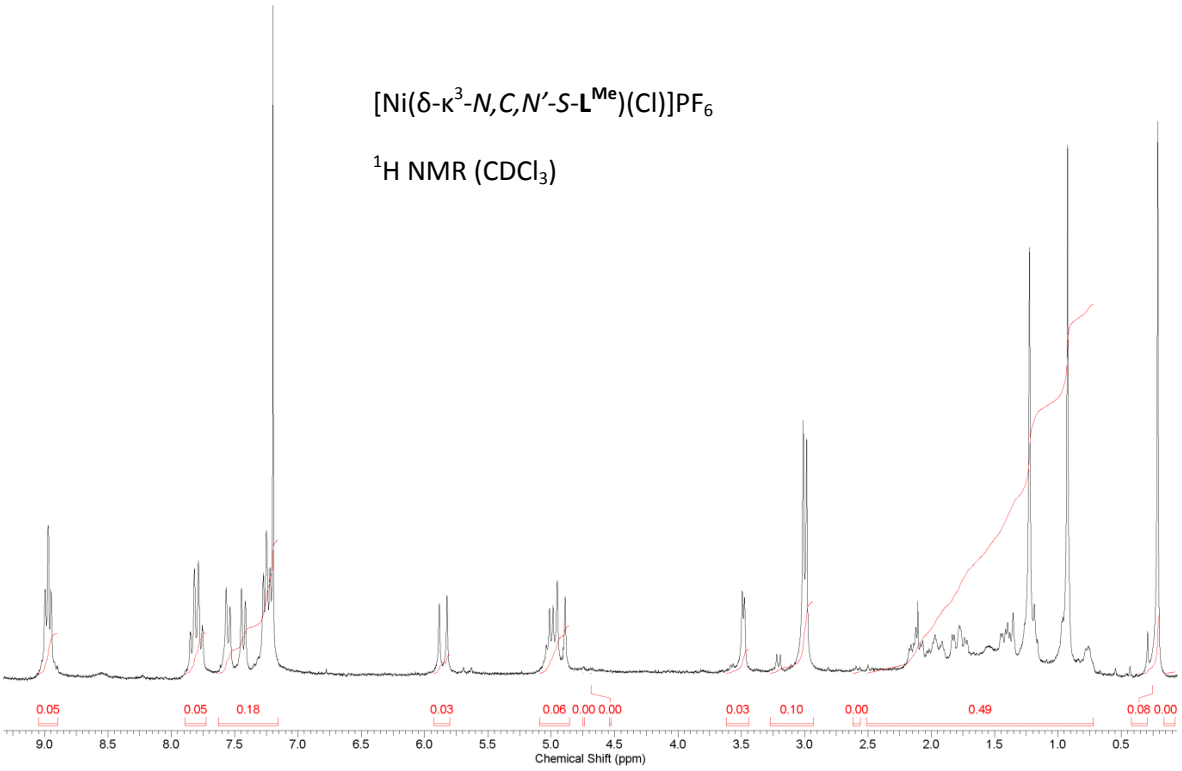
13/09/2013 12:17:45

endo,endo/exo,exo-[Ir(κ^3-*N,C,N'-R,S*-**L^{Me}**)(1,5-COD)]PF_6

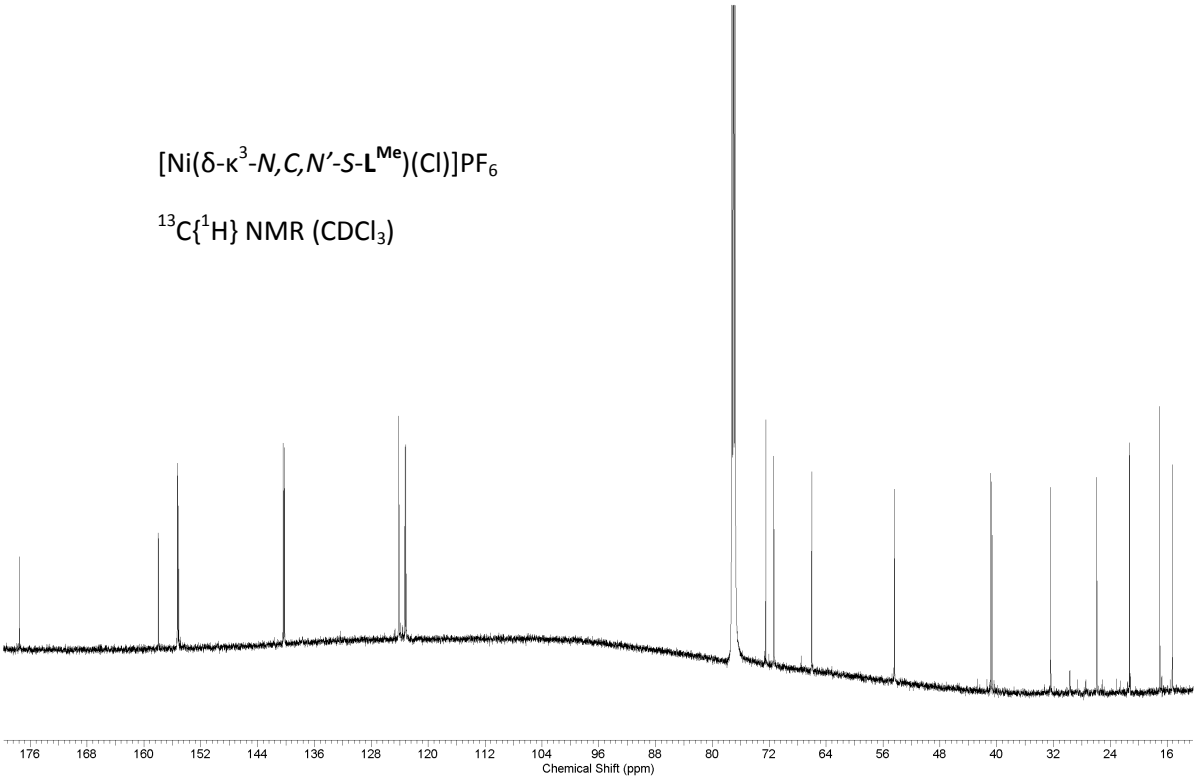
^1H NMR (CD_3CN)

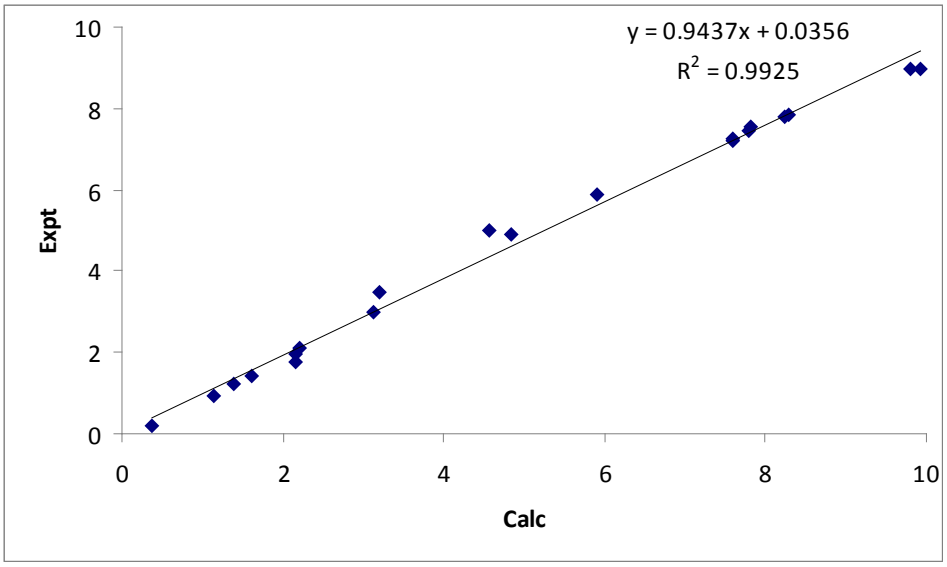


13/09/2013 13:48:59



24/09/2013 12:43:03





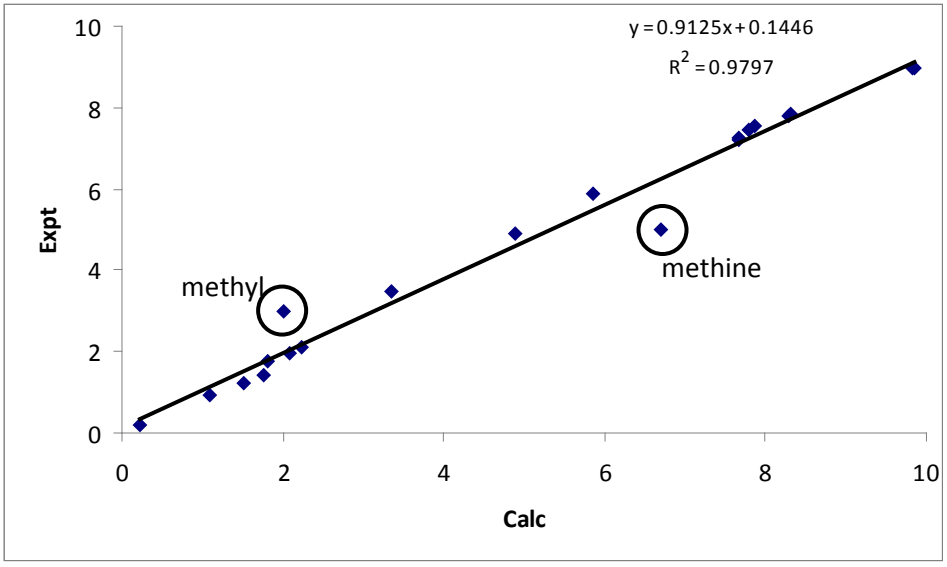


Table S1: Experimental vs. DFT predicted 1H chemical shifts for a) δ and b) λ conformers.

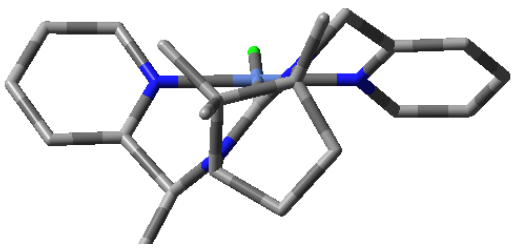


Fig S1: Geometry optimised molecular structure of [Ni(λ-κ^3-*N,C,N'*-*S*-**L^{Me}**)(Cl)]$^+$. Hydrogens are omitted for clarity.

Delta

C	3.13900000	-0.95190000	-0.68720000
H	3.25360000	-1.58990000	0.19620000
C	3.98860000	-1.05710000	-1.79570000
H	4.77650000	-1.82120000	-1.79880000
C	3.81950000	-0.17520000	-2.87320000
H	4.47760000	-0.22530000	-3.75160000
C	2.78480000	0.77270000	-2.81030000
H	2.60780000	1.47920000	-3.63140000
C	1.96030000	0.81210000	-1.67920000
C	0.76230000	1.72920000	-1.56180000
H	0.87630000	2.38670000	-0.67610000
H	0.67330000	2.37080000	-2.44930000
C	-0.50250000	0.19290000	-0.25490000
C	-1.52390000	0.78980000	-2.47250000
C	-2.76060000	1.59290000	-1.97890000
H	-2.44080000	2.53260000	-1.49050000
H	-3.40080000	1.86870000	-2.83910000
C	-3.51030000	0.62570000	-1.00170000
H	-3.58520000	1.03050000	0.02510000
H	-4.53760000	0.41740000	-1.35570000
C	-2.66220000	-0.67250000	-1.01890000
H	-3.23970000	-1.58810000	-0.80120000
C	-2.02010000	-0.70080000	-2.43190000
C	-1.00320000	1.23350000	-3.83950000
H	-0.06280000	0.71170000	-4.10810000
H	-0.83920000	2.32870000	-3.88390000

H	-1.76570000	0.99140000	-4.60250000
C	-3.11530000	-0.98660000	-3.48720000
H	-3.57920000	-1.97090000	-3.27180000
H	-2.67270000	-1.04030000	-4.50120000
H	-3.91790000	-0.22540000	-3.50150000
C	-0.90960000	-1.75220000	-2.61290000
H	-1.33220000	-2.77040000	-2.48430000
H	-0.07220000	-1.63430000	-1.89950000
H	-0.49680000	-1.68960000	-3.64020000
C	-1.68060000	-1.33880000	1.24860000
H	-2.73980000	-1.64140000	1.32620000
C	-1.38960000	-0.43450000	2.43680000
C	-2.26260000	-0.37040000	3.53320000
H	-3.16830000	-0.99060000	3.53670000
C	-1.96550000	0.48530000	4.60470000
H	-2.63710000	0.54780000	5.47150000
C	-0.80040000	1.26420000	4.53980000
H	-0.52610000	1.95720000	5.34500000
C	0.03560000	1.14390000	3.42470000
H	0.97350000	1.70240000	3.34030000
Cl	2.68380000	-0.14450000	2.32660000
Ni	0.97600000	0.12200000	0.92220000
N	2.14870000	-0.02950000	-0.62920000
N	-0.45680000	0.91460000	-1.39060000
N	-1.57310000	-0.57580000	-0.01420000
N	-0.25120000	0.30290000	2.40010000
C	-0.80980000	-2.61210000	1.24200000

H	-1.01550000	-3.21720000	2.14800000
H	-1.03990000	-3.21880000	0.34260000
H	0.26700000	-2.34650000	1.23760000

Lambda

C	-0.98050000	3.42140000	0.63390000
H	-1.49880000	3.22650000	1.57920000
C	-1.13170000	4.62360000	-0.06820000
H	-1.81430000	5.39080000	0.31900000
C	-0.39990000	4.82160000	-1.24870000
H	-0.49300000	5.75610000	-1.81860000
C	0.45720000	3.79990000	-1.69060000
H	1.04910000	3.91120000	-2.60820000
C	0.55510000	2.61630000	-0.94650000
C	1.42890000	1.45530000	-1.37420000
H	1.92470000	1.70360000	-2.32270000
H	2.21710000	1.28570000	-0.61060000
C	-0.11080000	-0.14000000	-0.47270000
C	0.62050000	-0.58610000	-2.82640000
C	-0.72910000	-0.29560000	-3.54530000
H	-1.00180000	0.77120000	-3.43470000
H	-0.63170000	-0.50120000	-4.62850000
C	-1.76810000	-1.25860000	-2.87810000
H	-2.61950000	-0.72040000	-2.42150000
H	-2.18000000	-1.97340000	-3.61550000
C	-0.95130000	-2.01640000	-1.80120000

H	-1.34660000	-3.01650000	-1.56950000
C	0.48370000	-2.08990000	-2.38620000
C	1.84910000	-0.30130000	-3.69130000
H	2.79060000	-0.41080000	-3.11670000
H	1.81380000	0.71060000	-4.14290000
H	1.86500000	-1.02330000	-4.52880000
C	0.49390000	-3.05650000	-3.59460000
H	0.14920000	-4.05760000	-3.26340000
H	1.52230000	-3.17170000	-3.99010000
H	-0.15920000	-2.72490000	-4.42360000
C	1.55280000	-2.57490000	-1.38970000
H	1.33470000	-3.62040000	-1.08780000
H	1.60960000	-1.95940000	-0.47230000
H	2.55090000	-2.56810000	-1.87330000
C	-1.65070000	-1.59620000	0.68920000
H	-2.16060000	-0.67600000	1.04080000
C	-0.60060000	-1.94660000	1.74340000
C	-0.47540000	-3.20150000	2.35230000
H	-1.19440000	-3.99520000	2.12230000
C	0.57230000	-3.42590000	3.26180000
H	0.68460000	-4.40480000	3.74760000
C	1.46680000	-2.38190000	3.53580000
H	2.30100000	-2.50880000	4.23750000
C	1.27680000	-1.14500000	2.90740000
H	1.91680000	-0.28030000	3.11470000
Cl	0.25550000	1.85320000	3.10530000
Ni	0.05150000	0.78680000	1.16860000

N	-0.15160000	2.44190000	0.20010000
N	0.63460000	0.21850000	-1.53360000
N	-0.91810000	-1.20830000	-0.55430000
N	0.26440000	-0.93720000	2.03330000
C	-2.73070000	-2.65650000	0.46900000
H	-3.31210000	-2.76750000	1.40530000
H	-3.42300000	-2.33560000	-0.33330000
H	-2.31490000	-3.64780000	0.20320000

Table S2: Coordinates for the Geometry optimised molecular structures of [Ni(δ-κ^3-*N,C,N'*-*S*-**L^{Me}**)(Cl)]$^+$ and [Ni(λ-κ^3-*N,C,N'*-*S*-**L^{Me}**)(Cl)]$^+$.