Supporting Information for:

# $CH_3$-X Reductive Elimination Reactivity of $Pt^{IV}Me$ Complexes Supported by a Sulfonated CNN Pincer Ligand (X = OH, $CF_3CO_2$, $PhNMe_2^+$)

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1. NMR spectra
2. DFT calculations

## 1. NMR spectra

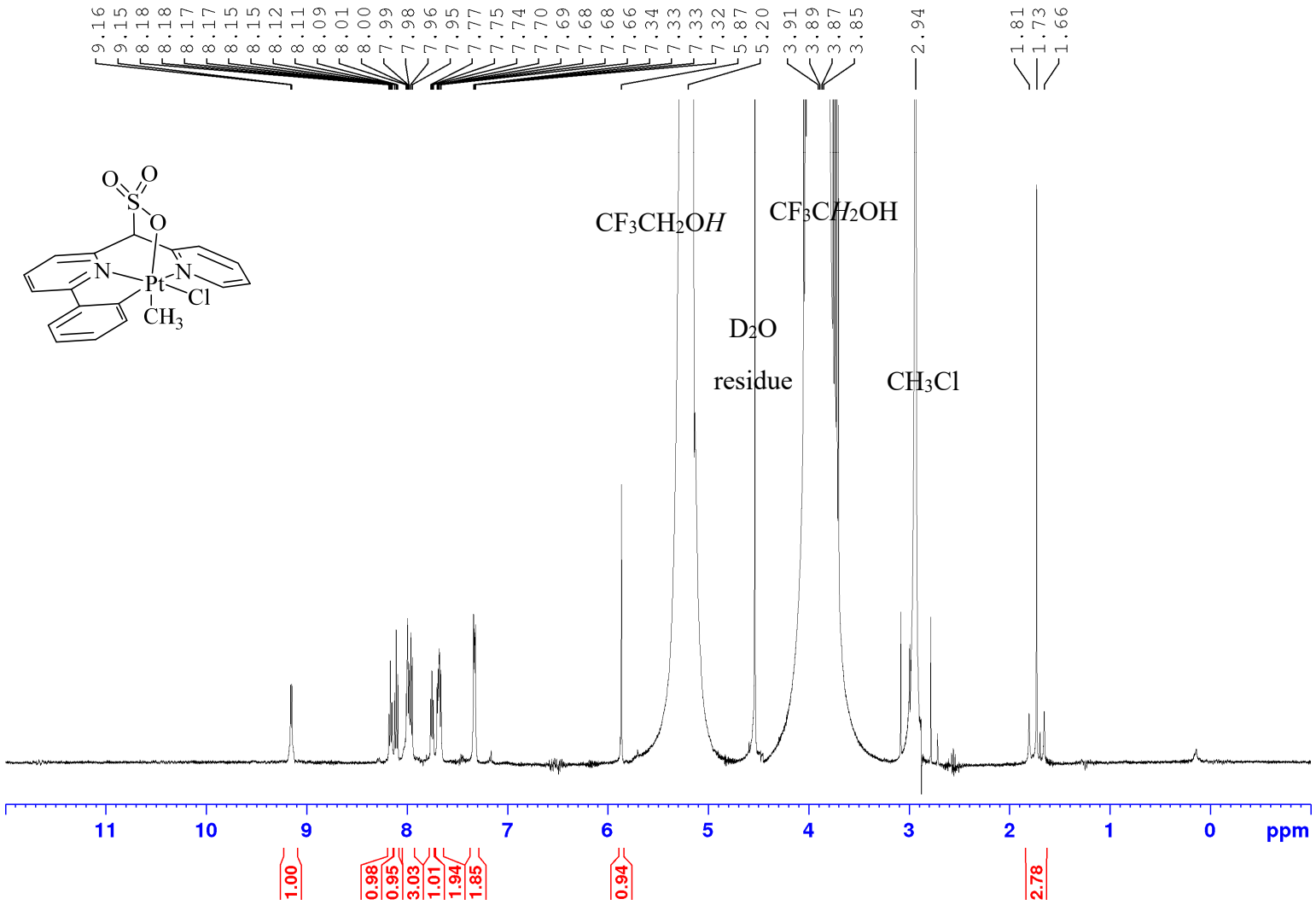



**Figure S1.** $^{1}$H NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)(Cl), **6**, in TFE. The signal at 2.94 ppm is $CH_3Cl$. The signal at 4.54 ppm is residual $H_2O$ in $D_2O$ in a capillary added for locking and shimming purposes.

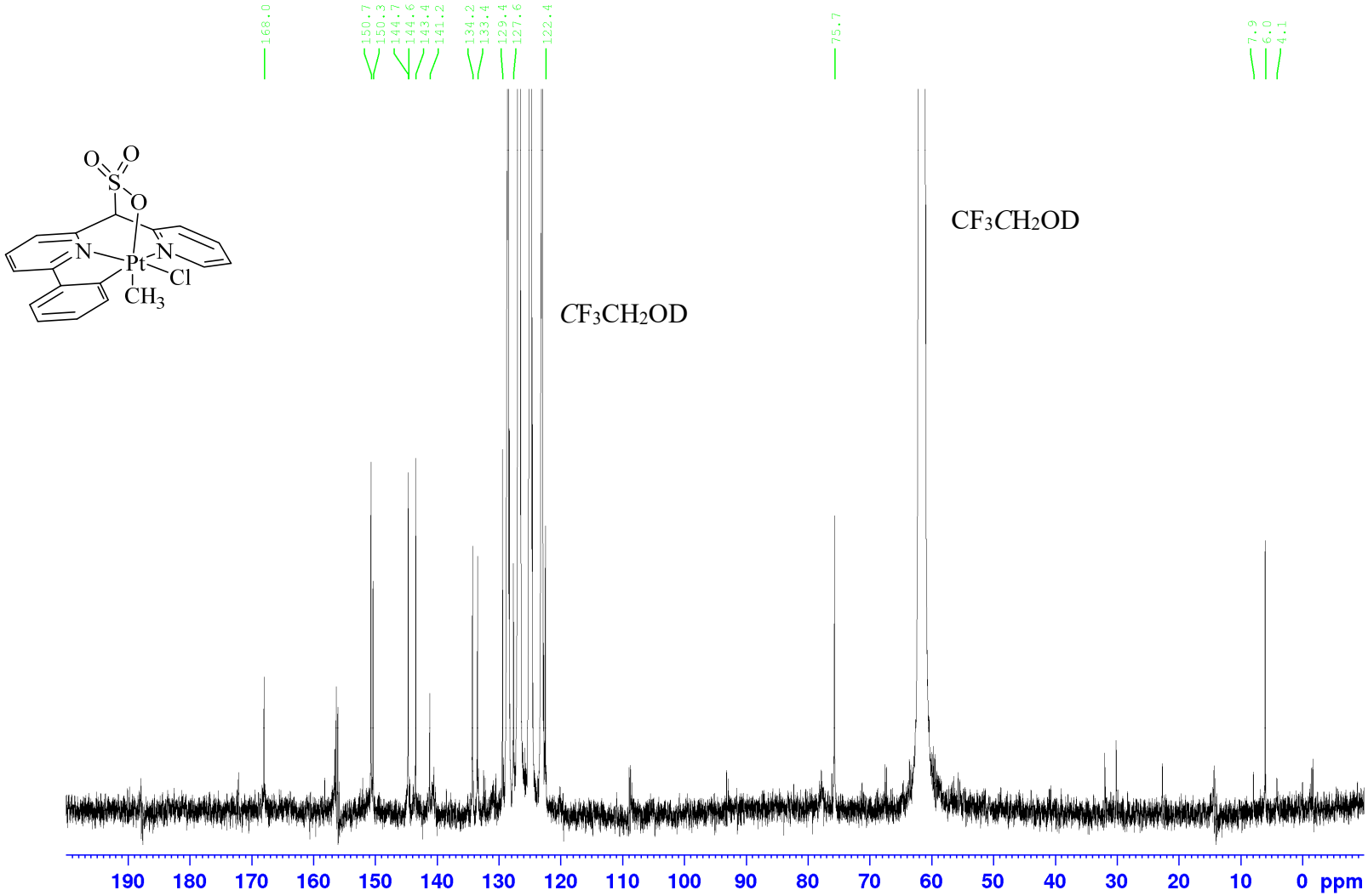



**Figure S2.** $^{13}$C NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)(Cl), **6**, in $CF_3CH_2OD$.

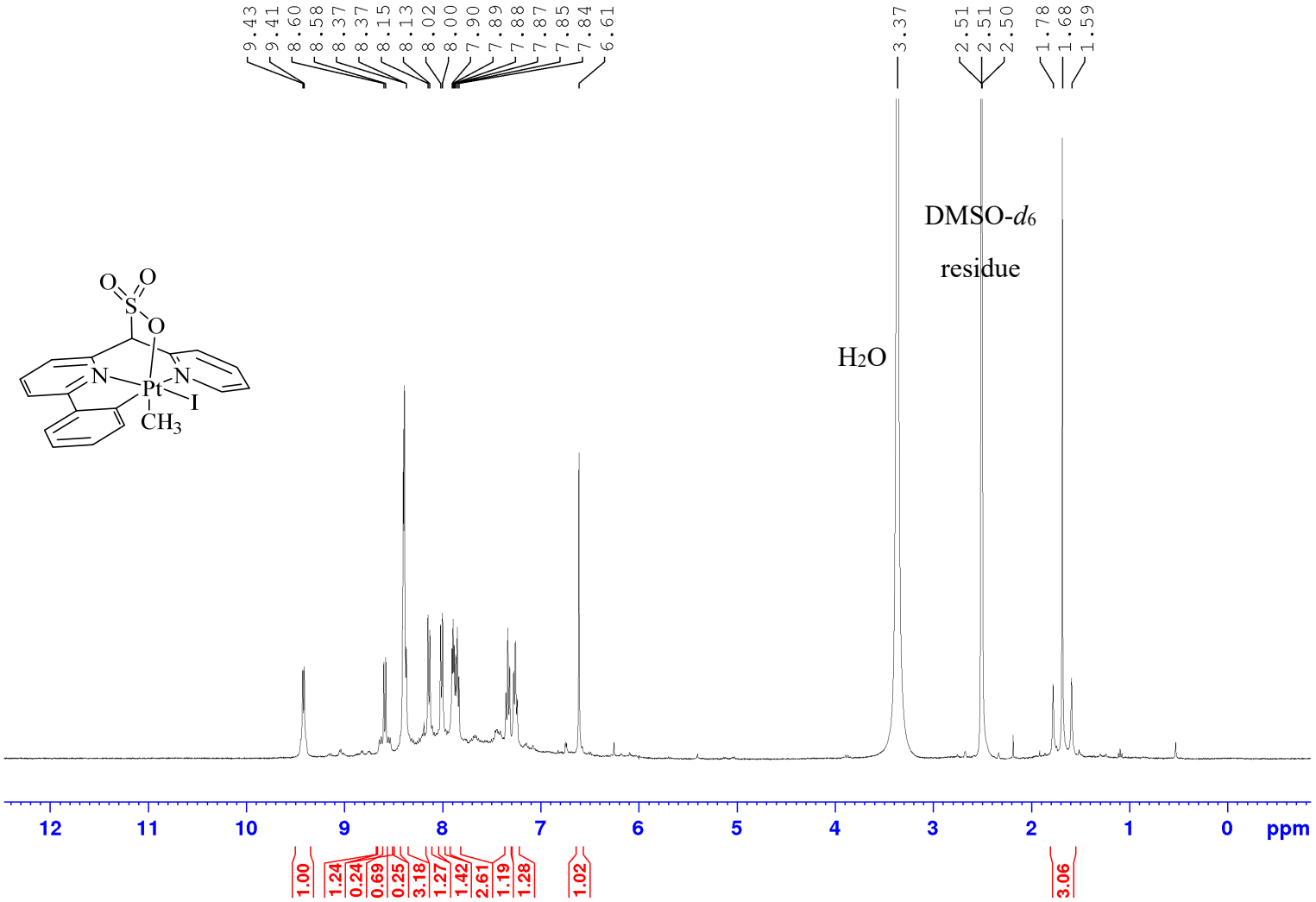



**Figure S3.** $^{1}$H NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)(I), **7**, in DMSO-$d_6$.

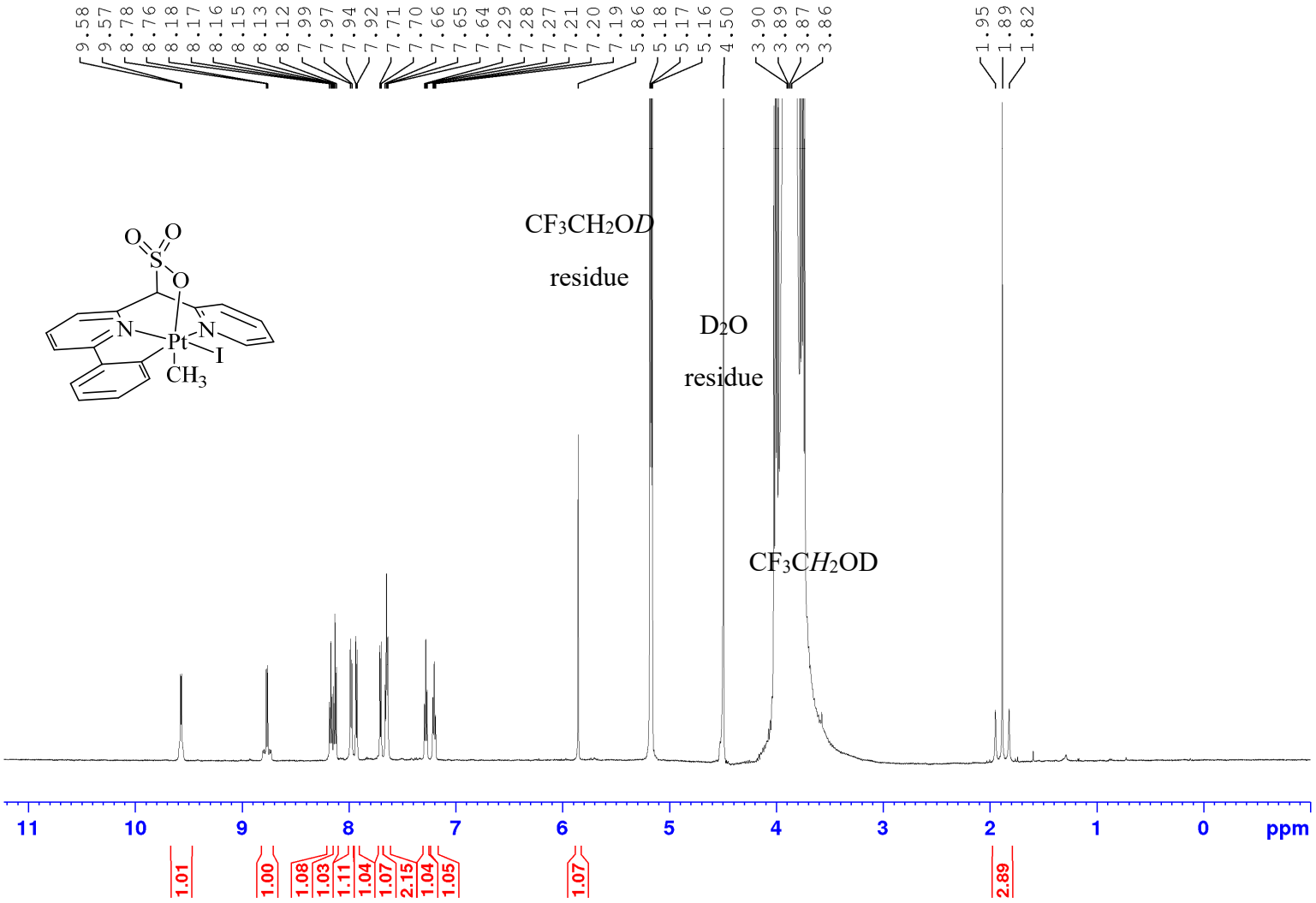



**Figure S4.** $^{1}$H NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)(I), **7**, in $CF_3CH_2OD$. The signal at 4.52 ppm is residual H in $D_2O$ in a capillary added intentionally for locking and shimming purposes.

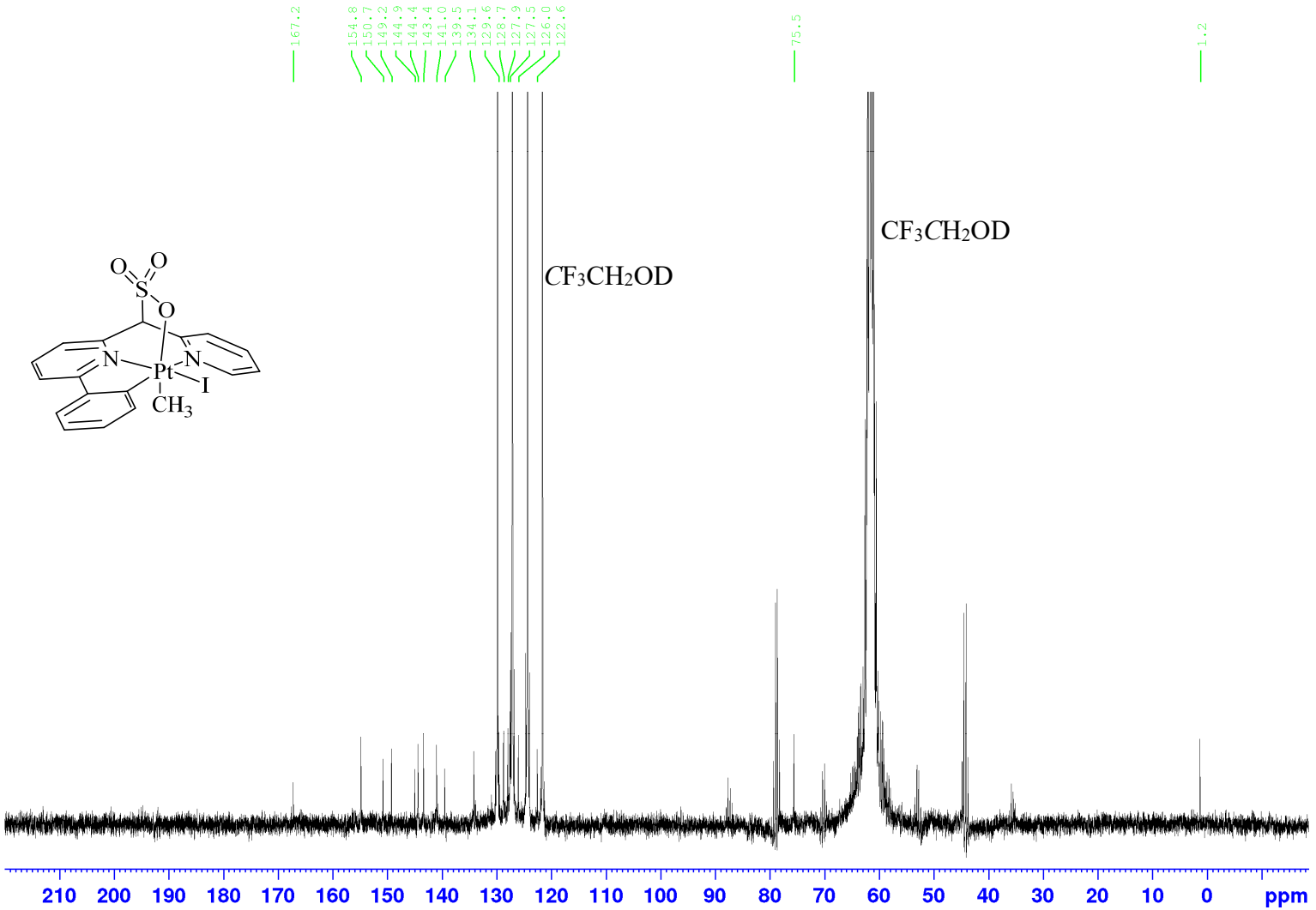



**Figure S5.** $^{13}$C NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)(I), **7**, in $CF_3CH_2OD$.

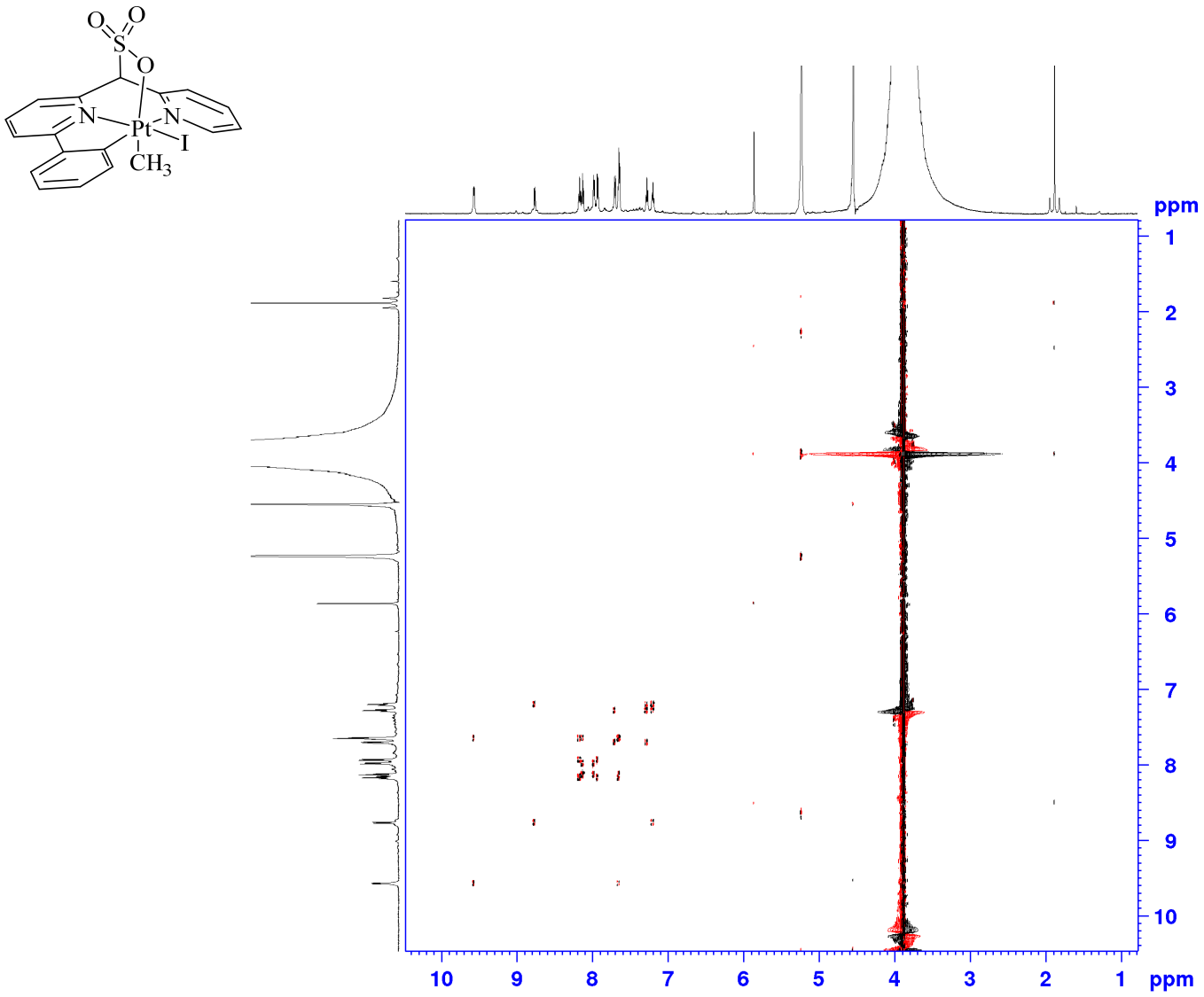



**Figure S6.** COSY of $(C_6H_4\text{-dpms})Pt^{IV}(Me)(I)$, **7**, in $CF_3CH_2OD$.

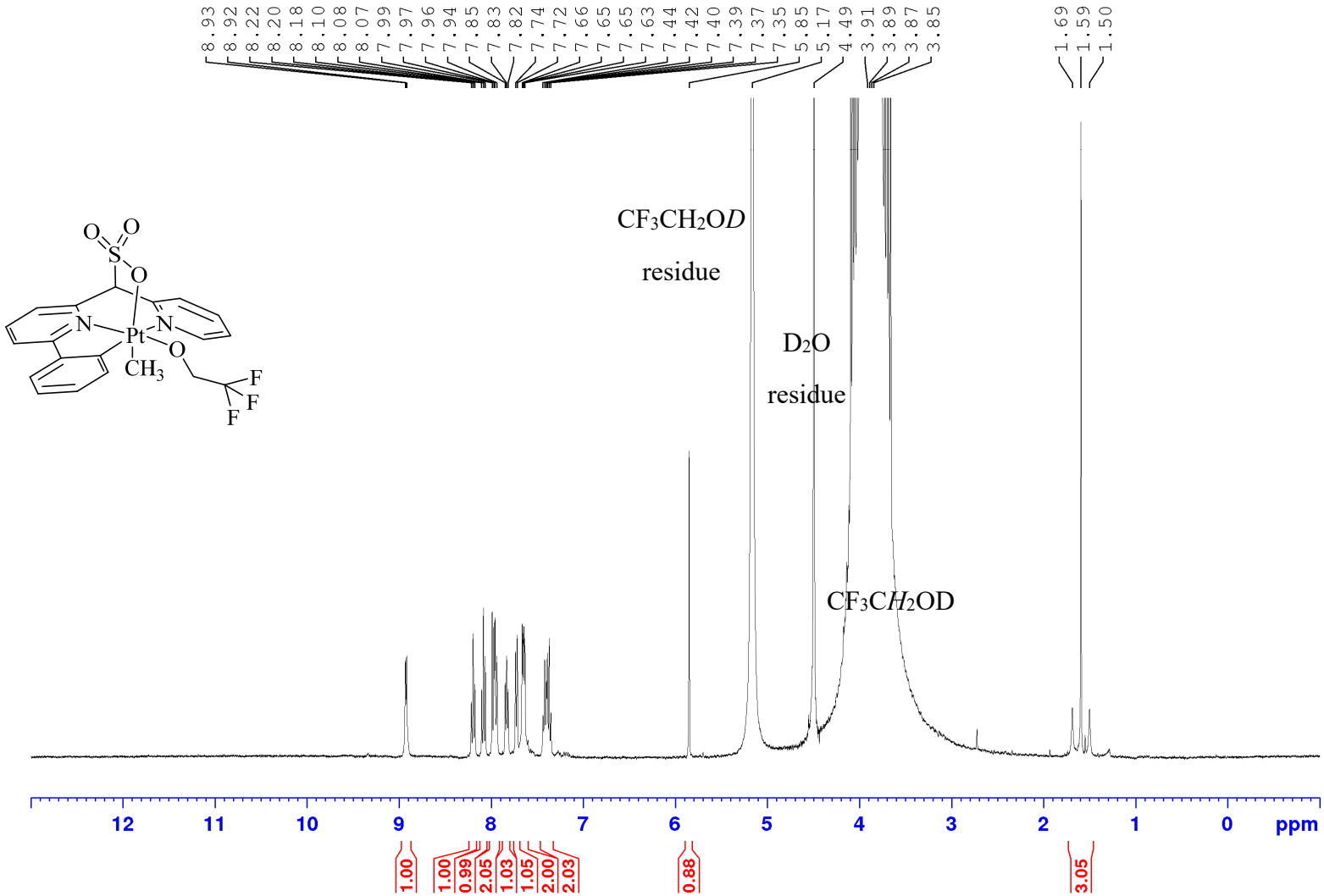



**Figure S7.** $^{1}$H NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)($OCH_2CF_3$), **8**, in TFE-$d_1$. The signal at 4.49 ppm is residual H in $D_2O$ in a capillary added intentionally for locking and shimming purposes.

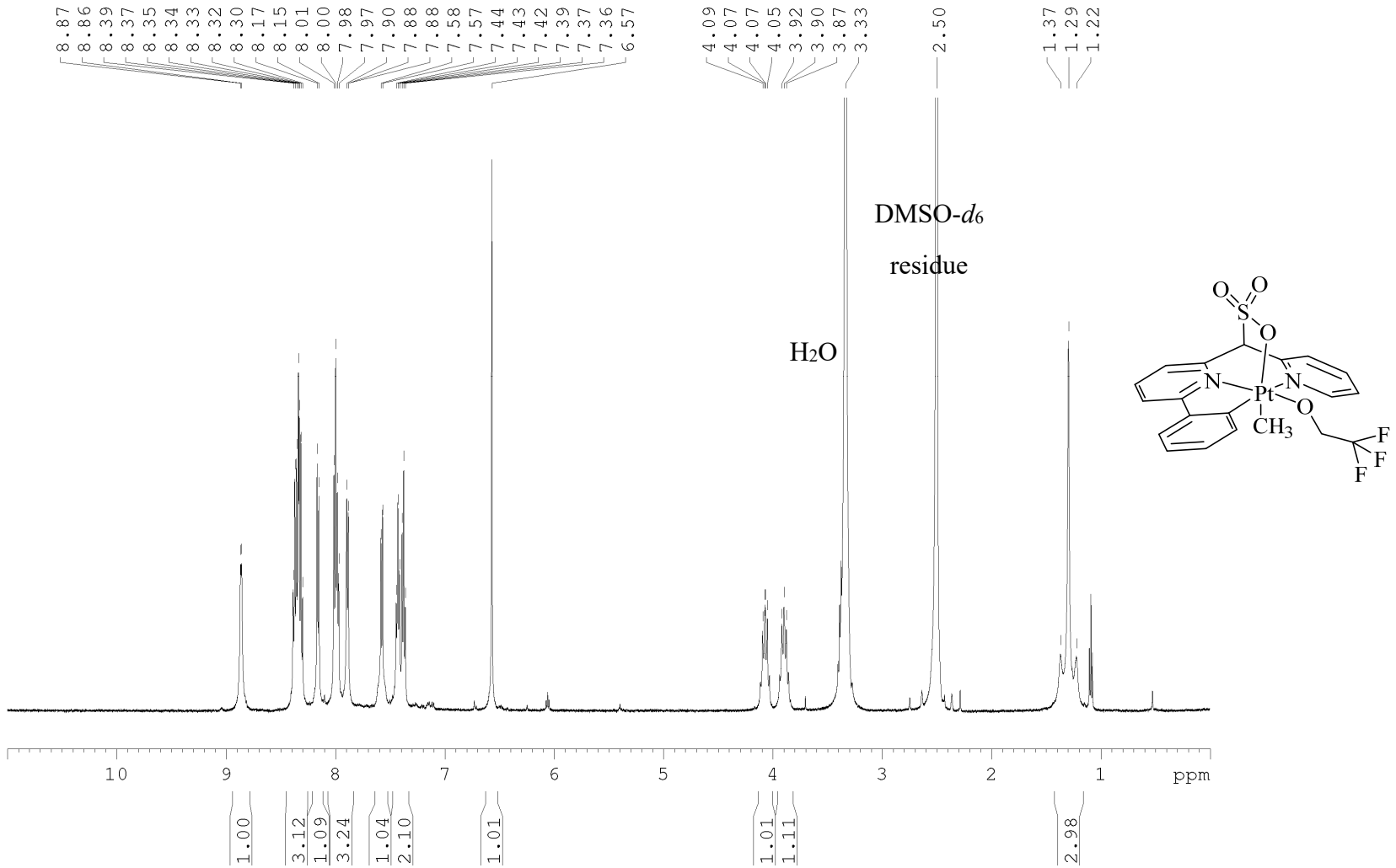



**Figure S8.** $^{1}$H NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)($OCH_2CF_3$), **8**, in DMSO-$d_6$.

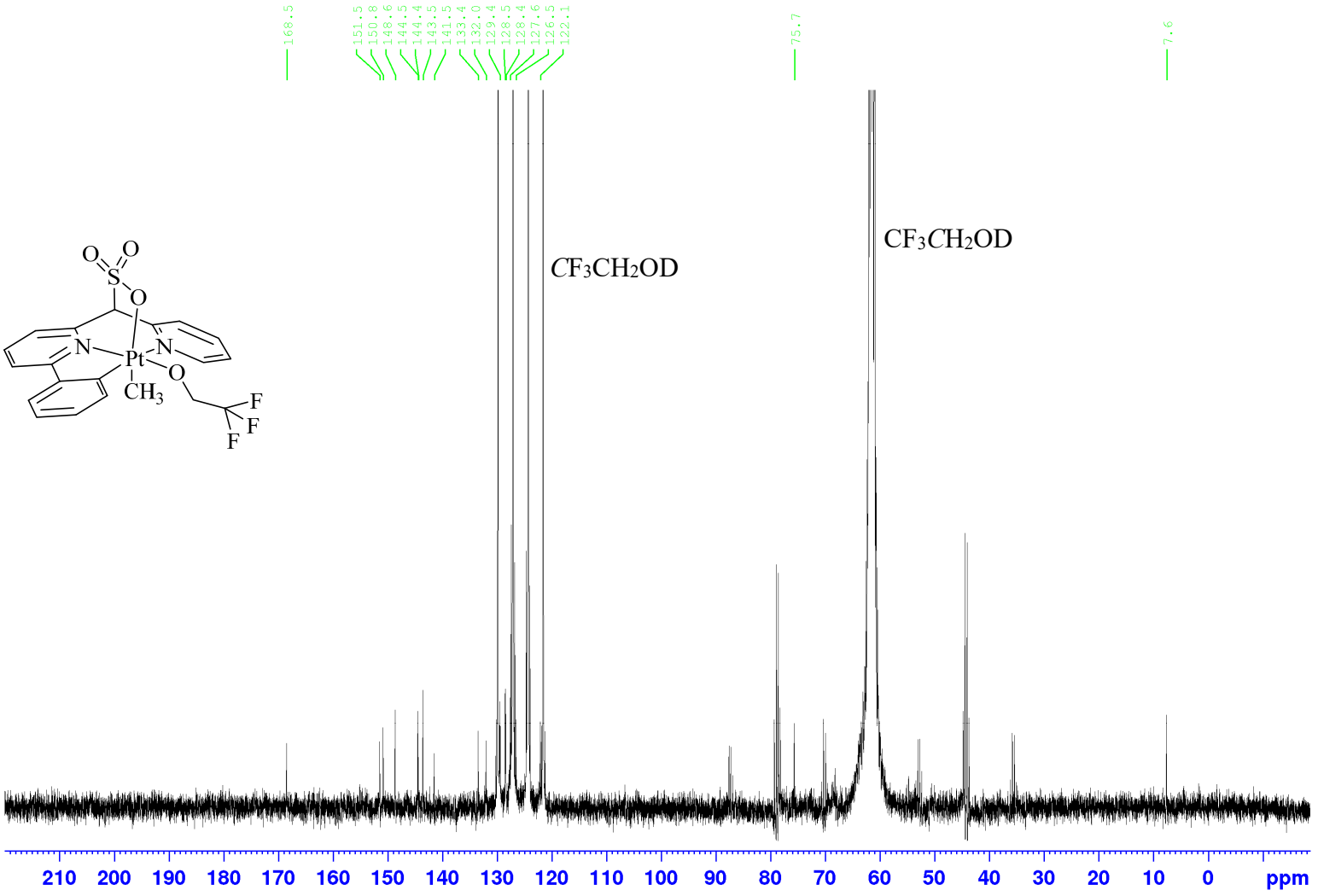



**Figure S9.** $^{13}$C NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)($OCH_2CF_3$), **8**, in TFE-$d_1$.

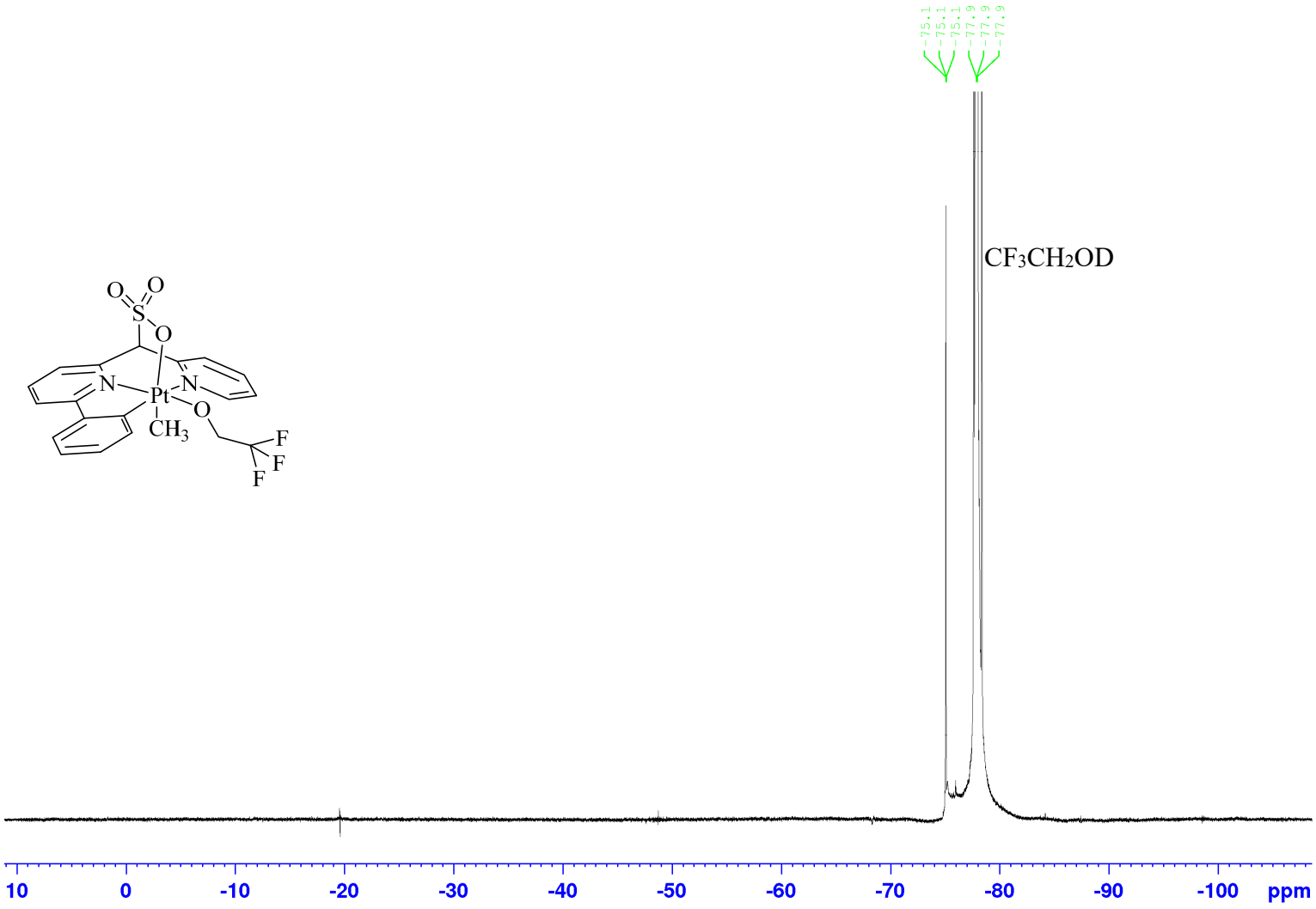



**Figure S10.** $^{19}$F NMR of ($C_6H_4$-dpms)$Pt^{IV}$(Me)($OCH_2CF_3$), **8**, in TFE-$d_1$.

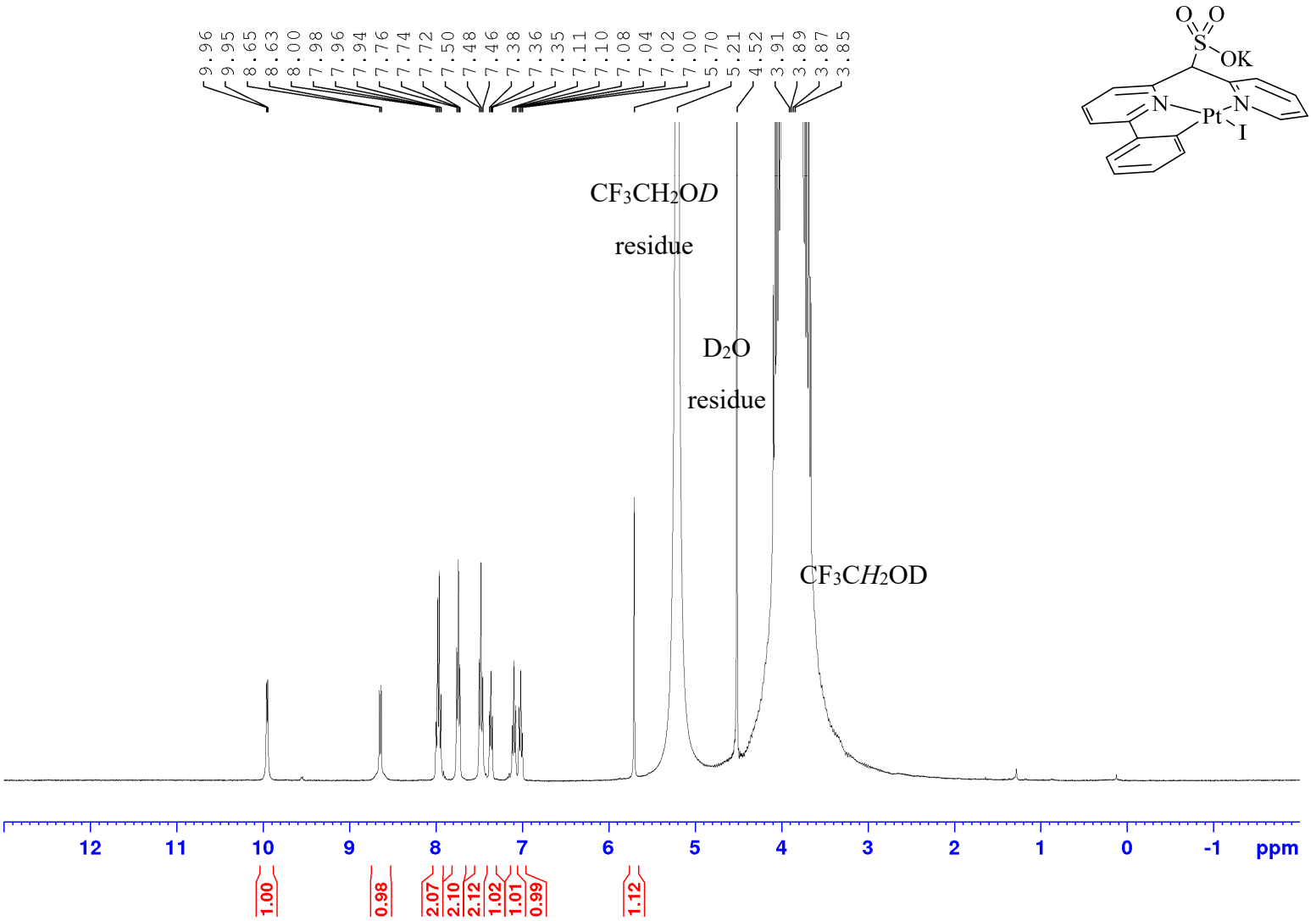



**Figure S11.** $^{1}$H NMR of K[($C_6H_4$-dpms)$Pt^{II}$(I)], **16**, in TFE-$d_1$.

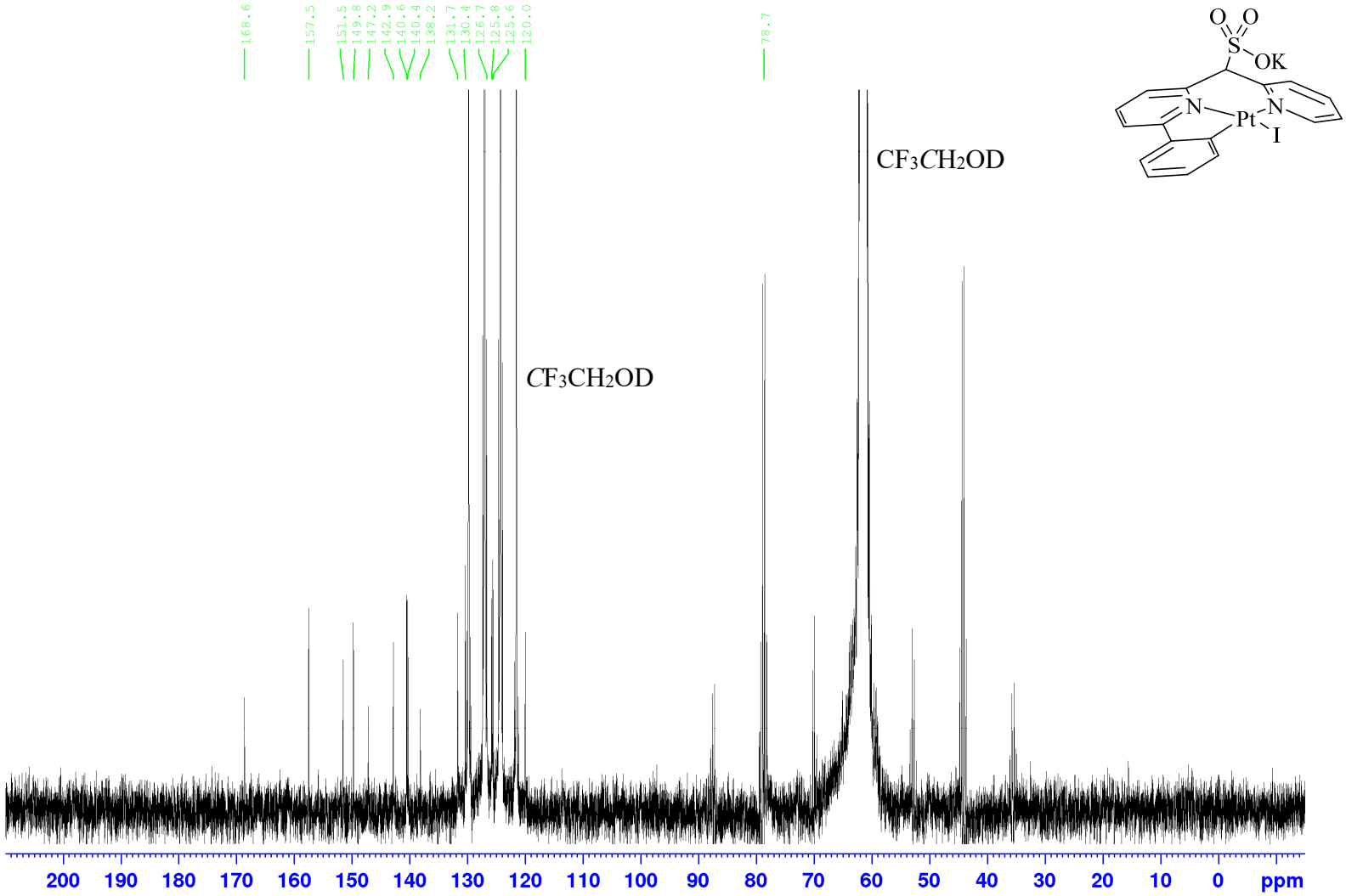



**Figure S12.** $^{13}$C NMR of K[($C_6H_4$-dpms)$Pt^{II}$(I)], **16**, in TFE-$d_1$.

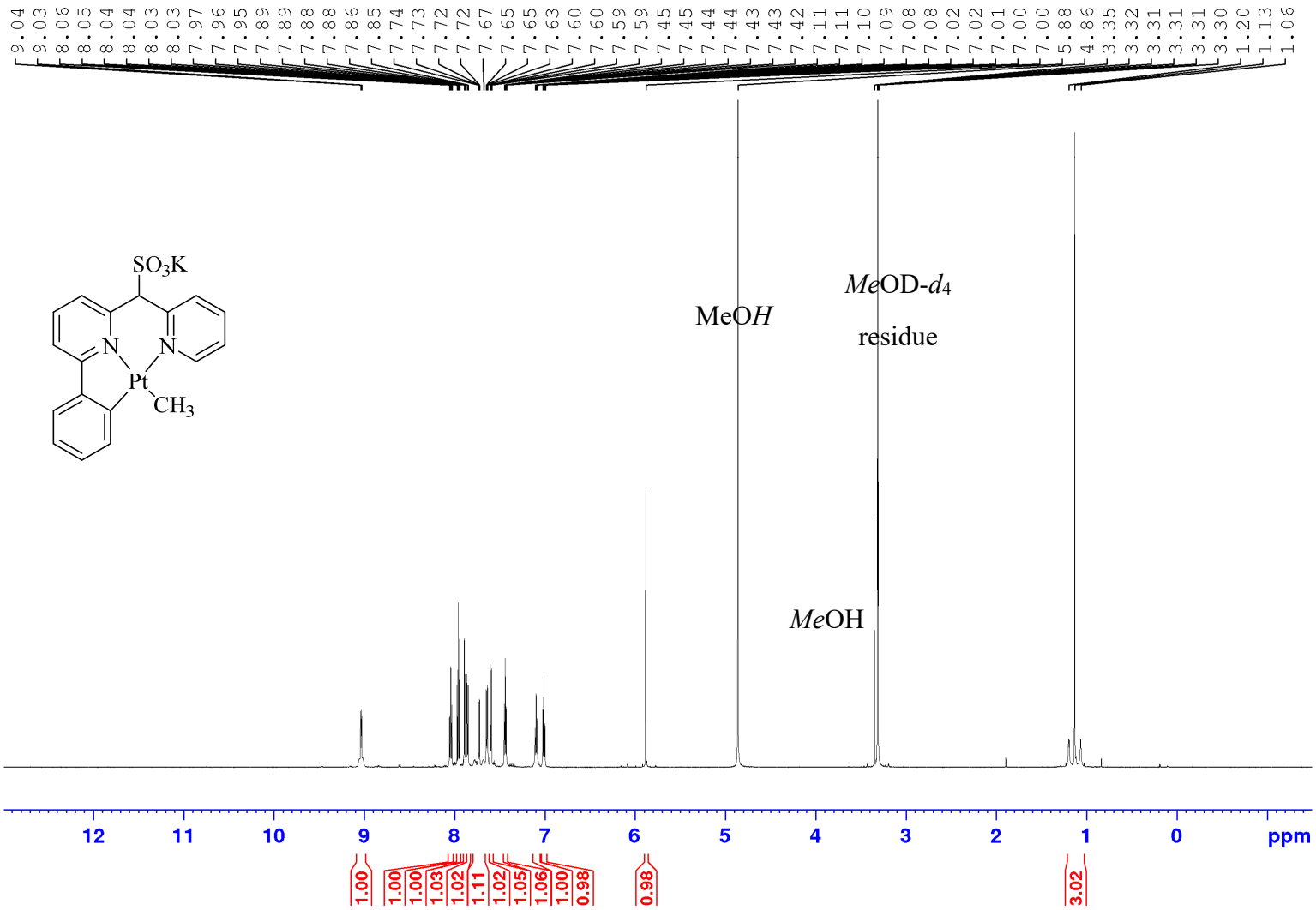



**Figure S13.** $^{1}$H NMR of K[($C_6H_4$-dpms)$Pt^{II}$Me], **13**, in MeOD-$d_4$.

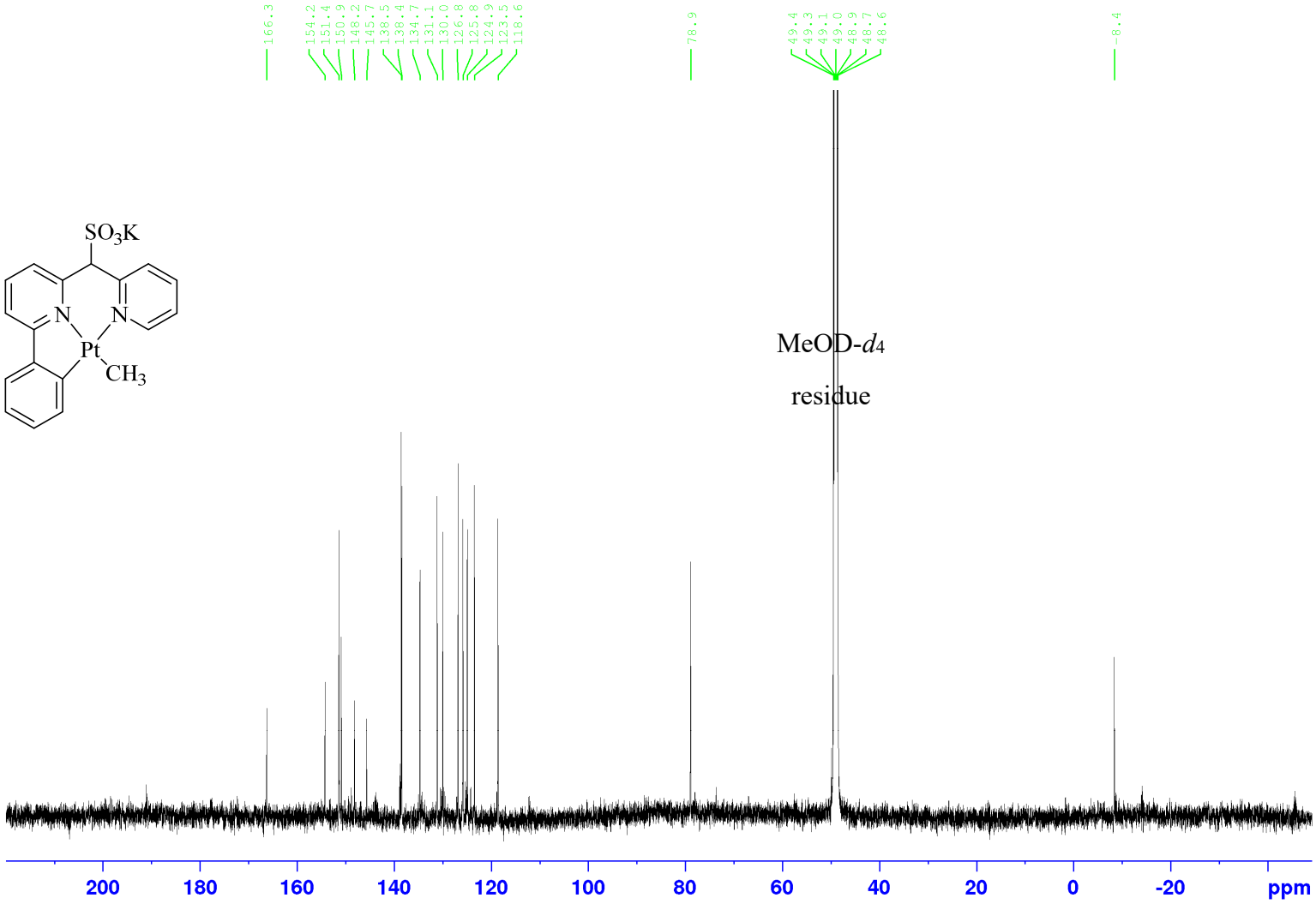



**Figure S14.** $^{13}$C NMR of [($C_6H_4$-dpms)$Pt^{II}$Me]K, **13**, in MeOD-$d_4$.

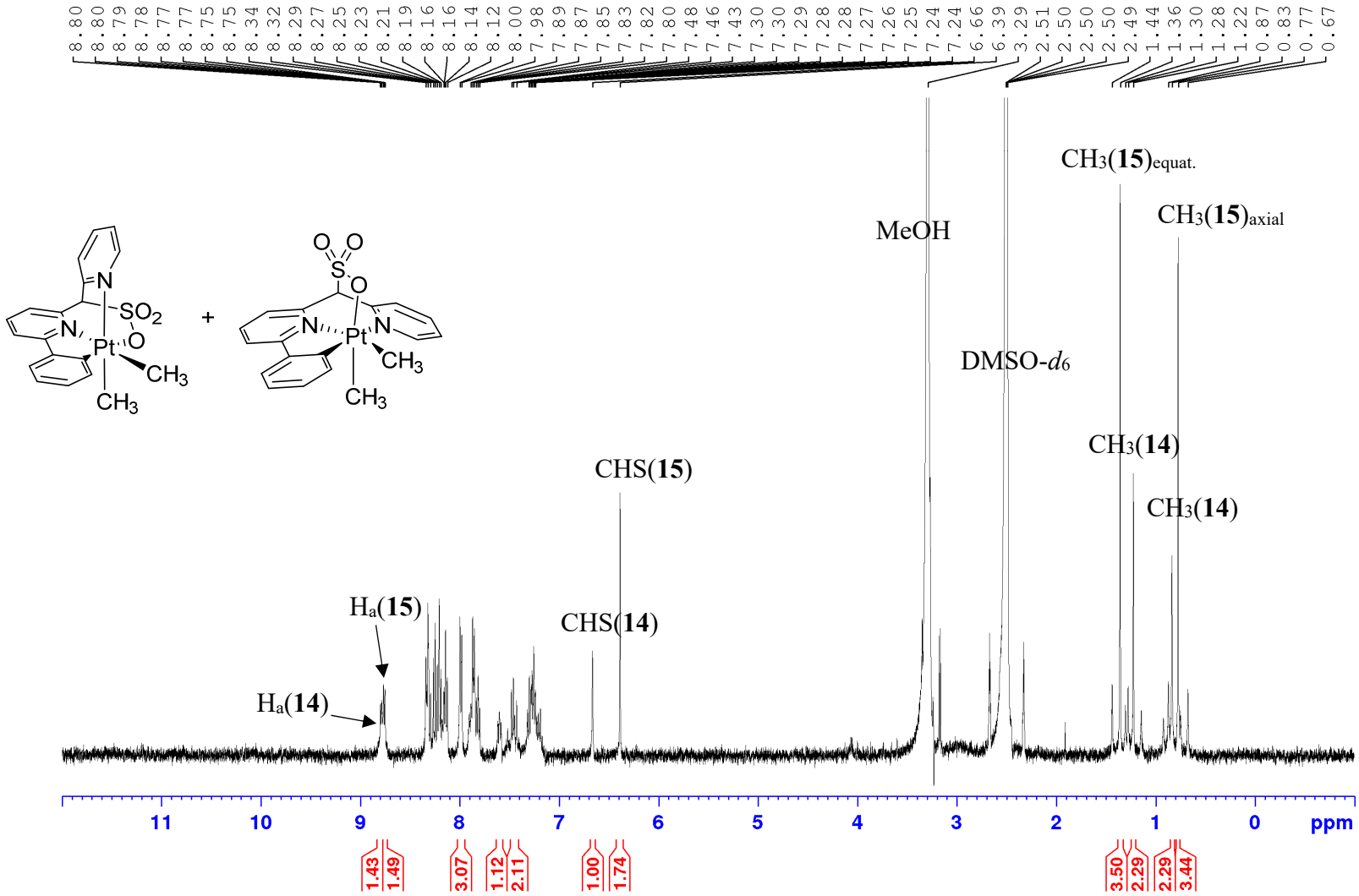
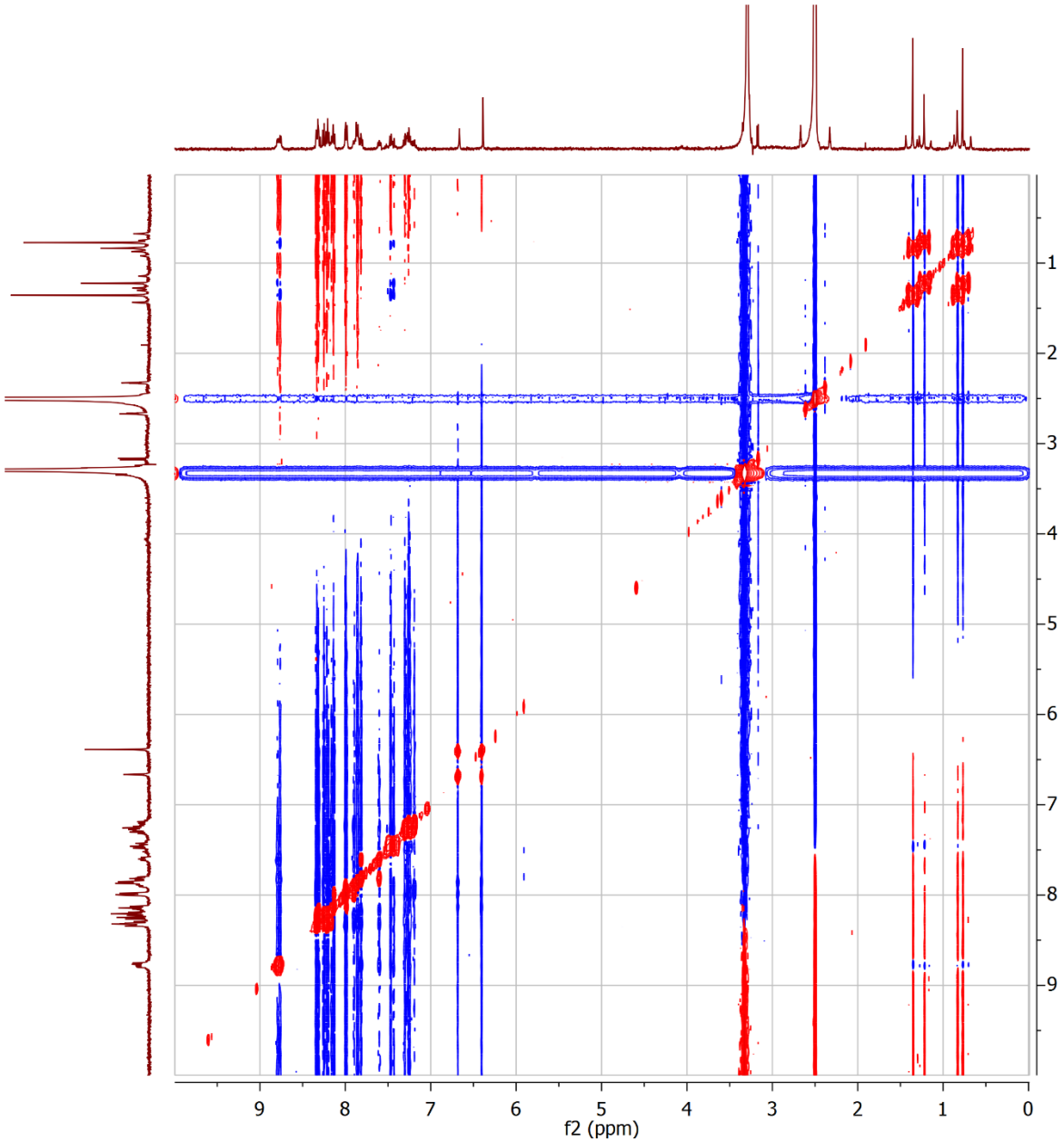



**Figure S15.** $^{1}$H NMR of $(C_6H_4\text{-dpms})Pt^{IV}Me_2$, **14**+**15**, in DMSO-$d_6$.



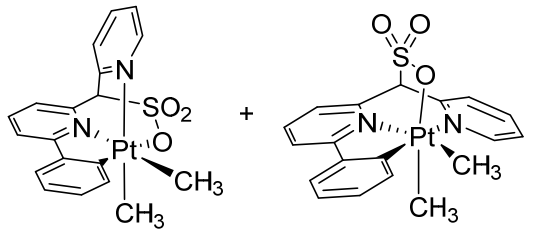




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**Figure S16.** 2D NOE of ($C_6H_4$-dpms)$Pt^{IV}Me_2$, **14**+**15**, in DMSO-*d*6.

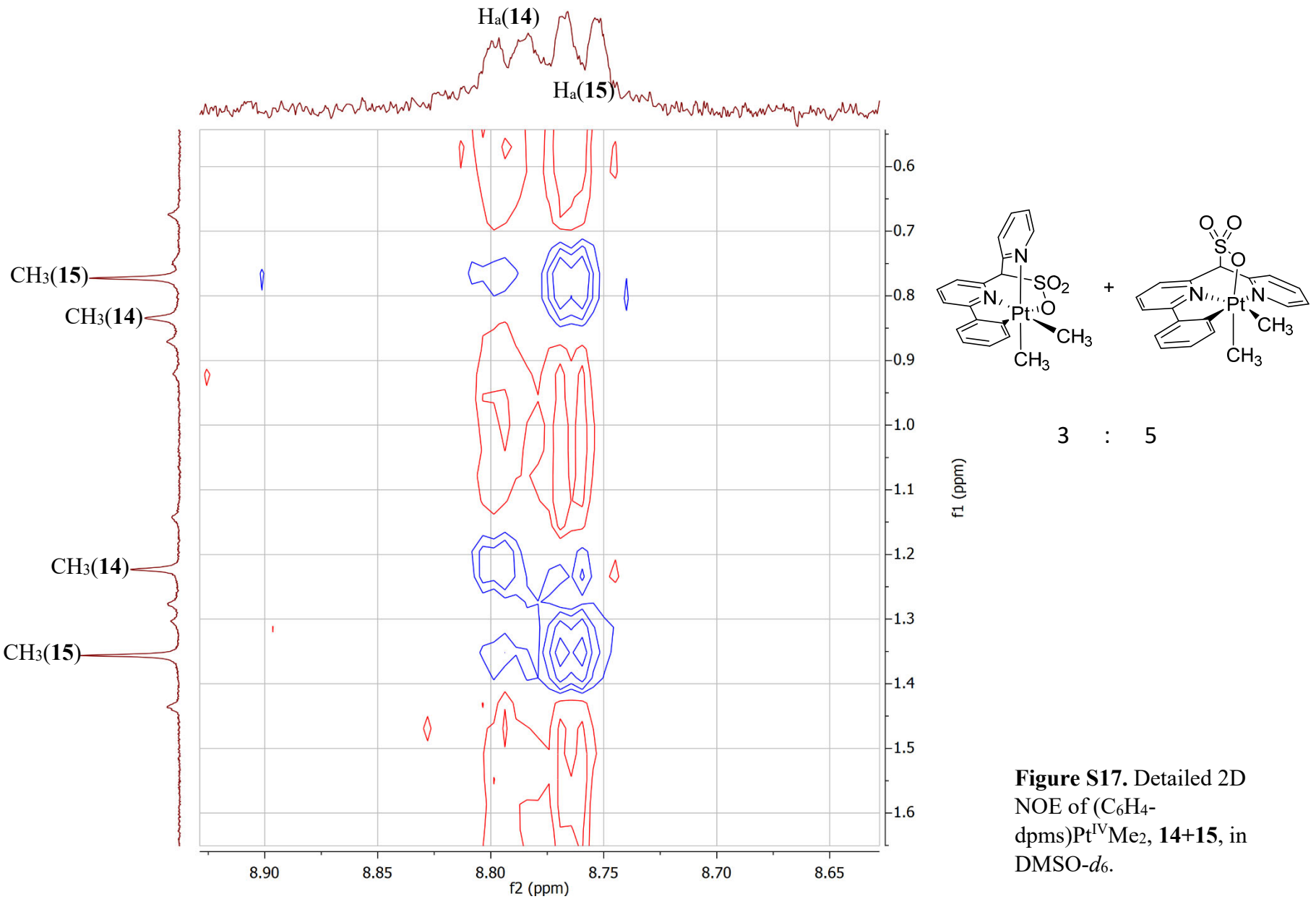


**Figure S17.** Detailed 2D NOE of ($C_6H_4$-dpms)$Pt^{IV}Me_2$, **14+15**, in DMSO-*d*6.

## 2. DFT calculations

The dispersion-corrected Gibbs energy Gtot-D3 values have been calculated as follows:
Gtot-D3 = Gtot – (SCF energy: DFT(pbe)) + (SCF energy: DFT(pbe-d3))

The standard reaction Gibbs energies in TFE, $\Delta G_{rxn}$, in kcal/mol were calculated as
$\Delta G_{rxn} = 627.51\times[\Sigma(\text{Gtot-D3})_{products} - \Sigma(\text{Gtot-D3})_{reactants}]_{gas\ phase} + \Sigma(Gsolv)_{products} - \Sigma(Gsolv)_{reactants} + \Delta nRT\ln(RT/P)$,

where $\Delta n$ is the change in the number of moles in a balanced reaction equation when going from reactants to products. The standard state for all solutes is 1 M concentration.

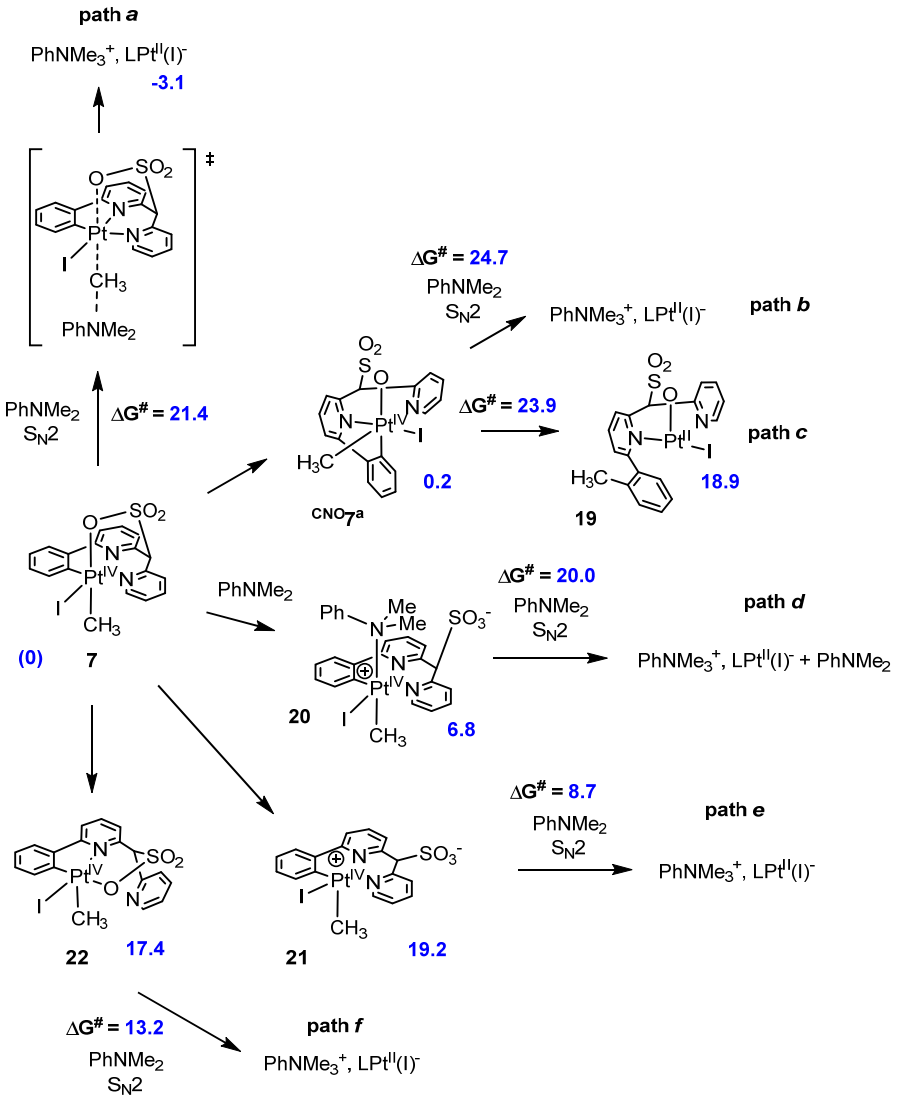


**Fig. S18.** Reaction pathways of complex **7** leading to C-N and C-C coupling. The standard reaction Gibbs energies (blue font) are for TFE solutions, in kcal/mol.

**Path a:**

**($C_6H_4$-dpms)$Pt^{IV}$Me(I), 7**

Total Gibbs free energy, Gtot (Htot - T*S):  -1557.277732 hartrees
SCF energy: DFT(pbe)  -1557.51676326430 hartrees
SCF energy: DFT(pbe-d3)  -1557.55924118277 hartrees
Gsolv = -20.7954 kcal/mol

**$PhNMe_2$**

Total Gibbs free energy, Gtot (Htot - T*S):  -365.599212 hartrees
SCF energy: DFT(pbe)  -365.73490609828 hartrees
SCF energy: DFT(pbe-d3)  -365.74285669215 hartrees
Gsolv = -3.9538 kcal/mol

**TS for the reaction in path a**

Total Gibbs free energy, Gtot (Htot - T*S):  -1922.814737 hartrees
SCF energy: DFT(pbe)  -1923.20929069308 hartrees
SCF energy: DFT(pbe-d3)  -1923.27181629502 hartrees
Gsolv = -32.8906 kcal/mol

**$PhNMe_3^+$,$LPt^{II}(I)^-$ ion pair**

Total Gibbs free energy, Gtot (Htot - T*S):  -1922.864287 hartrees
SCF energy: DFT(pbe)  -1923.26385159476 hartrees
SCF energy: DFT(pbe-d3)  -1923.32794667479 hartrees
Gsolv = -25.3388 kcal/mol

**Path b:**

**(mer-CNO-$C_6H_4$-dpms)$Pt^{IV}$(axial-Me)(I), $^{CNO}$7$^{a}$**

Total Gibbs free energy, Gtot (Htot - T*S):  -1557.278759 hartrees
SCF energy: DFT(pbe)  -1557.51775290507 hartrees
SCF energy: DFT(pbe-d3)  -1557.56024330523 hartrees
Gsolv = -19.9513 kcal/mol

**TS for the reaction in path b**

Total Gibbs free energy, Gtot (Htot - T*S):  -1922.828833 hartrees
SCF energy: DFT(pbe)  -1923.22336633032 hartrees
SCF energy: DFT(pbe-d3)  -1923.28411953092 hartrees
Gsolv = -21.6871 kcal/mol

**Path c:**

**TS for the reaction in path c**

Total Gibbs free energy, Gtot (Htot - T*S):  -1557.234137 hartrees
SCF energy: DFT(pbe)  -1557.47122312379 hartrees
SCF energy: DFT(pbe-d3)  -1557.51340741779 hartrees
Gsolv = -22.1520 kcal/mol

**19**

Total Gibbs free energy, Gtot (Htot - T*S):  -1557.250045 hartrees
SCF energy: DFT(pbe)  -1557.48550916232 hartrees
SCF energy: DFT(pbe-d3)  -1557.52575950778 hartrees
Gsolv = -20.5212 kcal/mol

**Path d**:

**20**

Total Gibbs free energy, Gtot (Htot - T*S):  -1922.850444 hartrees
SCF energy: DFT(pbe)  -1923.24886474720 hartrees
SCF energy: DFT(pbe-d3)  -1923.32224450406 hartrees
Gsolv = -18.3081 kcal/mol

**TS for the reaction in path d**

Total Gibbs free energy, Gtot (Htot - T*S):  -2288.399450 hartrees
SCF energy: DFT(pbe)  -2288.95474894208 hartrees
SCF energy: DFT(pbe-d3)  -2289.04113899192 hartrees
Gsolv = -26.6947 kcal/mol

**Path e**:

**21**

Total Gibbs free energy, Gtot (Htot - T*S):  -1557.244337 hartrees
SCF energy: DFT(pbe)  -1557.48141937480 hartrees
SCF energy: DFT(pbe-d3)  -1557.52148371699 hartrees
Gsolv = -24.0562 kcal/mol

**TS for the reaction in path e**

Total Gibbs free energy, Gtot (Htot - T*S):  -1922.821928 hartrees
SCF energy: DFT(pbe)  -1923.21786524277 hartrees
SCF energy: DFT(pbe-d3)  -1923.27845448081 hartrees
Gsolv = -23.0562 kcal/mol

**Path f**:

**22**

Total Gibbs free energy, Gtot (Htot - T*S):  -1557.260334 hartrees
SCF energy: DFT(pbe)  -1557.49582892156 hartrees
SCF energy: DFT(pbe-d3)  -1557.53489145778 hartrees
Gsolv = -16.4713 kcal/mol

**TS for the reaction in path f**

Total Gibbs free energy, Gtot (Htot - T*S):  -1922.815316 hartrees
SCF energy: DFT(pbe)  -1923.21184958863 hartrees
SCF energy: DFT(pbe-d3)  -1923.27193059787 hartrees
Gsolv = -24.8678 kcal/mol