Supporting Information

Structural diversity of late transition metal complexes with flexible tetra-NHC ligands

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Content

1. Detailed information on crystallographic data

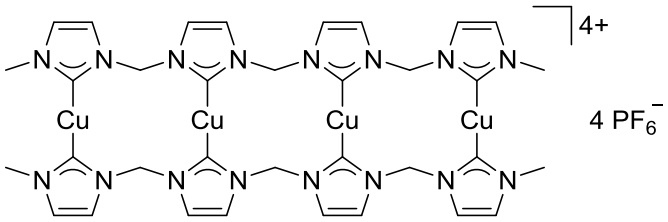
Table S1. Crystallographic Data for Tetra-NHC Complexes **3**, **5**, **6**, **7**, and **9**.

	3 (Cu_4(**L1**)$_2$(PF_6)$_4$)	**5** (Cu_2(**L2**)(PF_6)$_2$)	**6** (Au_2(**L2**)(PF_6)$_2$)	**7** (Ni(**L1**)(PF_6)$_2$)	**9** (Pt(**L1**)(PF_6)$_2$)
CCDC	1401411	1401412	1401413	1401414	1401415
formula	$C_{38}H_{46}Cu_4F_{24}N_{18}P_4$	$C_{19}H_{24}Cu_2F_{12}N_8P_2$	$C_{19}H_{24}Au_2F_{12}N_8P_2$	$C_{17}H_{20}F_{12}N_8NiP_2$	$C_{17}H_{20}F_{12}N_8P_2Pt$
fw	1588.97	781.48	1048.33	685.02	821.44
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	P-1 (No. 2)	P-1 (No. 2)
a [Å]	12.5785(9)	20.099(9)	20.5116(4)	10.286(2)	10.3598(6)
b [Å]	27.1993(19)	10.385(4)	10.3863(2)	11.806(5)	12.0333(6)
c [Å]	20.0728(13)	13.286(5)	13.2141(3)	12.097(3)	12.0391(8)
□ [°]	90	90	90	61.093(18)	60.019(2)
□ [°]	94.106(4)	91.55(4)	92.2120(10)	70.772(14)	71.750(3)
□ [°]	90	90	90	85.36(2)	77.024(2)
V [Å^3]	6849.8(8)	2772.2(2)	2813.03(10)	1208.7(8)	1230.38(13)
Z	4	4	4	4	2
T [K]	123	123	123	123	123
D_{calc} [g cm^{-3}]	1.541	1.872	2.475	1.876	2.217
μ [mm^{-1}]	1.426	1.759	10.640	1.051	5.950
R1/wR2 (I>2□(I))	0.0441/0.1235	0.0281/0.0640	0.0216/0.0392	0.0308/0.0728	0.0332/0.0767
R1/wR2 (all data)	0.0508/0.1284	0.0370/0.0677	0.0326/0.0419	0.0369/0.0754	0.0374/0.0783

Table S2. Crystallographic Data for Tetra-NHC Complexes **10**, **11**, **14**, and **16**.

	10 (Ni(**L2**)$(PF_6)_2$)	**11** (Pd(**L2**)$(PF_6)_2$)	**14** (Fe(**L1**)$(PMe_3)_2(PF_6)_2$)	**16** (Fe(**L2**)(PMe_3) $(MeCN)(PF_6)_2$)
CCDC	1401416	1401417	1401418	1401419
formula	$C_{21}H_{27}F_{12}N_9NiP_2$	$C_{57}H_{72}F_{36}N_{24}P_6$ Pd_3	$C_{13.5}H_{22}F_6Fe_{0.5}N_4P_2$	$C_{26}H_{39}F_{12}FeN_{10}P_3$
fw	754.17	2282.40	458.22	868.43
space group	*Pbca* (No. 61)	$P2_1$ (No. 4)	*Fdd*2 (No. 43)	$P2_1/n$ (No. 14)
a [Å]	10.6200(2)	14.7168(3)	19.9505(4)	12.5032(3)
b [Å]	13.0884(2)	11.1897(3)	26.1623(7)	14.0746(4)
c [Å]	40.5195(6)	24.0049(5)	14.5631(4)	20.8711(5)
□ [°]	90	90	90	90
□ [°]	90	93.7770(10)	90	90.0770(10)
□ [°]	90	90	90	90
V [$Å^3$]	5632.16(16)	3944.46(16)	7601.2(3)	3672.84(16)
Z	8	2	16	4
T [K]	123	123	123	123
D_{calc} [g cm^{-3}]	1.779	1.922	1.602	1.571
μ [mm^{-1}]	0.915	0.941	0.661	0.638
R1/wR2 (*I*>2□(*I*))	0.0351/0.0765	0.0437/0.0780	0.0281/0.0655	0.0405/0.0819
R1/wR2 (all data)	0.0537/0.0841	0.0515/0.0805	0.0328/0.0675	0.0605/0.0894

2. NMR spectra of compound 3 ($Cu_4[L1]_2[PF_6]_4$)



3

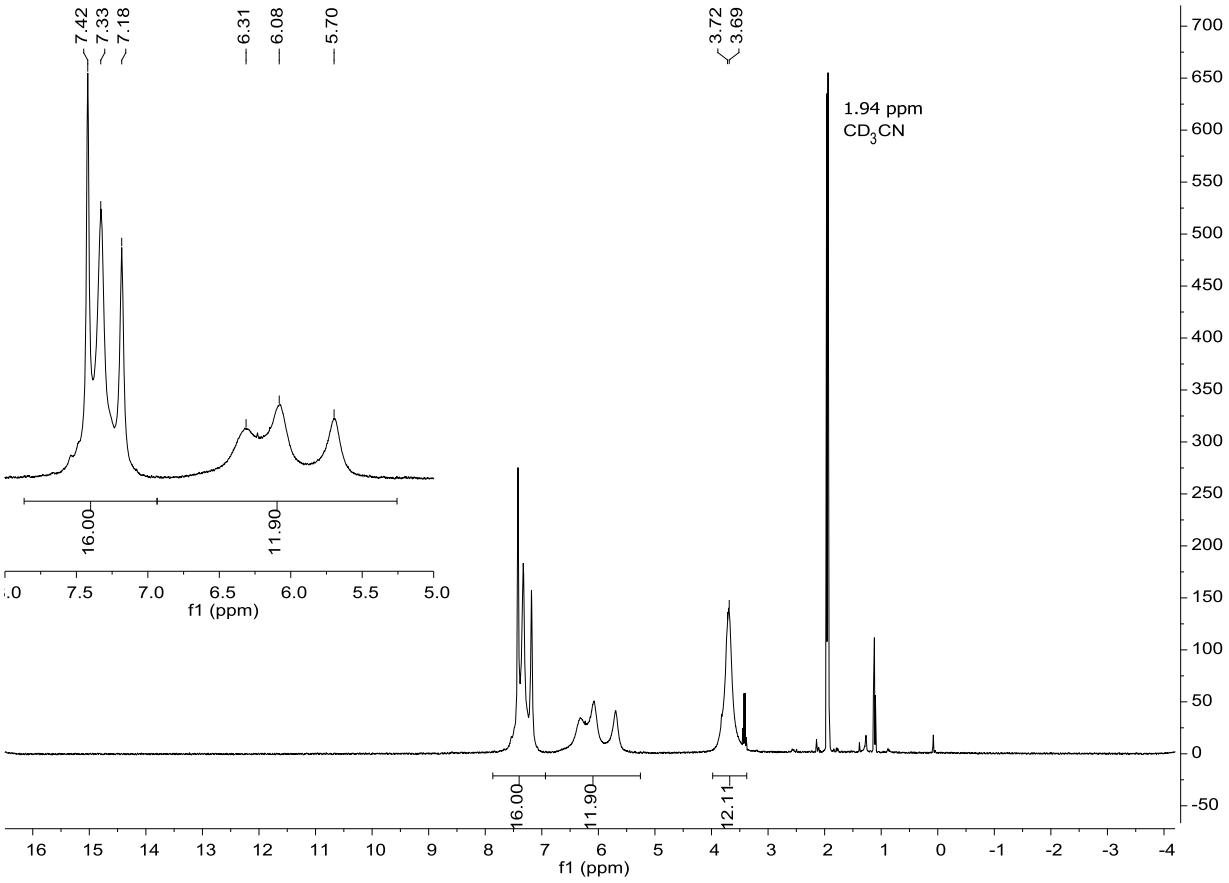


Figure S1: ^{1}H NMR of 3 in CD_3CN at 400.13 MHz.

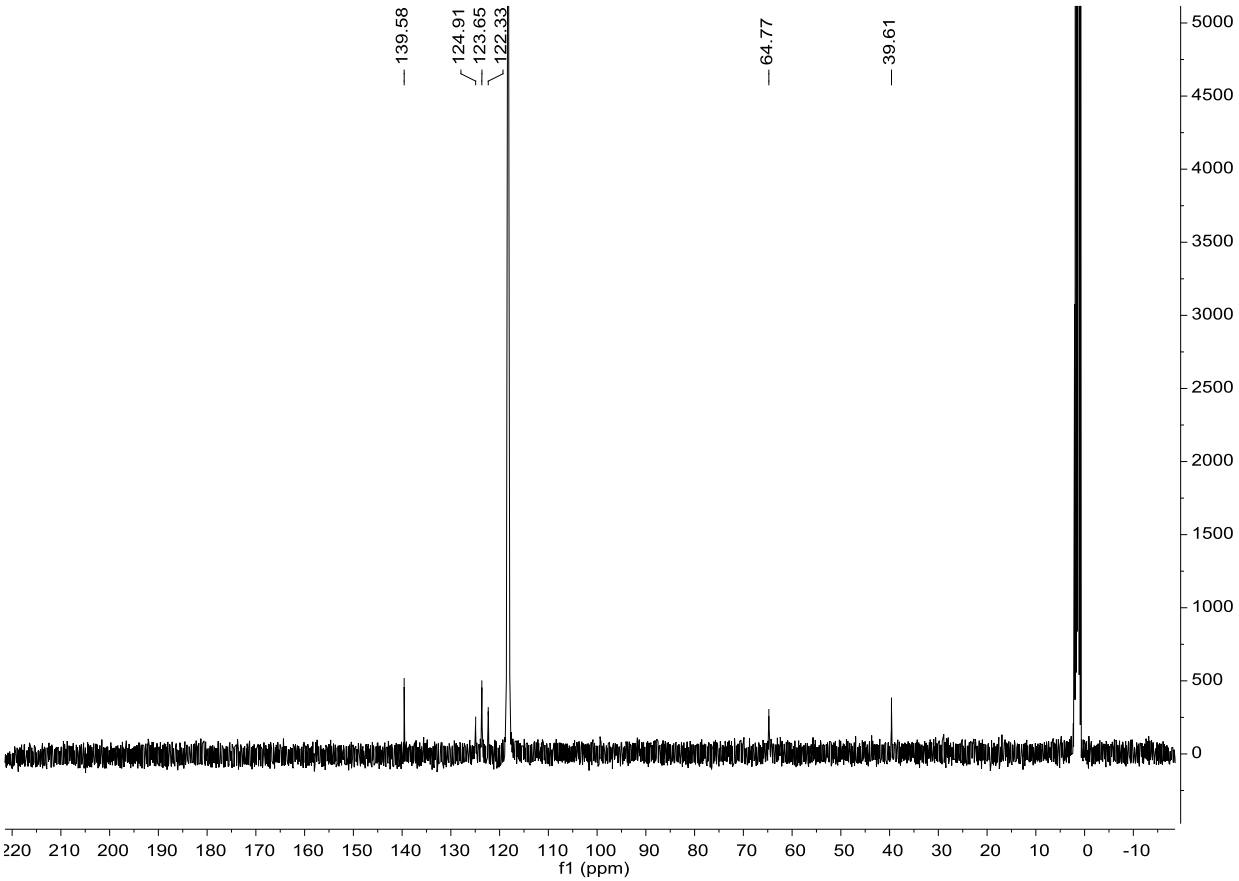


Figure S2: $^{13}C\{^{1}H\}$ NMR of 3 in CD_3CN at 100.62 MHz and 343.2 K (70 °C).

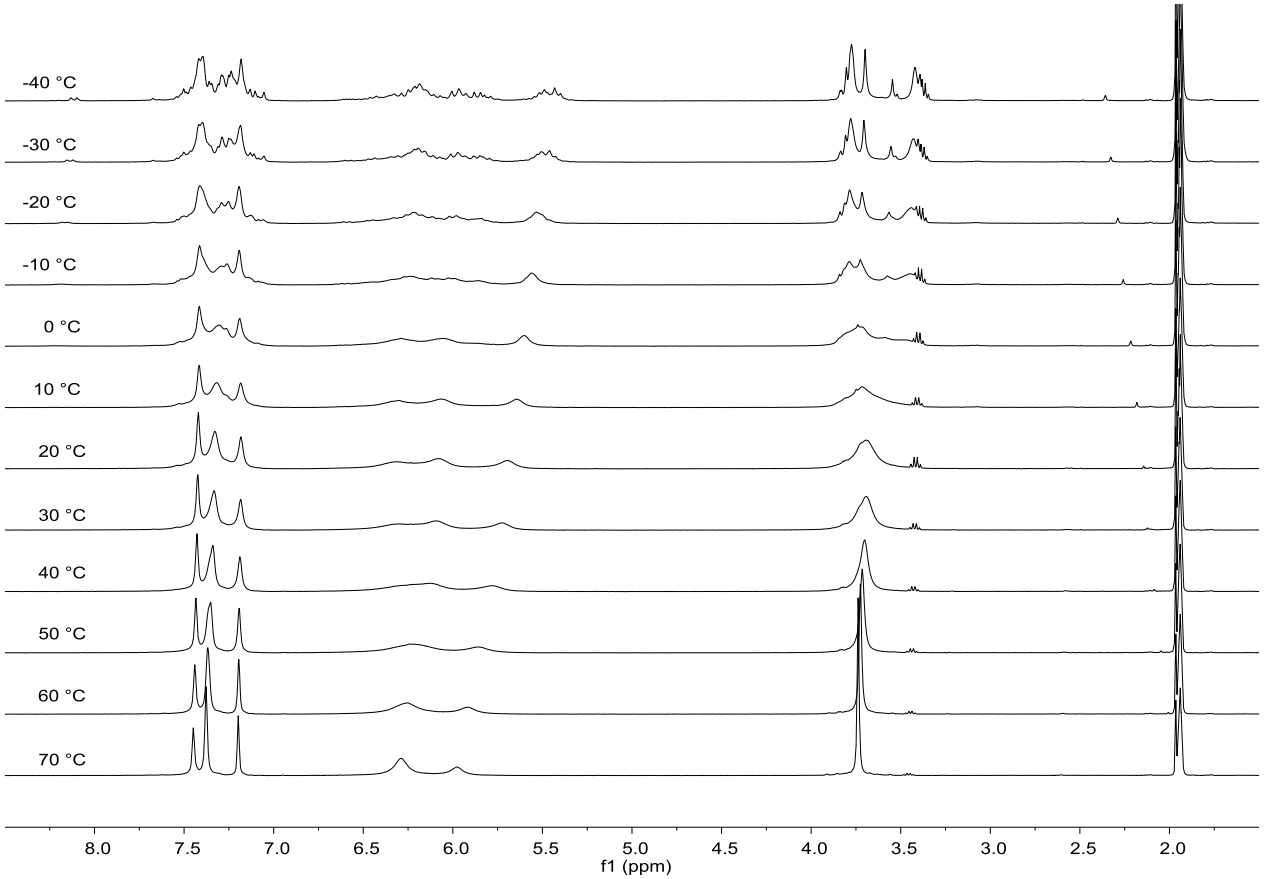
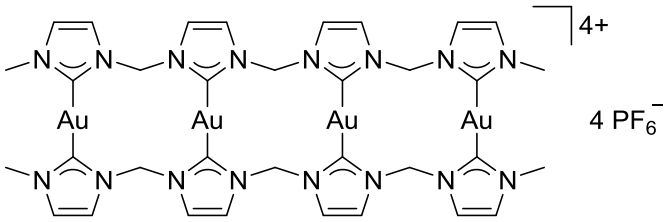


Figure S3: Variable temperature ^{1}H NMR of 3 in CD_3CN at 400.13 MHz.

3. NMR spectra of compound 4 ($Au_4[L1]_2[PF_6]_4$)



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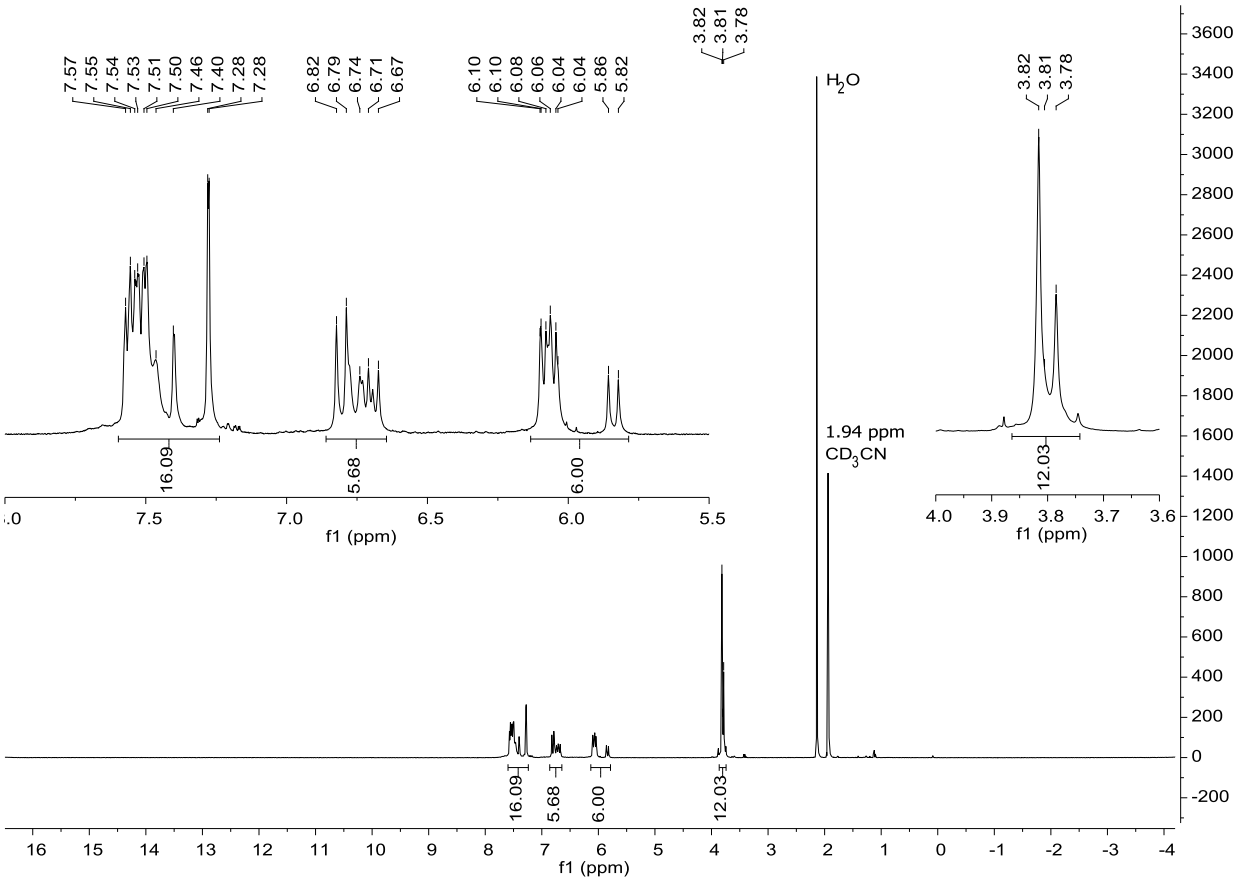


Figure S4: ^{1}H NMR of 4 in CD_3CN at 400.13 MHz.

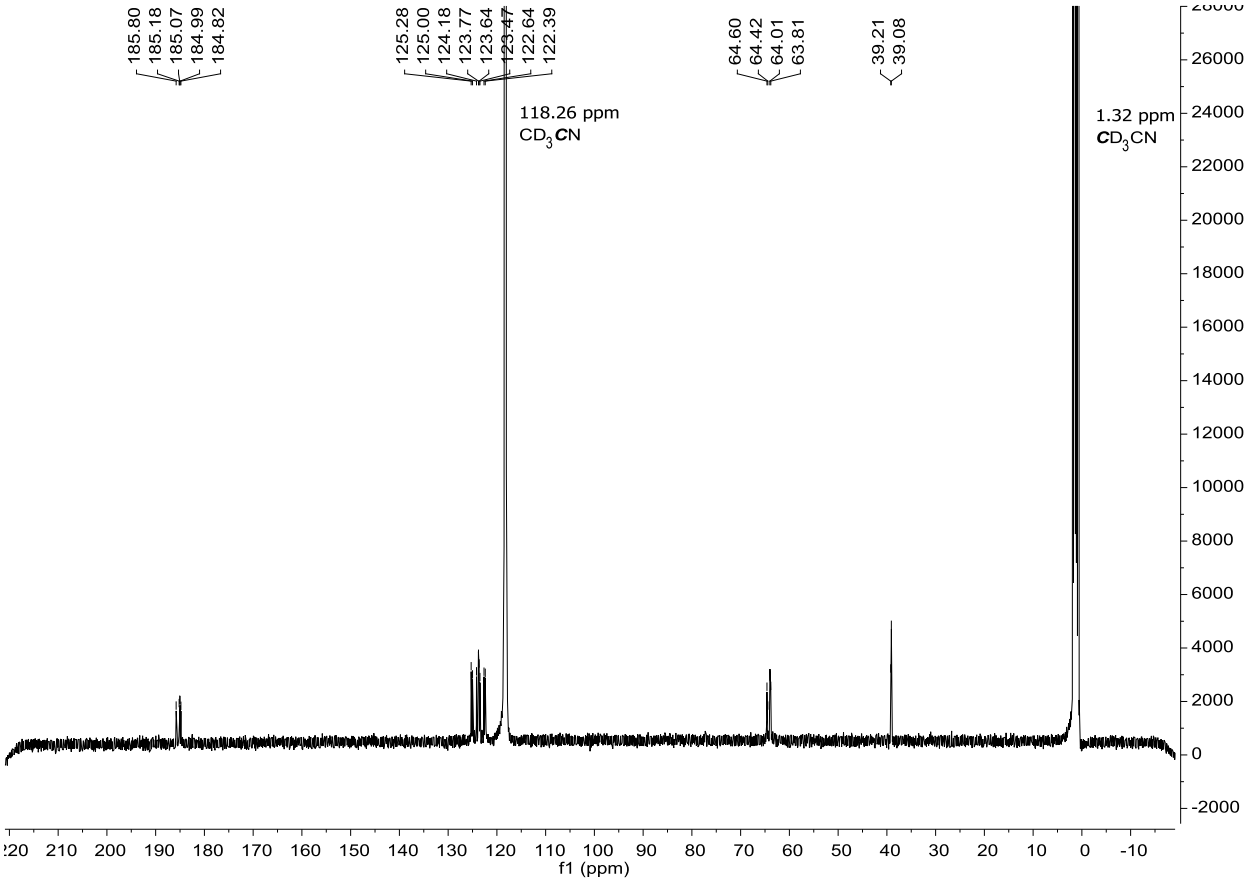


Figure S5: $^{13}C\{^{1}H\}$ NMR of 4 in CD_3CN at 100.62 MHz.

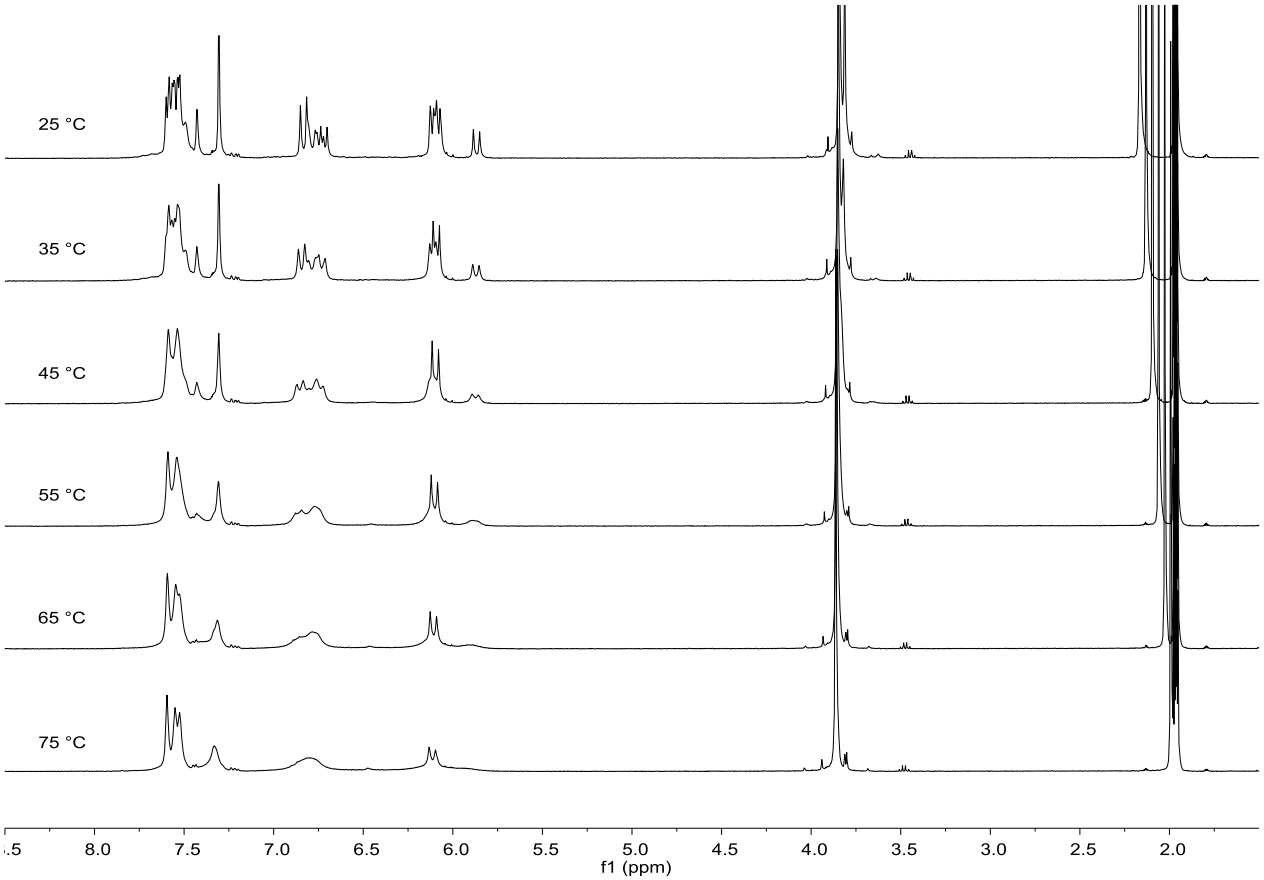


Figure S6: Variable temperature ^{1}H NMR of 4 in CD_3CN at 400.13 MHz.

4. High temperature ^{13}C NMR spectra of 1,3, and 4

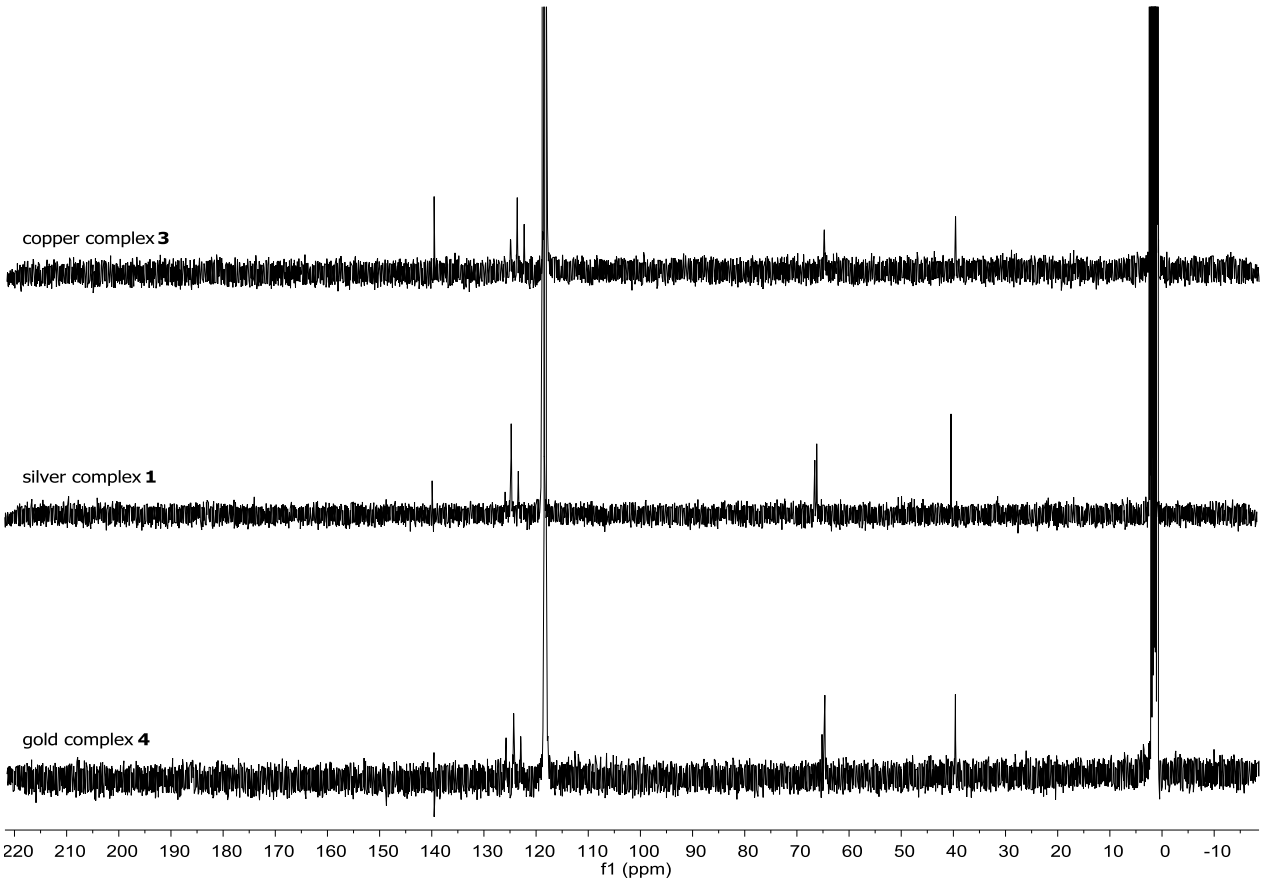
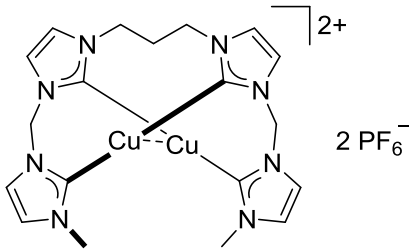


Figure S7: $^{13}C\{^{1}H\}$ NMR of 1,3, and 4 in CD_3CN at 100.62 MHz and 70 °C.

5. NMR spectra of compound 5 ($Cu_2[L2][PF_6]_4$)



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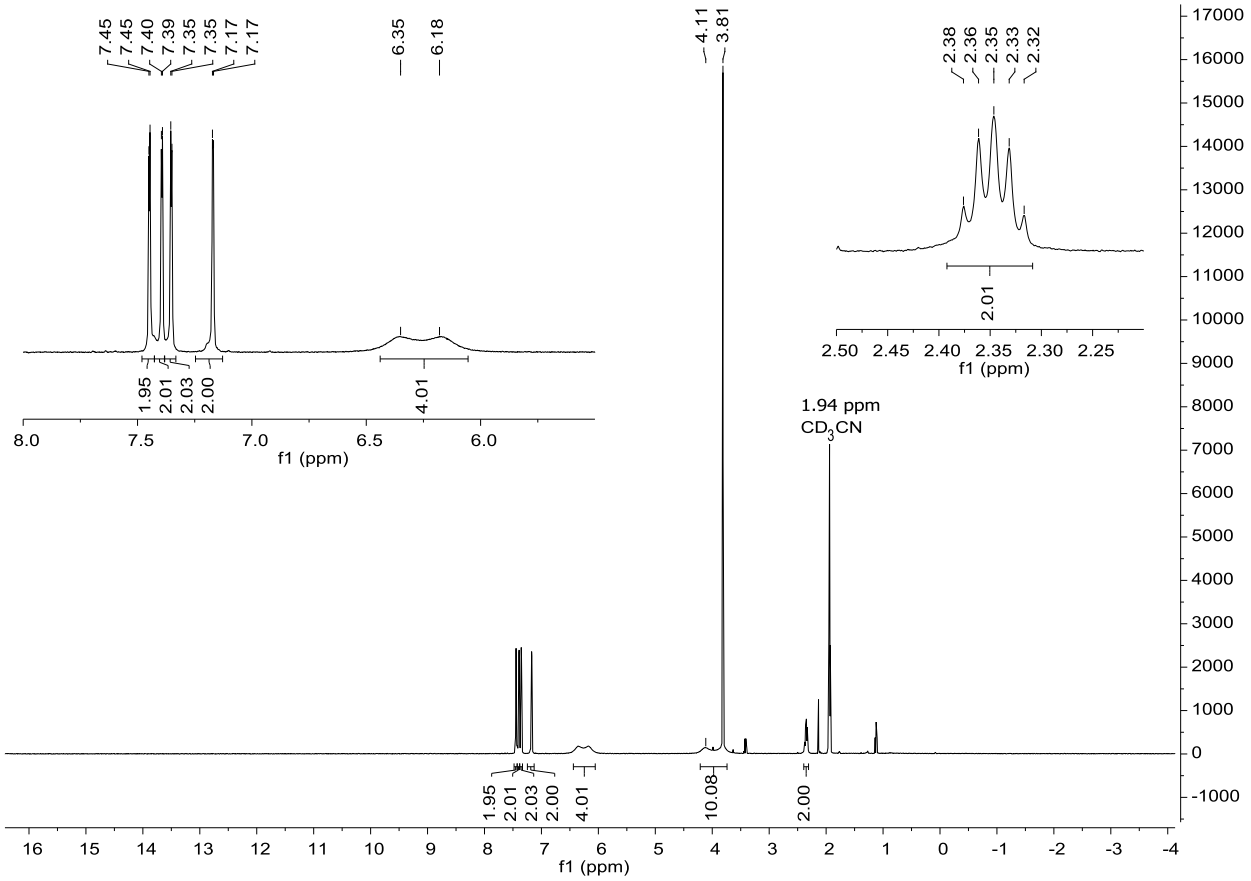


Figure S8: ^{1}H NMR of 5 in CD_3CN at 400.13 MHz.

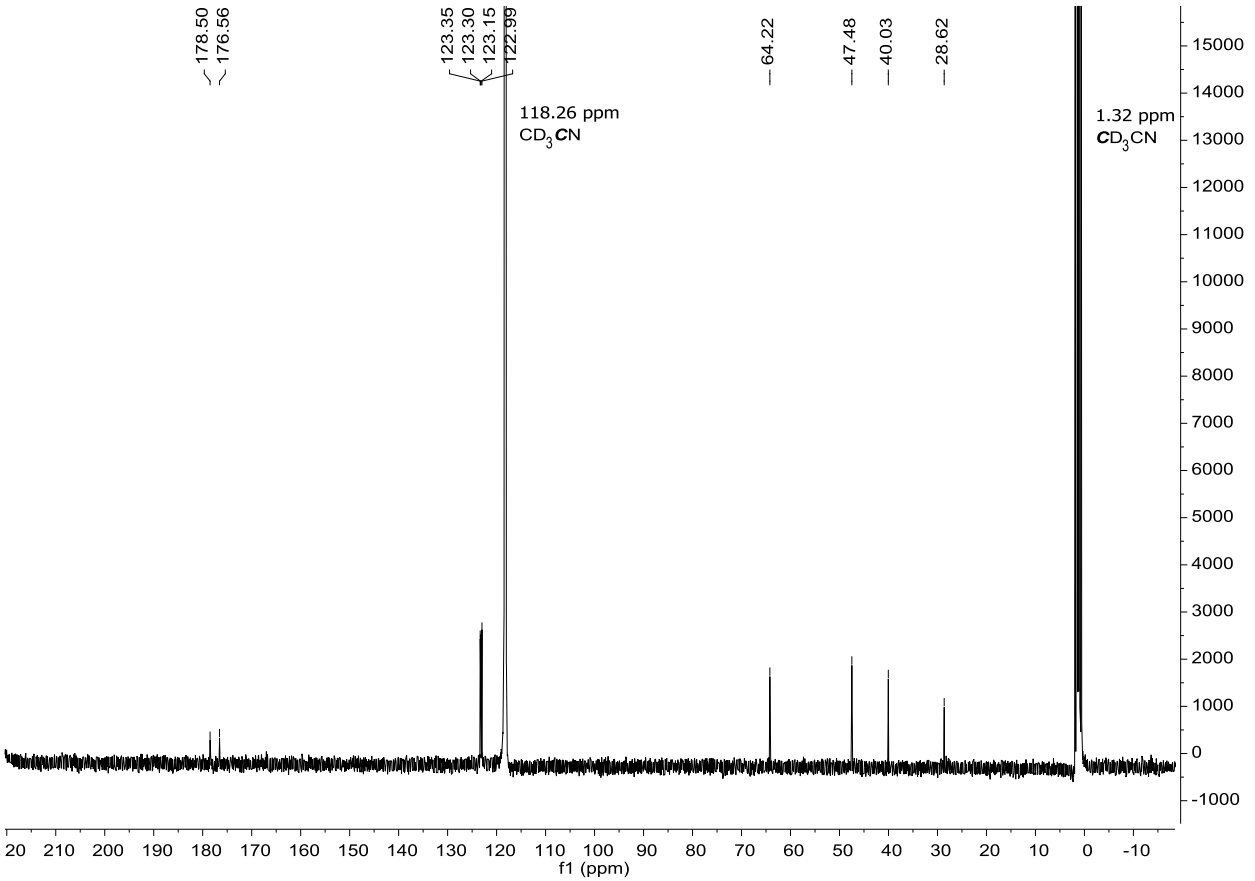


Figure S9: $^{13}C\{^{1}H\}$ NMR of 5 in CD_3CN at 100.62 MHz.

6. NMR spectra of compound 6 ($Au_2[L2][PF_6]_4$)

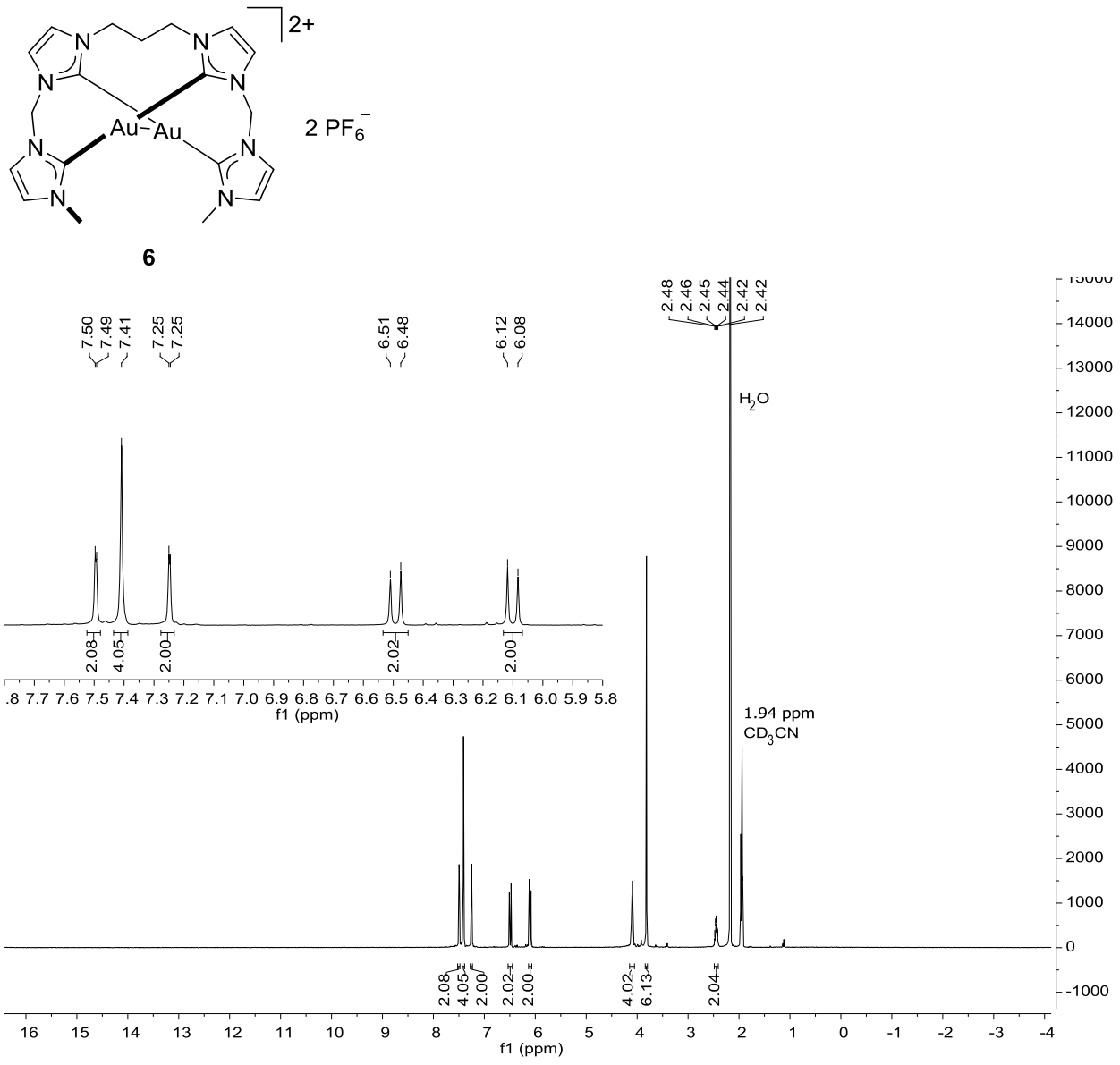


Figure S10: ^{1}H NMR of 6 in CD_3CN at 400.13 MHz and 296.6 K (ambient temperature).

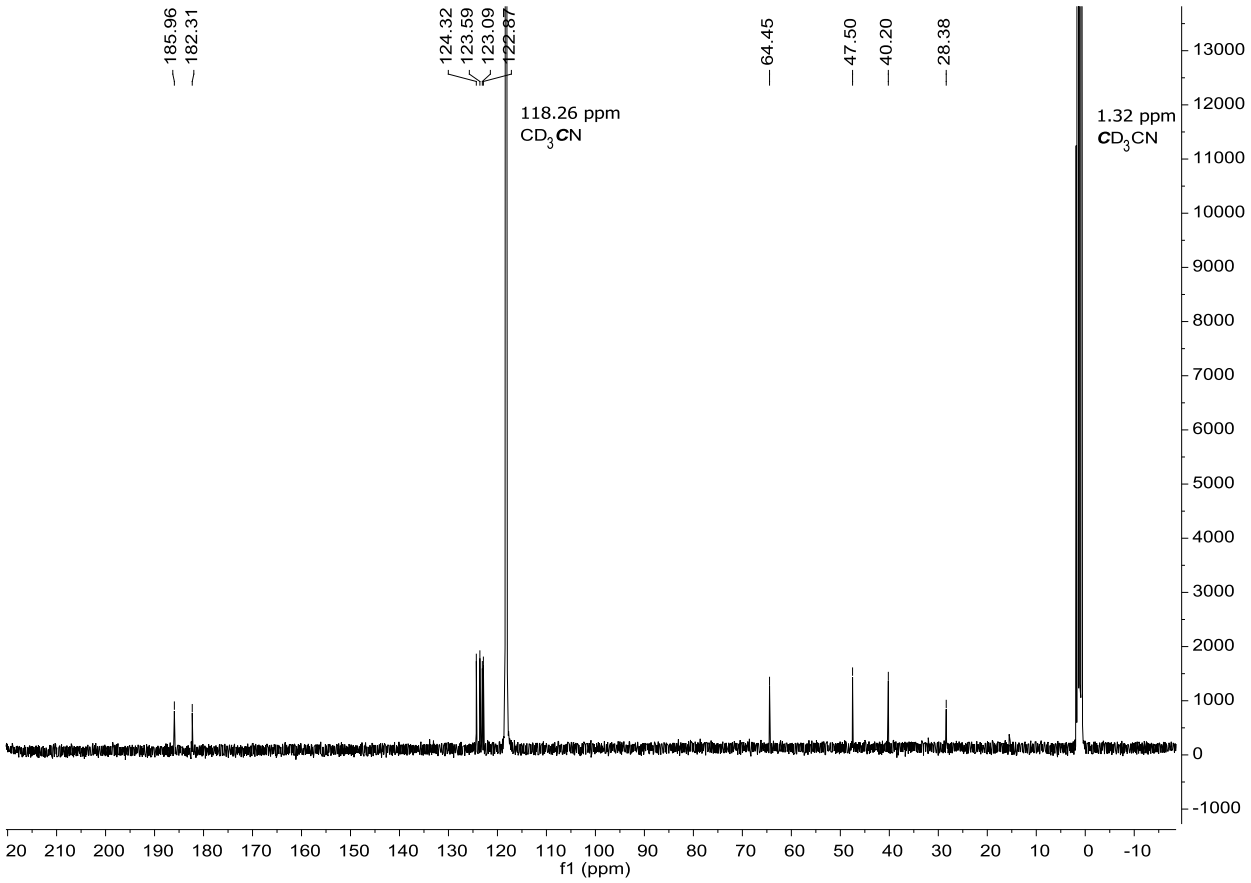
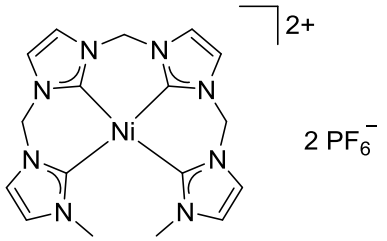


Figure S11: $^{13}C\{^{1}H\}$ NMR of 6 in CD_3CN at 100.62 MHz.

7. NMR spectra of compound 7 ($Ni[L1][PF_6]_2$)



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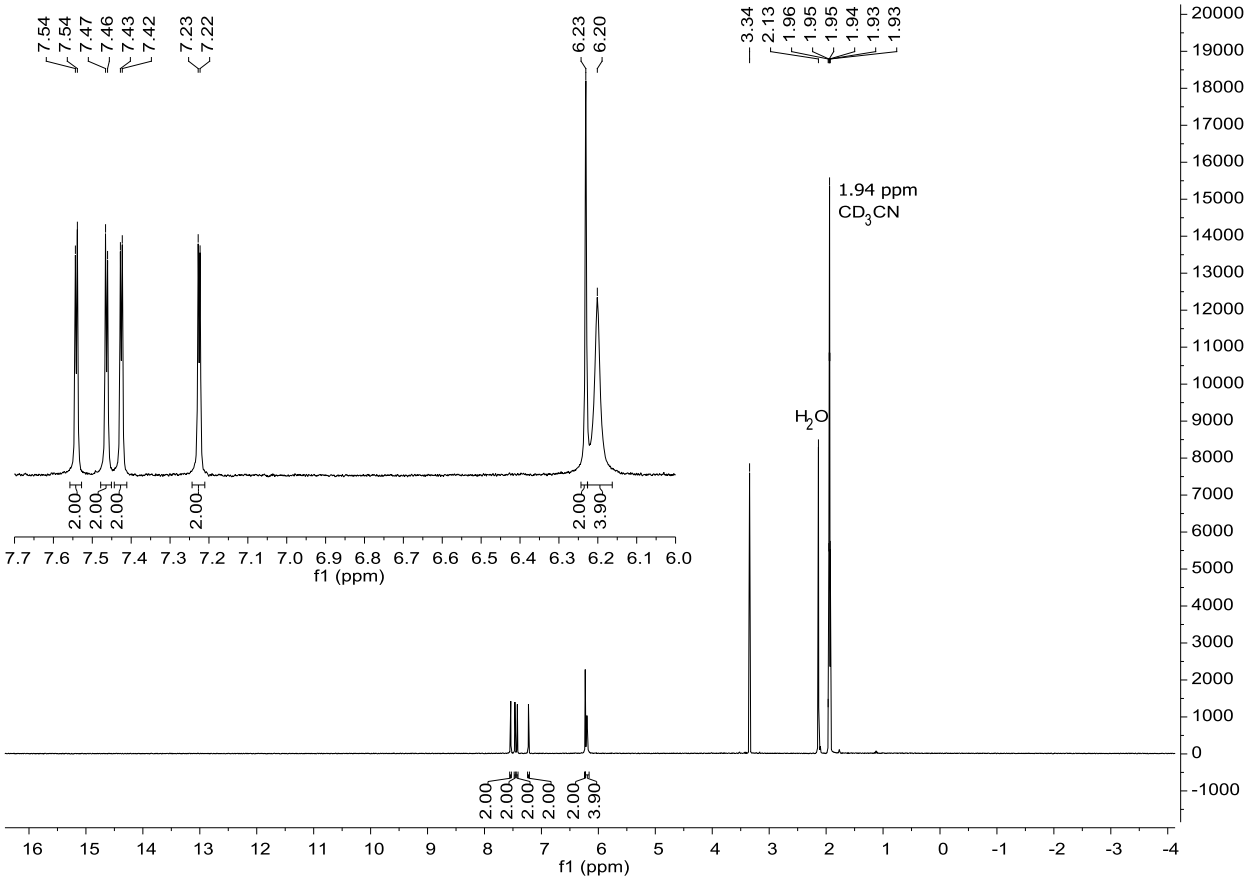


Figure S12: ^{1}H NMR of 7 in CD_3CN at 400.13 MHz.

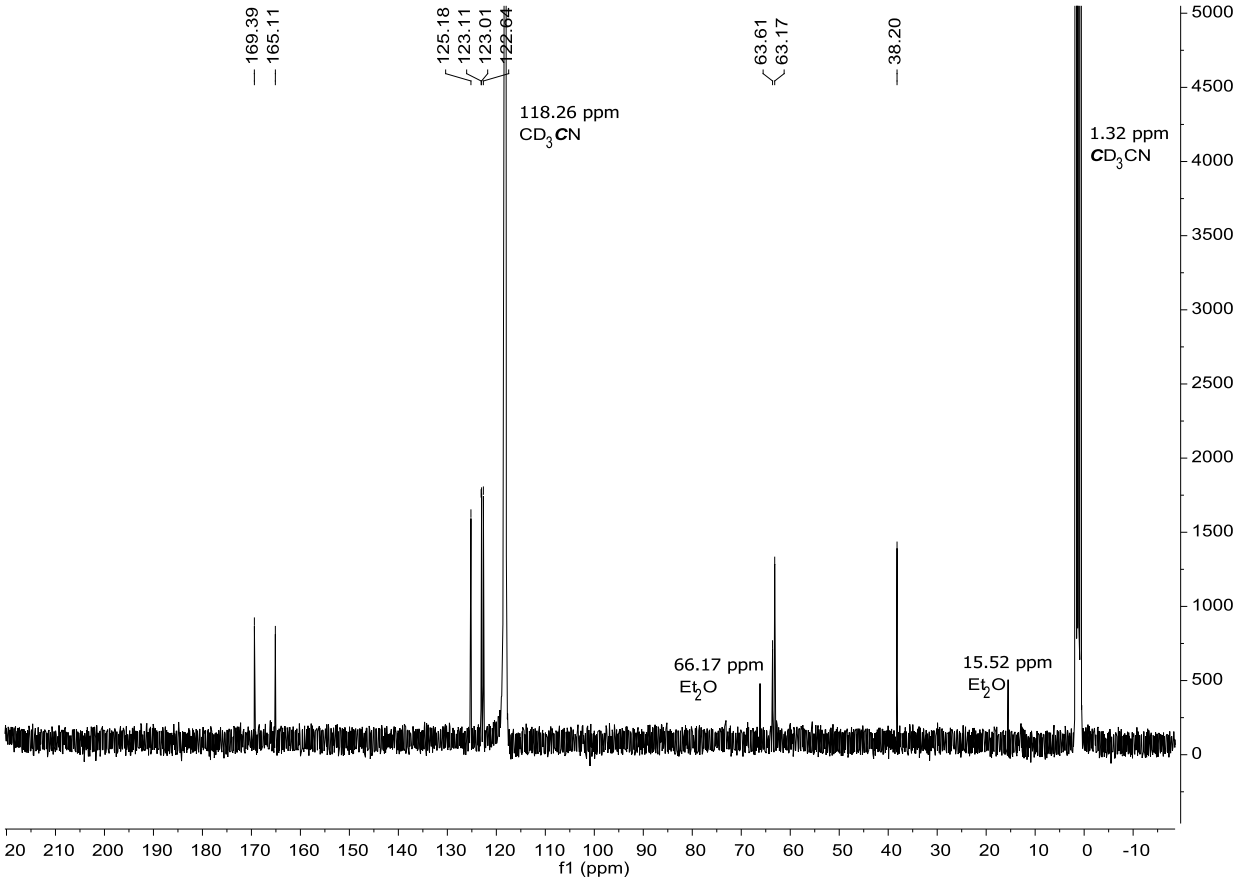
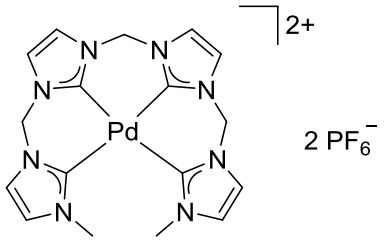


Figure S13: $^{13}C\{^{1}H\}$ NMR of 7 in CD_3CN at 100.62 MHz.

8. NMR spectra of compound 8 ($Pd[L1][PF_6]_2$)



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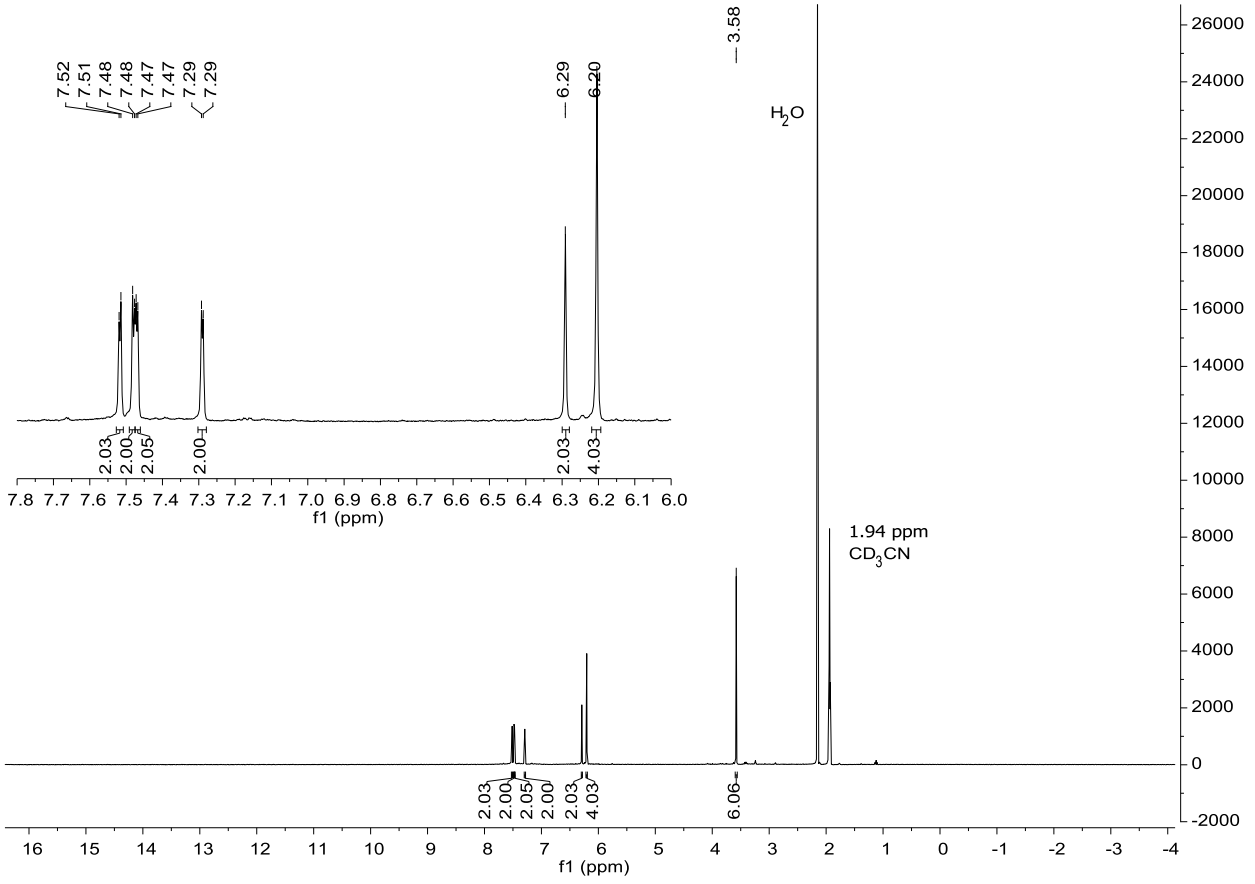


Figure S14: ^{1}H NMR of 8 in CD_3CN at 400.13 MHz.

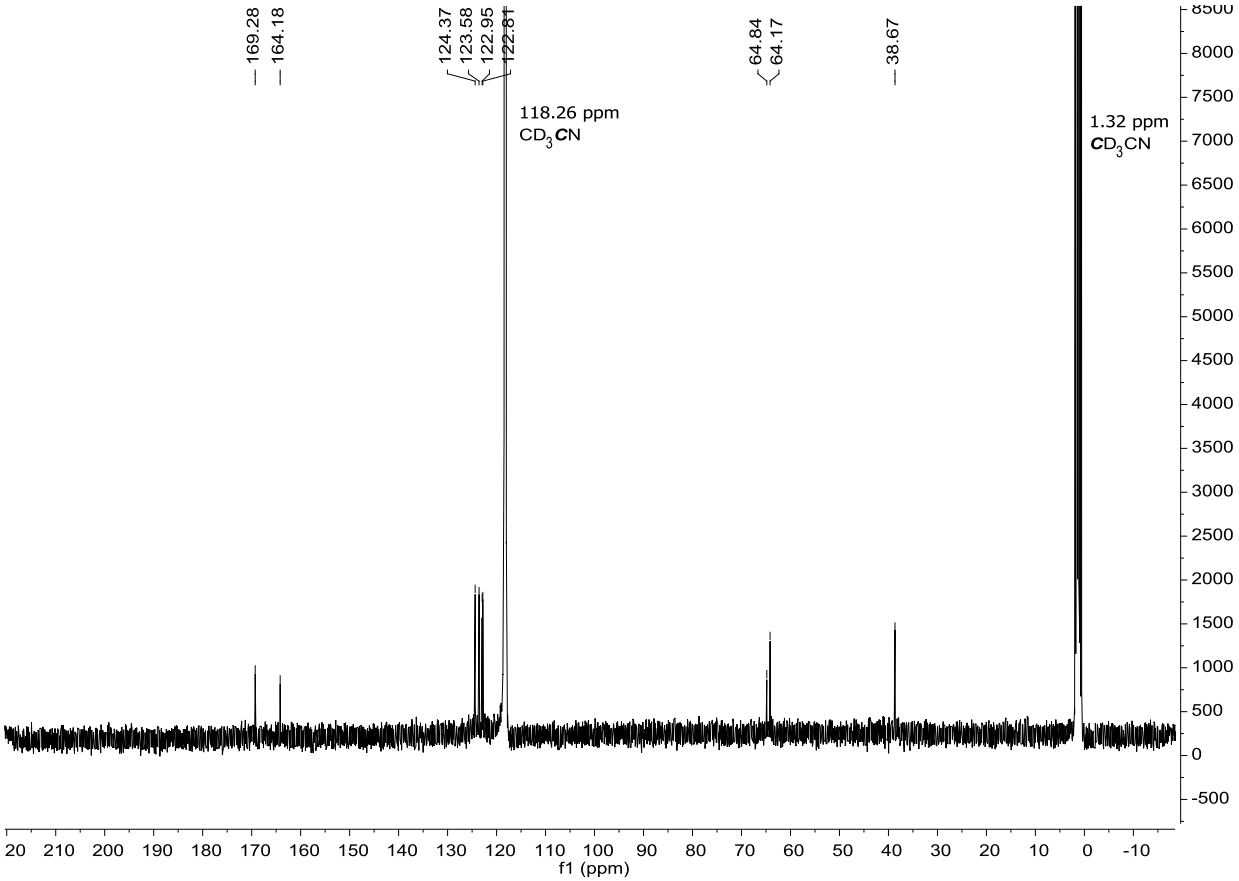
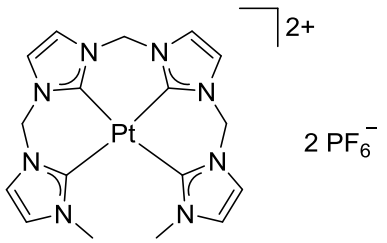


Figure S15: $^{13}C\{^{1}H\}$ NMR of 8 in CD_3CN at 100.62 MHz.

9. NMR spectra of compound 9 ($Pt[L1][PF_6]_2$)



2 PF_6^-

9

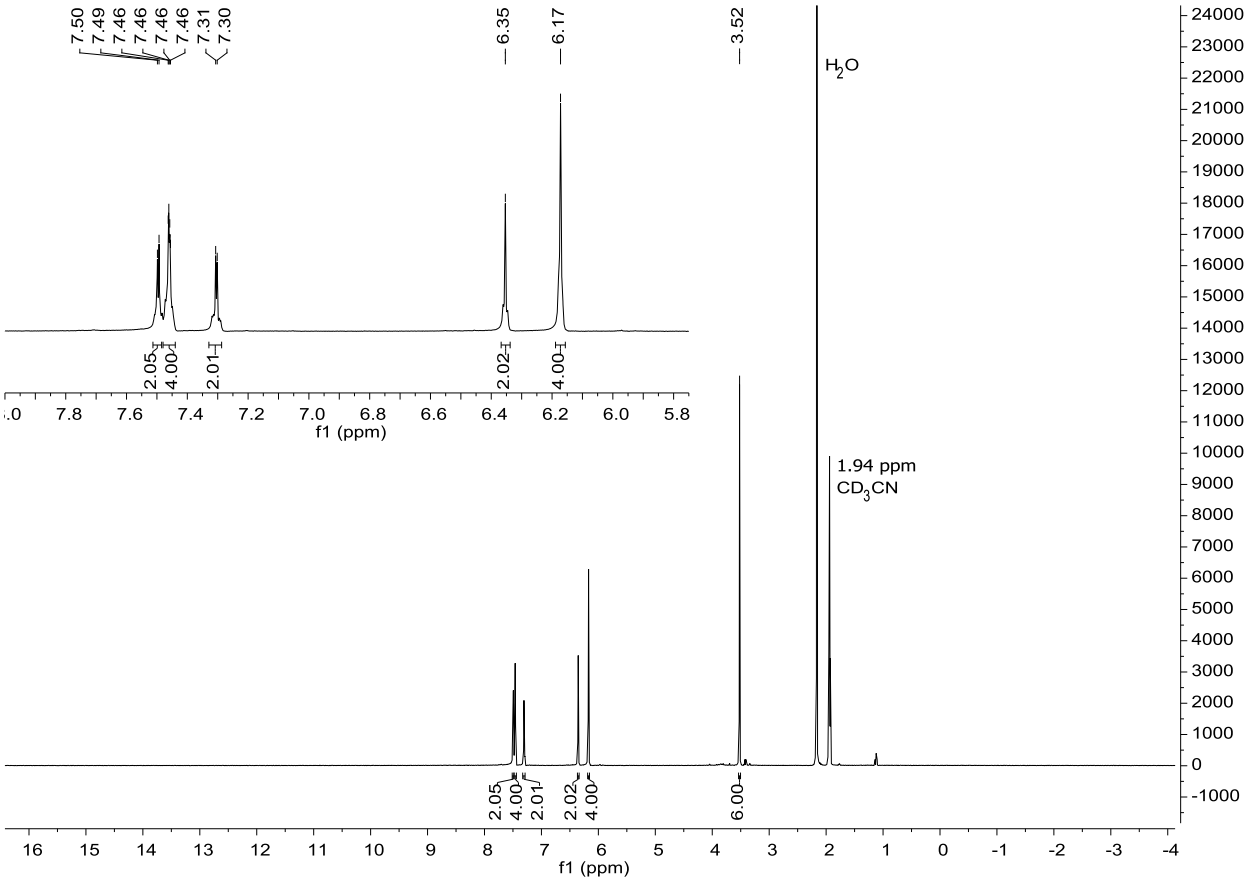


Figure S16: ^{1}H NMR of 9 in CD_3CN at 400.13 MHz.

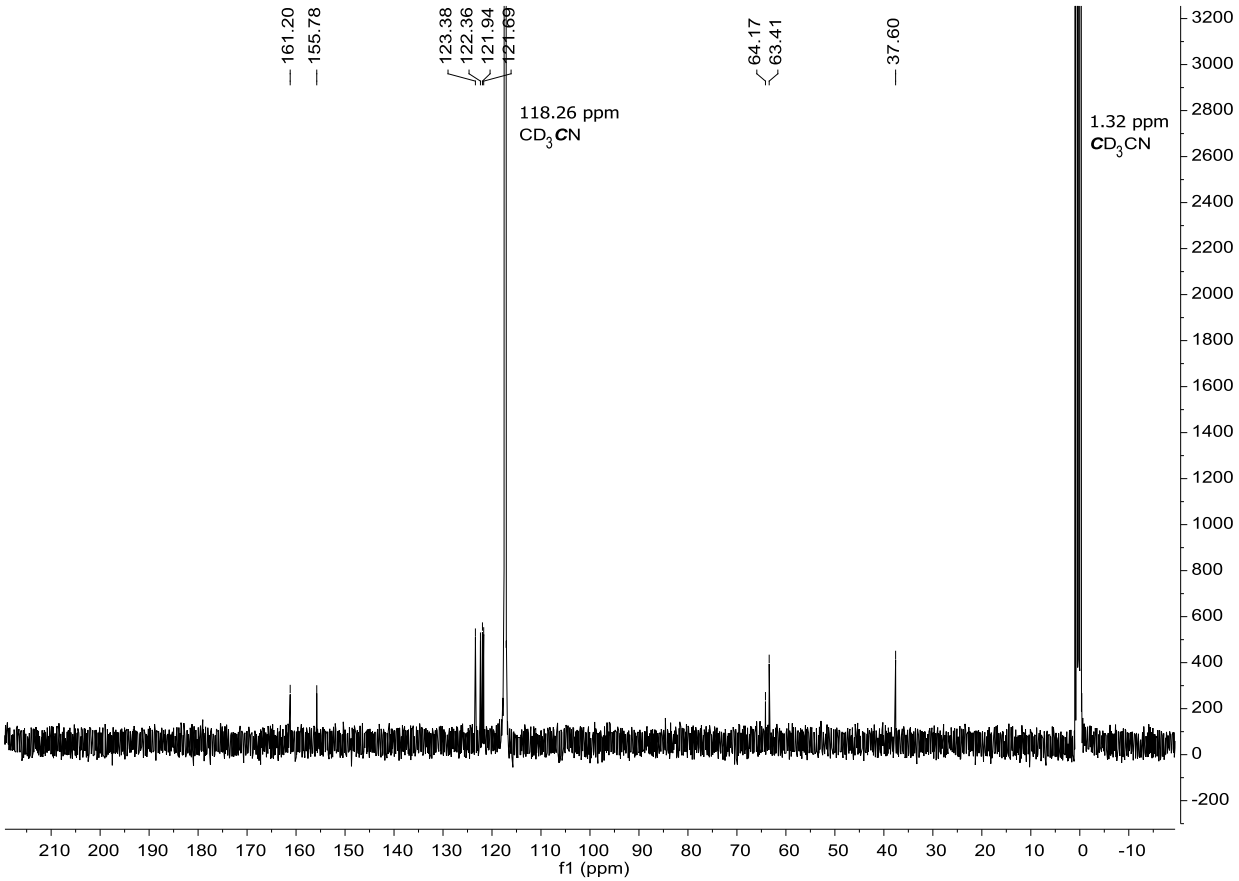
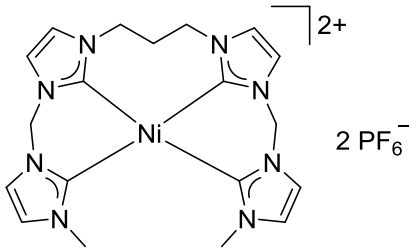


Figure S17: $^{13}C\{^{1}H\}$ NMR of 9 in CD_3CN at 100.62 MHz.

10. NMR spectra of compound 10 ($Ni[L2][PF_6]_2$)



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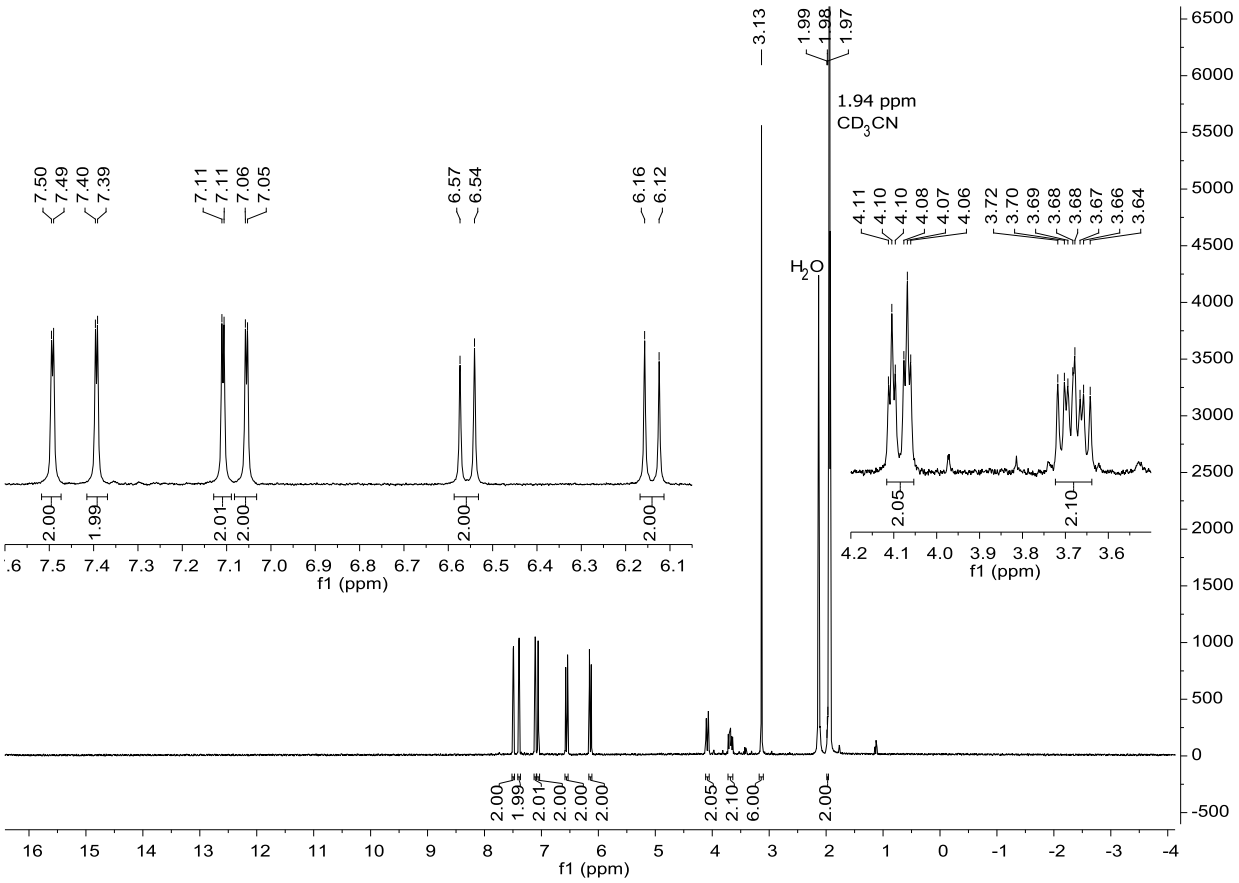


Figure S18: ^{1}H NMR of 10 in CD_3CN at 400.13 MHz.

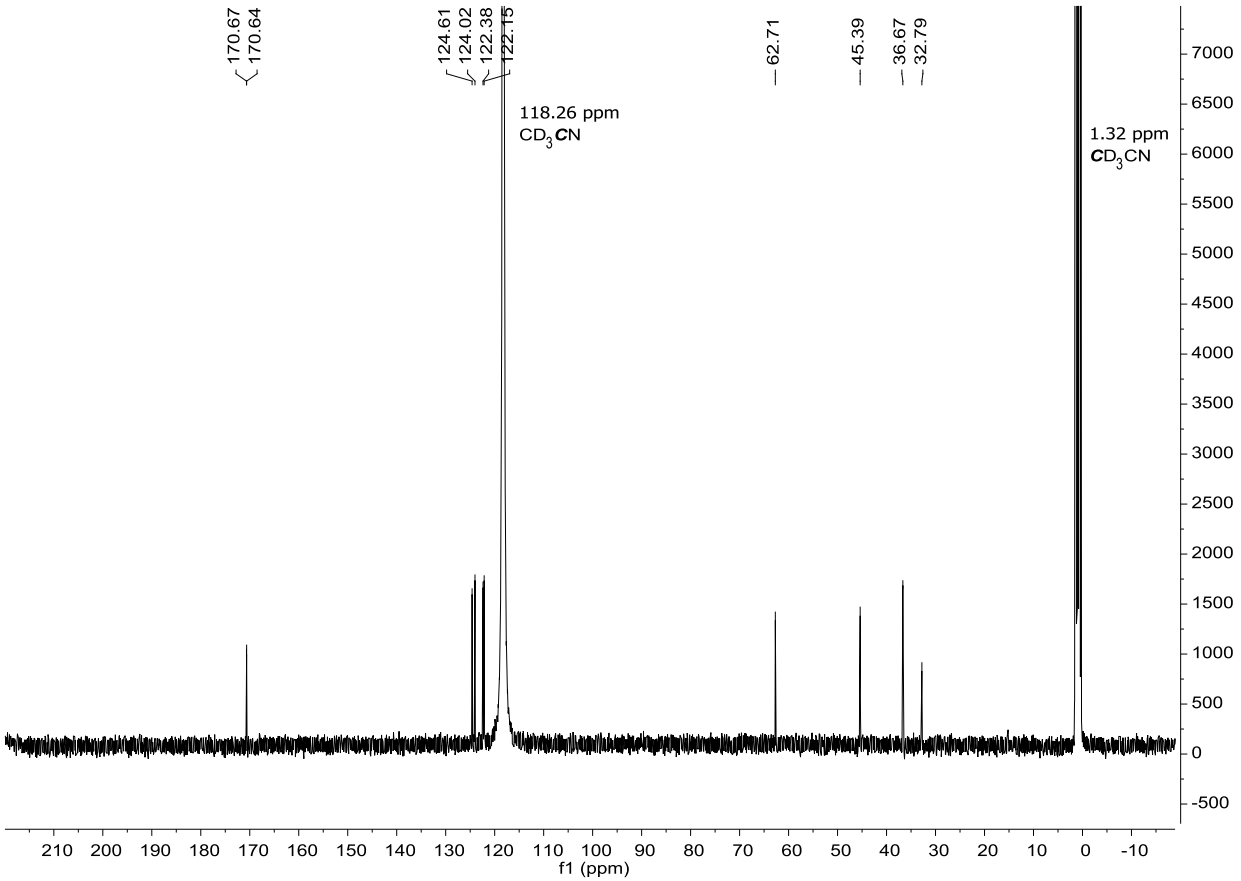
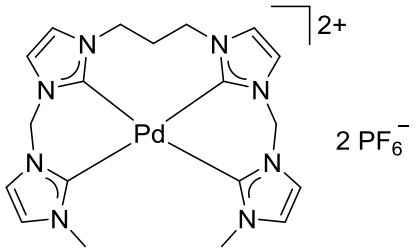


Figure S19: $^{13}C\{^{1}H\}$ NMR of 10 in CD_3CN at 100.62 MHz.

11. NMR spectra of compound 11 ($Pd[L2][PF_6]_2$)



11

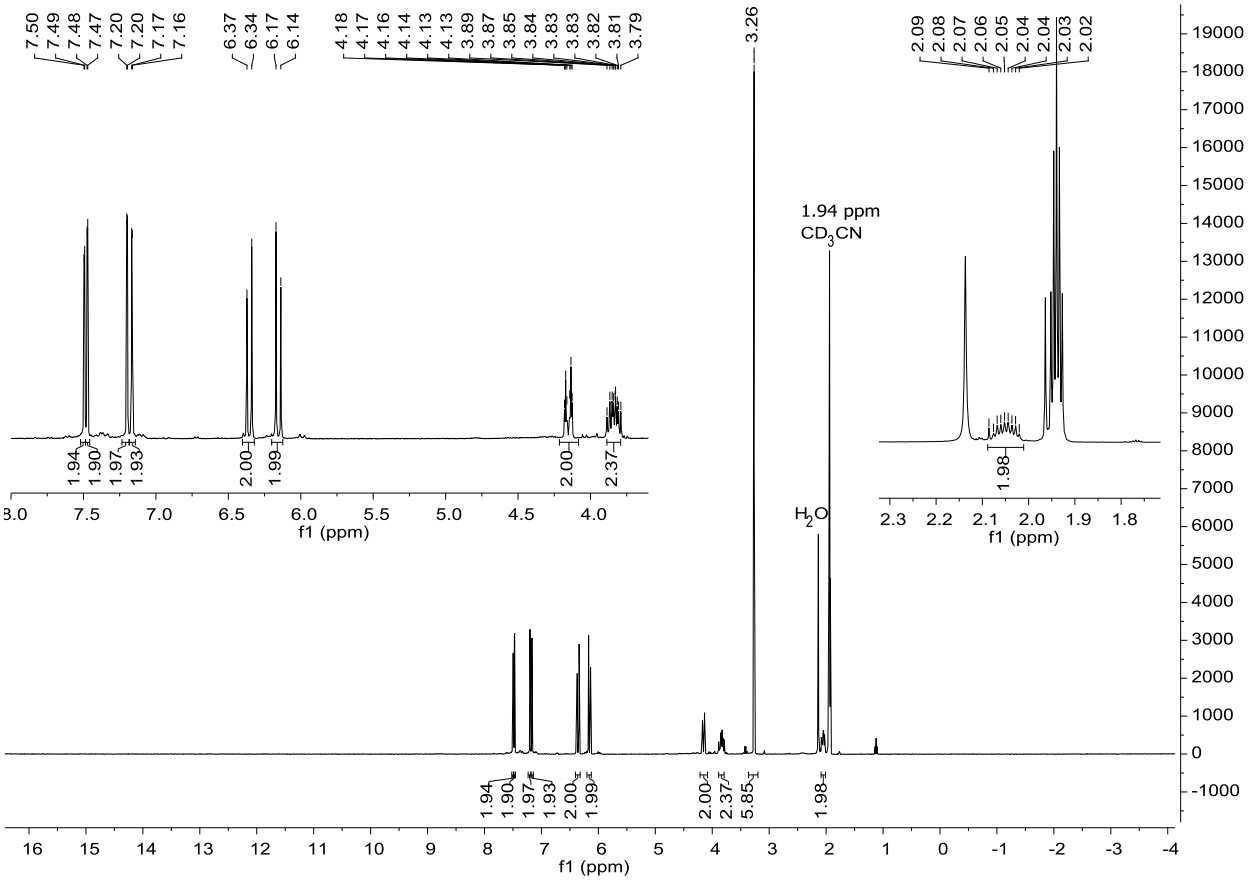


Figure S20: ^{1}H NMR of 11 in CD_3CN at 400.13 MHz.

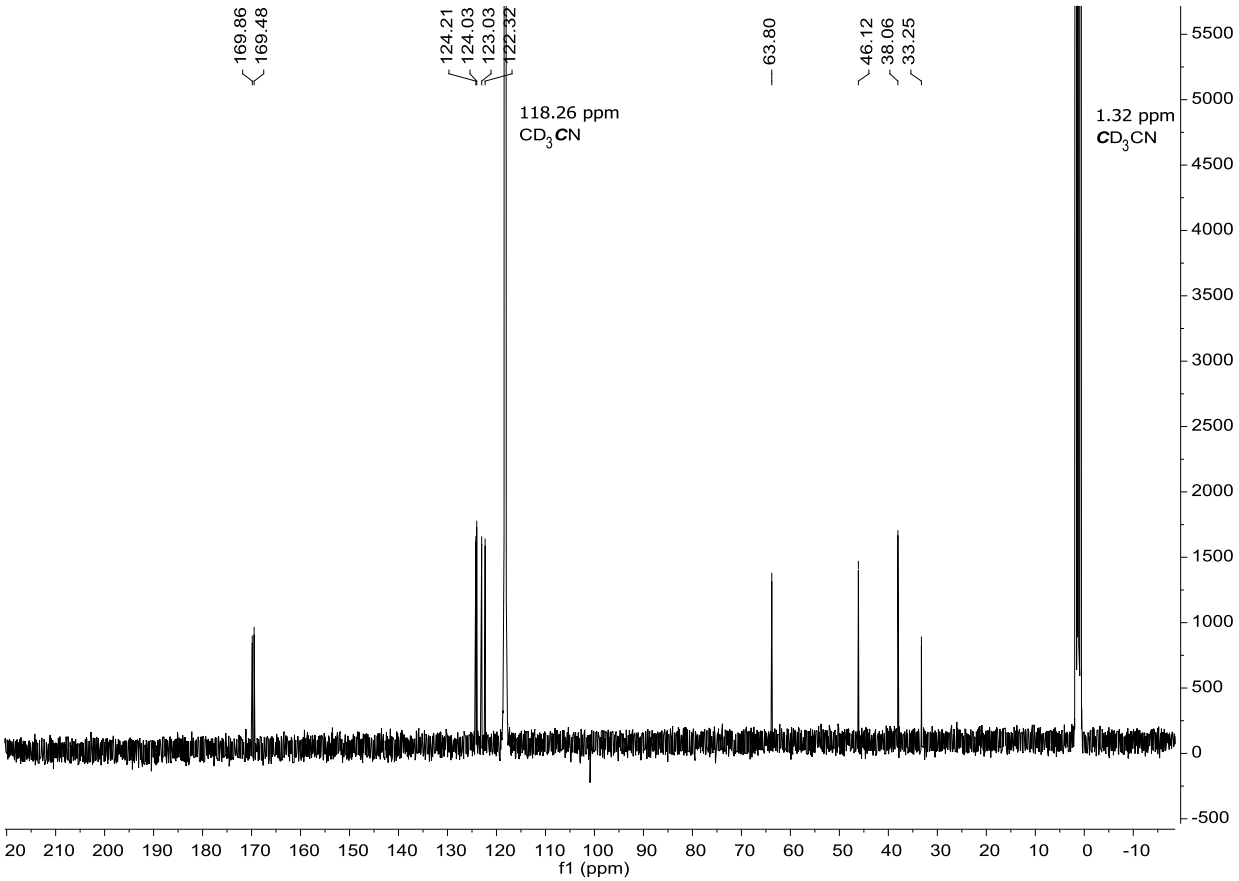
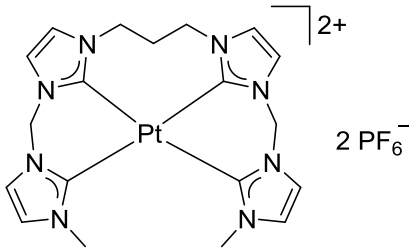


Figure S21: $^{13}C\{^{1}H\}$ NMR of 11 in CD_3CN at 100.62 MHz.

12. NMR spectra of compound 12 ($Pt[L2][PF_6]_2$)



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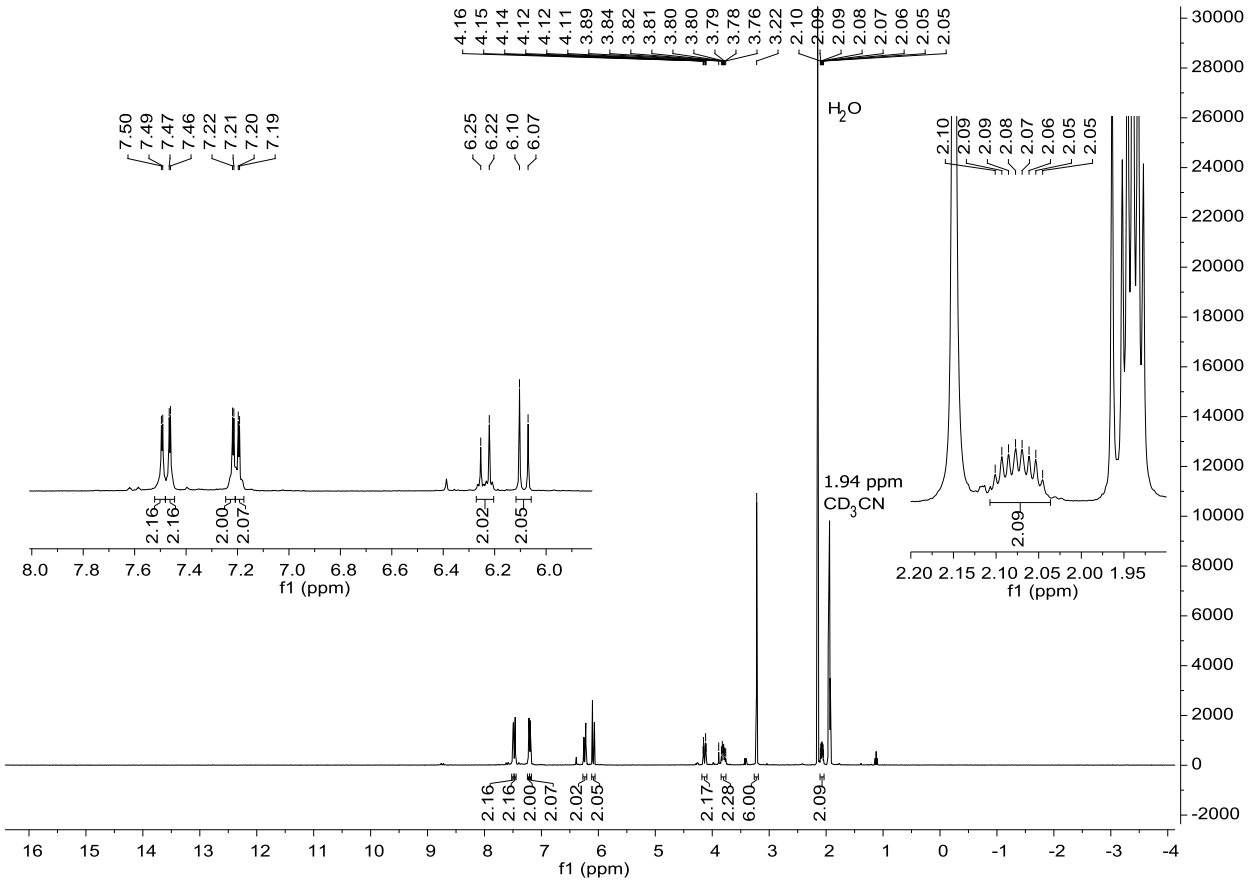


Figure S22: ^{1}H NMR of 12 in CD_3CN at 400.13 MHz.

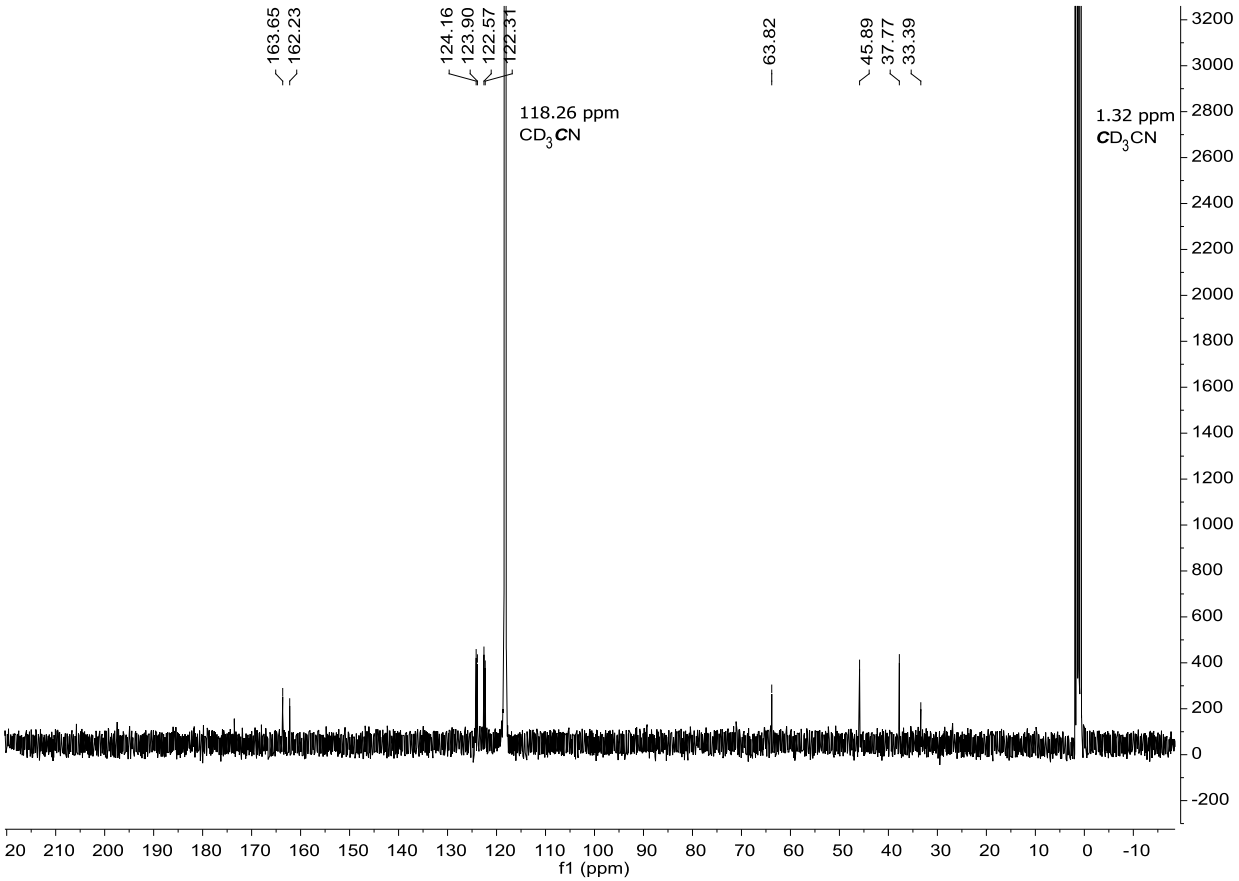
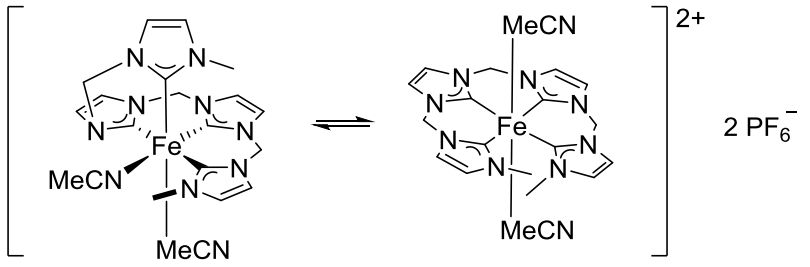


Figure S23: $^{13}C\{^{1}H\}$ NMR of 12 in CD_3CN at 100.62 MHz.

13. NMR spectra of compound 13 ($Fe[L1][MeCN]_2[PF_6]_2$)



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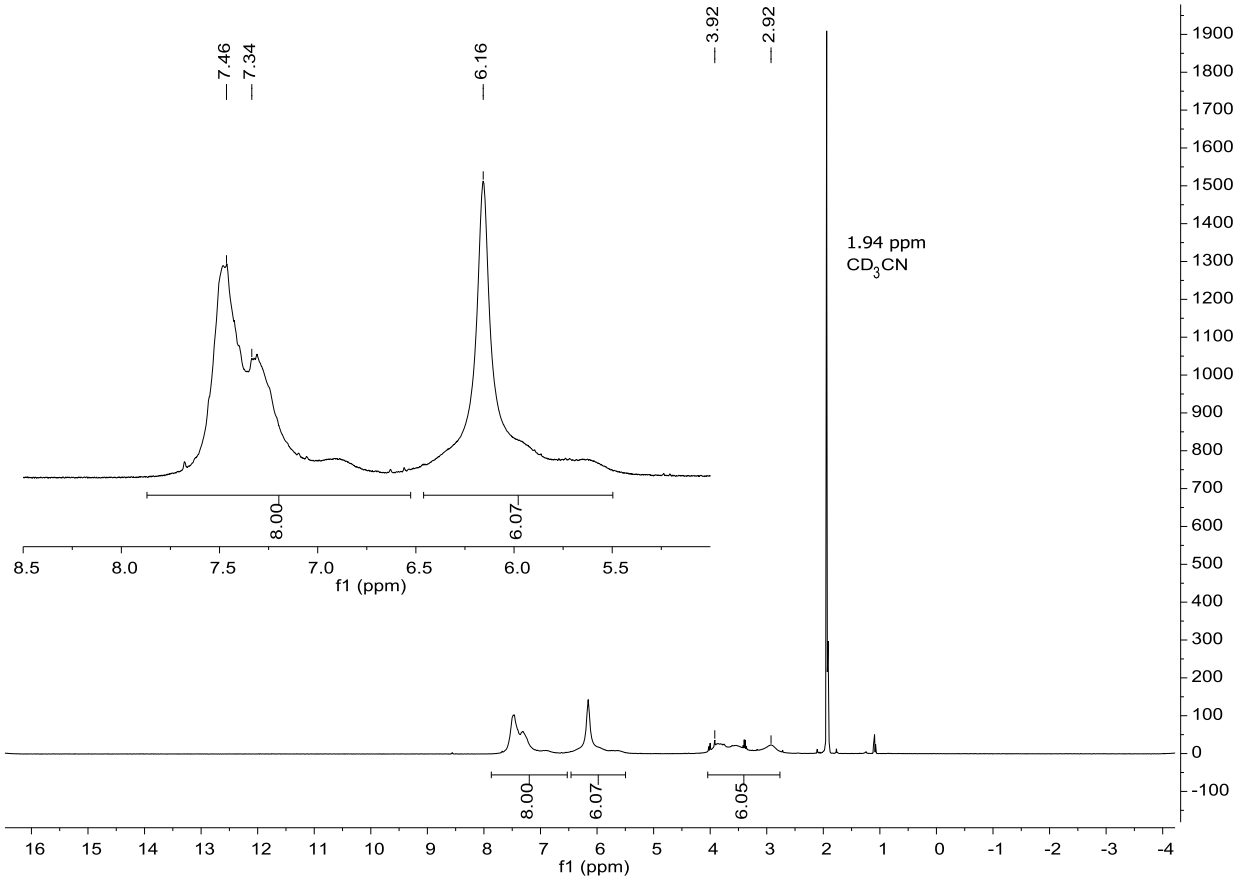


Figure S24: ^{1}H NMR of 13 in CD_3CN at 400.13 MHz.

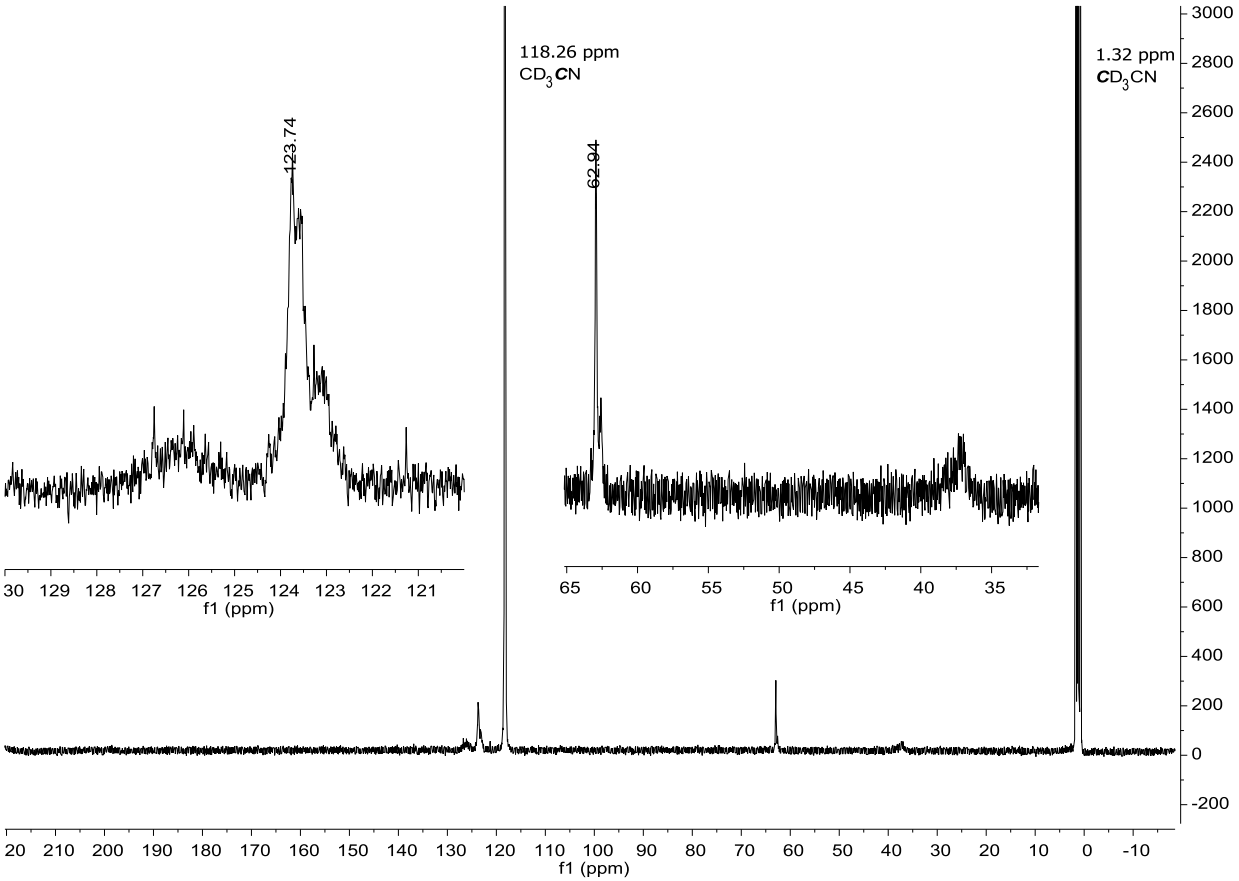


Figure S25: $^{13}C\{^{1}H\}$ NMR of 13 in CD_3CN at 100.62 MHz.

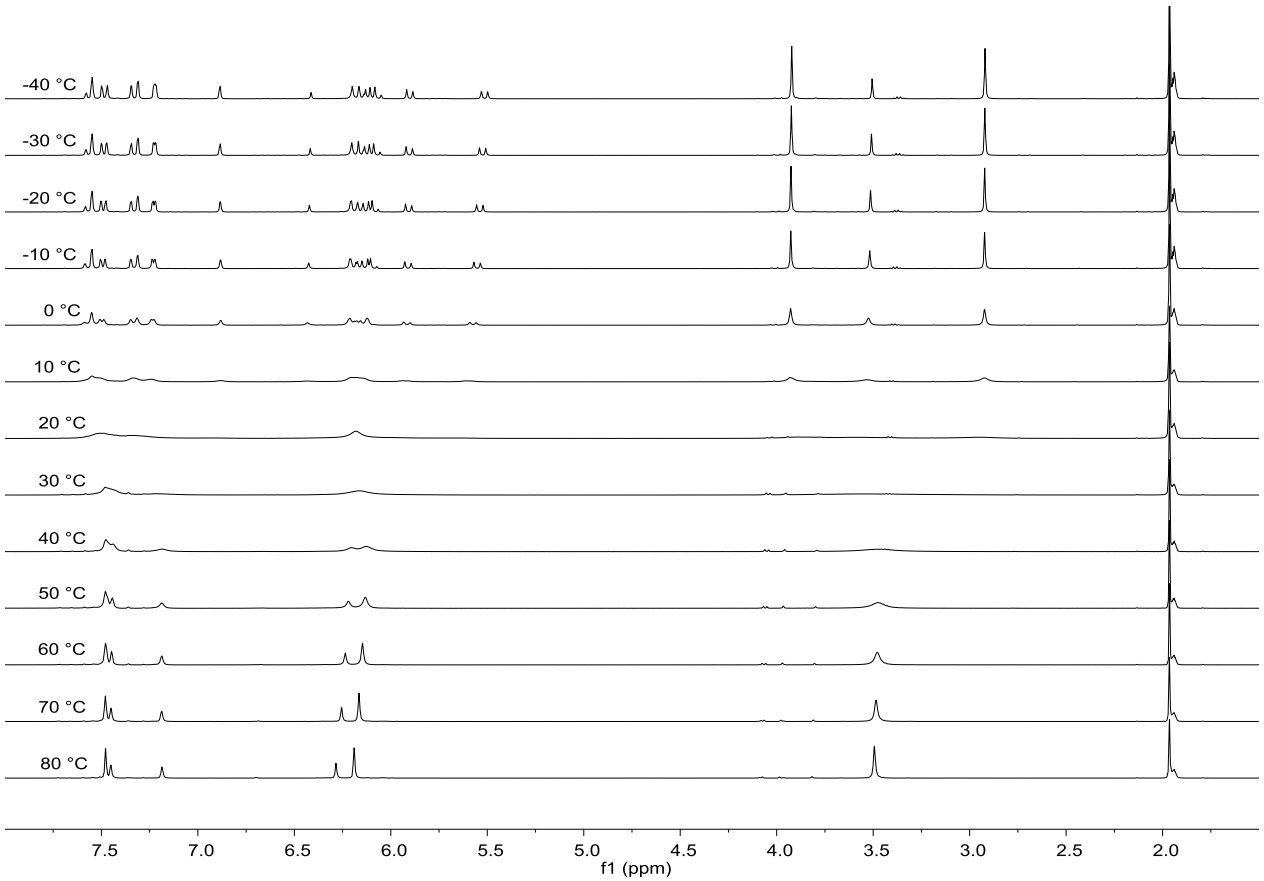
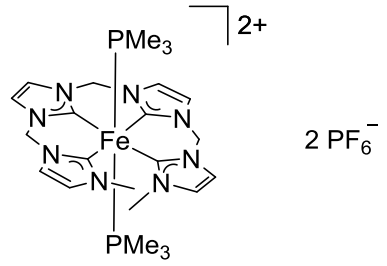


Figure S26: Variable temperature ^{1}H NMR of 13 in CD_3CN at 100.62 MHz.

14. NMR spectra of compound 14 ($Fe[L1][PMe_3]_2[PF_6]_2$)



2 PF_6^-

14

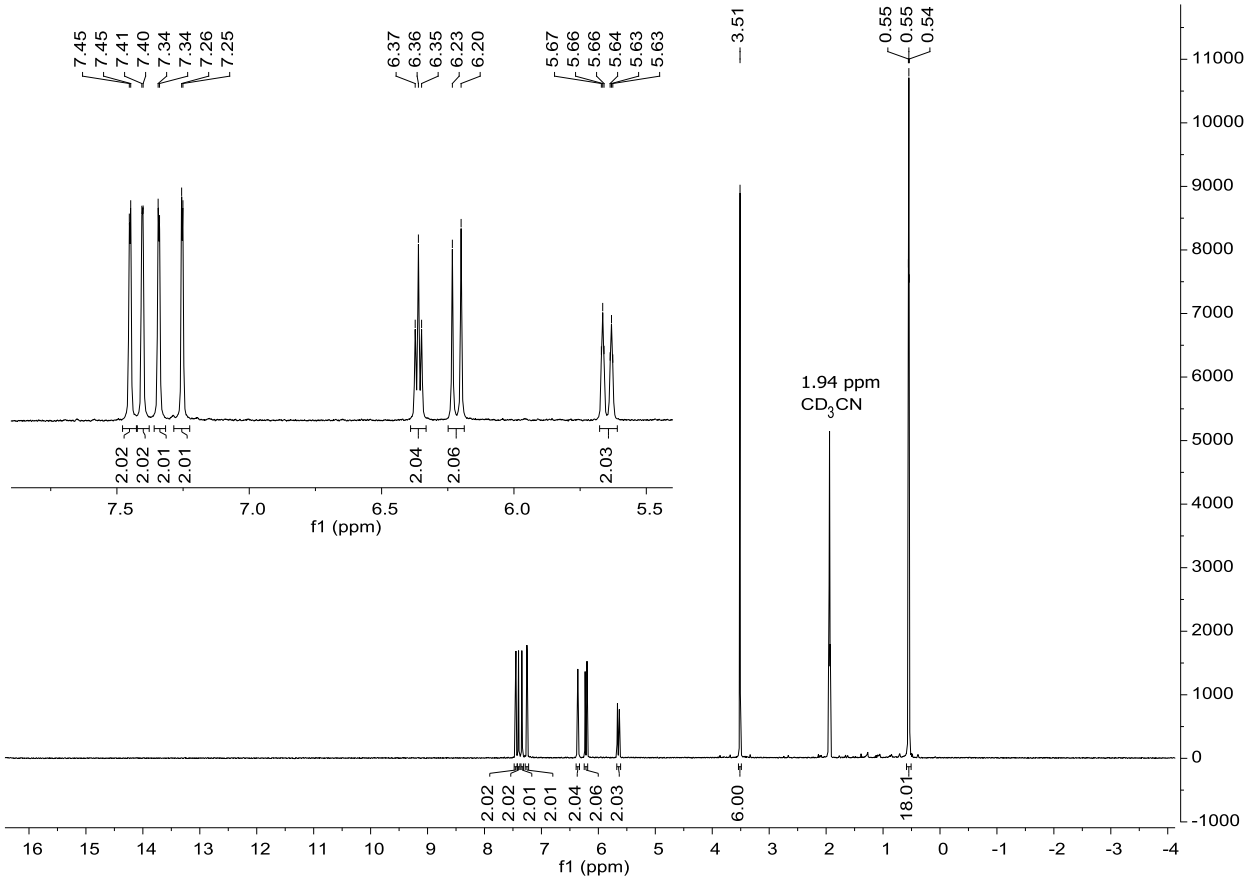


Figure S27: ^{1}H NMR of 14 in CD_3CN at 400.13 MHz.

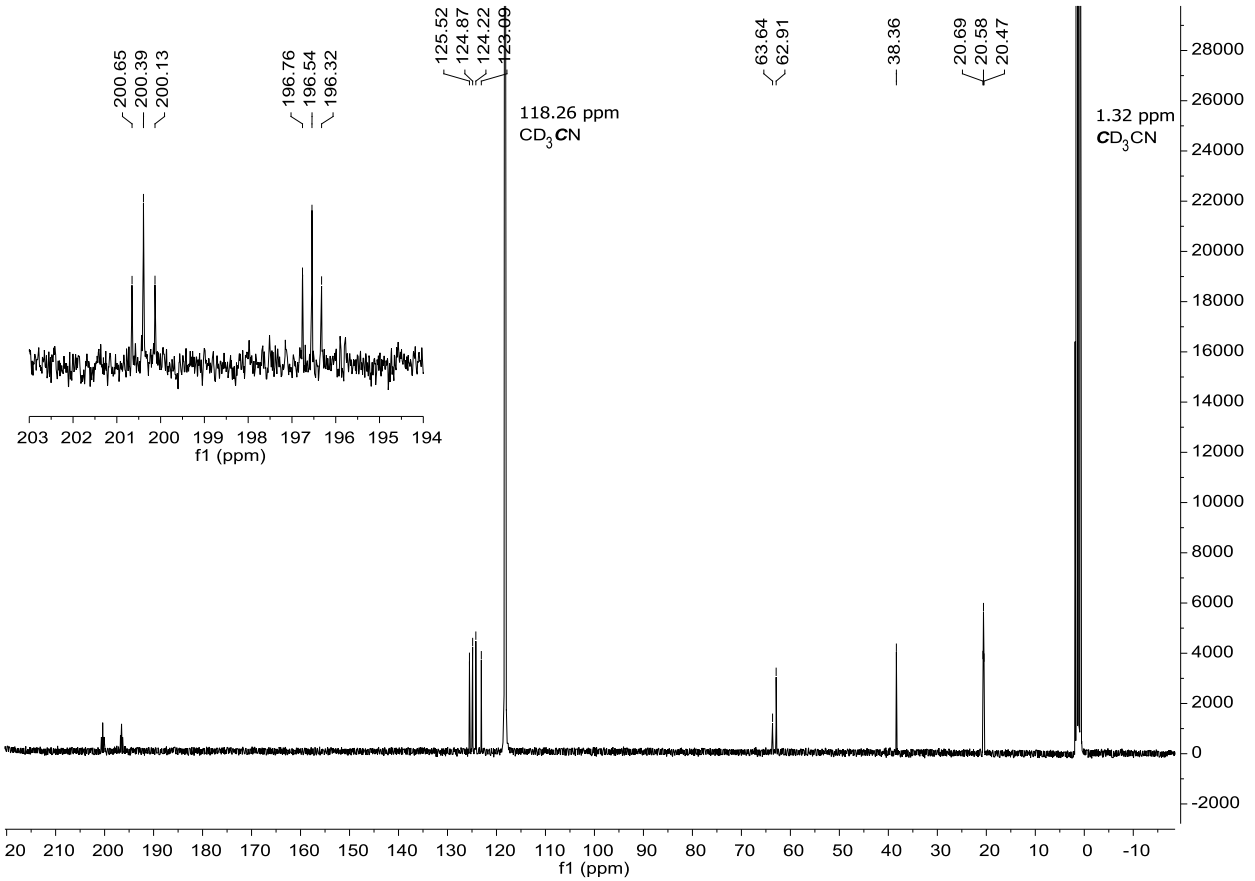


Figure S28: $^{13}C\{^{1}H\}$ NMR of 14 in CD_3CN at 100.62 MHz.

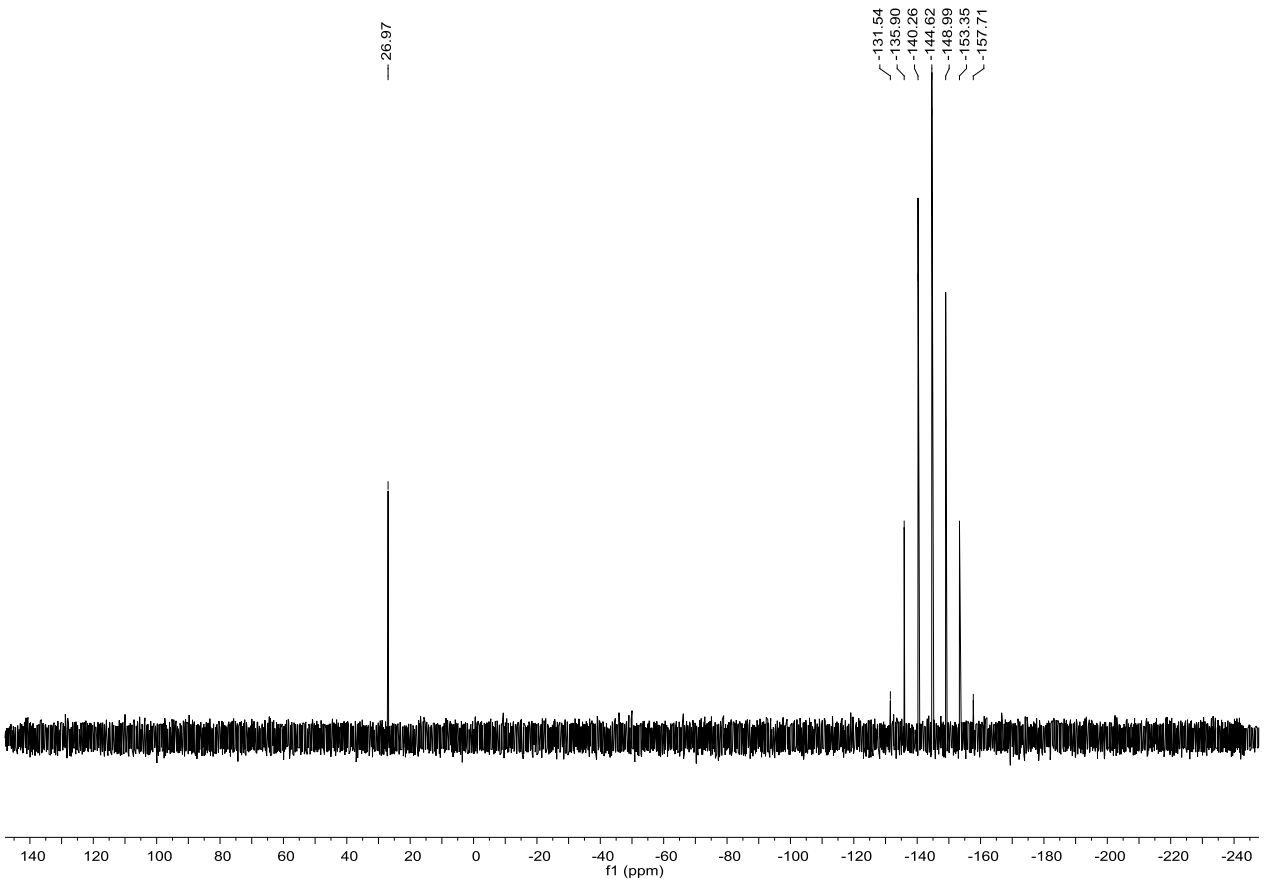
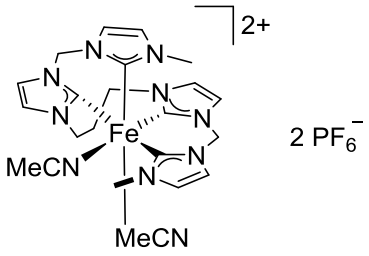


Figure S29: $^{31}P\{^{1}H\}$ NMR of 14 in CD_3CN at 161.97 MHz.

15. NMR spectra of compound 15 ($Fe[L2][MeCN]_2[PF_6]_2$)



15

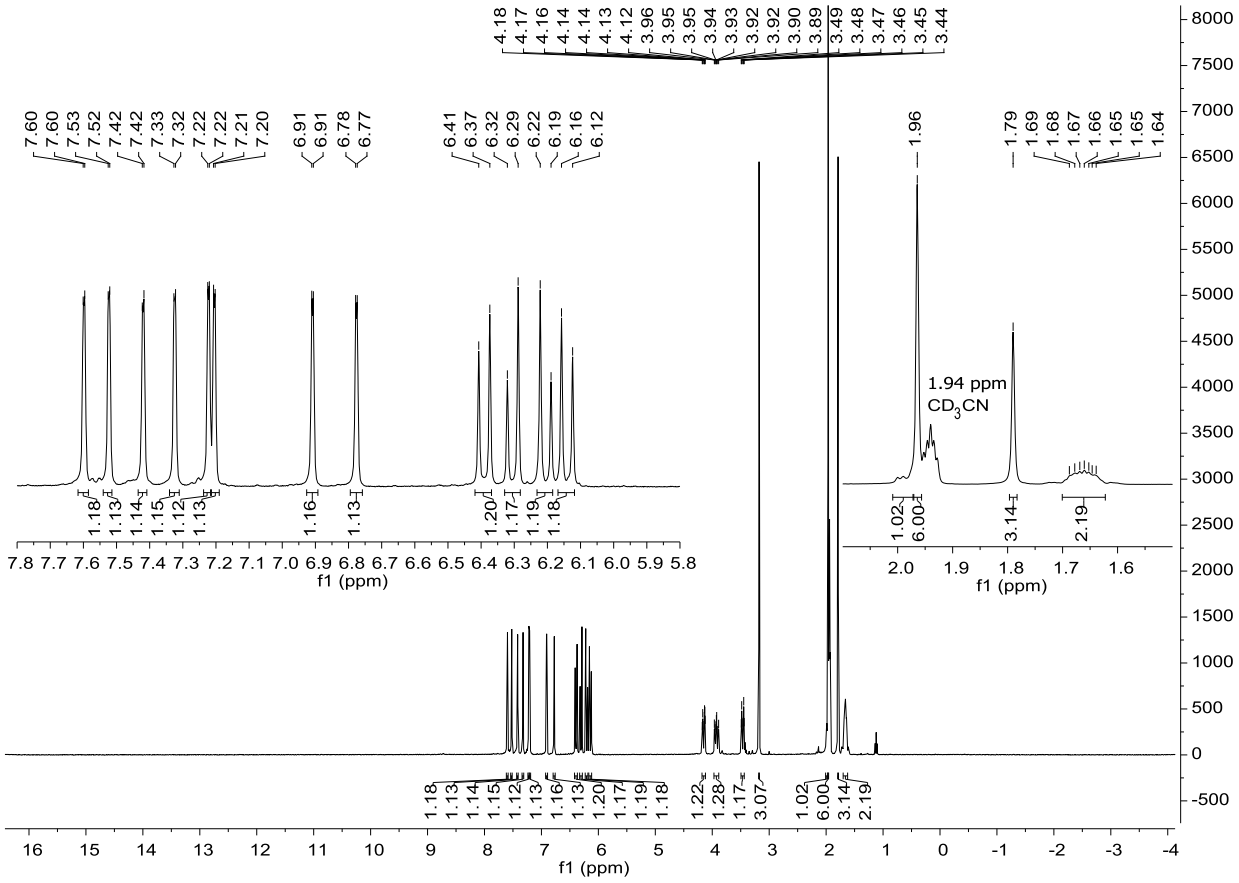


Figure S30: ^{1}H NMR of 15 in CD_3CN at 400.13 MHz.

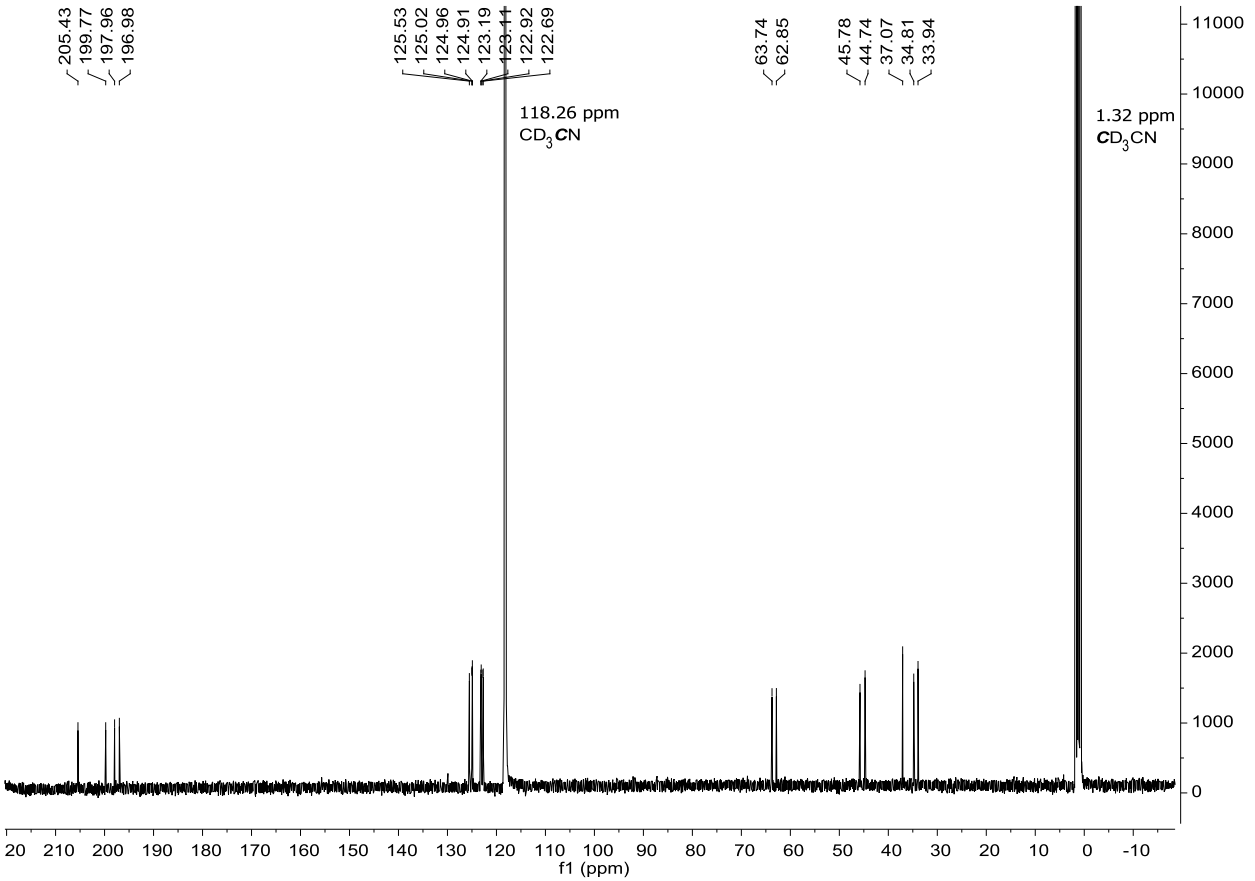
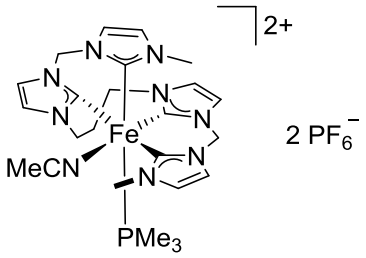


Figure S31: $^{13}C\{^{1}H\}$ NMR of 15 in CD_3CN at 100.62 MHz.

16. NMR spectra of compound 16 (Fe[L2][MeCN][PMe_3][PF_6]$_2$)



16

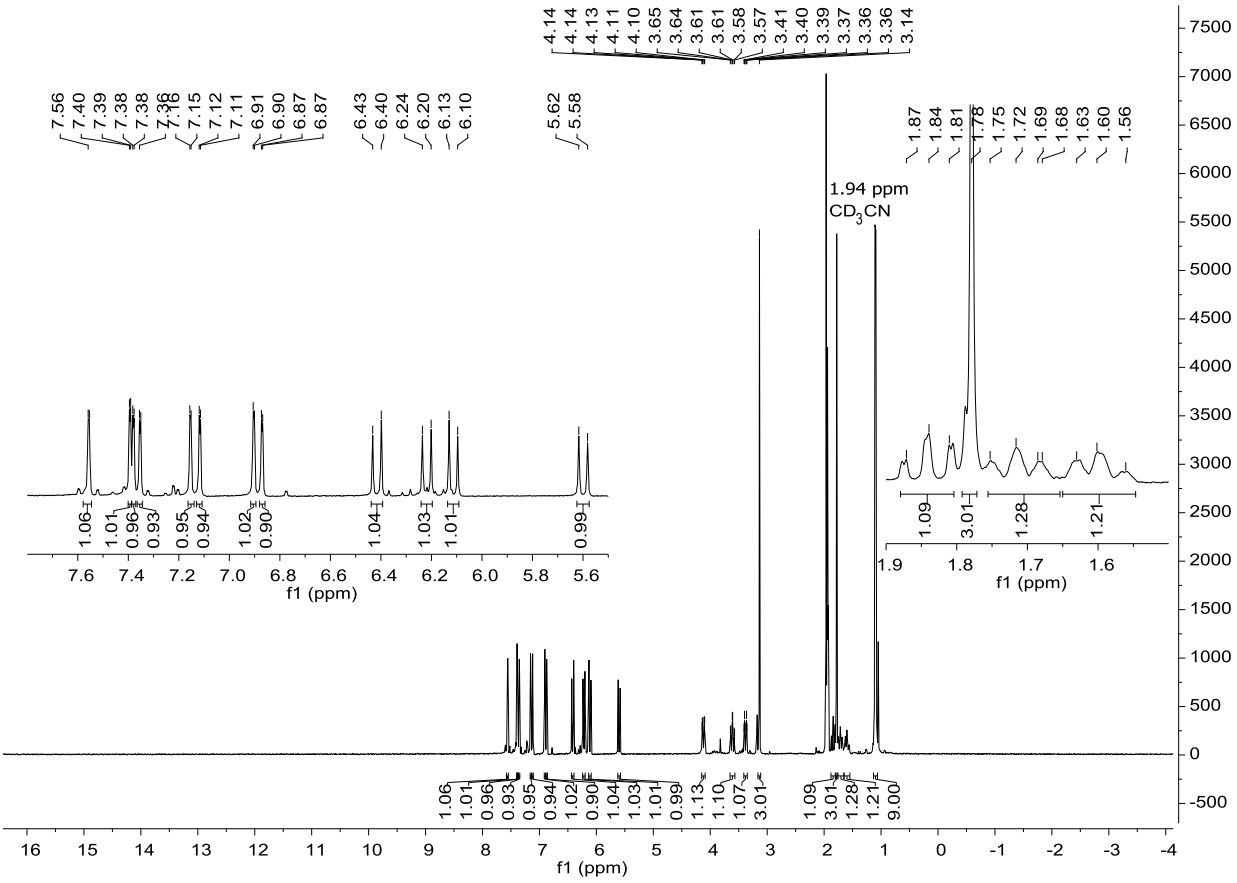


Figure S32: ^{1}H NMR of 16 in CD_3CN at 400.13 MHz.

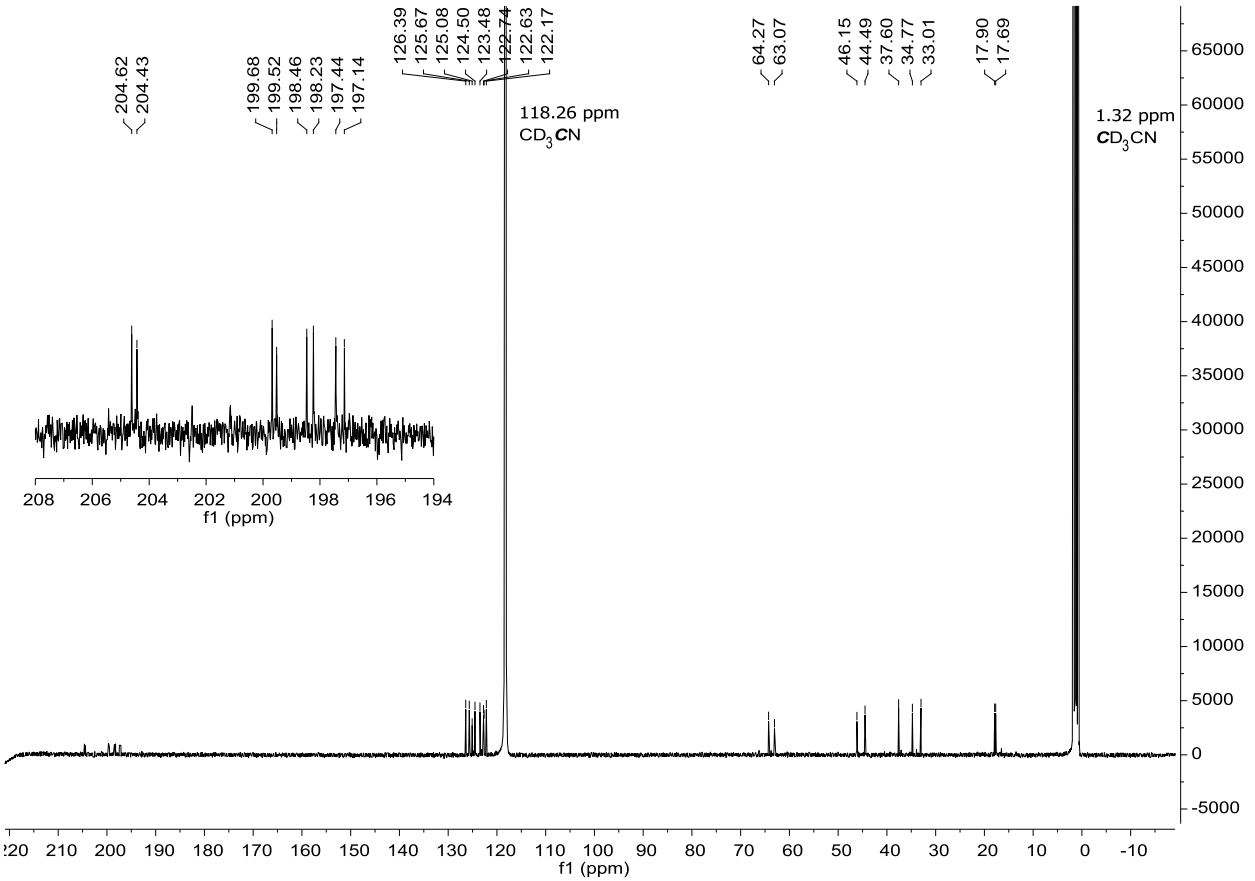


Figure S33: $^{13}C\{^{1}H\}$ NMR of 16 in CD_3CN at 100.62 MHz.

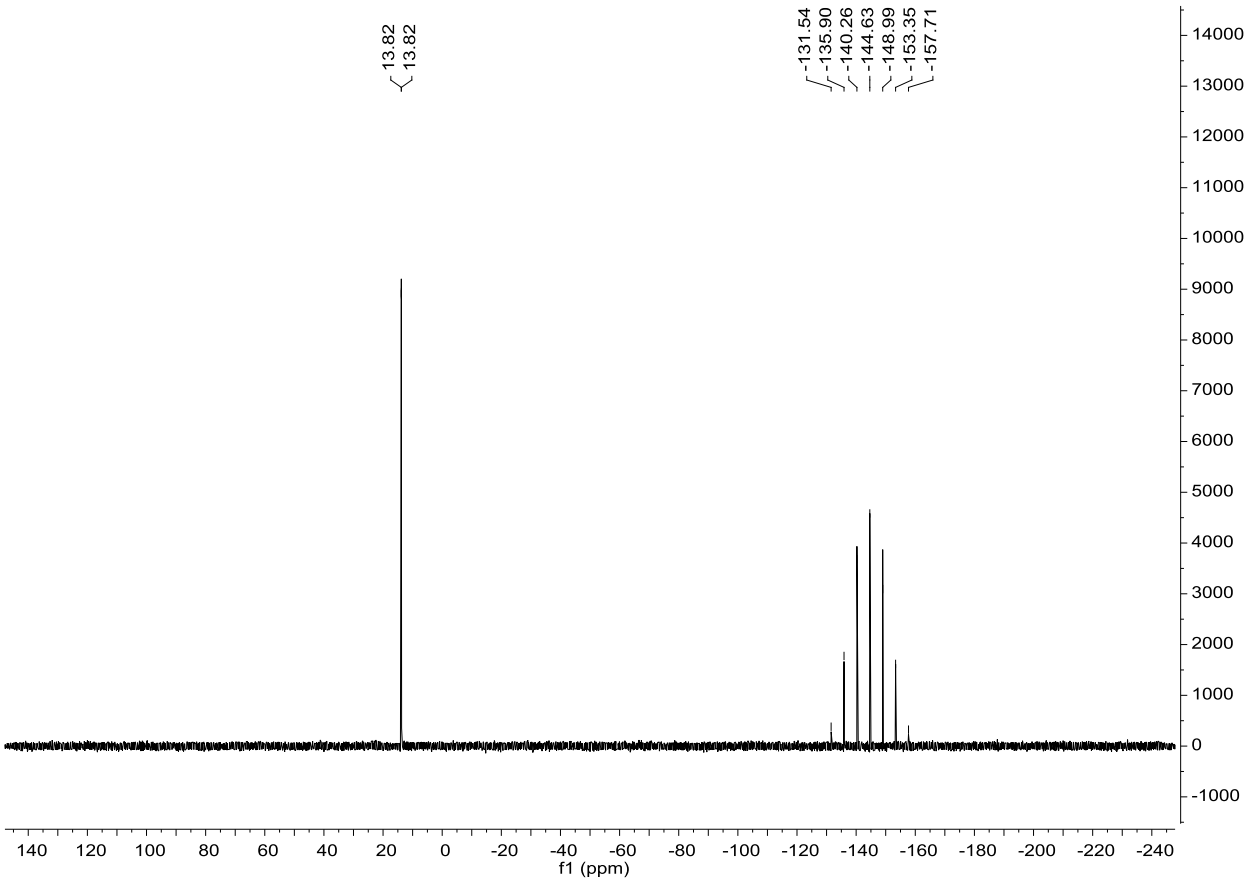


Figure S34: $^{31}P\{^{1}H\}$ NMR of 16 in CD_3CN at 161.97 MHz.