

NHC-Au(I) complexes bearing Trispyrazolyl borate (Tp) ligands: Efficient platforms for bimetallic species

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Experimental section

Commercially available reagents and solvents were used as received. NHC-Gold complexes **1** and **2** and KTP^{Me_2} and KTP^{H} were synthesized as reported in the literature.^{1,2} All manipulations related to the synthesis of gold complexes was performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. NMR spectroscopy was obtained with a Bruker Ascend (400 MHz) spectrometer. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin Elmer Series II CHNS/O 2400 instruments. X-Ray diffraction analyses were collected in an Agilent Gemini Diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures were solved using direct methods, using SHELXT and refined by SHELXL full matrix least squares against F^2 .^{3,4} All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters. The crystallographic data and some details of the data collection and refinement are given in Table 1.

Table 1. Crystallographic Data and Summary of Data Collection and Structure Refinement.

	3	4	6
Formula	$\text{C}_{41}\text{H}_{55}\text{AuBN}_{10}$	$\text{C}_{42}\text{H}_{59}\text{AuB}_2\text{N}_8$	$\text{C}_{36}\text{H}_{46}\text{AuBN}_8$
Fw	897.74	883.74	798.58
cryst syst	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
T , K	293(2)	293(2)	293(2)
a , \AA	11.3365(3)	10.6045(4)	10.7562(4)
b , \AA	11.3427(3)	11.9711(4)	12.2016(4)
c , \AA	17.7686(6)	20.2522(8)	16.3263(5)
α , deg	71.578(3)	97.609(3)	92.925(3)
β , deg	80.431(2)	102.029(3)	97.466(3)
γ , deg	80.447(2)	93.076(3)	115.809(4)
V , \AA^3	2121.79(11)	2483.60(16)	1898.67(13)
Z	2	2	2
d_{calc} g.cm ⁻³	1.405	1.182	1.397
μ , mm ⁻¹	6.824	2.994	3.909
refl collected	32588	56017	68532
$T_{\text{min}}/T_{\text{max}}$	0.843	0.912	0.971
N_{measd}	8941	12705	10089
$[R_{\text{int}}]$	0.0397	0.0757	0.0533
$R [I > 2\sigma(I)]$	0.0318	0.0409	0.0307
R (all data)	0.0362	0.0938	0.0547
$R_w [I > 2\sigma(I)]$	0.0795	0.0728	0.0476
R_w (all data)	0.0825	0.0887	0.0547
GOF	1.010	1.008	1.059

Computational details

Geometry optimizations of the ligands were performed with the Gaussian 09 software⁶ at the B3LYP/Def2SVP+LANL2DZ level of theory with Grimme's D3 correction⁷, using Def2SVP basis set⁸ for light atoms and LANL2DZ pseudopotential⁹ for Au atoms. Both complexes were calculated as closed shell neutral molecules. The initial geometries of the complexes were built from the optimized ligands, inserting the NiCl₂/PtCl₂ fragment and considering two possible conformations (one with the Cl atoms in the complex facing towards the trimethylbenzene ring and the other with these Cl atoms facing away of it). Then geometry optimizations followed by frequency analyses of the ligand were performed at the same level of theory, using Def2SVP basis set for Cl atoms and LANL2DZ pseudopotential for Ni and Pd atoms. All optimized geometries were confirmed to be actual minima in the potential energy surface by checking that all vibrational frequencies were real. In both complexes the most stable conformation was the one with the Cl atoms facing towards the trimethylbenzene ring as shown in Figure 3. The energy difference (ΔU) between the two NiCl₂ complex conformations was around 2.8 kcal/mol and the free energy difference (ΔG) at 298.15 K was of around 4.7 kcal/mol. On the other hand, ΔU between the two PtCl₂ complex conformations was around 3.6 kcal/mol and ΔG at 298.15 K was of around 3.8 kcal/mol. These free energy differences are above the assessed accuracy of less than 2.0 kcal/mol for B3LYP-D3 in metal complex systems,¹⁰ supporting the relevance of our calculations.

Optimized coordinates for complex 7

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Au	2.2062	0.0911	0.7035
N	2.1745	2.5063	-1.0307
N	1.2826	-1.2845	1.9880
N	3.9820	1.3885	-1.4149
N	-0.0411	-1.5529	1.8358
N	-2.5693	-1.9524	-0.8867
N	-2.0920	-0.1558	1.4986
N	-1.3595	-1.9647	-0.2636
C	2.8749	1.4171	-0.6352
C	4.9794	0.3554	-1.3393
N	-3.3981	-0.2323	1.1125
C	0.9039	2.8819	-0.4541
C	1.7569	-2.0413	2.9879
C	-0.4219	-2.4839	2.7425
C	-0.2780	2.4518	-1.0811
C	0.7033	-2.8207	3.4977
H	0.7507	-3.5416	4.3104
C	6.1052	0.5646	-0.5272
C	4.7618	-0.8428	-2.0405
C	3.9778	2.4584	-2.3023
H	4.7796	2.6121	-3.0184
C	0.9099	3.5954	0.7576

C	2.8355	3.1612	-2.0575
H	2.4298	4.0580	-2.5165
C	5.7342	-1.8436	-1.9259
H	5.5859	-2.7854	-2.4618
C	-1.4929	2.7964	-0.4744
H	-2.4289	2.4778	-0.9359
C	-2.7147	-3.0797	-1.5945
C	-1.8246	-2.9906	2.8383
H	-2.5023	-2.2096	3.2177
H	-1.8678	-3.8502	3.5205
H	-2.2098	-3.2969	1.8550
C	6.8840	-1.6733	-1.1414
C	-1.5369	3.5129	0.7298
C	-2.0226	0.4695	2.7049
C	-0.3283	3.8962	1.3327
H	-0.3519	4.4435	2.2800
C	7.0493	-0.4662	-0.4473
H	7.9326	-0.3253	0.1819
C	-0.6900	-3.0958	-0.6368
C	-4.1675	0.2637	2.0928
C	-3.3270	0.7239	3.1218
H	-3.6297	1.2065	4.0481
C	3.1874	-1.9696	3.4166
H	3.8568	-1.9235	2.5435
H	3.4562	-2.8471	4.0211
H	3.3736	-1.0681	4.0239
C	-1.5330	-3.8287	-1.4648
H	-1.3103	-4.7858	-1.9304
C	6.2565	1.8424	0.2586
H	6.2617	2.7271	-0.3986
H	7.1881	1.8451	0.8411
H	5.4123	1.9719	0.9563
C	2.2067	3.9747	1.4292
H	2.7276	3.0802	1.8131
H	2.0306	4.6527	2.2762
H	2.9017	4.4713	0.7327
C	-0.2431	1.6025	-2.3266
H	0.1956	2.1476	-3.1796
H	-1.2490	1.2619	-2.6117
H	0.3778	0.7056	-2.1629
C	-3.9579	-3.4021	-2.3543
H	-4.8462	-3.2156	-1.7314
H	-3.9493	-4.4556	-2.6686
H	-4.0466	-2.7499	-3.2351
B	-0.9103	-0.8494	0.7401
H	-0.2152	-0.0215	0.1920
C	7.9305	-2.7576	-1.0667
H	7.4794	-3.7598	-1.1290
H	8.5109	-2.6987	-0.1336
H	8.6445	-2.6691	-1.9040
C	-0.7454	0.8318	3.3950
H	-0.3061	-0.0108	3.9526

H	-0.9438	1.6424	4.1102
H	0.0053	1.1886	2.6753
C	0.7174	-3.4440	-0.2637
H	1.3976	-2.5910	-0.4026
H	1.0606	-4.2630	-0.9112
H	0.8210	-3.7773	0.7803
C	3.5055	-1.0503	-2.8475
H	2.6256	-1.1238	-2.1865
H	3.5608	-1.9724	-3.4421
H	3.3134	-0.2091	-3.5317
C	-2.8581	3.8727	1.3615
H	-3.6738	3.2646	0.9463
H	-3.0979	4.9339	1.1731
H	-2.8275	3.7304	2.4531
C	-5.6560	0.2927	2.0024
H	-6.0215	-0.6038	1.4803
H	-5.9875	1.1579	1.4097
H	-6.0998	0.3384	3.0077
Pt	-3.6773	-0.2533	-0.9249
Cl	-3.5823	-0.1621	-3.2930
Cl	-4.9335	1.7698	-0.9097

Optimized coordinates for complex **8**

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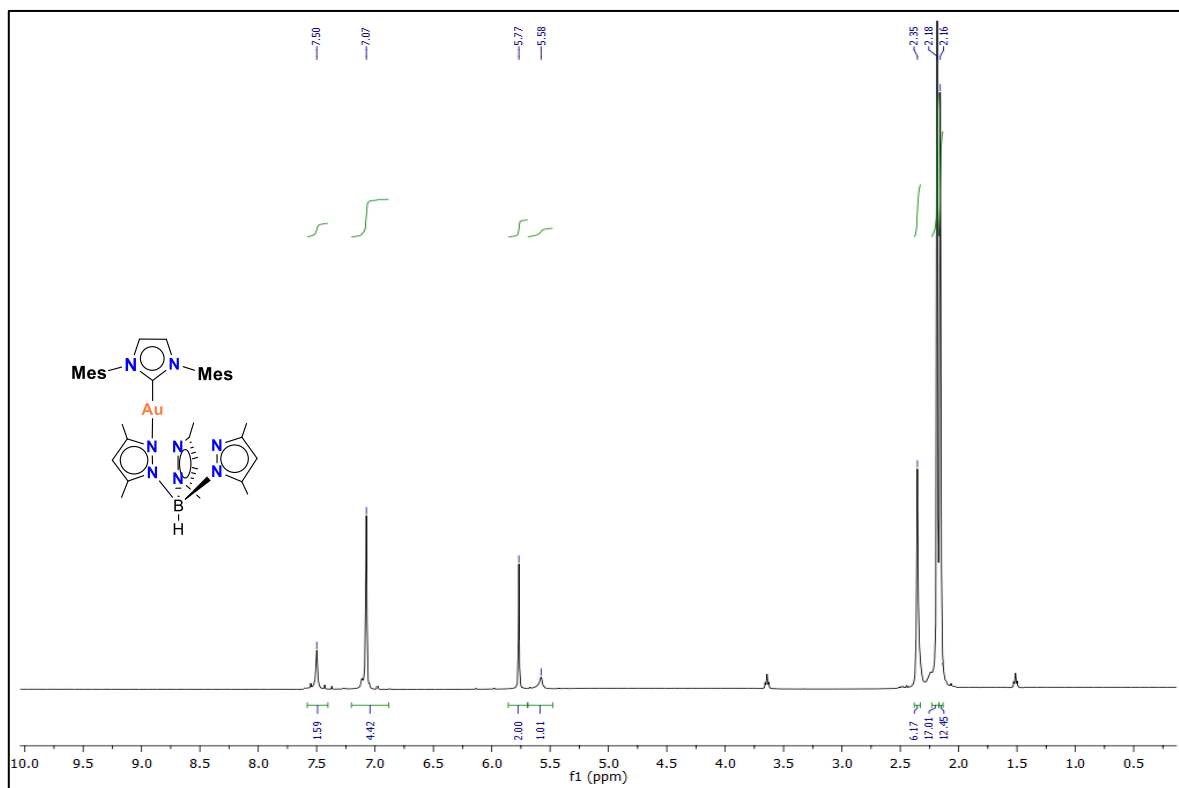
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N	-1.7849	-1.9489	-0.5584
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C	4.6882	0.4091	-1.1353
N	-3.8598	-0.3444	0.7851
C	0.5469	2.8859	-0.4464
C	1.2047	-2.1942	2.8151
C	-0.9620	-2.6122	2.4504
C	-0.5700	2.4280	-1.1671
C	0.1262	-2.9885	3.2415
H	0.1327	-3.7431	4.0244
C	5.7427	0.5553	-0.2198
C	4.5212	-0.7430	-1.9220
C	3.7653	2.5680	-2.0543
H	4.6197	2.7582	-2.6971
C	0.4382	3.5821	0.7687

C	2.6046	3.2575	-1.8640
H	2.2330	4.1770	-2.3067
C	5.4777	-1.7576	-1.7927
H	5.3688	-2.6634	-2.3958
C	-1.8393	2.7209	-0.6508
H	-2.7271	2.3654	-1.1806
C	-3.1356	-2.9869	-1.9369
C	-2.3687	-3.1165	2.4550
H	-3.0727	-2.3269	2.7600
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C	-2.5433	0.3987	2.4164
C	-0.8501	3.8460	1.2443
H	-0.9632	4.3825	2.1912
C	6.6722	-0.4872	-0.1279
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C	-1.1105	-3.0550	-0.9887
C	-4.6608	0.1273	1.7492
C	-3.8632	0.6087	2.8042
H	-4.2029	1.0750	3.7261
C	2.6163	-2.1492	3.3062
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H	2.8151	-2.9816	3.9952
H	2.8180	-1.2054	3.8392
C	-1.9545	-3.7466	-1.8516
H	-1.7324	-4.6781	-2.3671
C	5.8288	1.7766	0.6597
H	5.8730	2.7048	0.0674
H	6.7164	1.7417	1.3063
H	4.9357	1.8532	1.3027
C	1.6669	3.9742	1.5509
H	2.1775	3.0801	1.9498
H	1.4068	4.6221	2.3998
H	2.4021	4.5072	0.9263
C	-0.4068	1.6055	-2.4196
H	0.0522	2.1931	-3.2330
H	-1.3739	1.2182	-2.7714
H	0.2531	0.7414	-2.2333
C	-4.3641	-3.2388	-2.7471
H	-5.2495	-2.8281	-2.2401
H	-4.5053	-4.3172	-2.9124
H	-4.2892	-2.7234	-3.7163
B	-1.3508	-0.8921	0.4975
H	-0.6178	-0.0558	0.0142
C	7.5954	-2.7406	-0.8174
H	7.1630	-3.7275	-1.0415
H	8.0527	-2.7838	0.1827
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C	-1.2900	0.7753	3.1408
H	-0.8434	-0.0726	3.6847

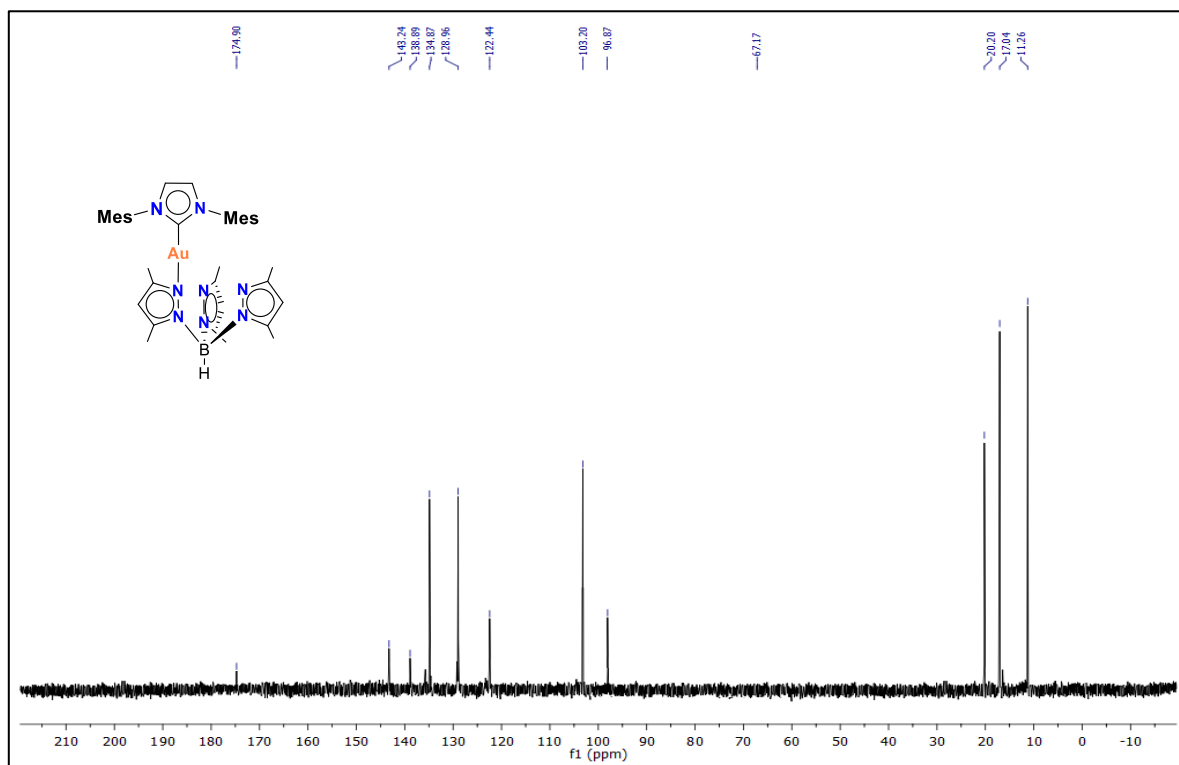
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H	0.3803	-3.7932	0.4166
C	3.3264	-0.8954	-2.8286
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C	-6.1487	0.1227	1.6320
H	-6.4662	-0.5457	0.8212
H	-6.5198	1.1264	1.3788
H	-6.6052	-0.2029	2.5802
Ni	-4.0120	-0.2718	-1.1703
Cl	-3.6519	-0.0405	-3.3532
Cl	-5.2826	1.5473	-1.1311

References:

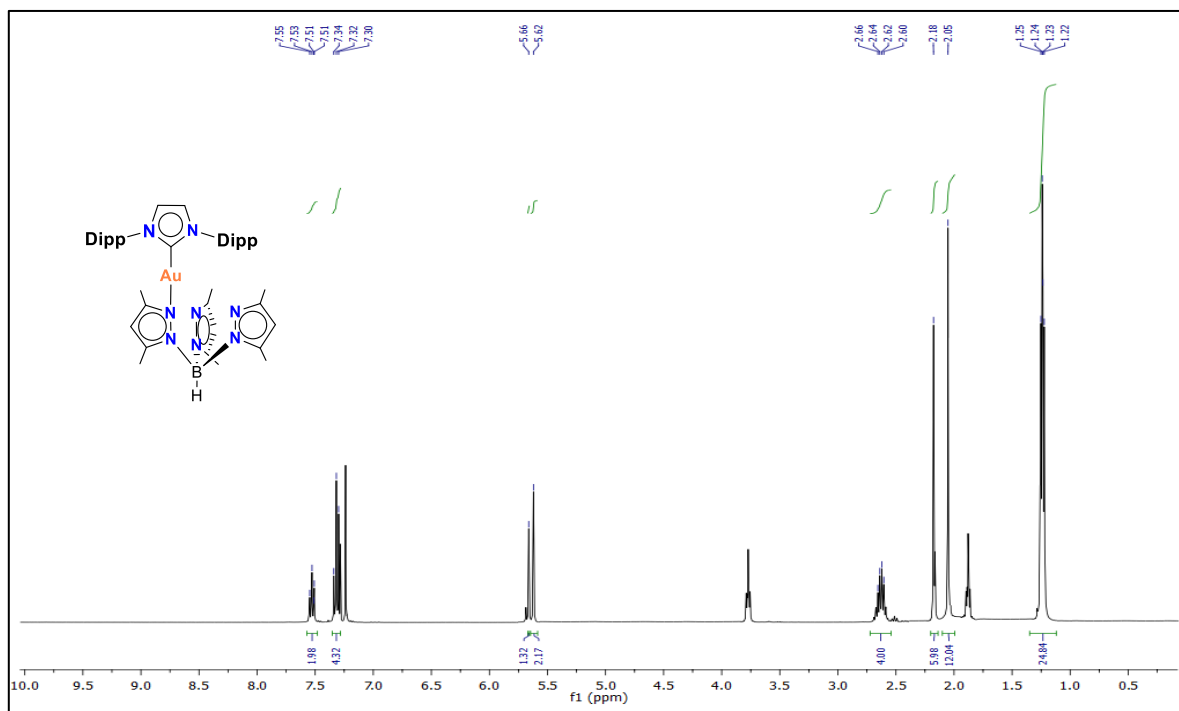
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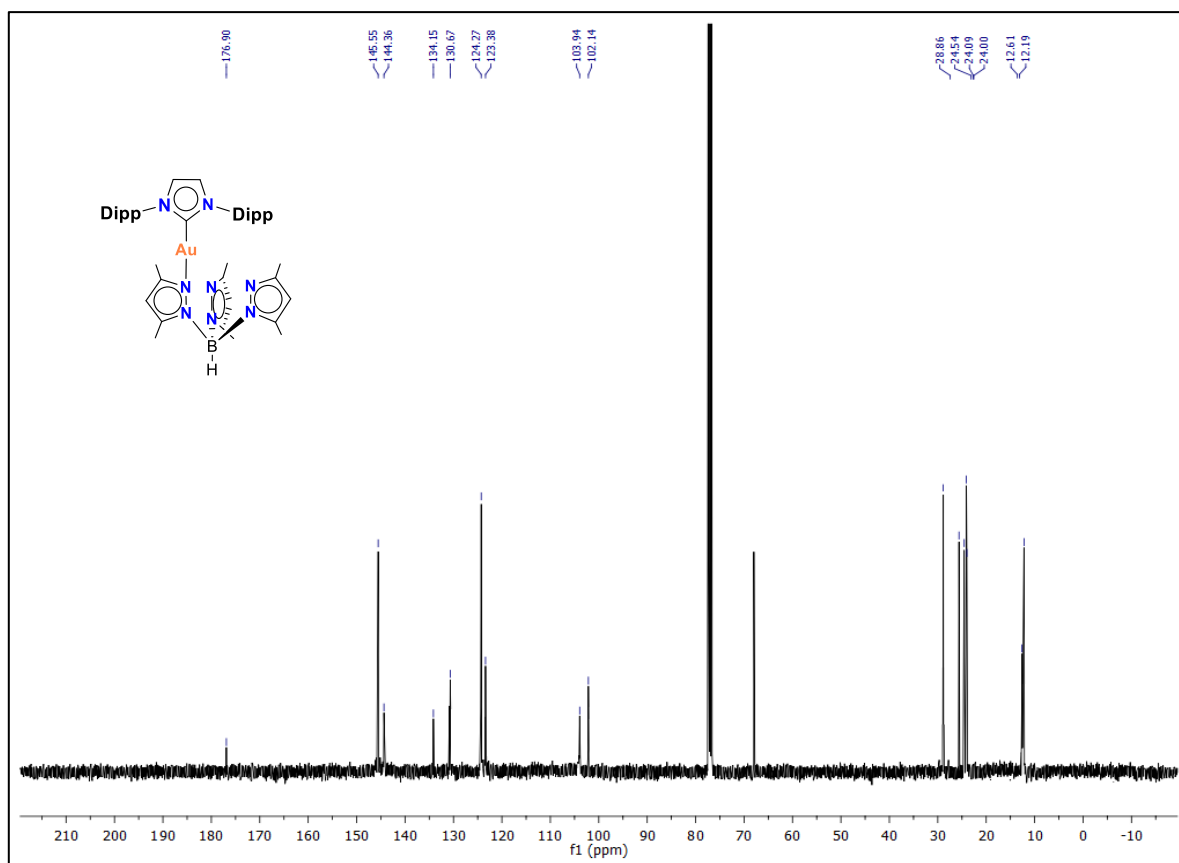
$^1\text{H-NMR}$ (400 MHz) spectra for complex **3** in CDCl_3



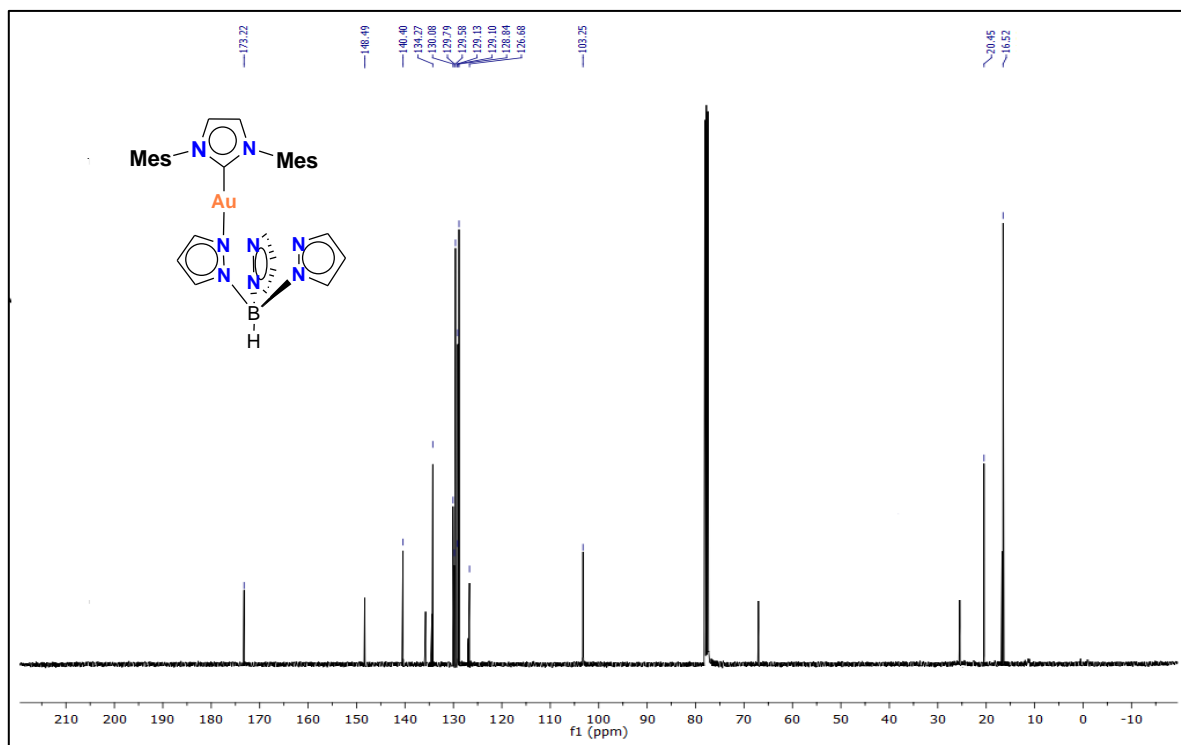
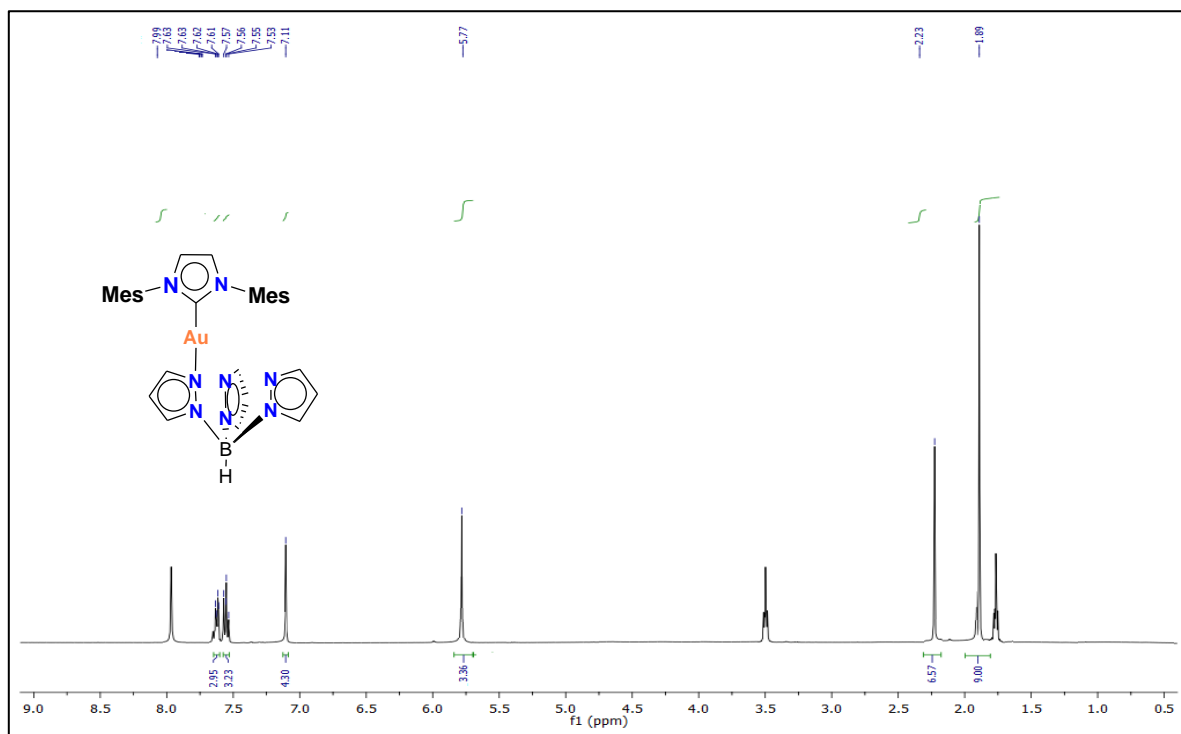
$^{13}\text{C-NMR}$ (100 MHz) spectra for complex **3** in CDCl_3

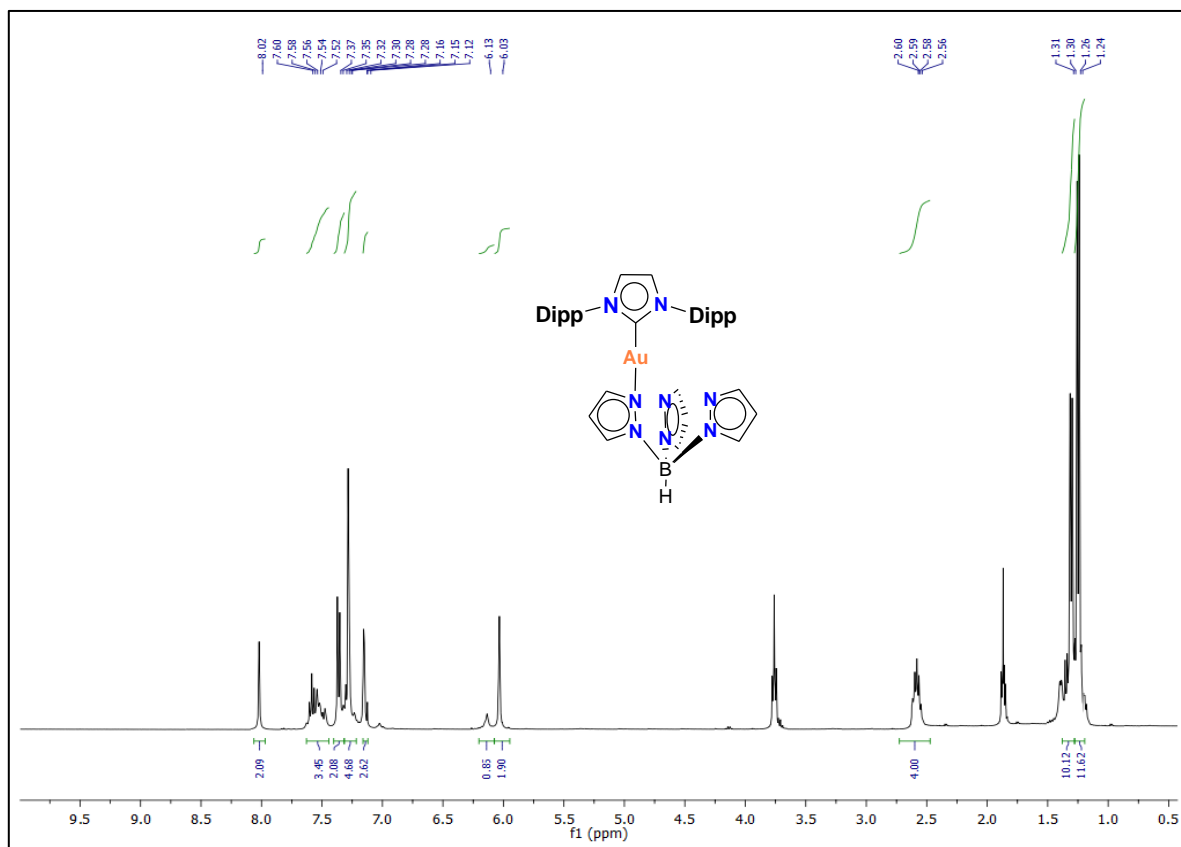


¹H-NMR (400 MHz) spectra for complex **4** in CDCl₃

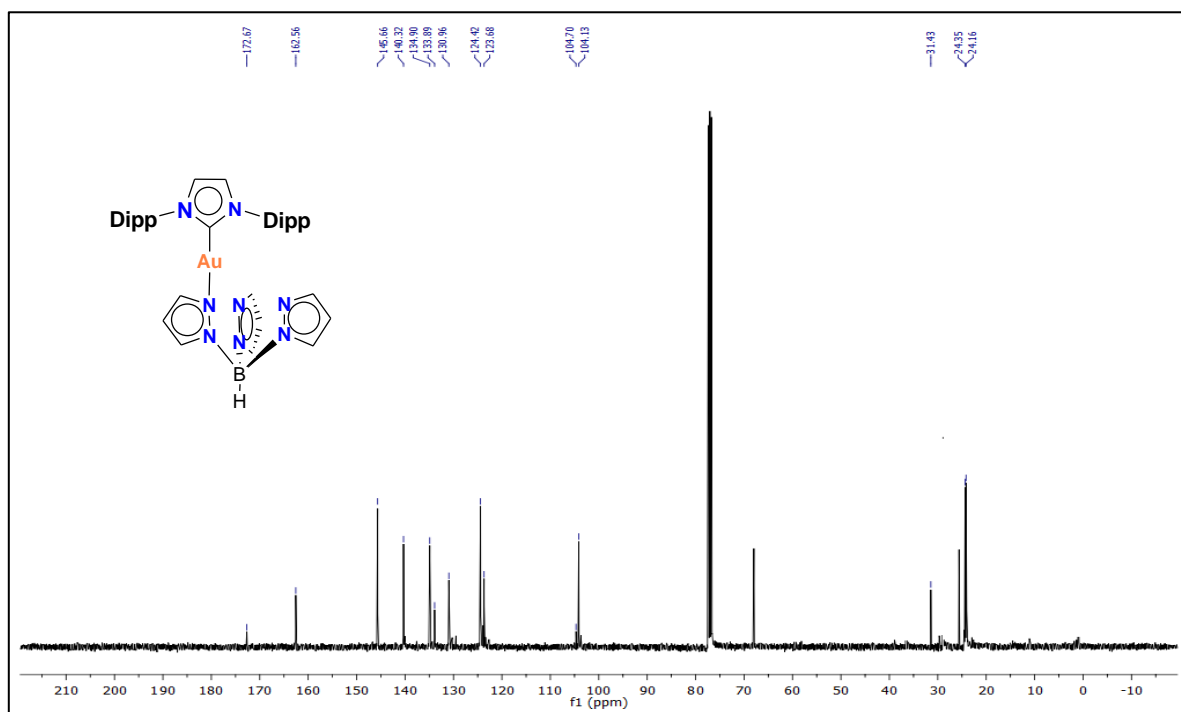


¹³C-NMR (100 MHz) spectra for complex **4** in CDCl₃

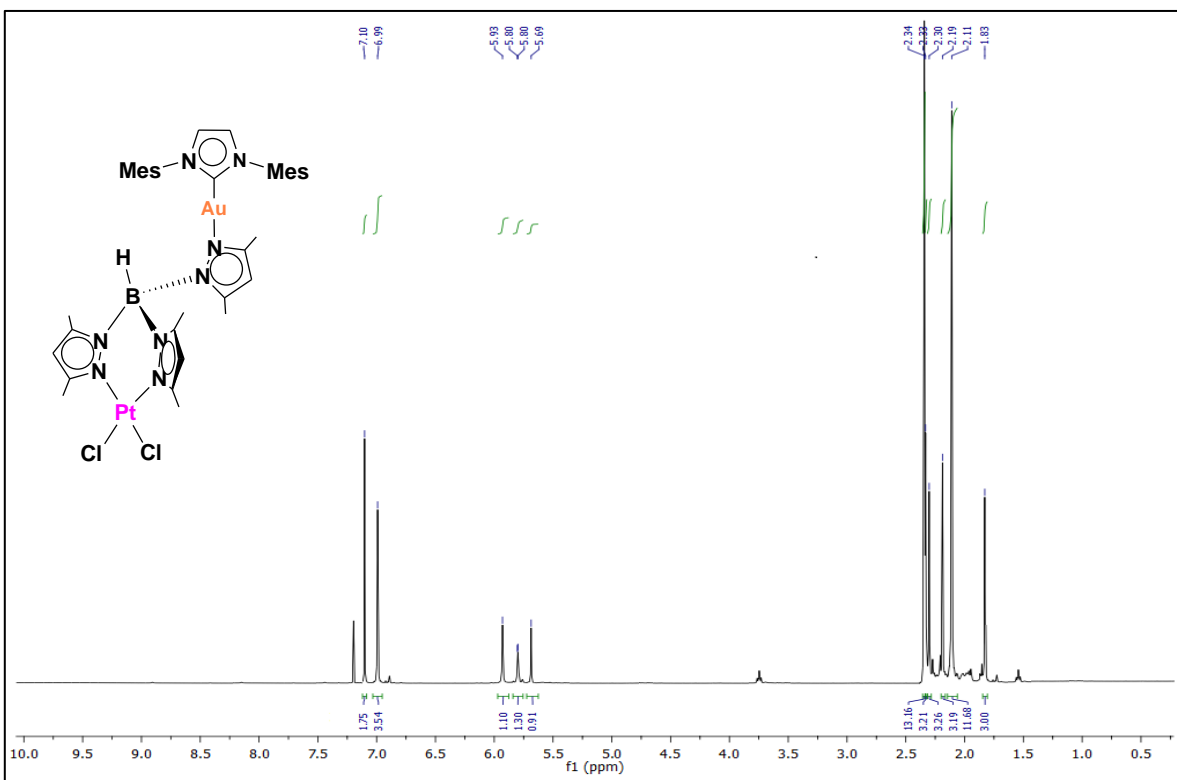




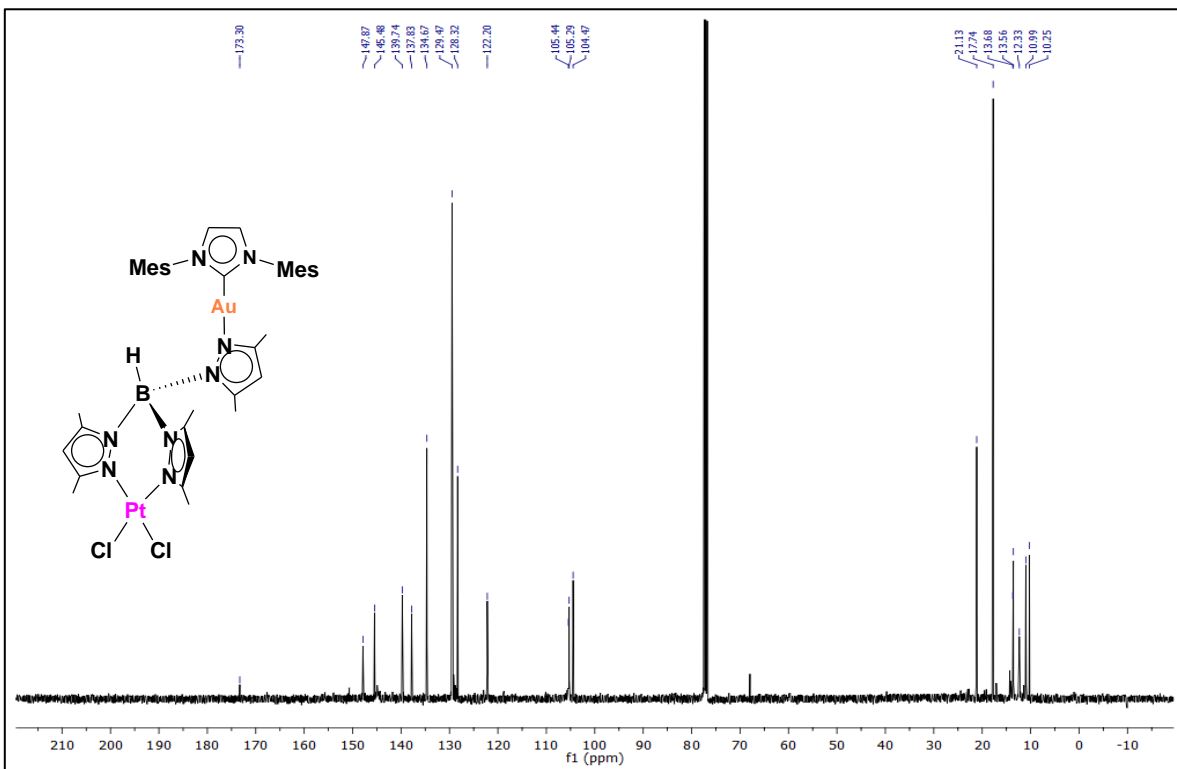
$^1\text{H-NMR}$ (400 MHz) spectra for complex **6** in CDCl_3



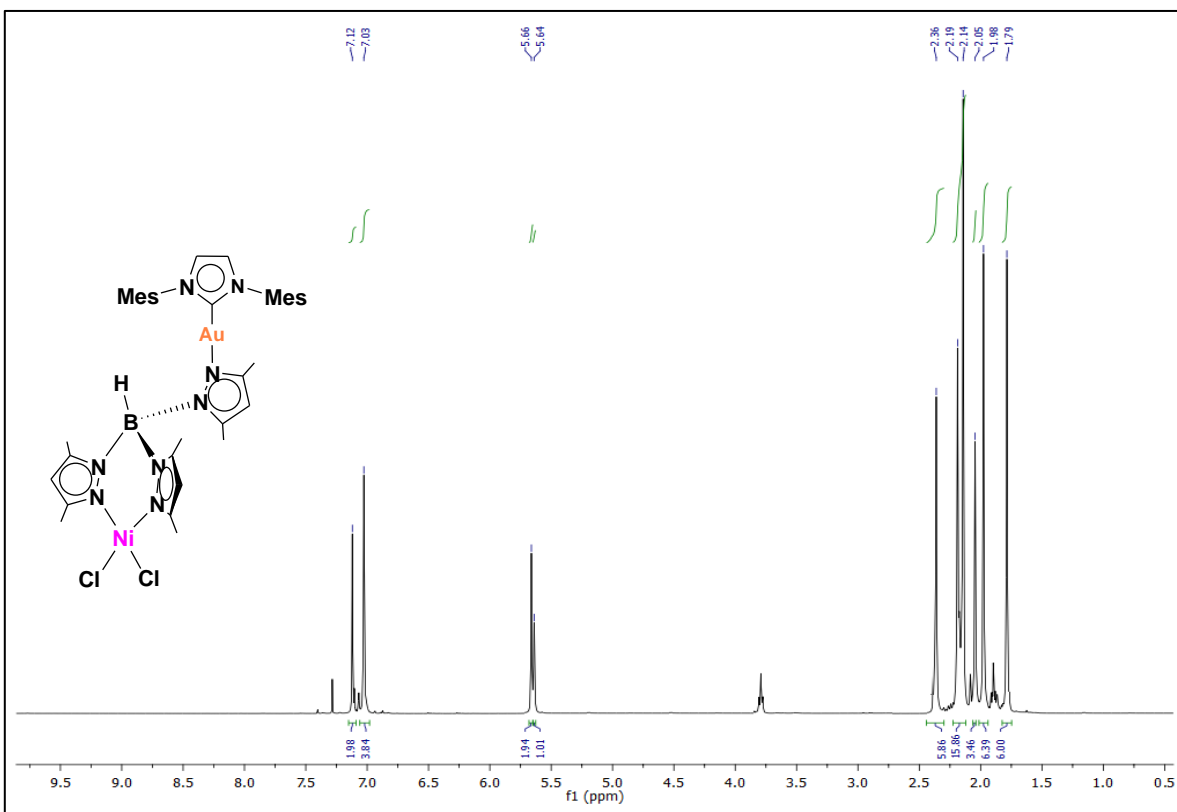
$^{13}\text{C-NMR}$ (100 MHz) spectra for complex **6** in CDCl_3



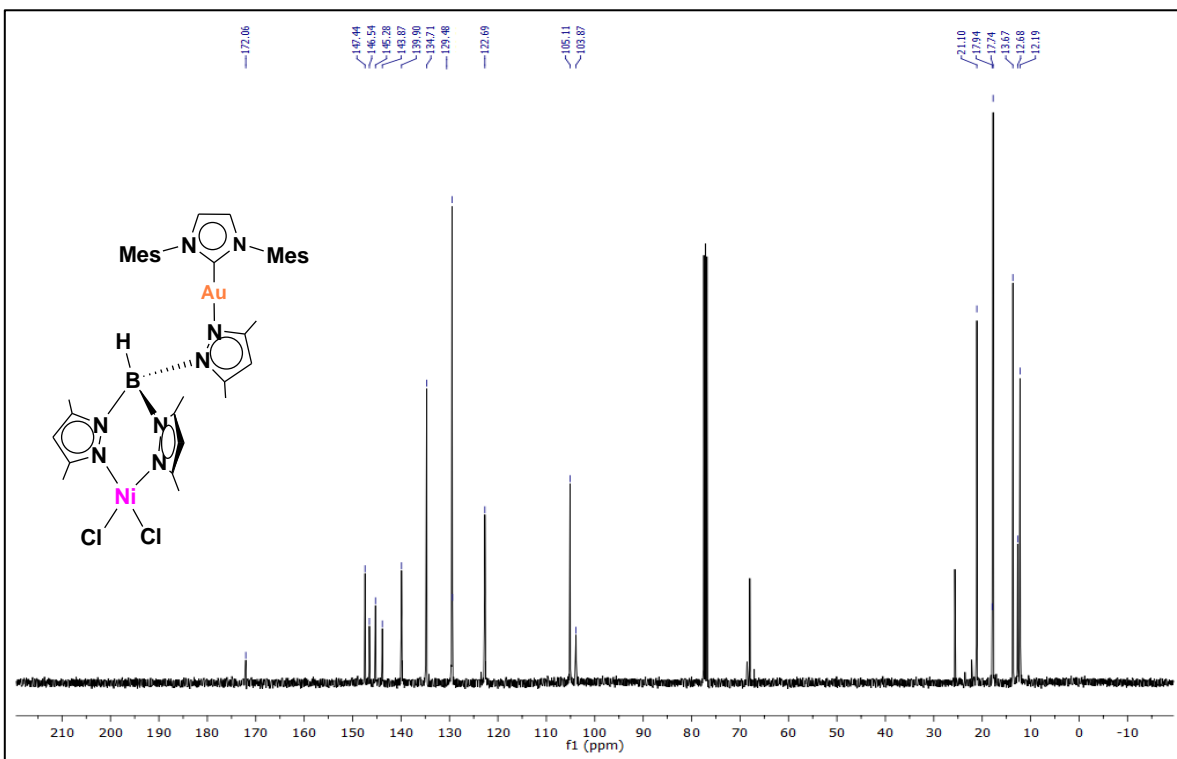
¹H-NMR (400 MHz) spectra for complex 7 in CDCl₃



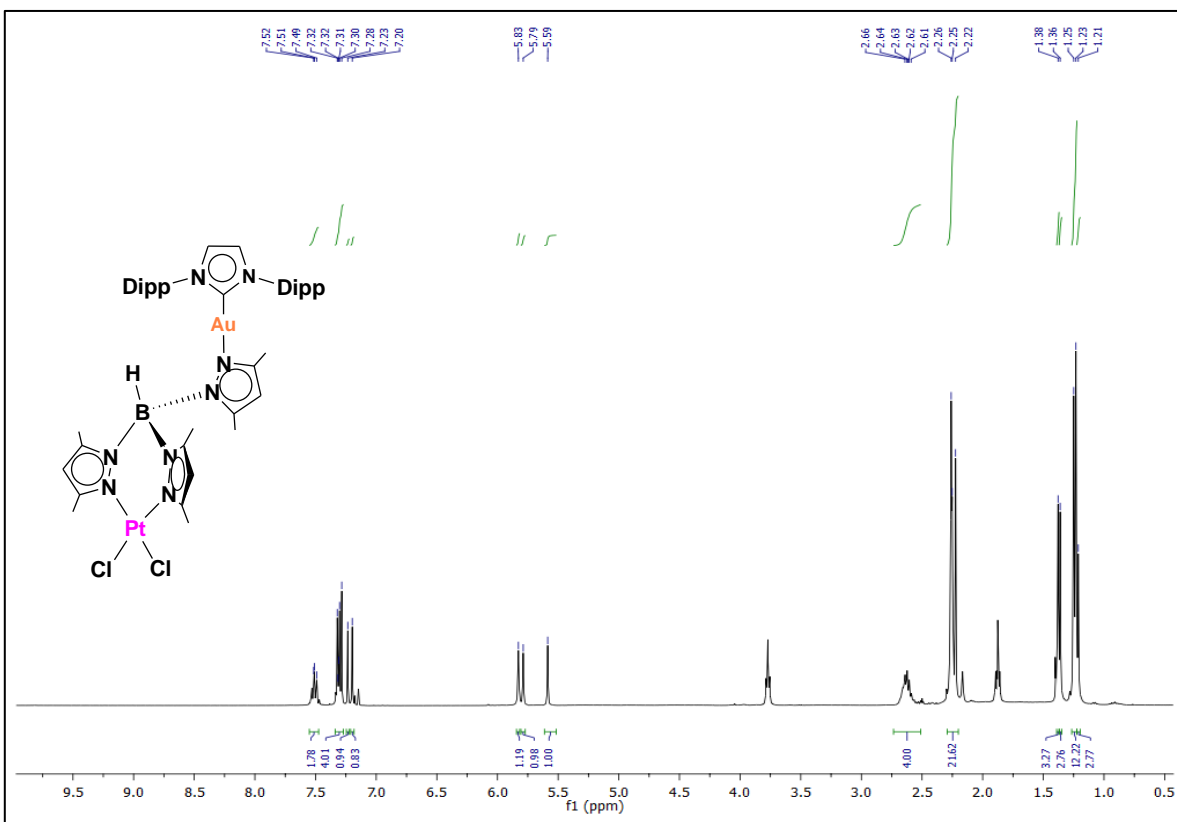
¹³C-NMR (100 MHz) spectra for complex 7 in CDCl₃



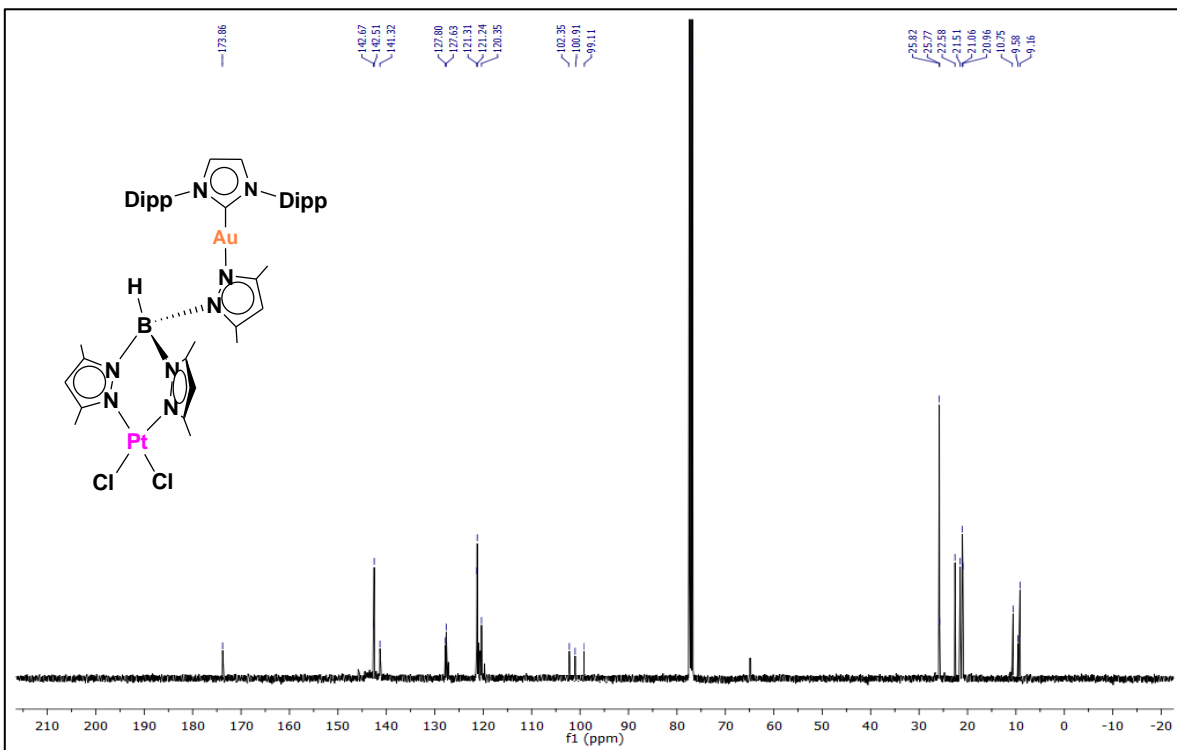
¹H-NMR (400 MHz) spectra for complex **8** in CDCl₃



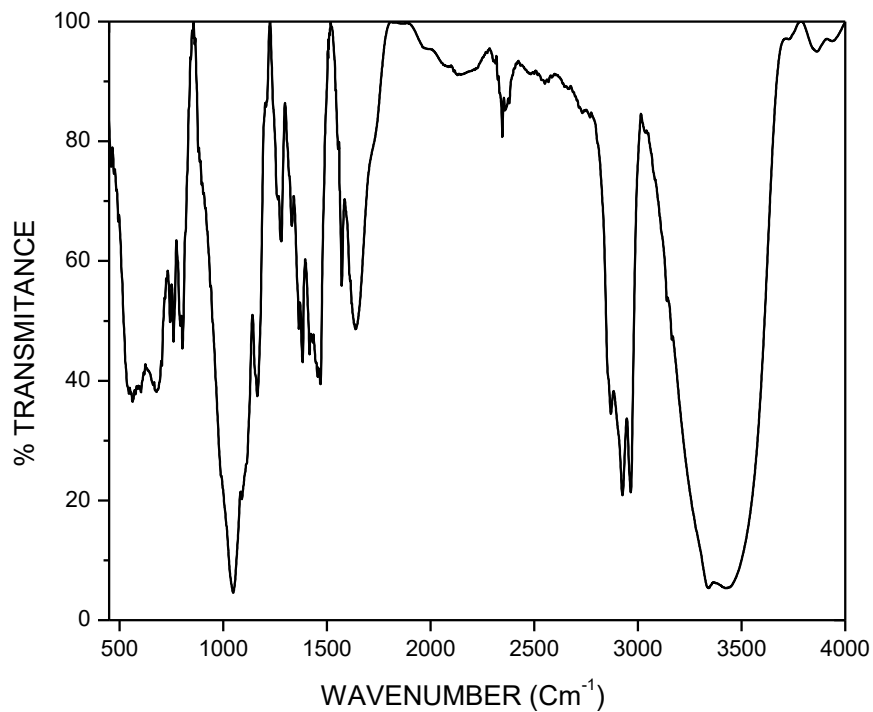
¹³C-NMR (100 MHz) spectra for complex **8** in CDCl₃



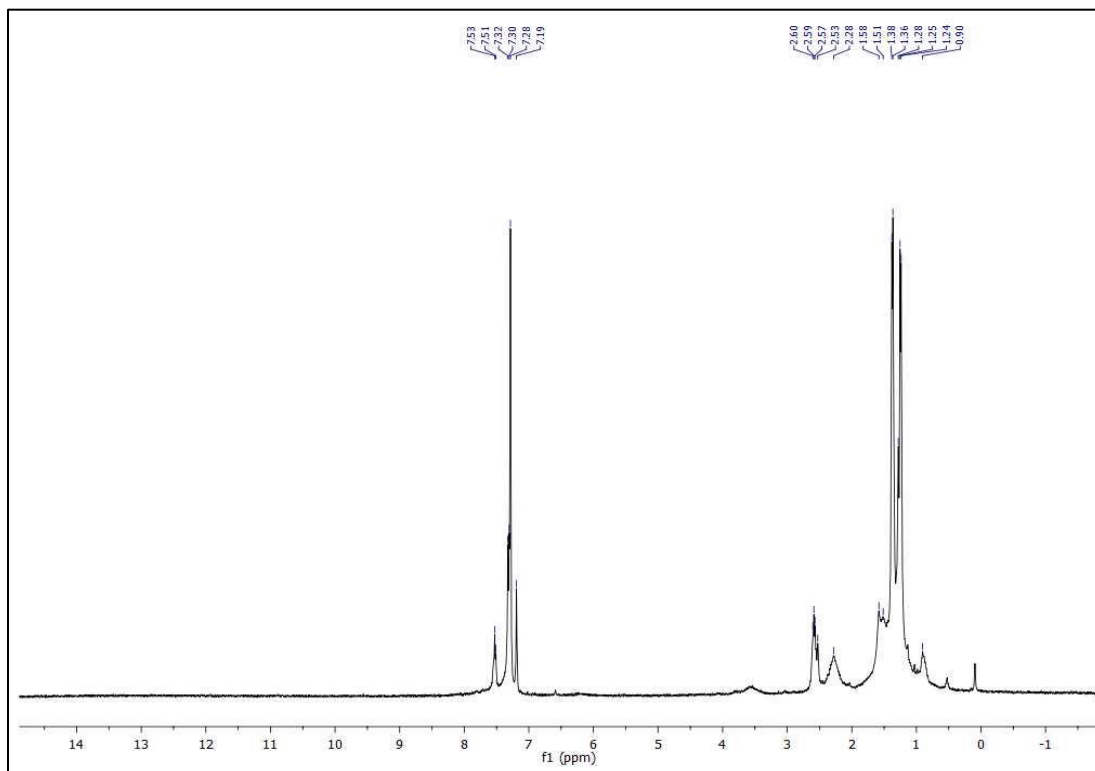
¹H-NMR (400 MHz) spectra for complex **9** in CDCl₃



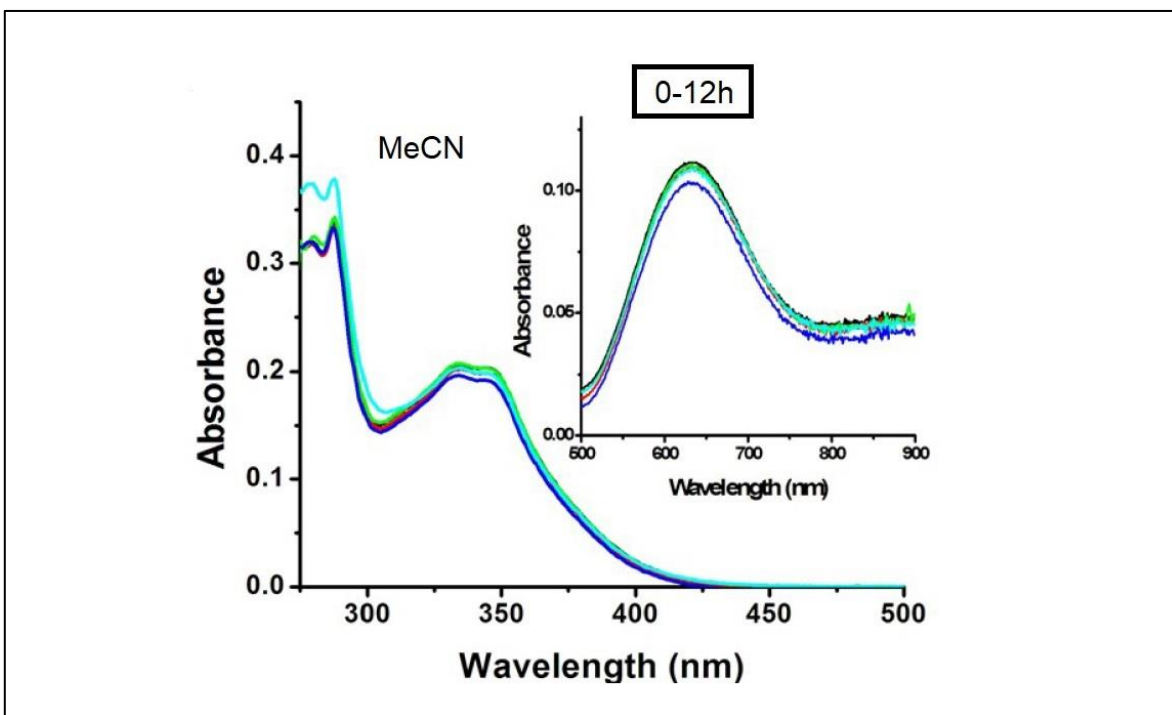
¹³C-NMR (100 MHz) spectra for complex **9** in CDCl₃



FT-IR Spectra for complex **10** in KBr: 3444, 2966 (CH-Ar), 2925 (CH-Ar), 2868, 2350, 1636(C=N), 1572 (C=N), 1440, 1376, 1272, 1160, 1048(C-N), 682, 563 cm⁻¹



¹H-NMR (400 MHz) spectra for complex **10** in CDCl₃



UV- Visible absorption spectra of complex **10** in MeCN up to 12 h at room temperature.