Supporting Information

Stereoelectronic Effects in C-H Bond Oxidation Reactions of Ni(I) N-Heterocyclic Carbene Complexes

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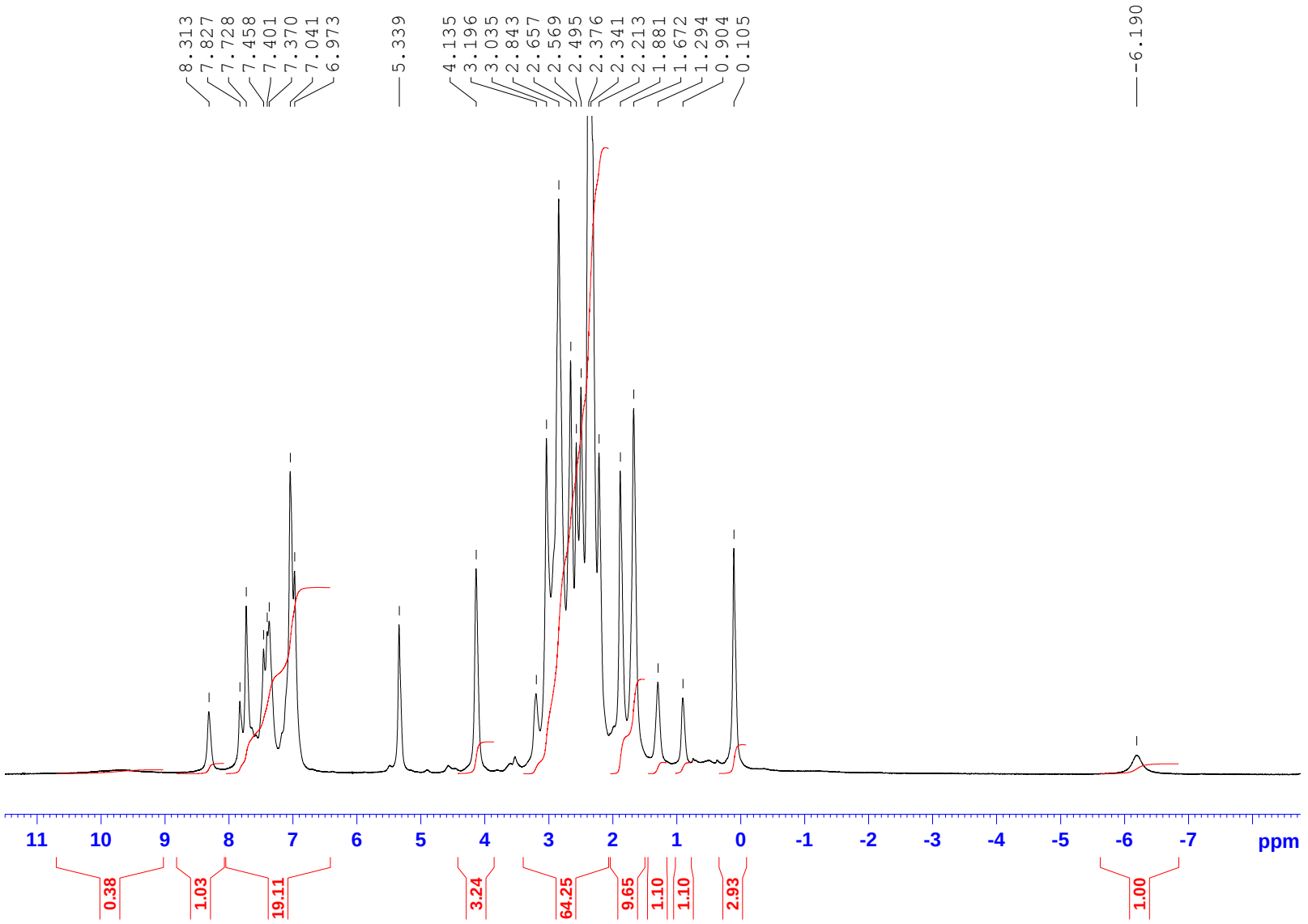
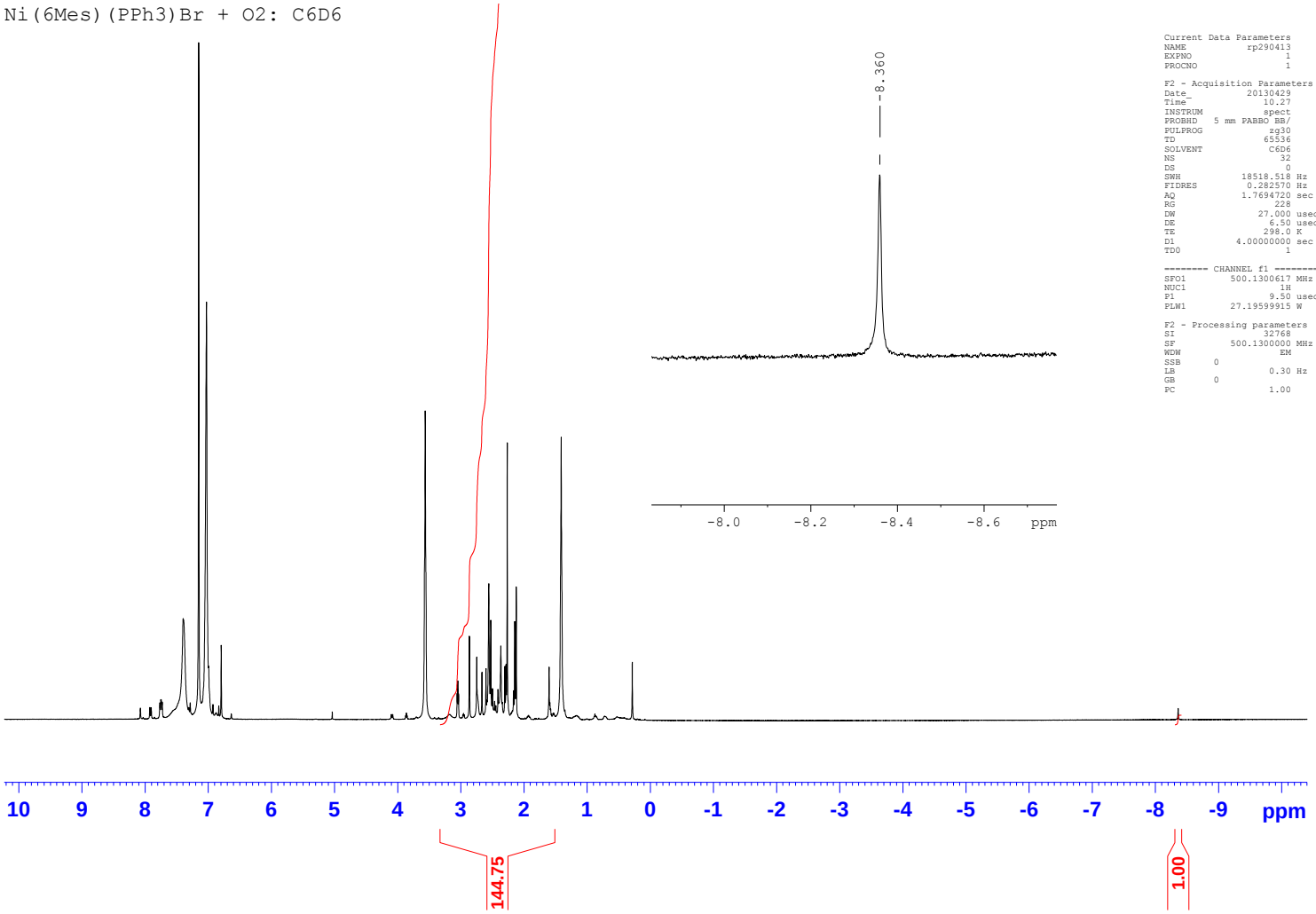
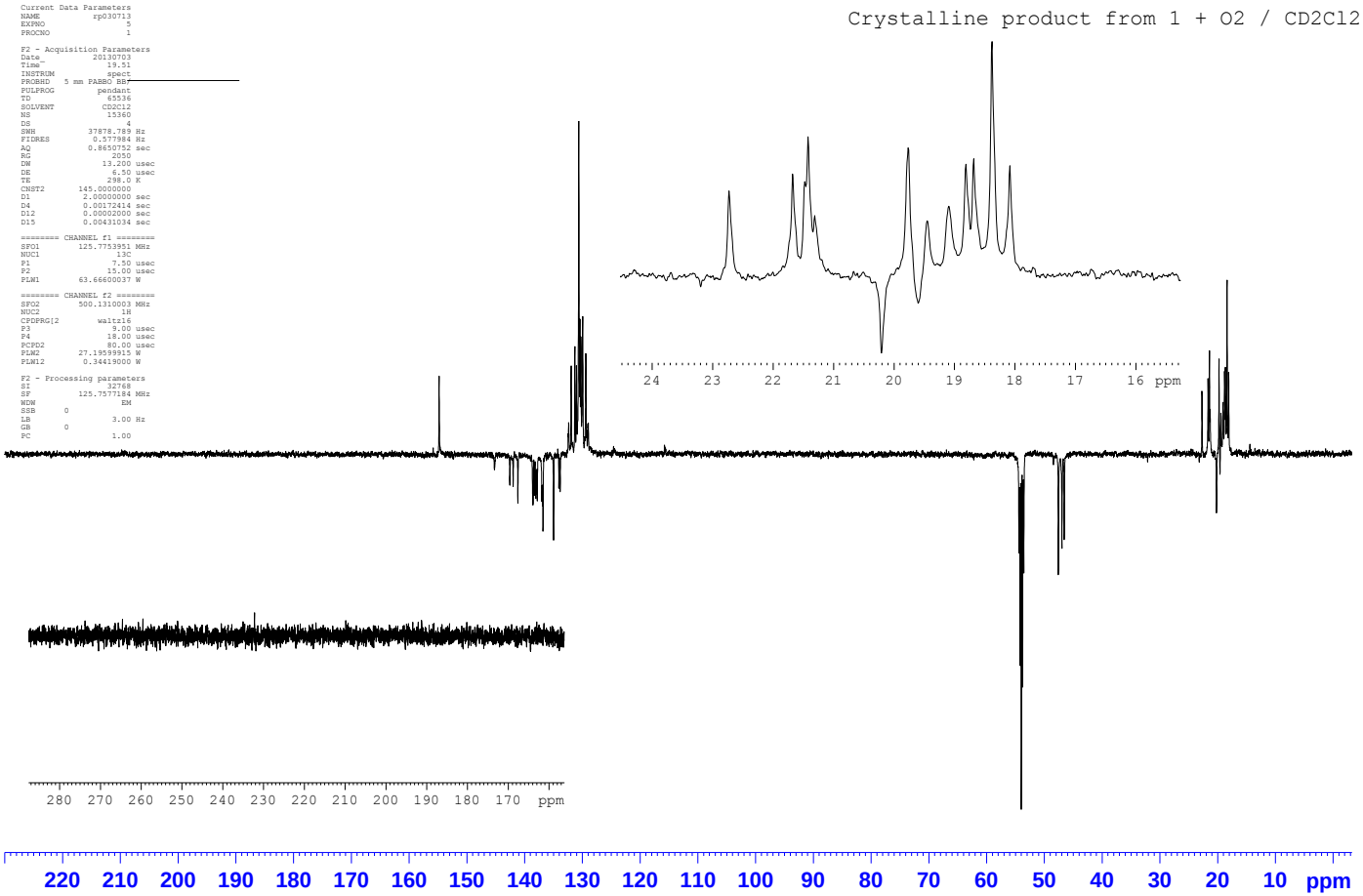


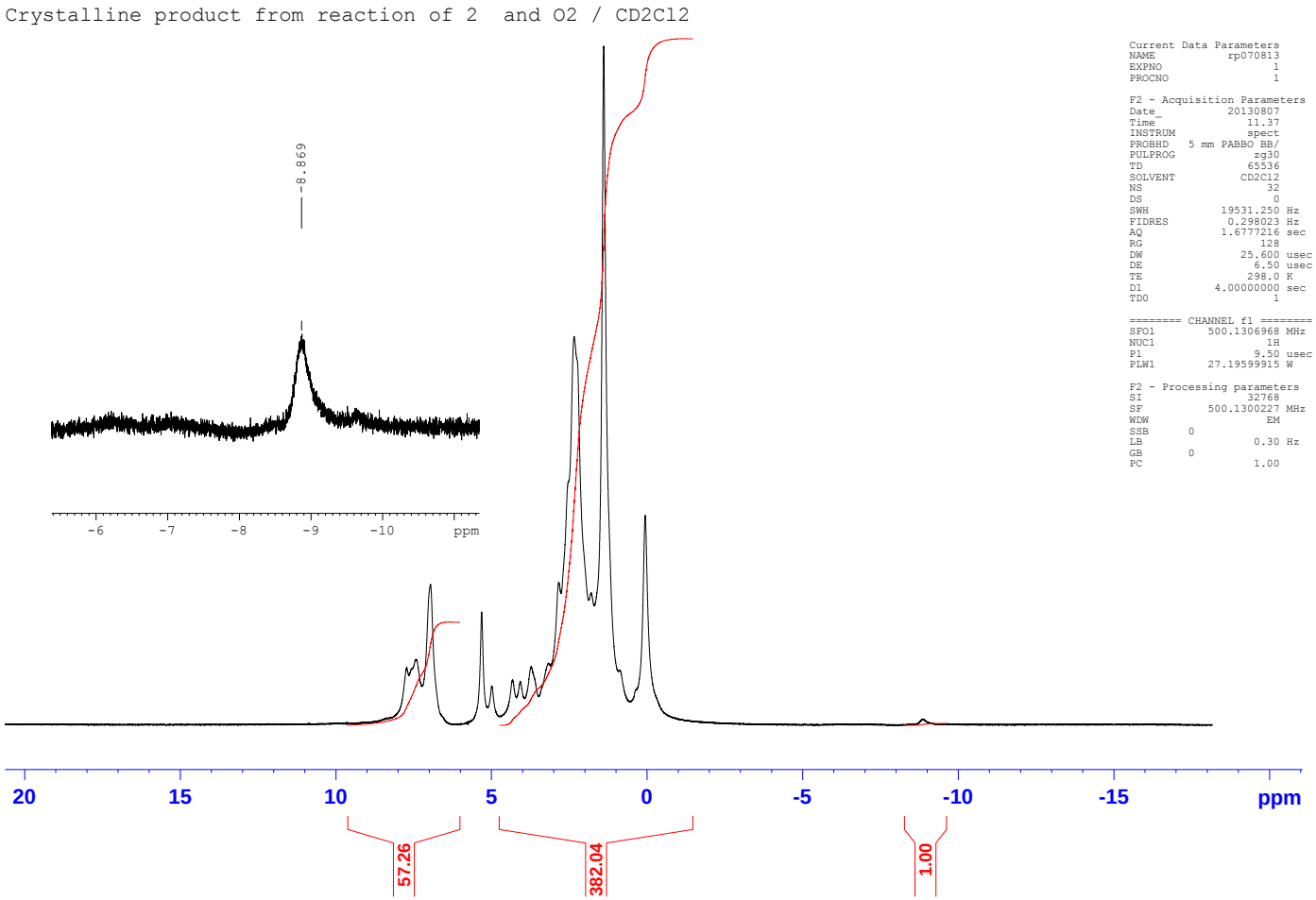
^{1}H NMR spectrum (500 MHz, 298 K) of redissolved microcrystalline solid isolated from reaction of **1** with O_2 recorded in CD_2Cl_2.



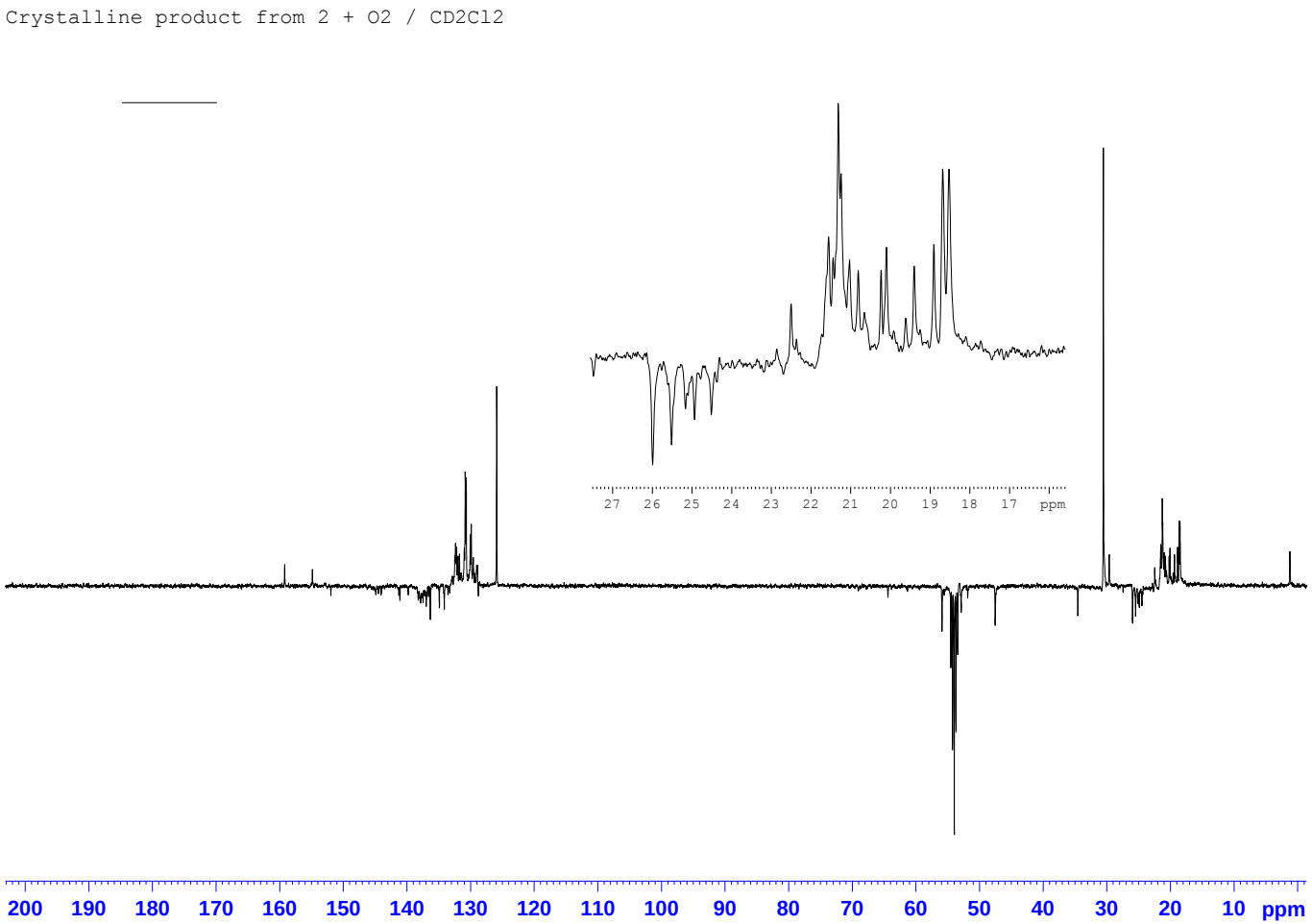
^{1}H NMR spectrum (500 MHz, 298 K) of redissolved microcrystalline solid isolated from reaction of **1** with O_2 recorded in C_6D_6.



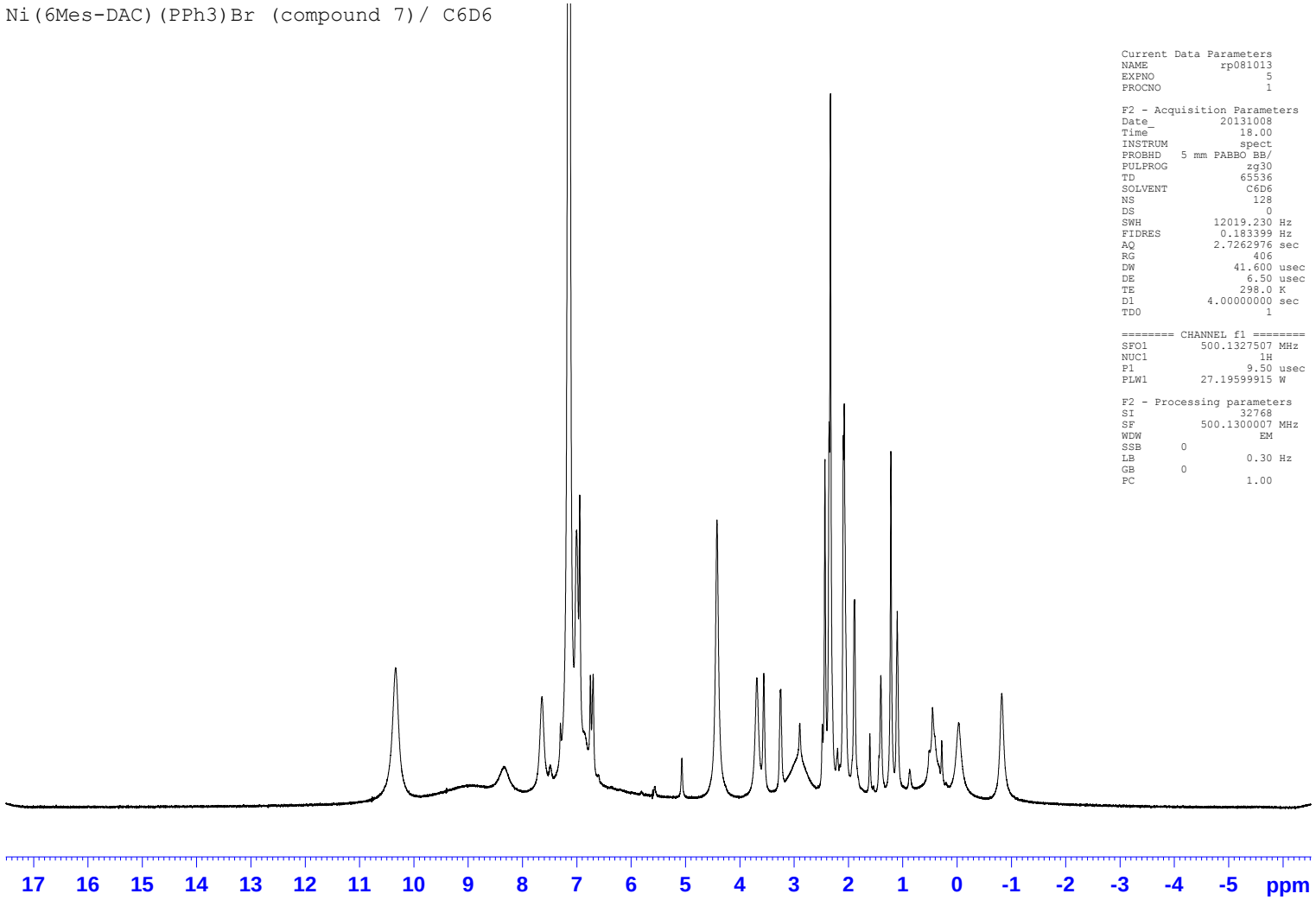
$^{13}C\{^{1}H\}$ PENDANT NMR spectrum (126 MHz, 298 K) of redissolved microcrystalline solid isolated from reaction of **1** with O_2 recorded in CD_2Cl_2. Insets highlight (i) lack of high frequency carbenic signals and (ii) extensive number of methyl carbons.



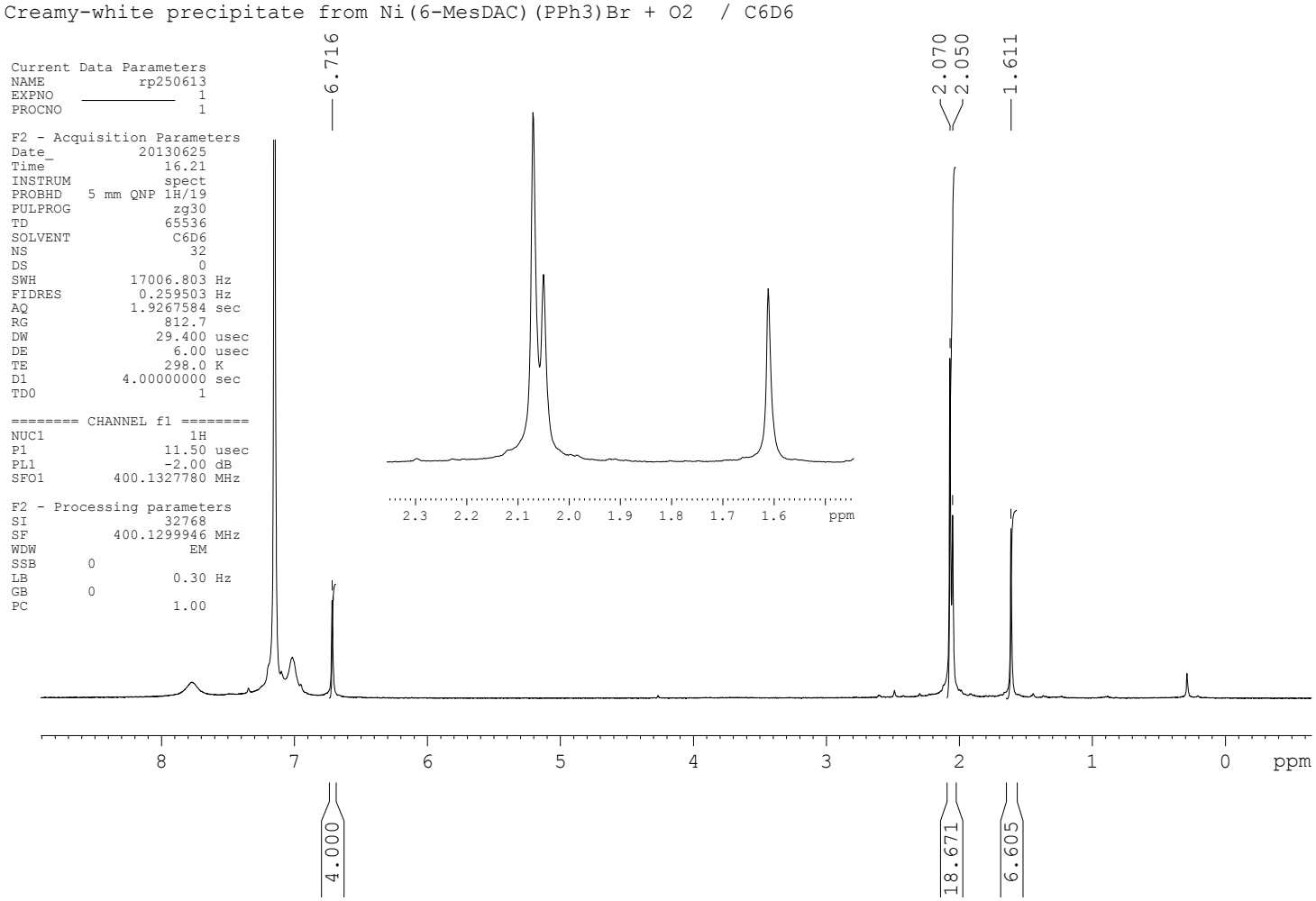
^{1}H NMR spectrum (500 MHz, 298 K) of redissolved microcrystalline solid isolated from reaction of **2** with O_2 recorded in CD_2Cl_2.



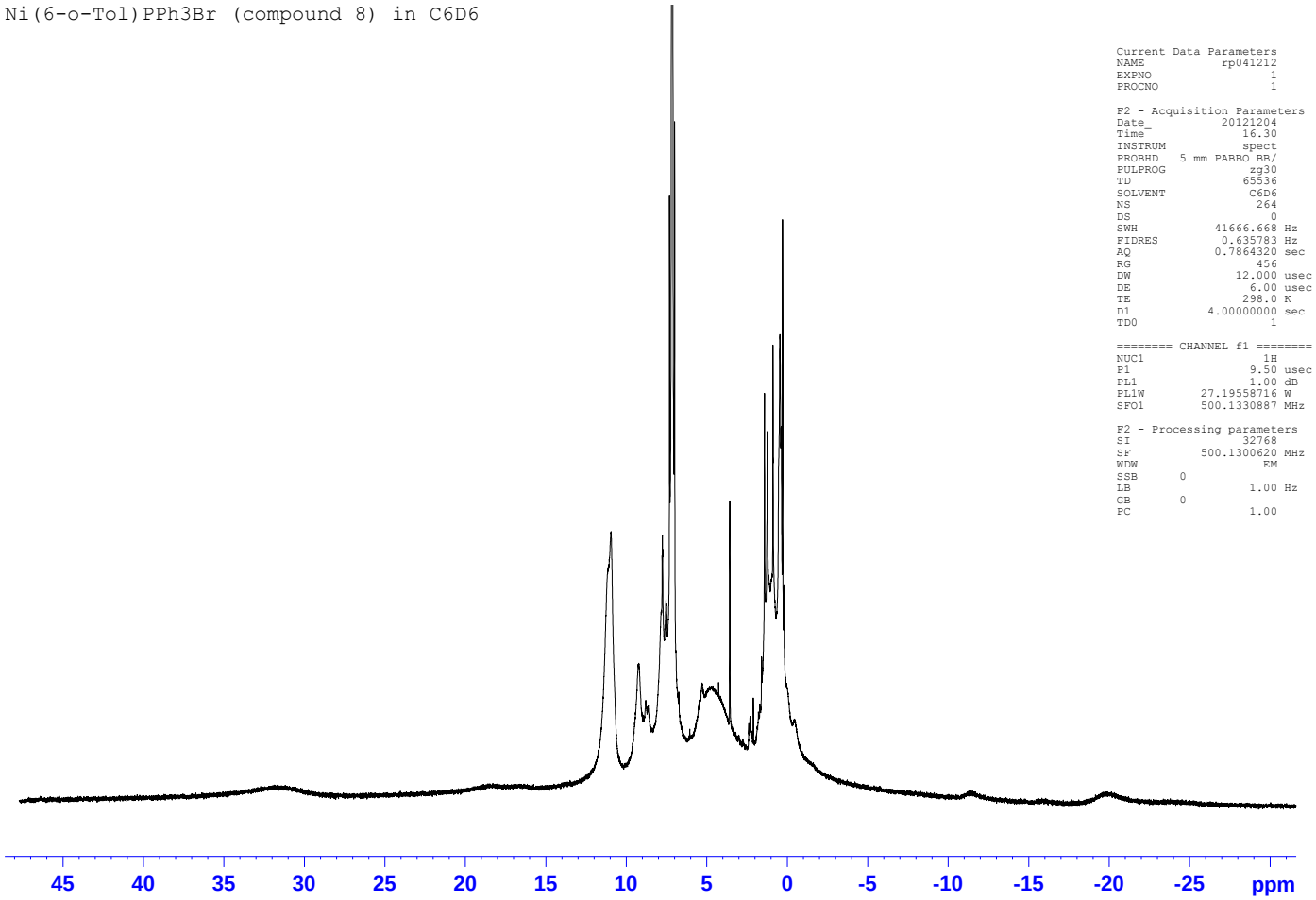
$^{13}C\{^{1}H\}$ PENDANT NMR spectrum (126 MHz, 298 K) of redissolved microcrystalline solid isolated from reaction of **2** with O_2 recorded in CD_2Cl_2. Inset highlights the extensive number of methyl carbons.



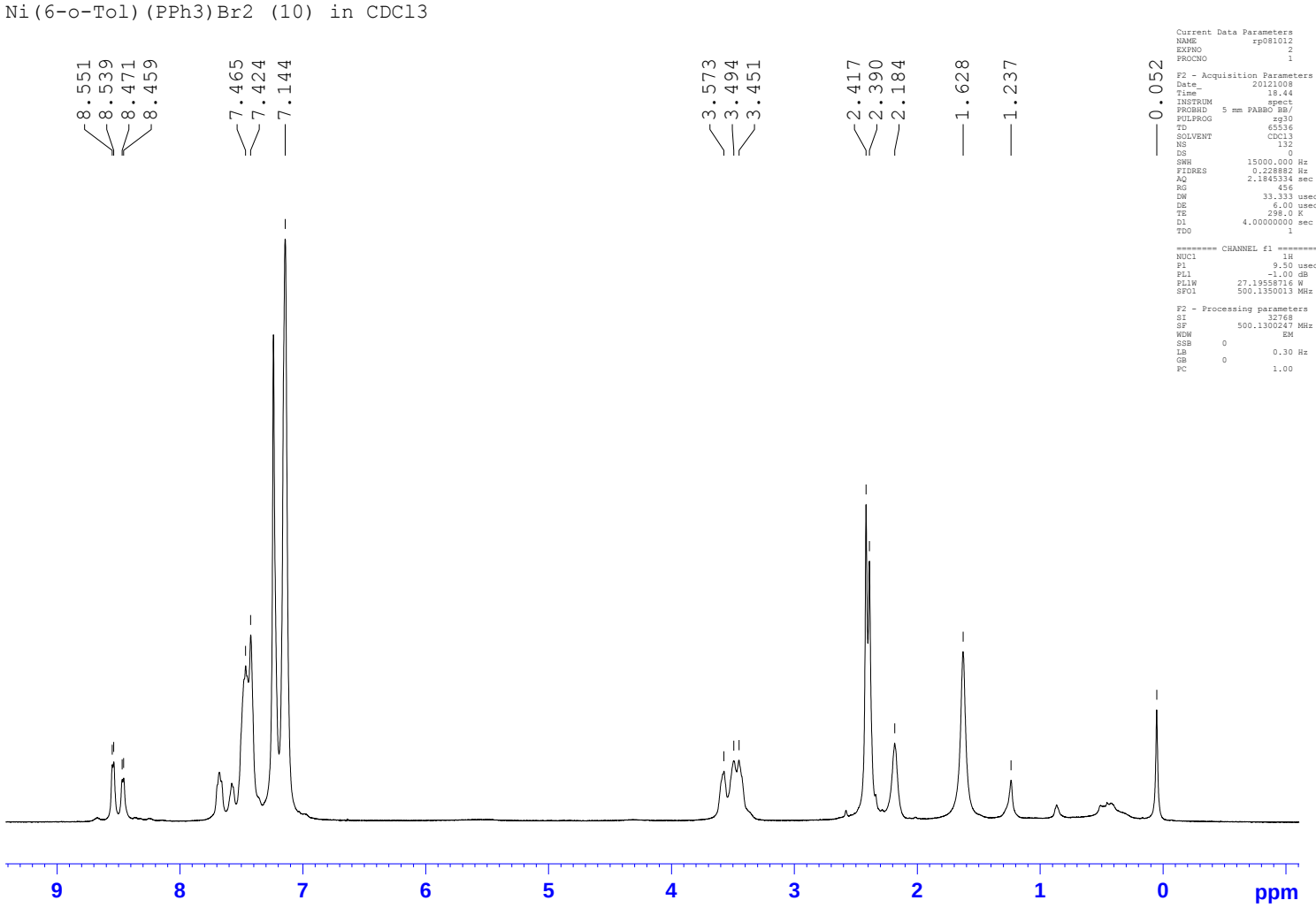
^{1}H NMR spectrum (500 MHz, 298 K) of Ni(6-MesDAC)(PPh_3)Br (**7**) in C_6D_6.



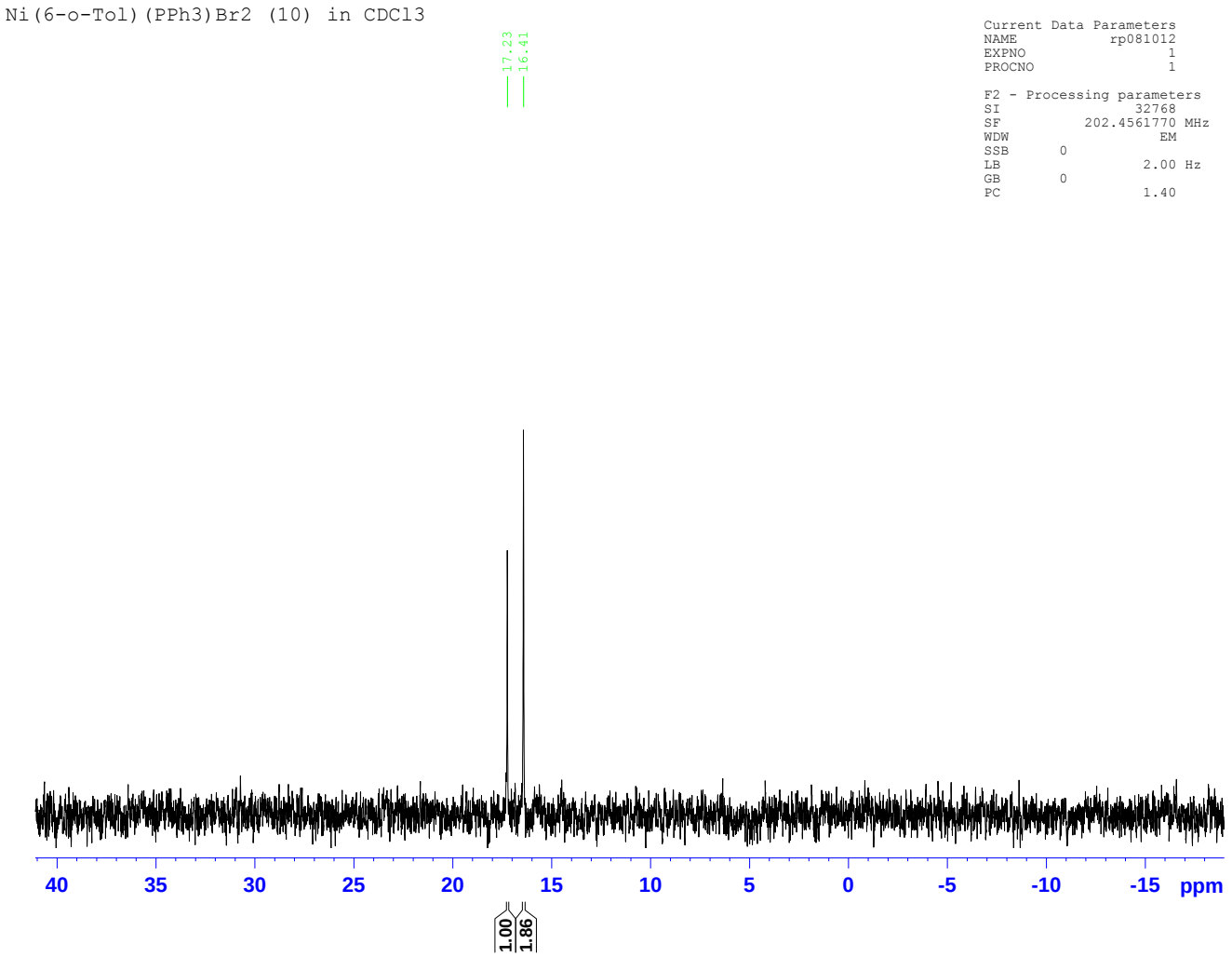
^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of a mixture of $Ni(O{=}PPh_3)_2Br_2$ and (6-MesDAC)=O formed from reaction of **7** with O_2.



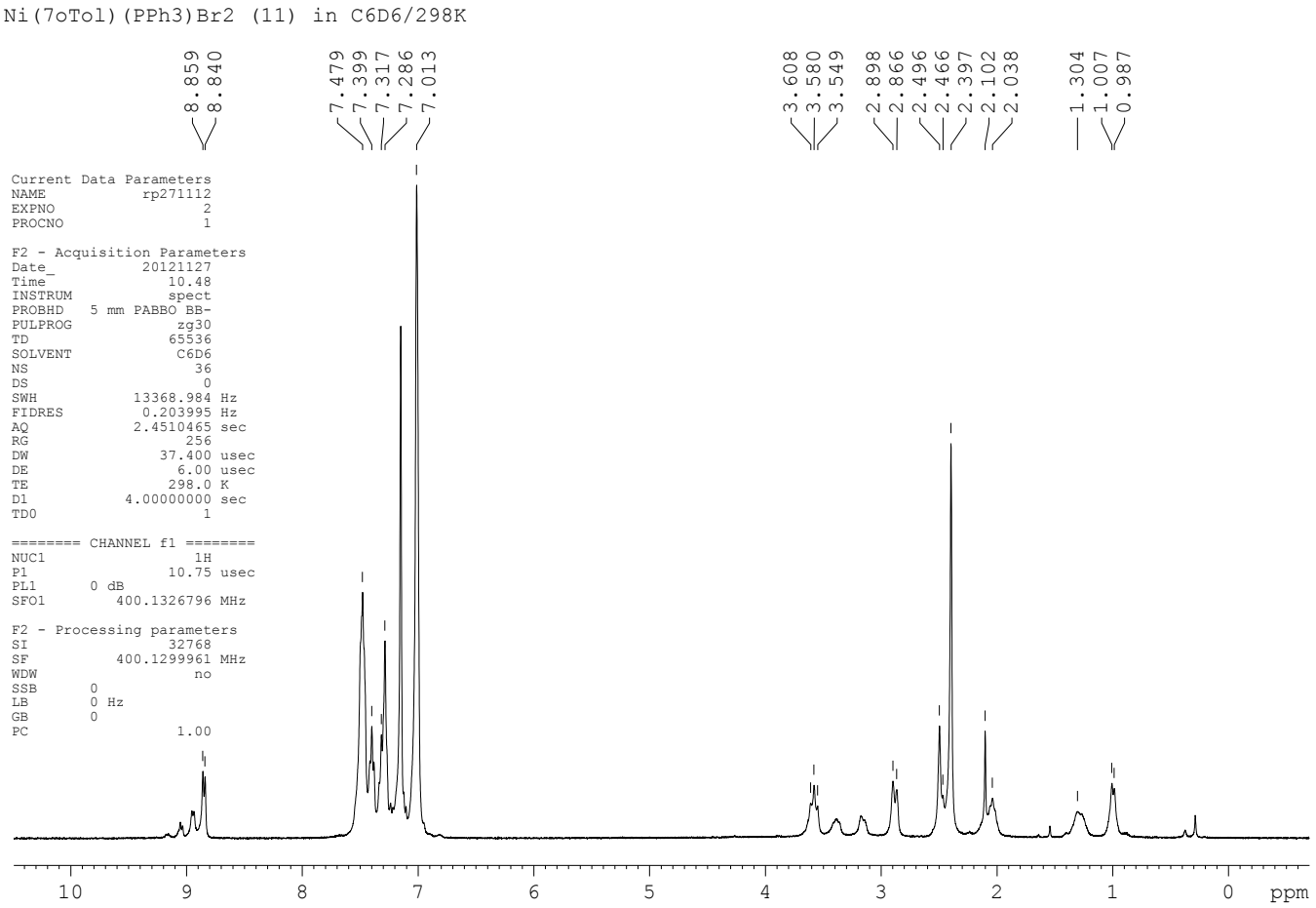
^{1}H NMR spectrum (500 MHz, 298 K) of Ni(6-*o*-Tol)(PPh_3)Br (**8**) in C_6D_6.



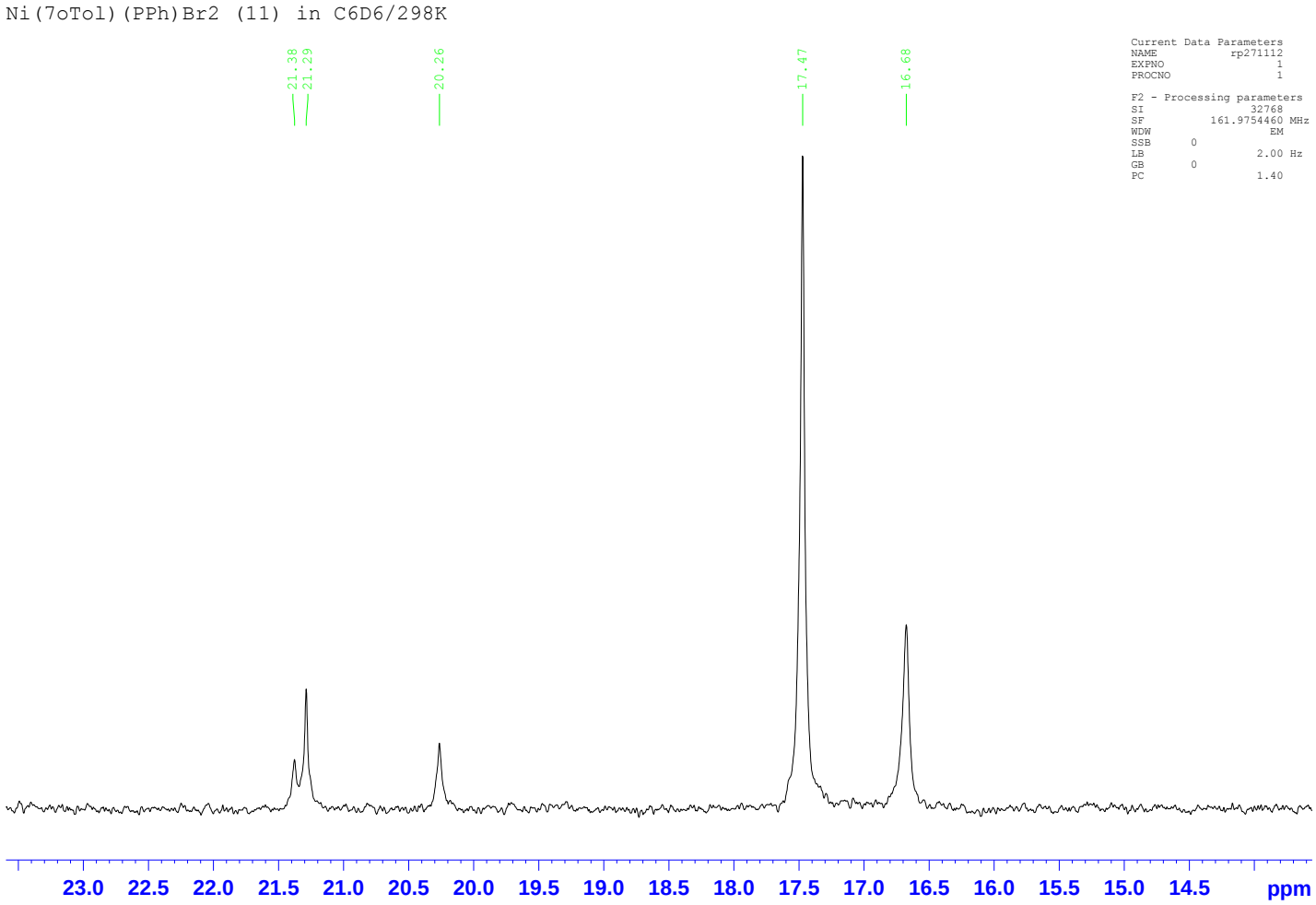
^{1}H NMR spectrum (500 MHz, 298 K) of Ni(6-*o*-Tol)(PPh_3)Br_2 (**10**) in $CDCl_3$.



$^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 298 K) of Ni(6-*o*-Tol)(PPh_3)Br_2 (**10**) in $CDCl_3$.

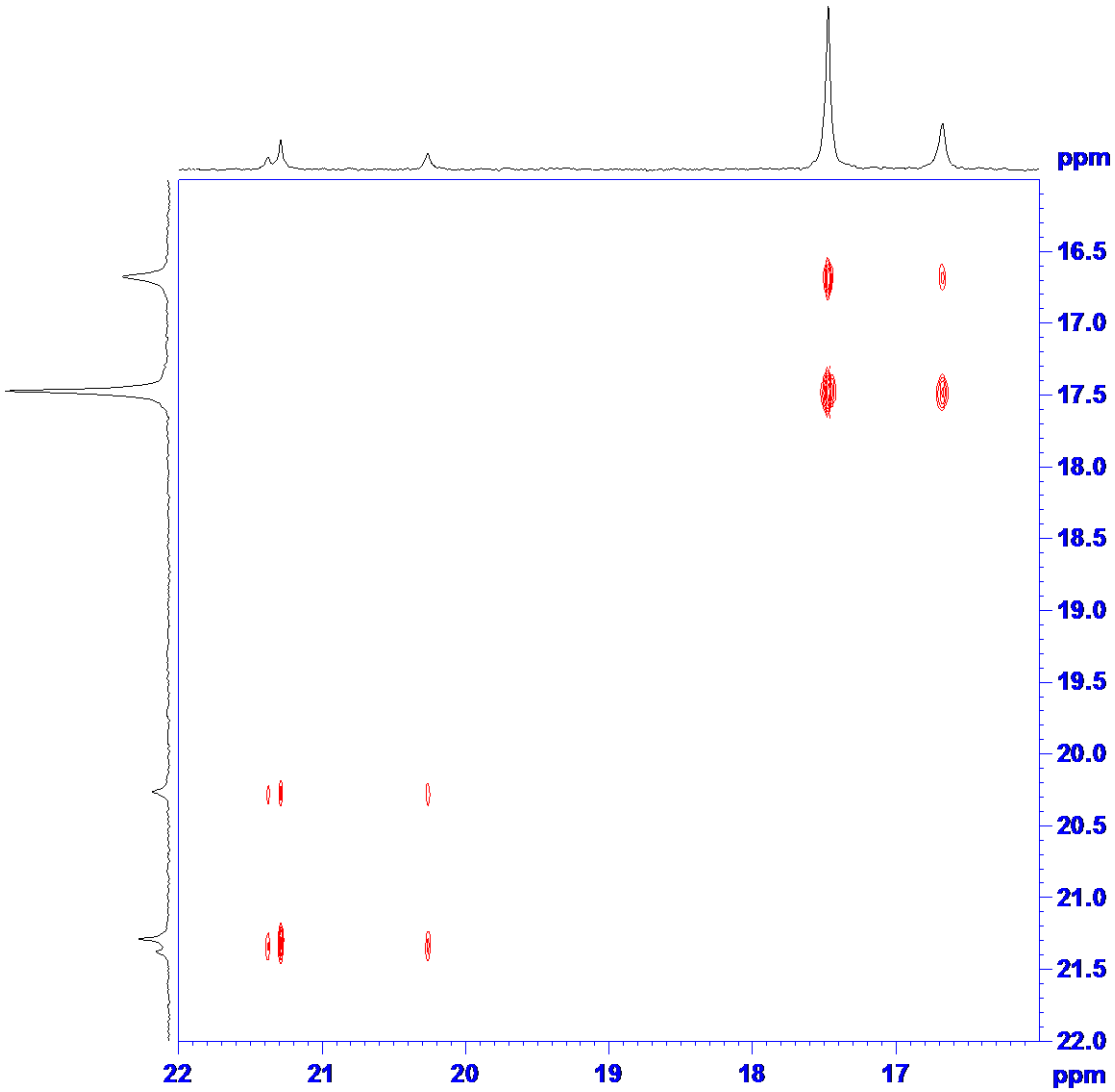


^{1}H NMR spectrum (400 MHz, 298 K) of Ni(7-*o*-Tol)(PPh_3)Br_2 (**11**) in C_6D_6.



$^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 298 K) of Ni(7-*o*-Tol)(PPh_3)Br_2 (**11**) in C_6D_6.

^{31}P-^{31}P EXSY for **11** (202 MH, C_6D_6, 298 K)



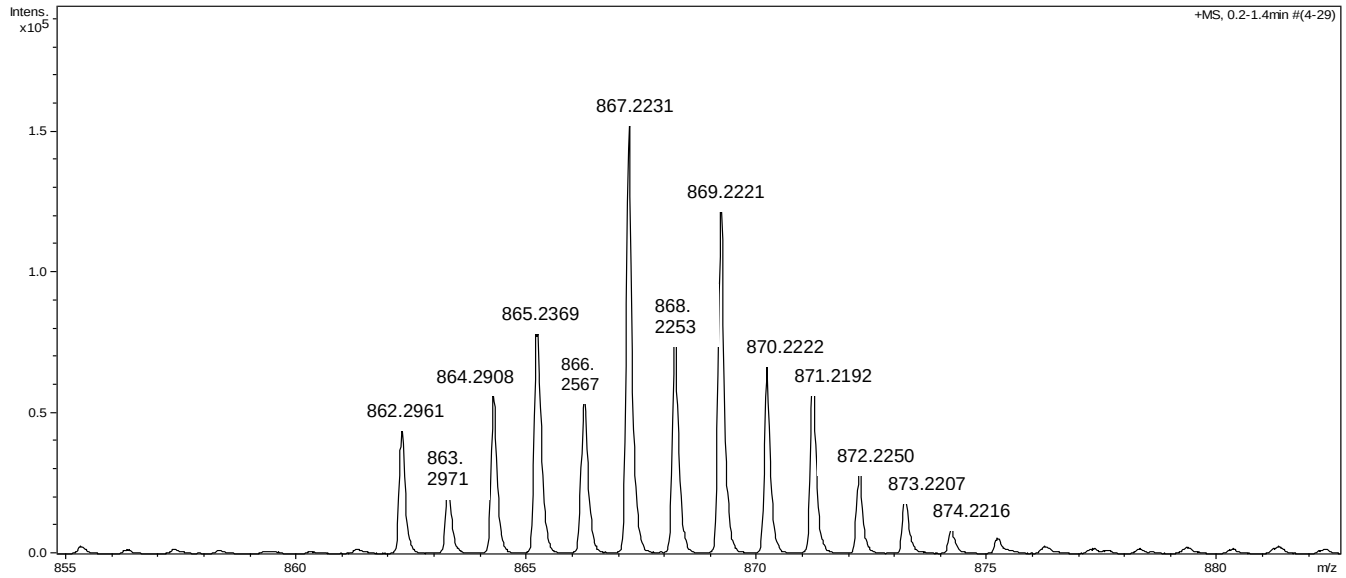
Mass Spectrometer data for **3/5**

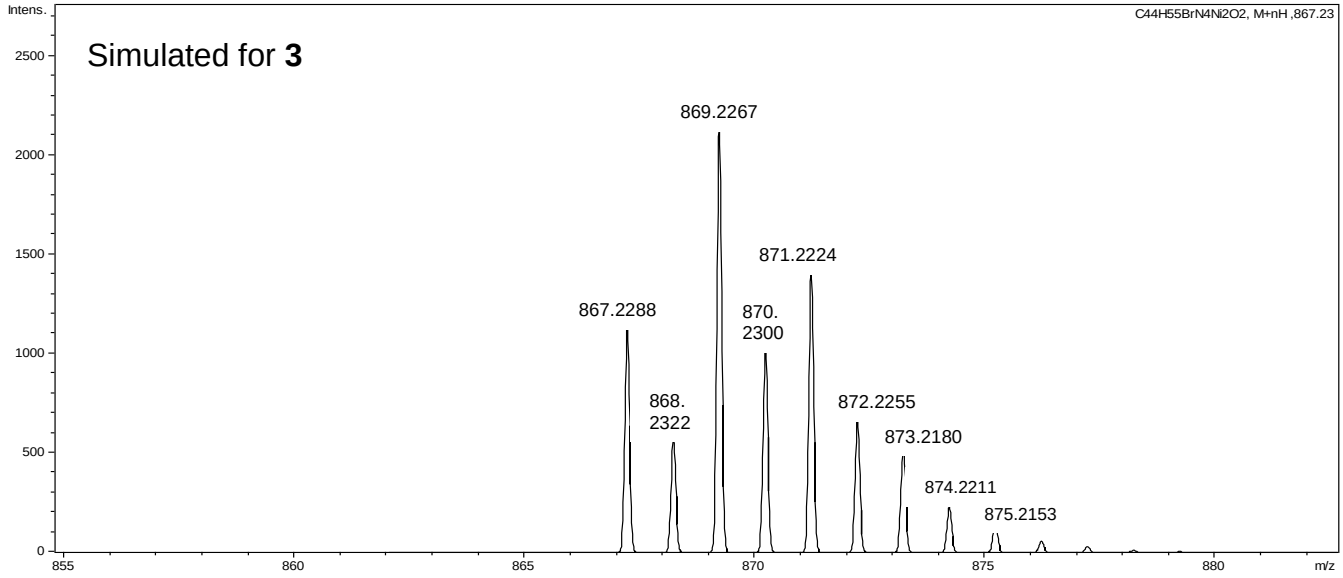
$[M - HBr + H]^+$

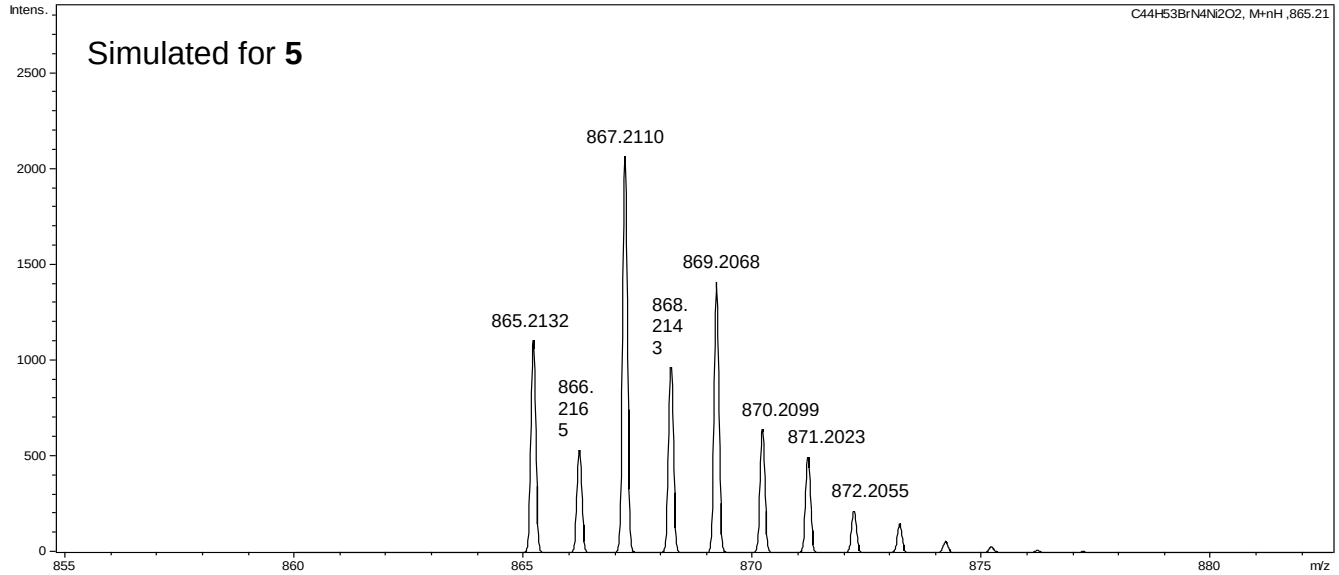
$[C_{44}H_{53}BrN_4Ni_2O_2 + H]^+$

Theoretical m/z = 867.2106

Measured m/z = 867.2231







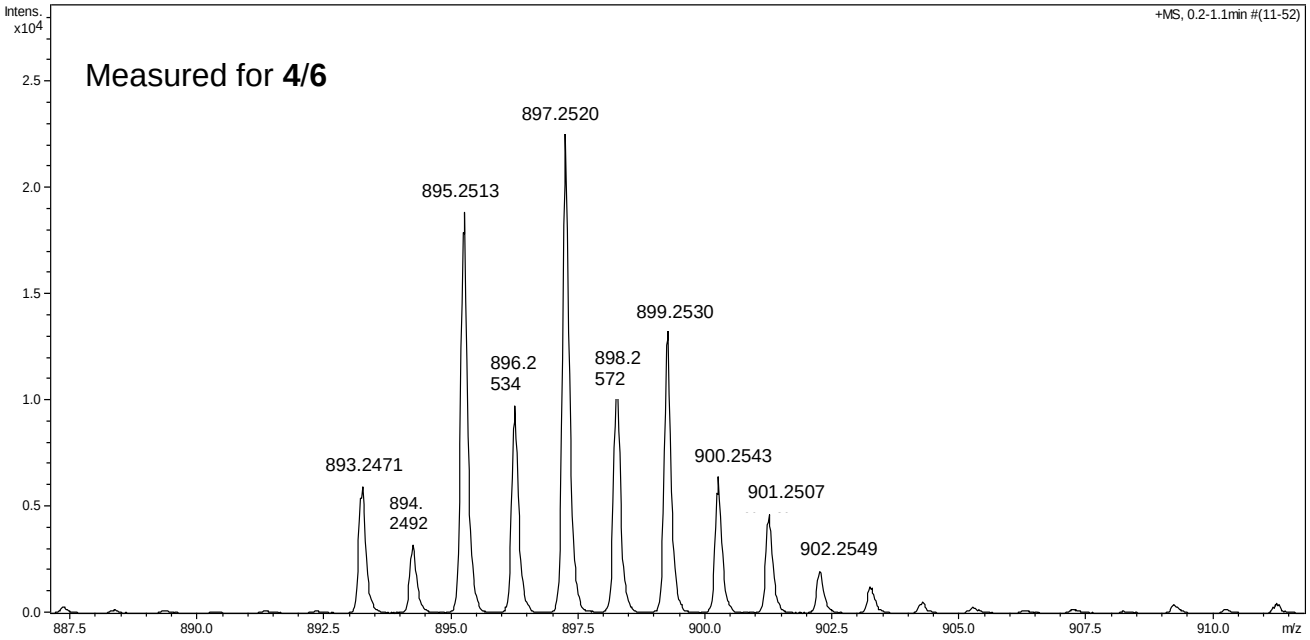
Mass Spectrometer data for **4/6**

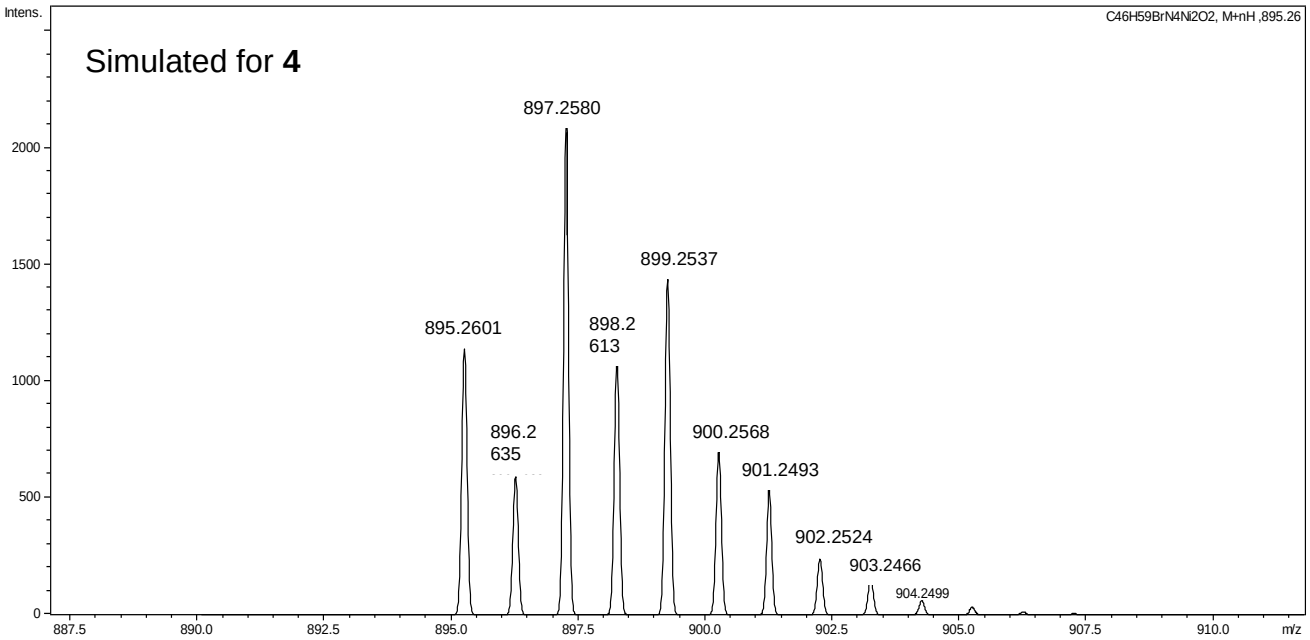
$[M - HBr + H]^+$

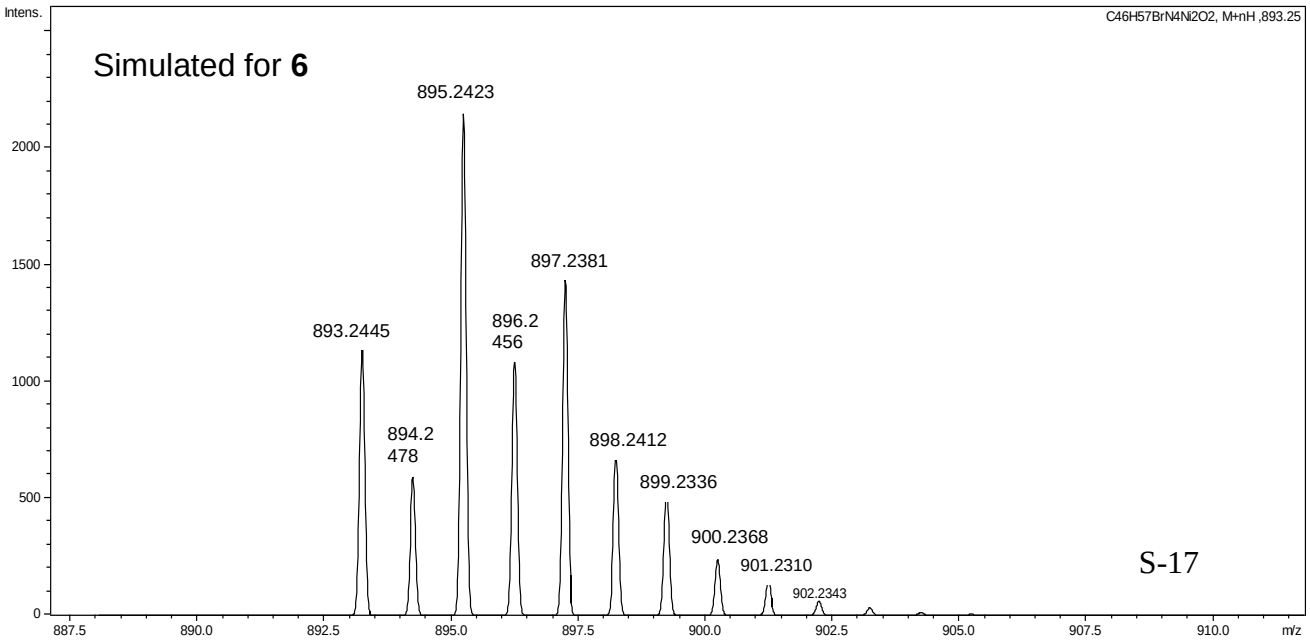
$[C_{46}H_{59}BrN_4Ni_2O_2 + H]^+$

Theoretical m/z = 897.7615

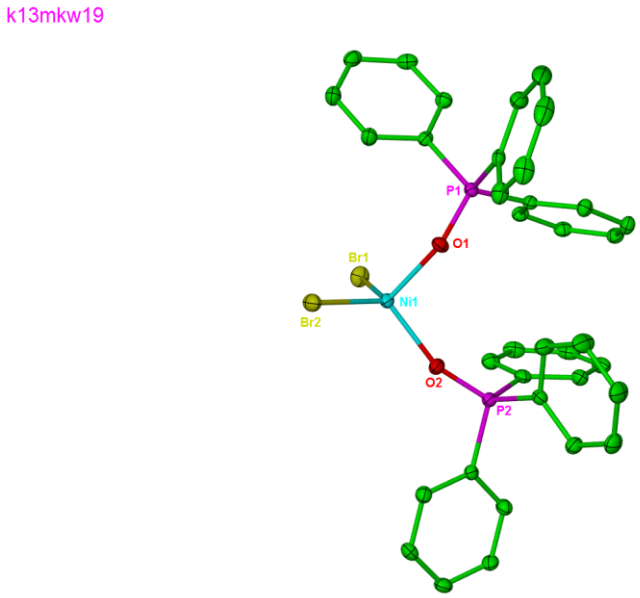
Measured m/z = 897.2520







X-ray crystal structure of $Ni(O{=}PPh_3)_2Br_2$

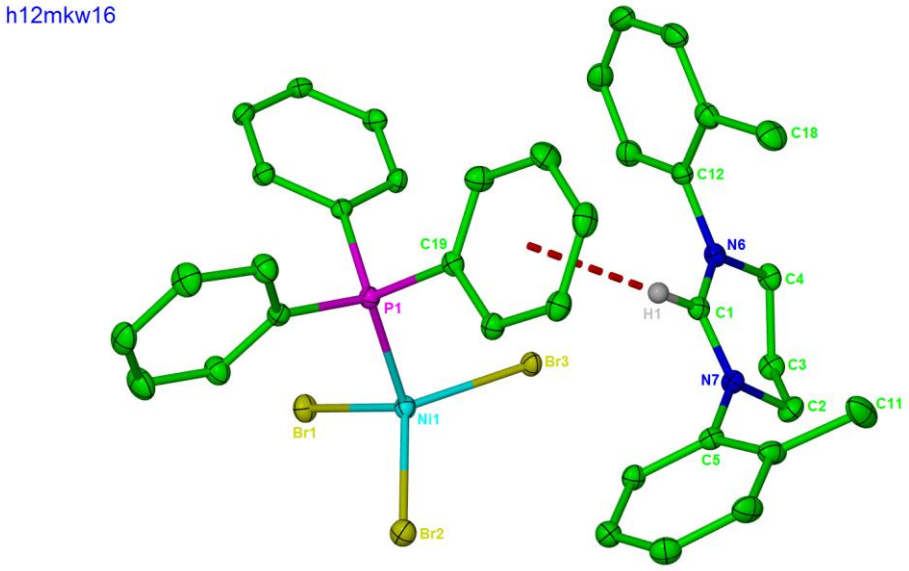


Molecular structure of $Ni(O{=}PPh_3)_2Br_2$. Ellipsoids are shown at the 30% level. All hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (°): Ni(1)-O(1) 1.9447(18), Ni(1)-O(2) 1.9561(19), Ni(1)-Br(1) 2.3622(4), Ni(1)-Br(2) 2.3734(4), P(1)-O(1) 1.5103(19), Br(1)-Ni(1)-Br(2) 116.512(16), O(1)-Ni(1)-O(2) 100.72(8), Br(1)-Ni(1)-O(1) 111.75(6).

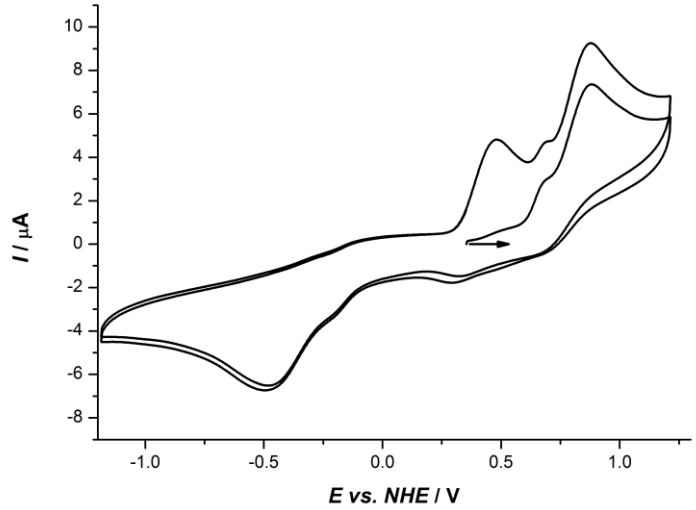
Characterisation of [6-*o*-TolH][Ni(PPh$_3$)Br$_3$]

[6-*o*-TolH][$Ni(PPh_3)Br_3$]. A toluene solution (20 mL) of 6-*o*-Tol (prepared *in-situ* by reaction of [6-*o*-TolH][BF_4] (345 mg, 1.30 mmol) with $KN(SiMe_3)_2$ (257 mg, 1.29 mmol) was added to a toluene solution (10 mL) of $Ni(PPh_3)_2Br_2$ (959 mg, 1.29 mmol). The mixture was stirred at room temperature for 1 h. After cannula filtration, the volatiles removed under vacuum and the residue washed with hexane (15 mL). The resulting purple-green residue was extracted with toluene (10 mL), reduced to dryness and recrystallized from toluene/hexane to afford the Ni(II) complex Ni(6-*o*-

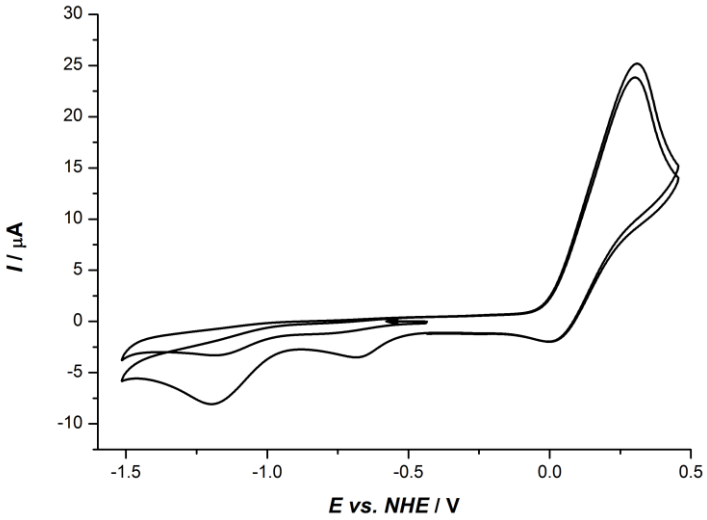
Tol)(PPh_3)Br_2 (**10**). The filtrate was removed, reduced to dryness and recrystallized from CH_2Cl_2/hexane to give X-ray quality crystals of [6-*o*-TolH][Ni(PPh_3)Br_3]. Yield 15 mg. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 19.55, 12.56, 10.48, 9.38, 8.20, 8.06, 8.04, 7.95, 7.58, 4.09, 2.94, 0.48, 0.09, -4.85. Anal. calcd for $C_{36}H_{36}N_2PBr_3Ni$ (MW 826.02) C, 52.34; H, 4.39; N, 3.39. Found: C, 52.17; H, 4.49; N, 3.56.



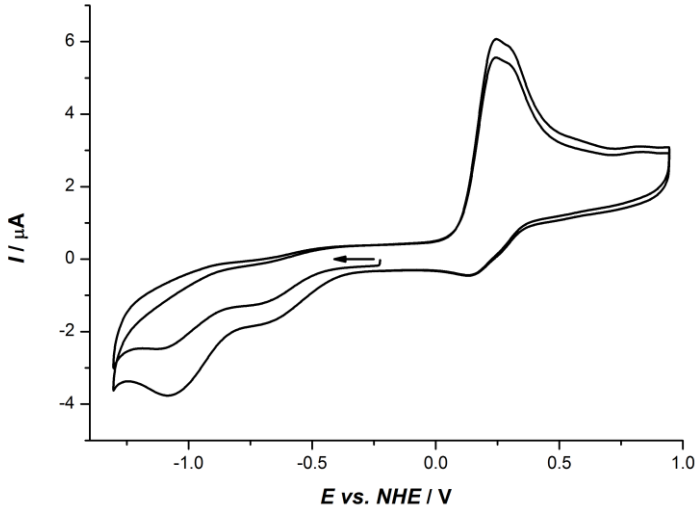
Molecular structure of [6-*o*-TolH][Ni(PPh_3)Br_3]**.** Ellipsoids are shown at 30 % probability with all hydrogen atoms, except H(1), removed for clarity. Selected bond lengths (Å) and angles (°): Ni(1)-P(1) 2.3133(10), Ni(1)-Br(1) 2.3780(6), Ni(1)-Br(2) 2.3772(6), Ni(1)-Br(3) 2.3728(5), P(1)-Ni(1)-Br(1) 101.14(3), Br(1)-Ni(1)-Br(2) 110.73(2).



Cyclic voltammogram for **2** at 100 mV/s scan rate *vs*. NHE. The arrow indicates the initial scanning potential and the scan direction.



Cyclic voltammogram for **8** at 100 mV/s scan rate *vs*. NHE. The arrow indicates the initial scanning potential and the scan direction.



Cyclic voltammogram for **9** at 100 mV/s scan rate *vs*. NHE. The arrow indicates the initial scanning potential and the scan direction.