Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Selectfluor promoted NHC-Oxazoline gold(I) complexes catalyzed cycloaddition/oxidation reaction of enynones with alkenes

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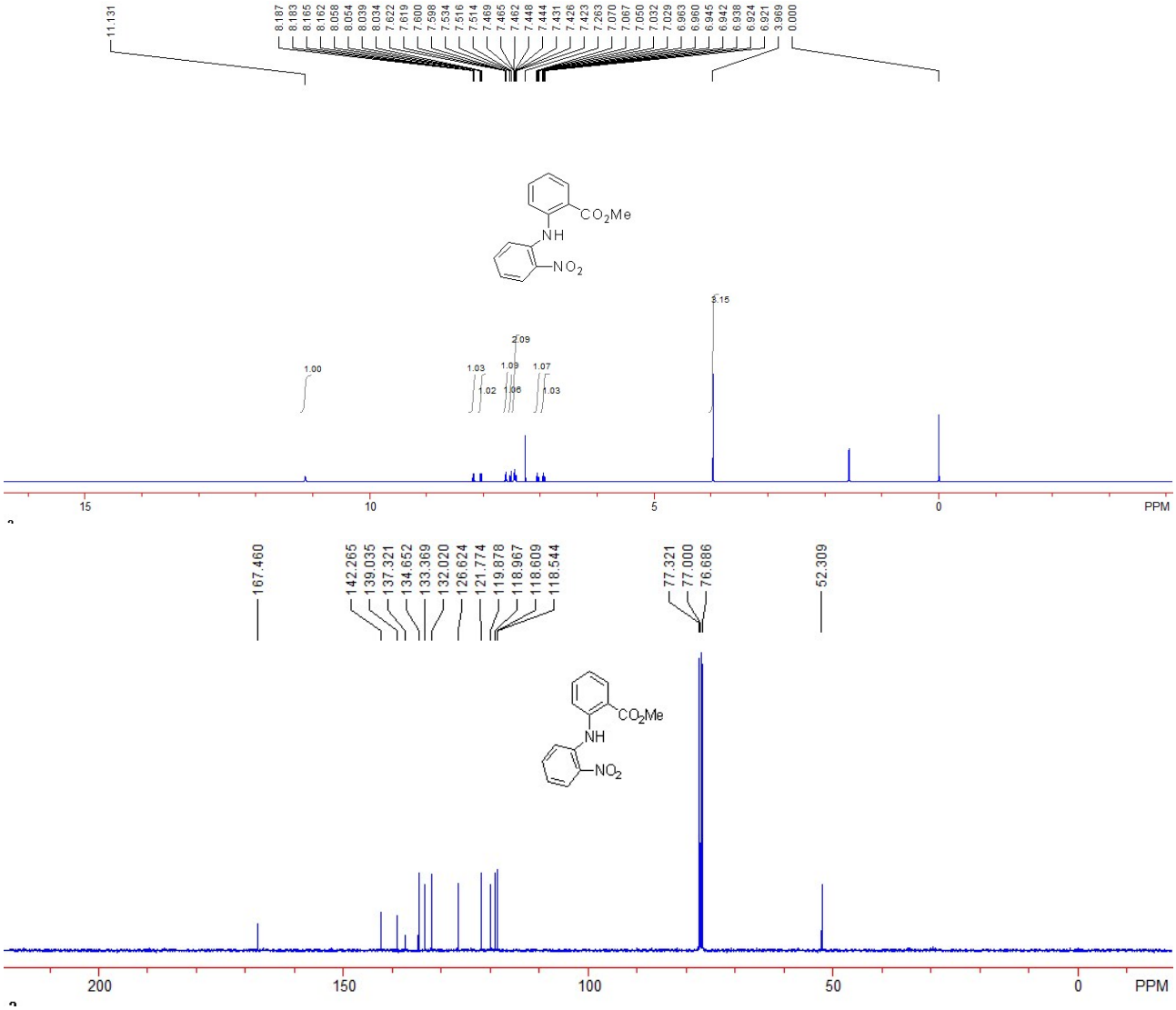
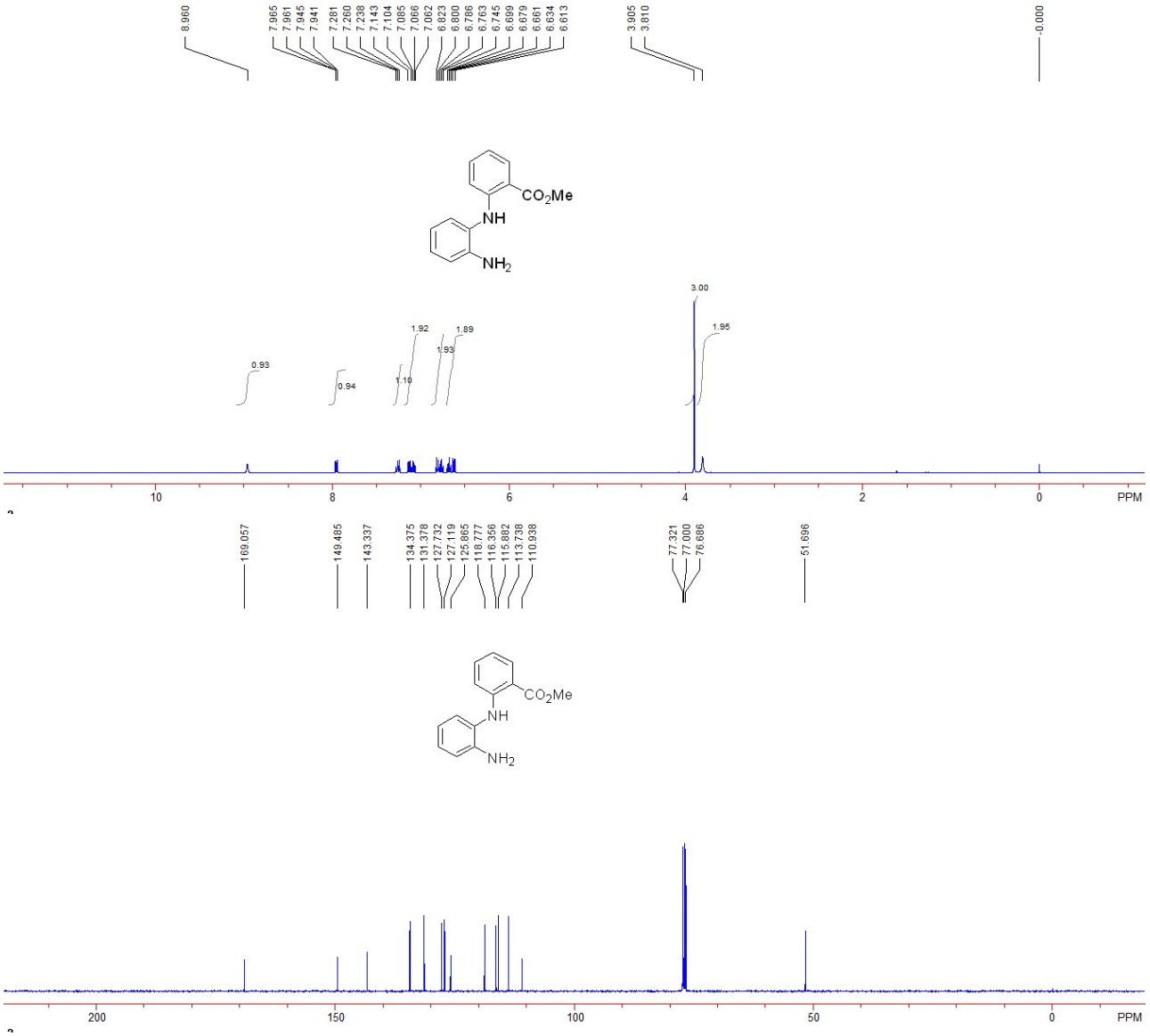
1. NMR spectra of compounds 2-7

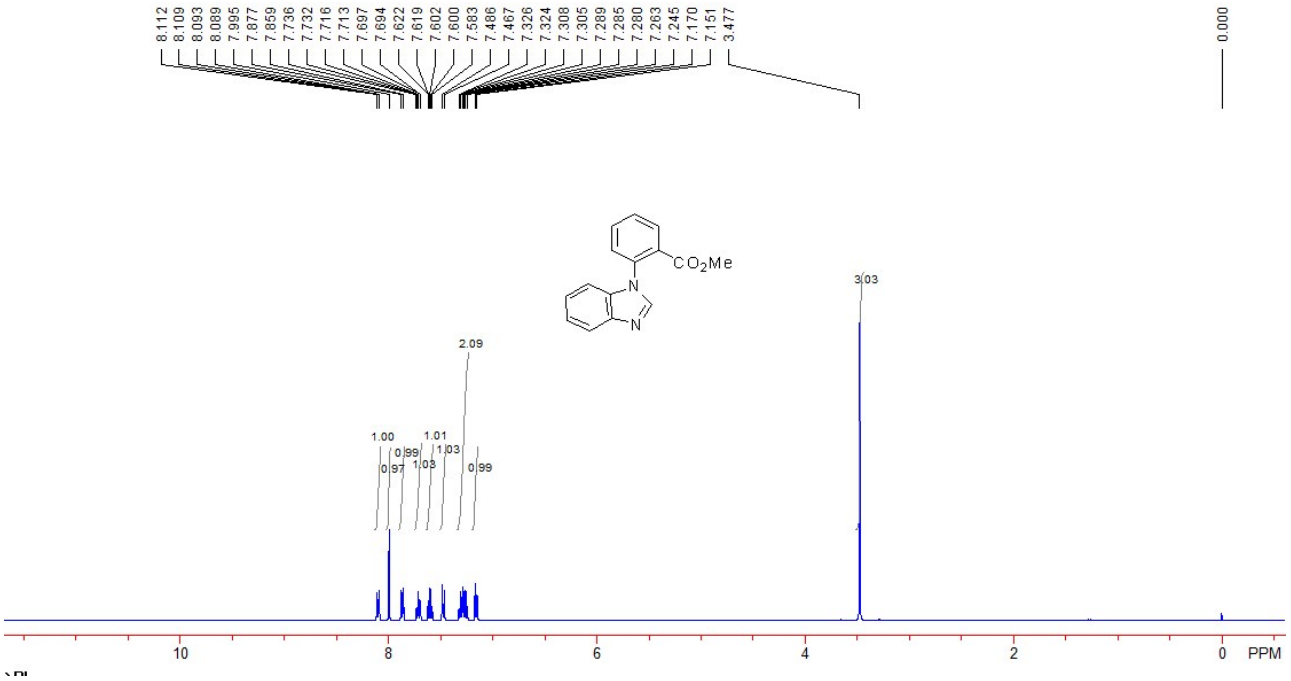
^{1}H NMR and ^{13}C NMR spectra of compound **2**

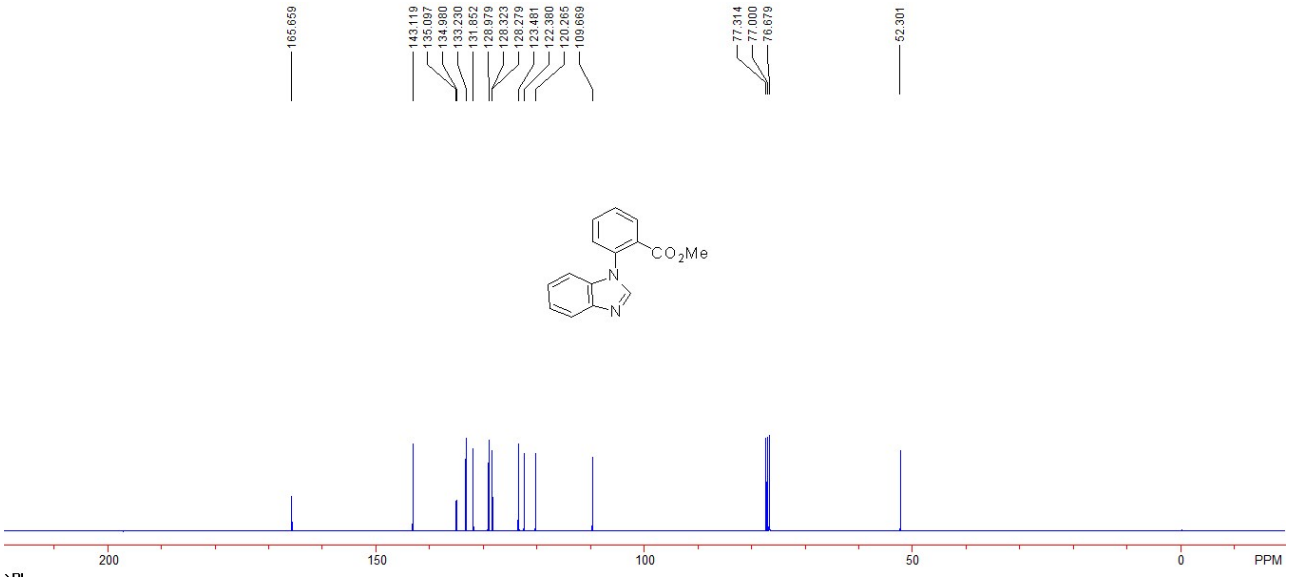


^{1}H NMR and ^{13}C NMR spectra of compound **3**

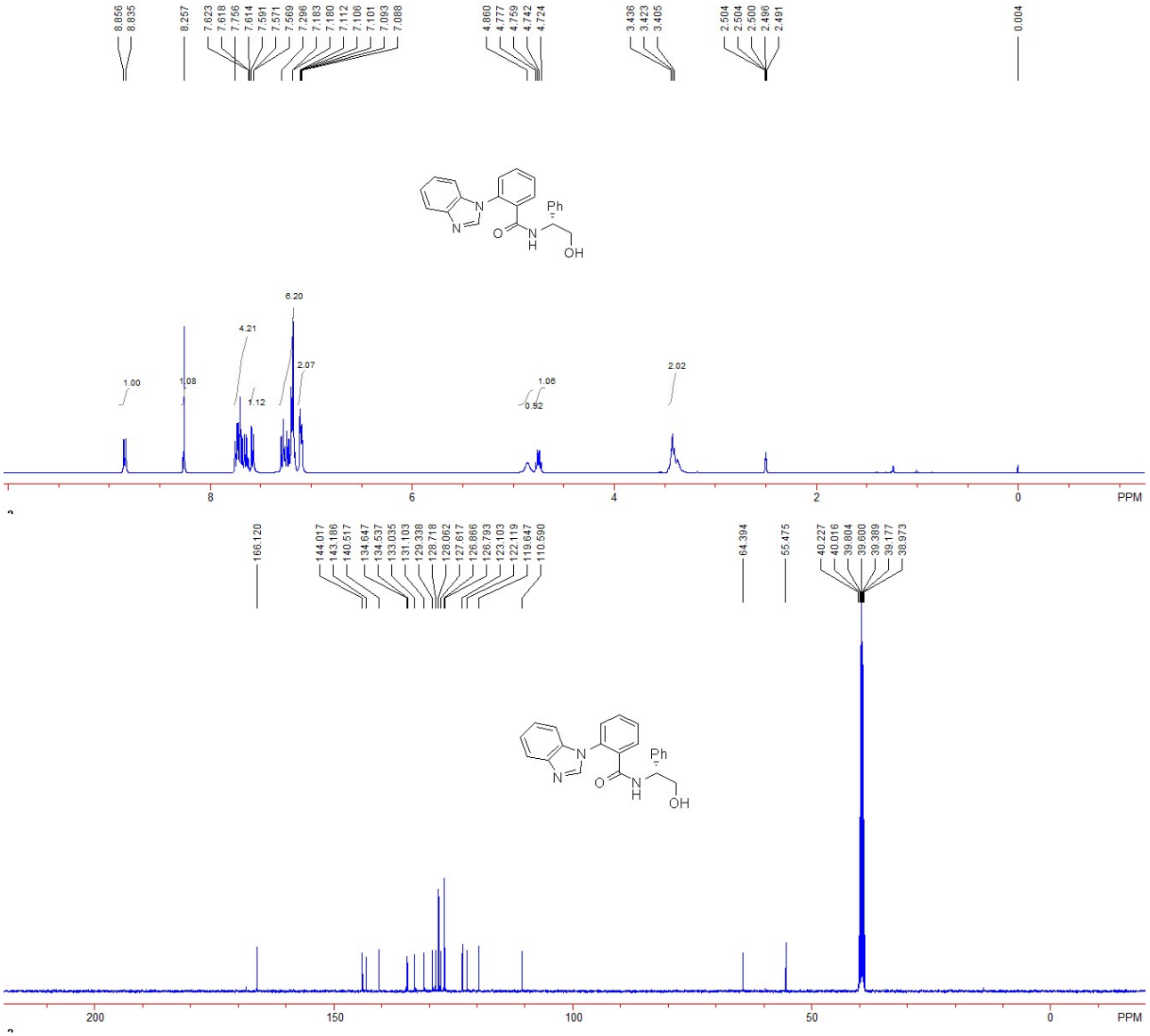


^{1}H NMR and ^{13}C NMR spectra of compound **4**

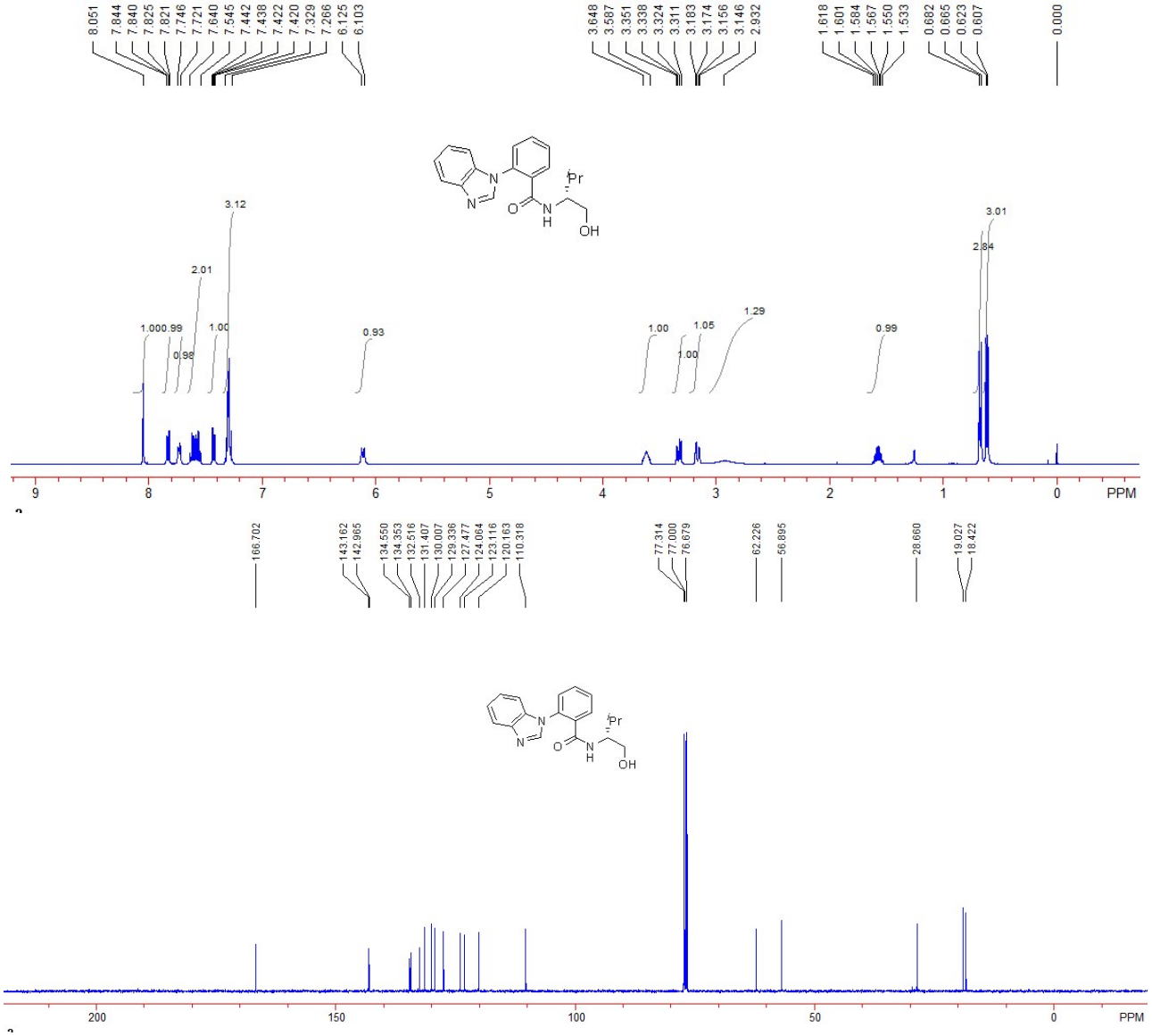




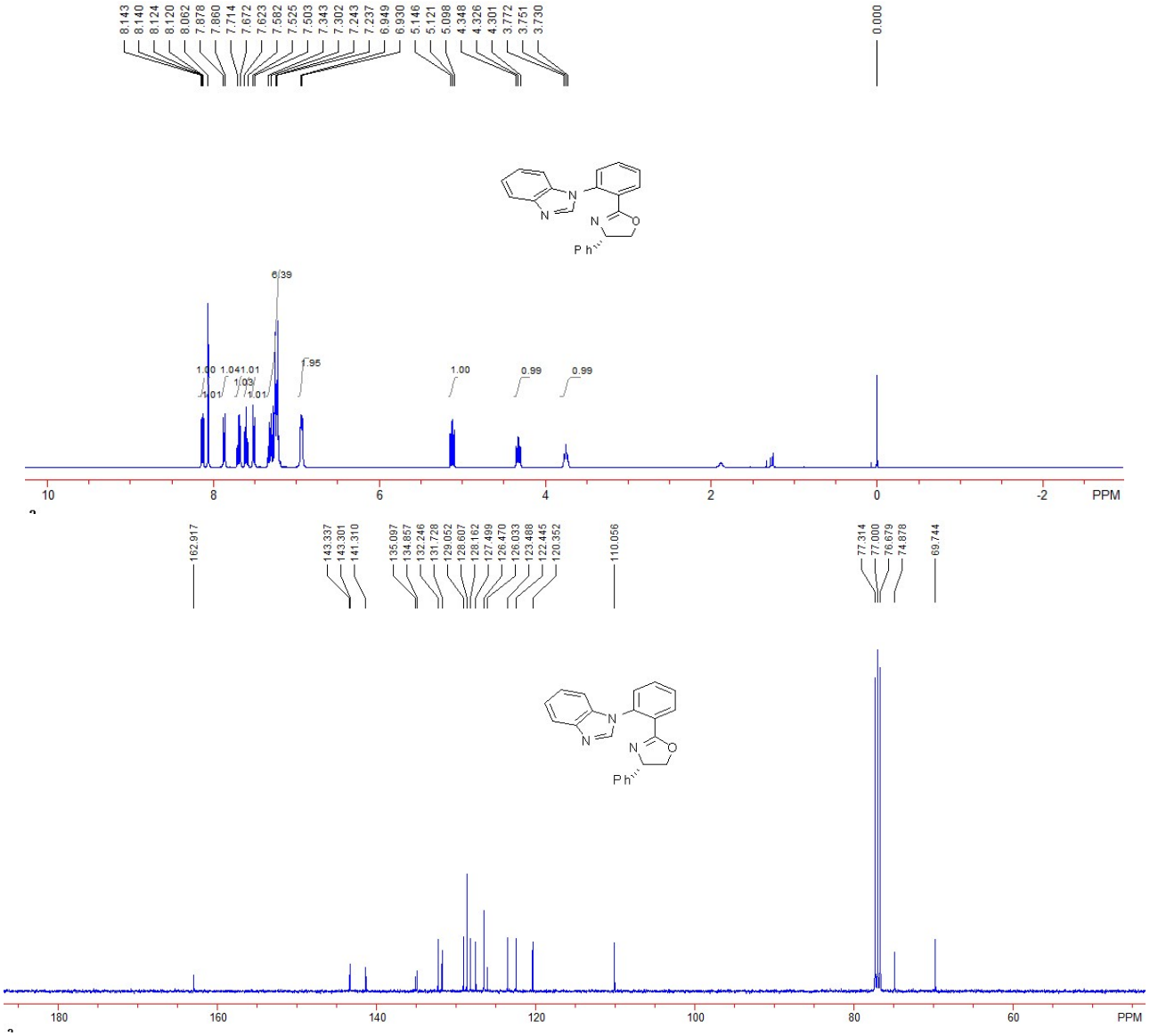
^{1}H NMR and ^{13}C NMR spectra of compound **5a**



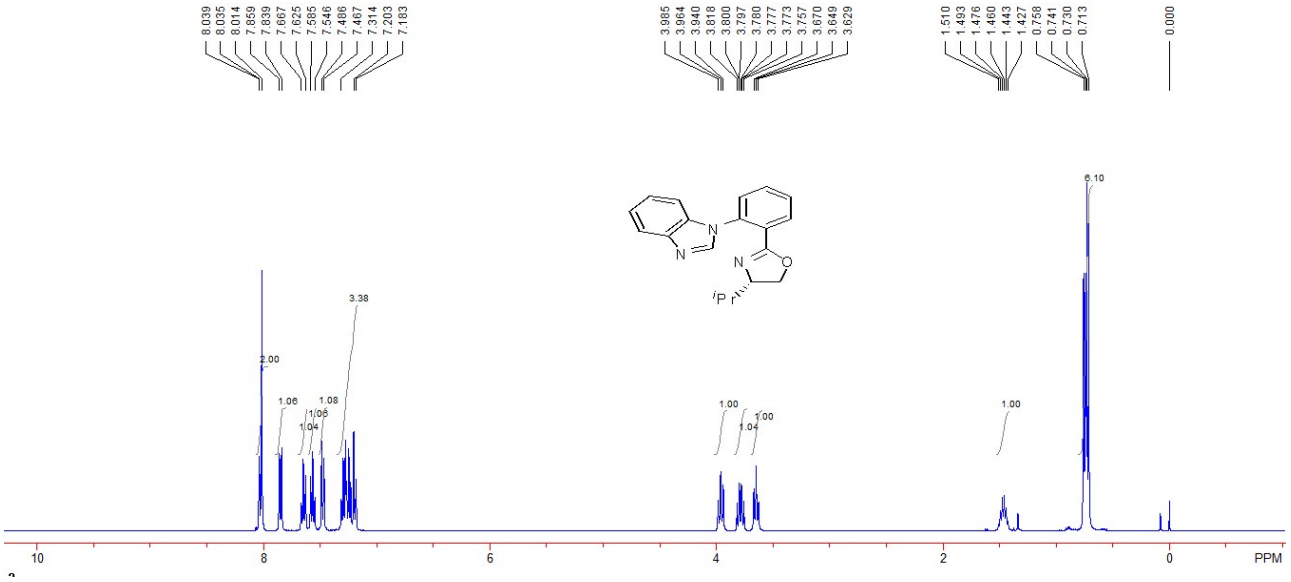
^{1}H NMR and ^{13}C NMR spectra of compound **5b**

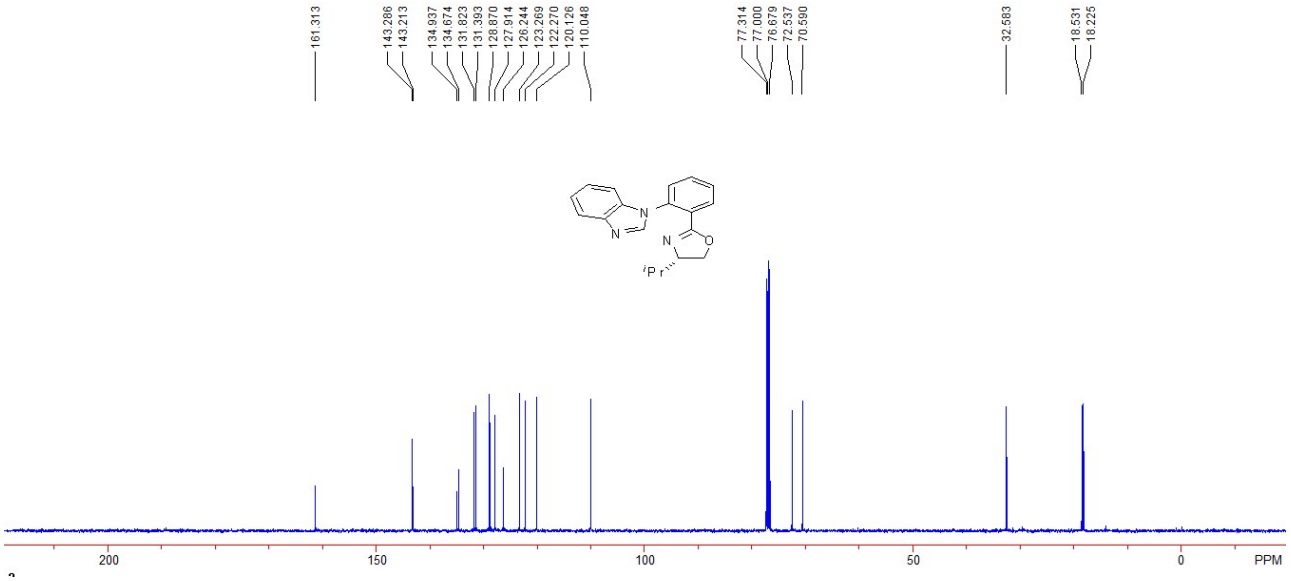


^{1}H NMR and ^{13}C NMR spectra of compound **6a**



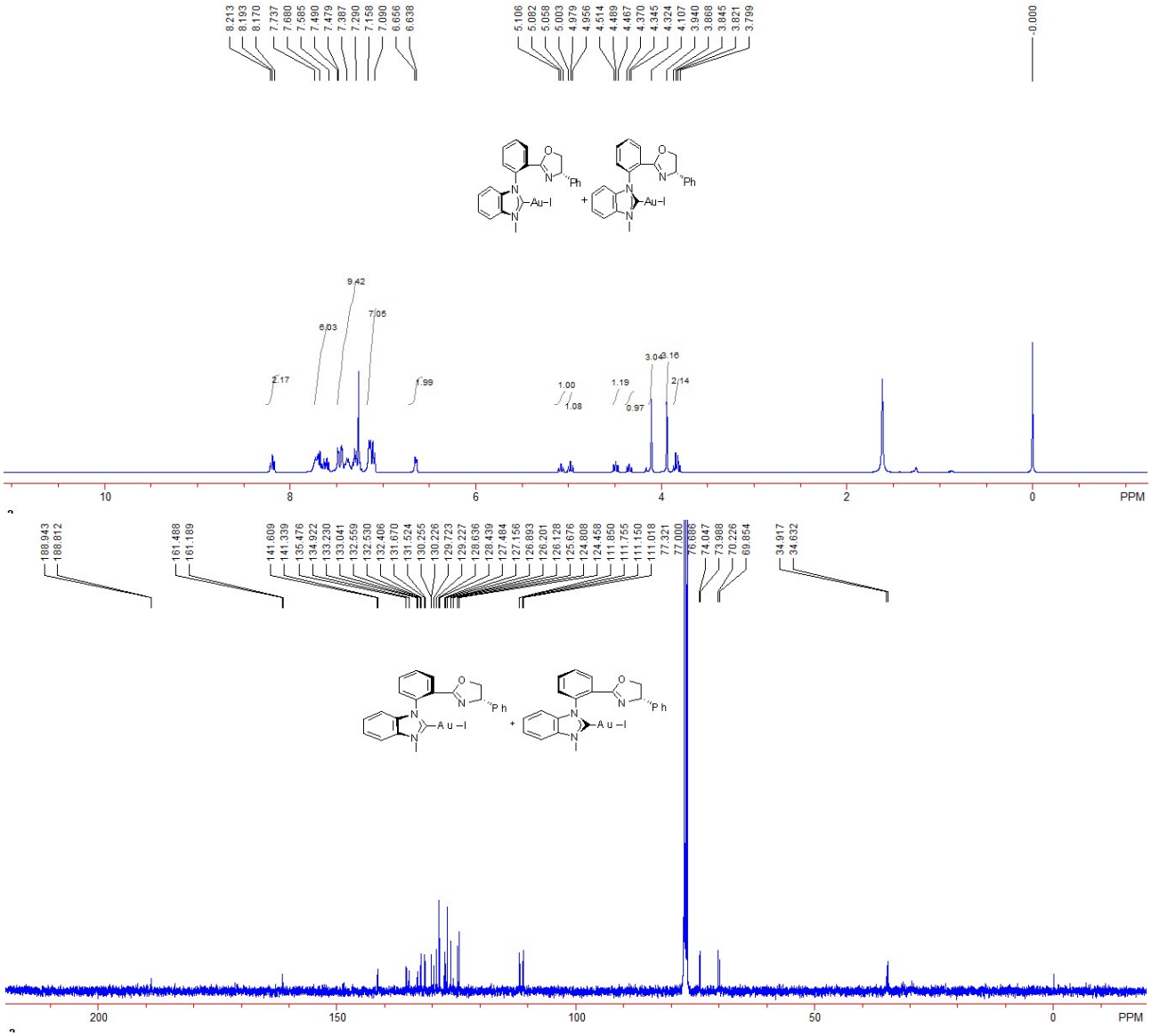
^{1}H NMR and ^{13}C NMR spectra of compound **6b**



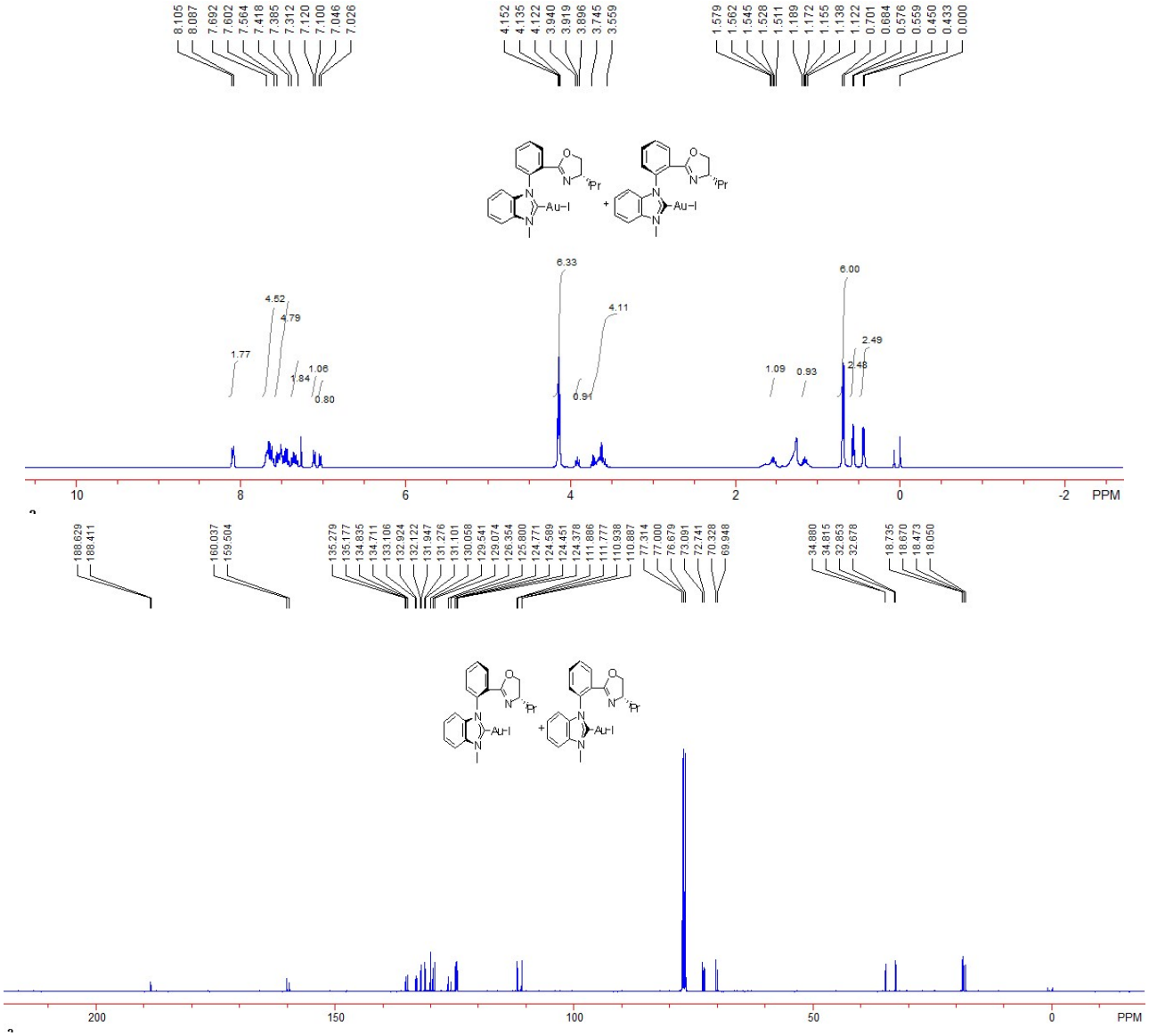


2. **NMR spectra of NHC-gold complex 8**

^{1}H NMR, ^{13}C NMR spectra of NHC-gold complex **8a**

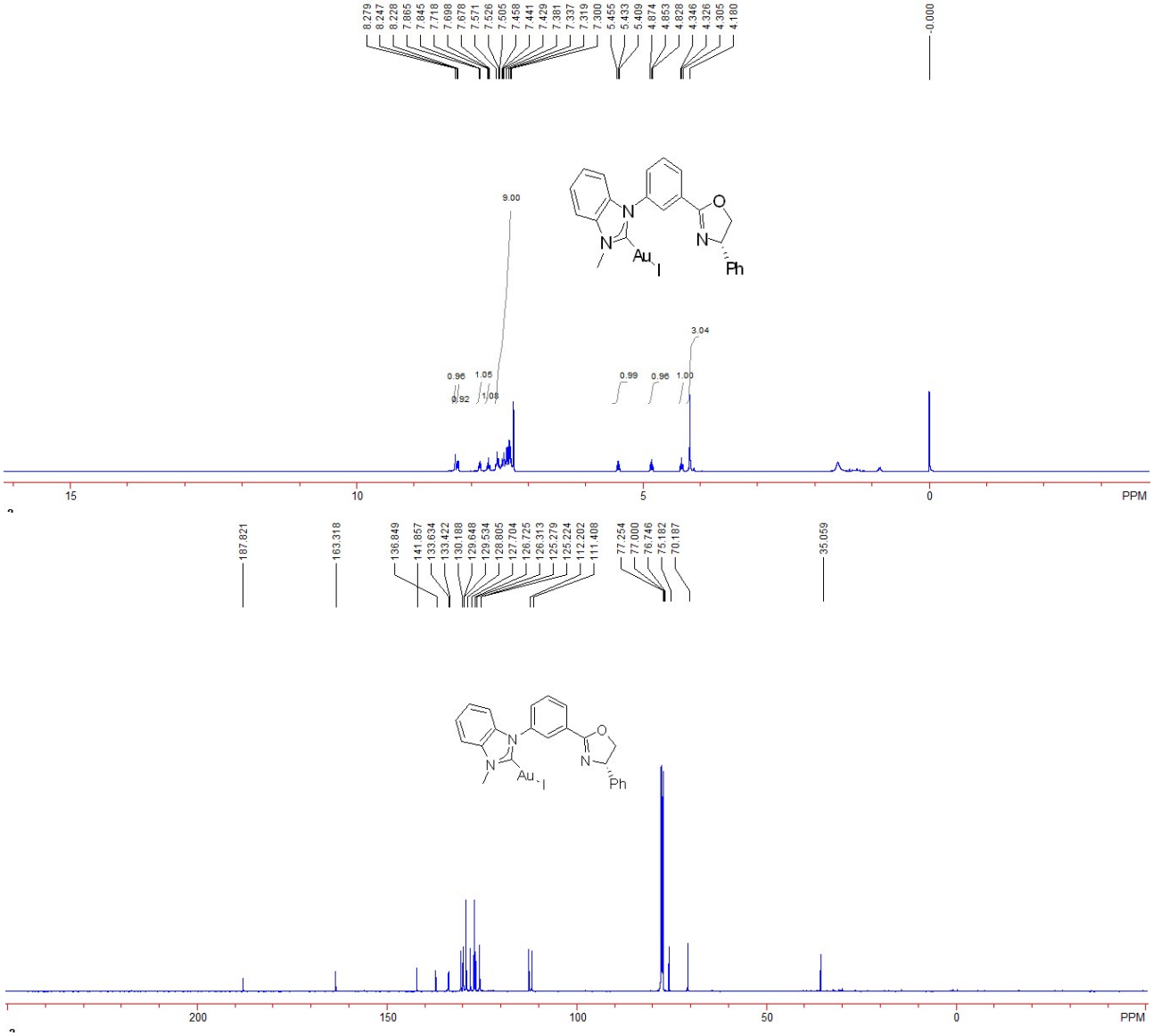


^{1}H NMR, ^{13}C NMR spectra of NHC-gold complex **8b**

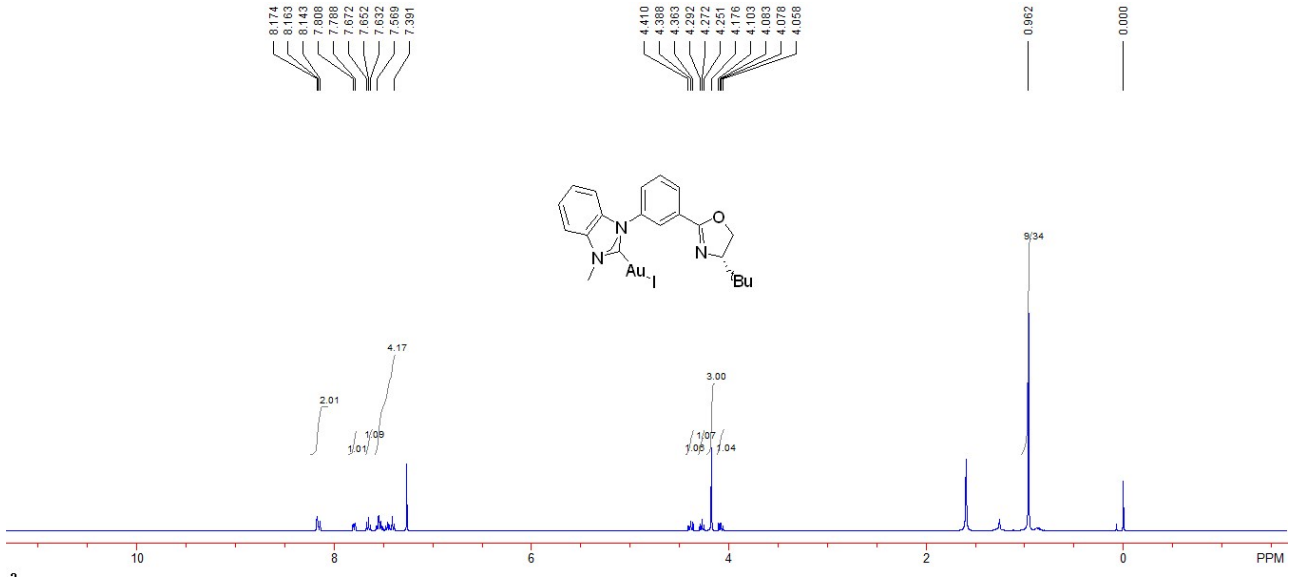


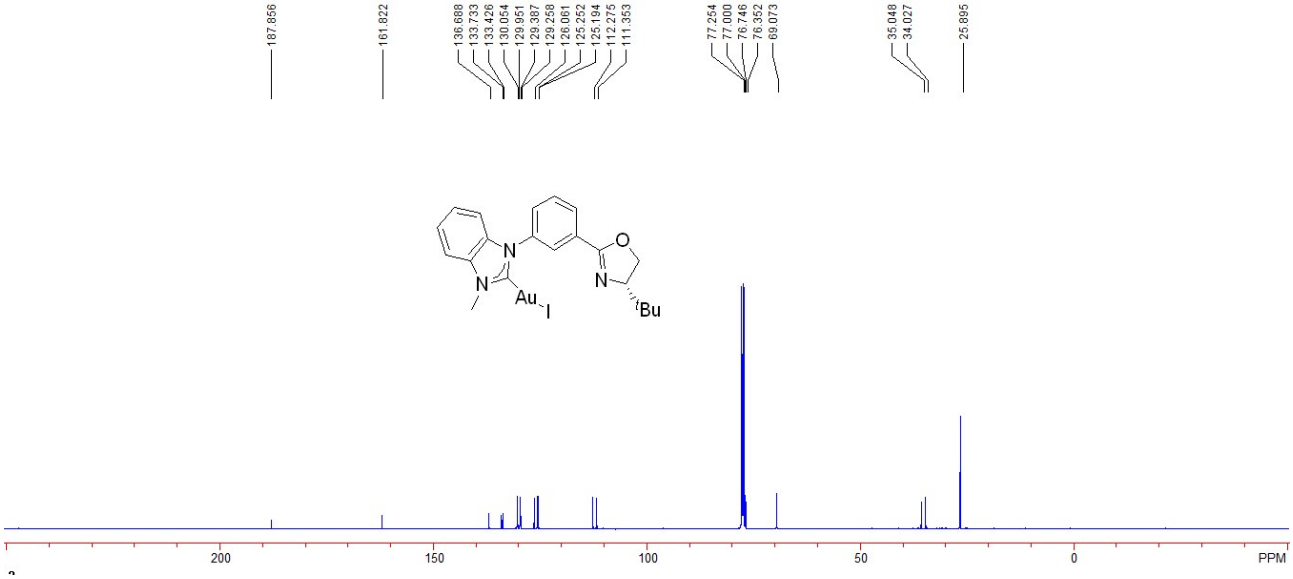
3. NMR spectra of NHC-gold(I) complex 10

^{1}H NMR, ^{13}C NMR spectra of NHC-gold complex **10a**

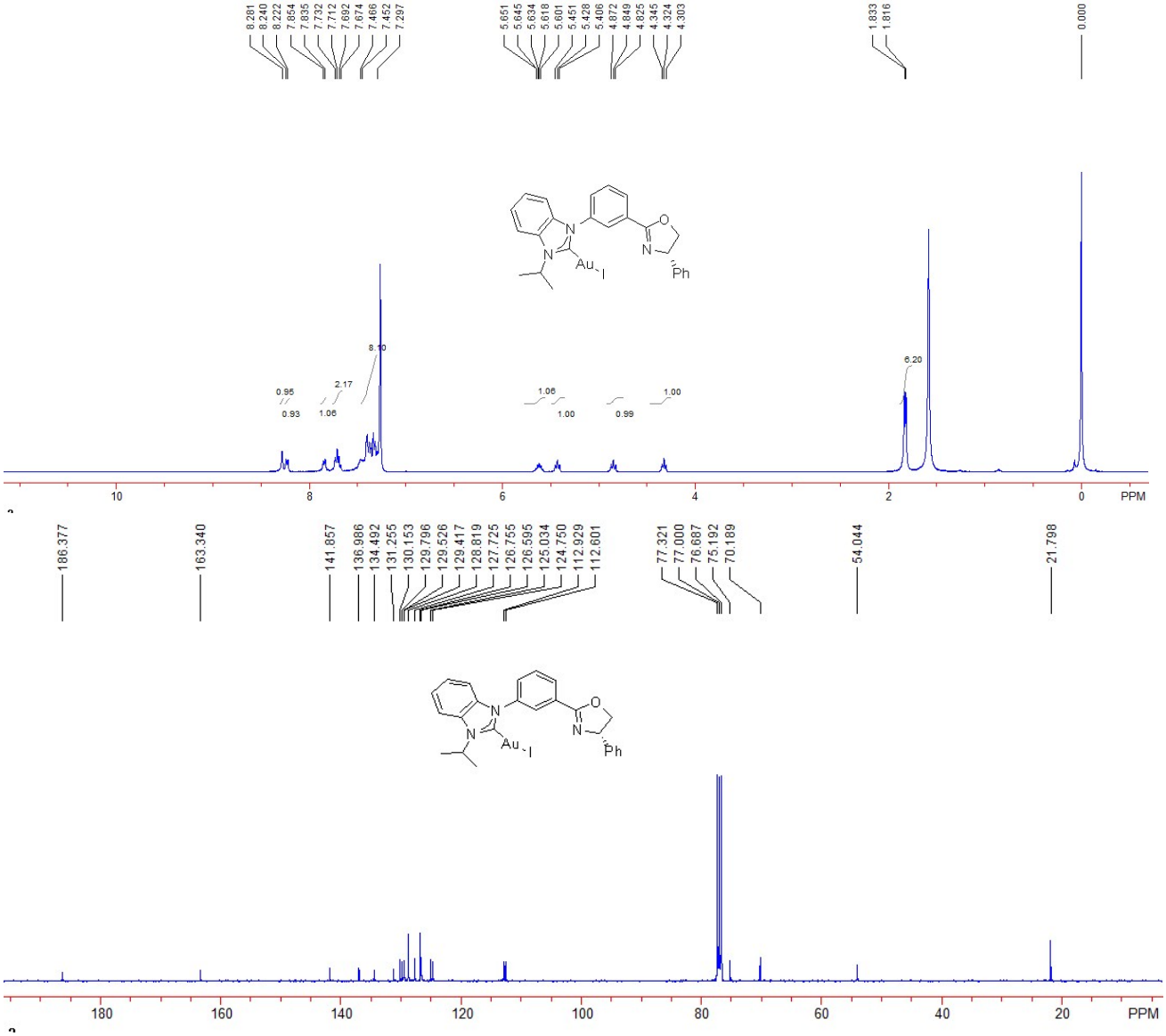


^{1}H NMR, ^{13}C NMR spectra of NHC-gold complex **10b**



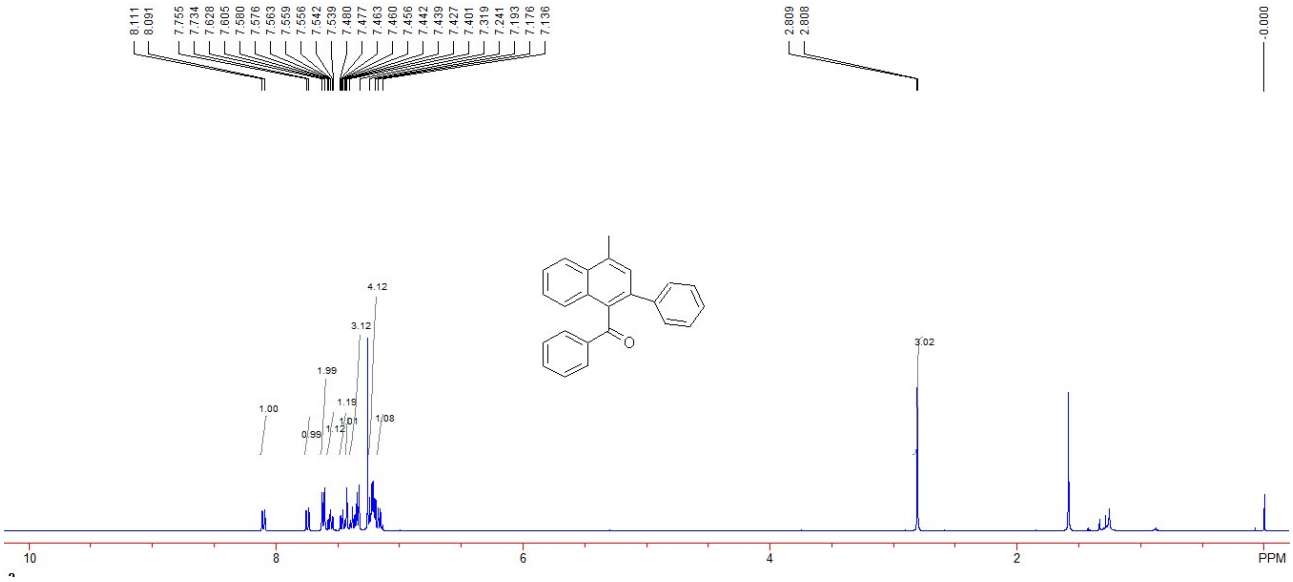


^{1}H NMR, ^{13}C NMR spectra of NHC-gold complex **10c**

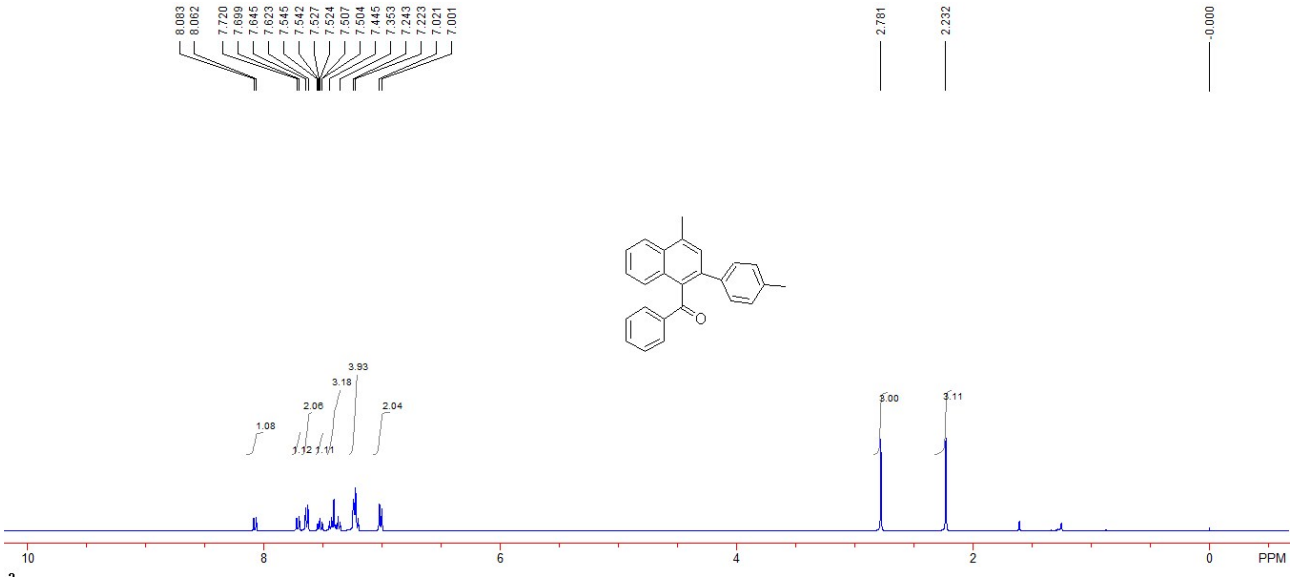


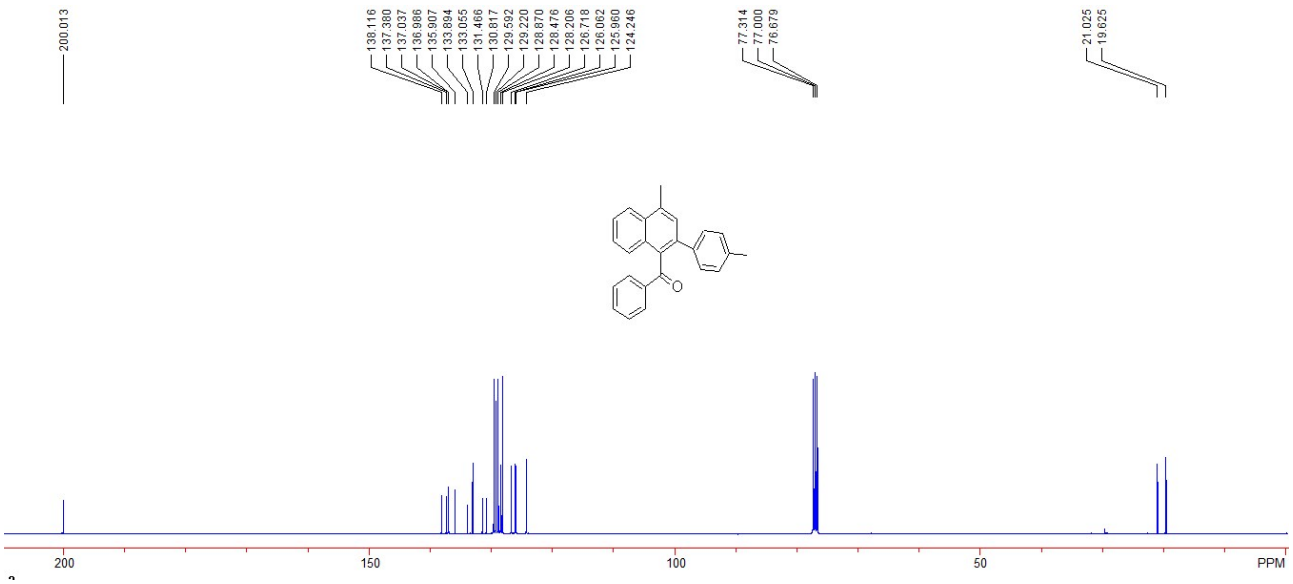
4. NMR spectra of product 13

^{1}H NMR spectra of compound **13a**

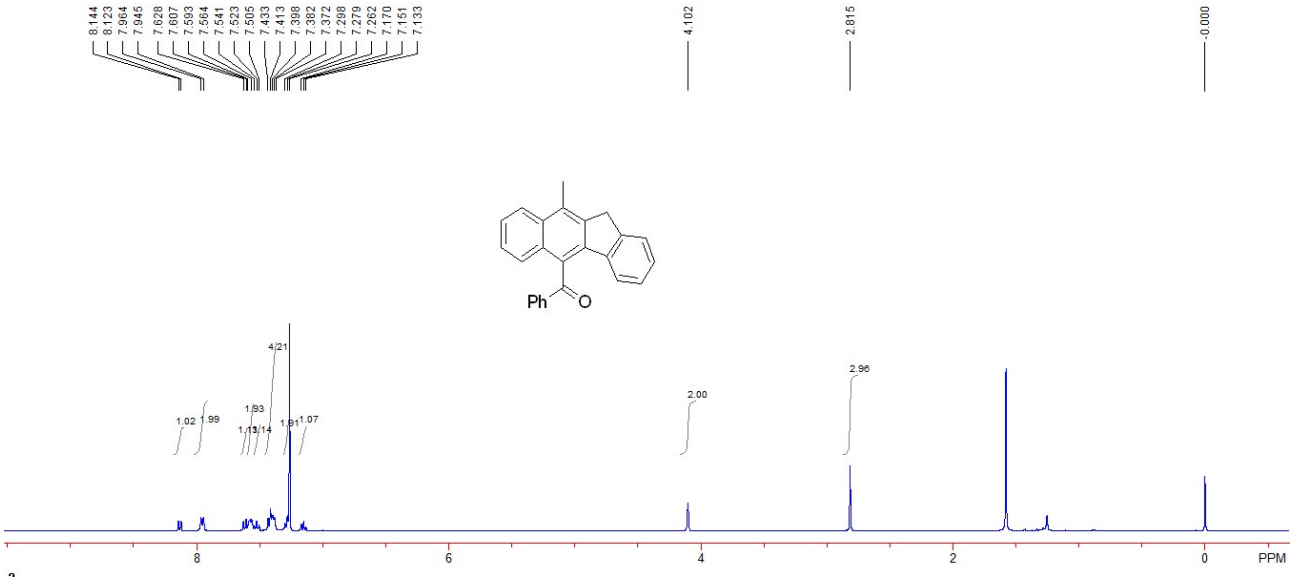


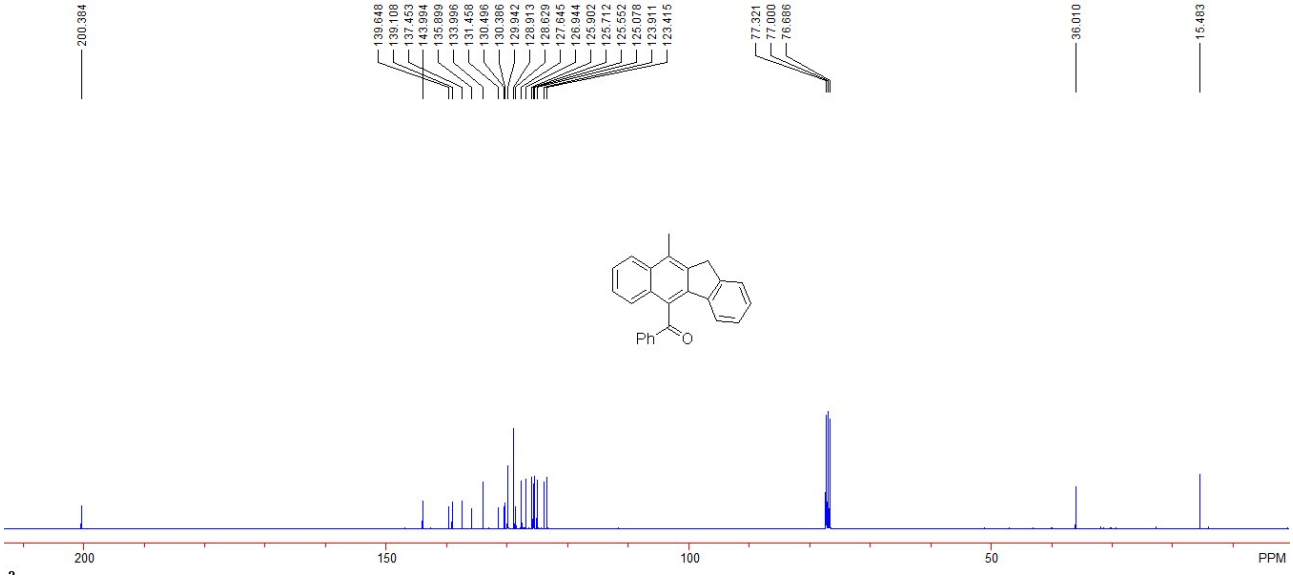
^{1}H NMR and ^{13}C NMR spectra of compound **13b**



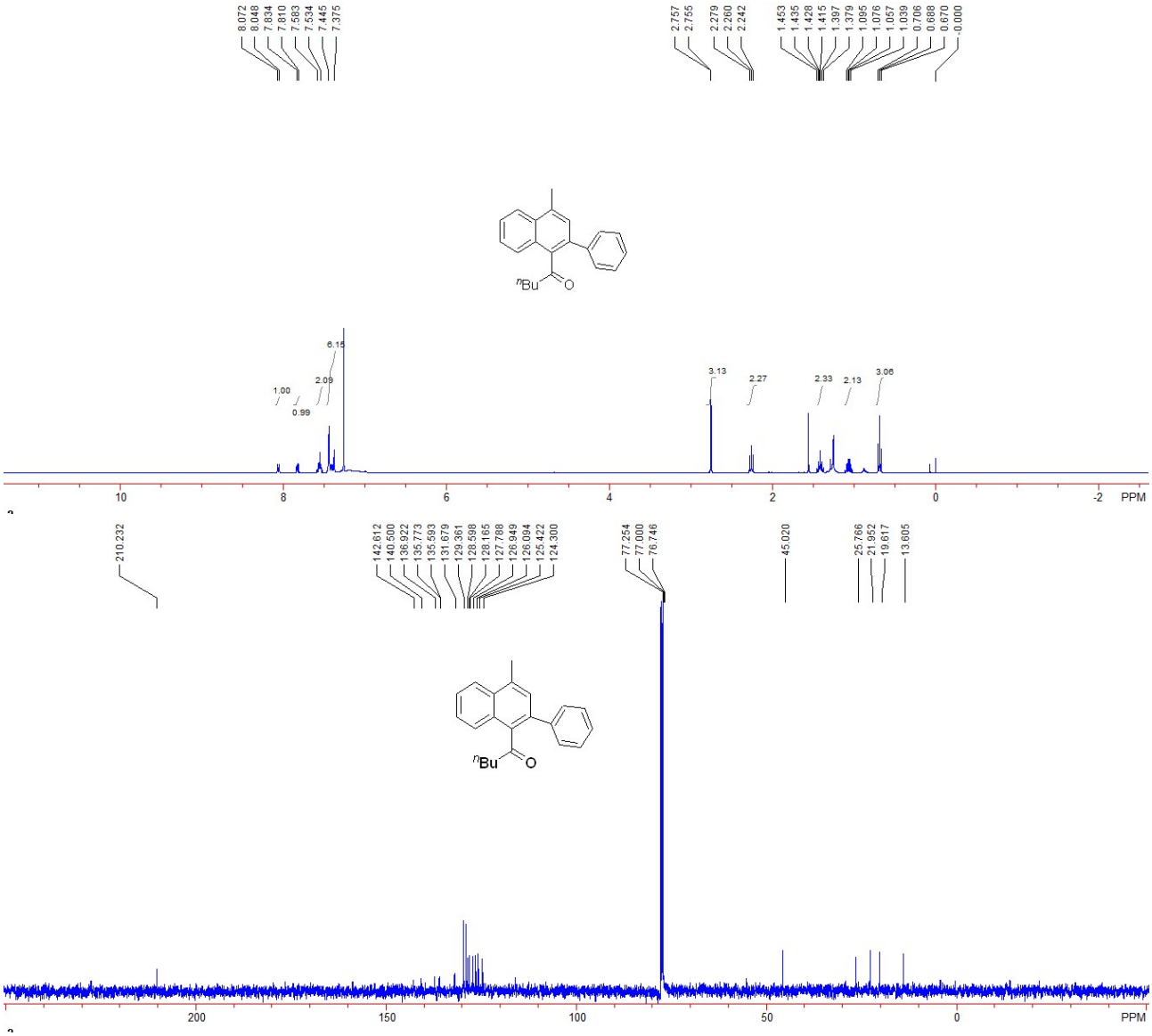


^{1}H NMR and ^{13}C NMR spectra of compound **13c**

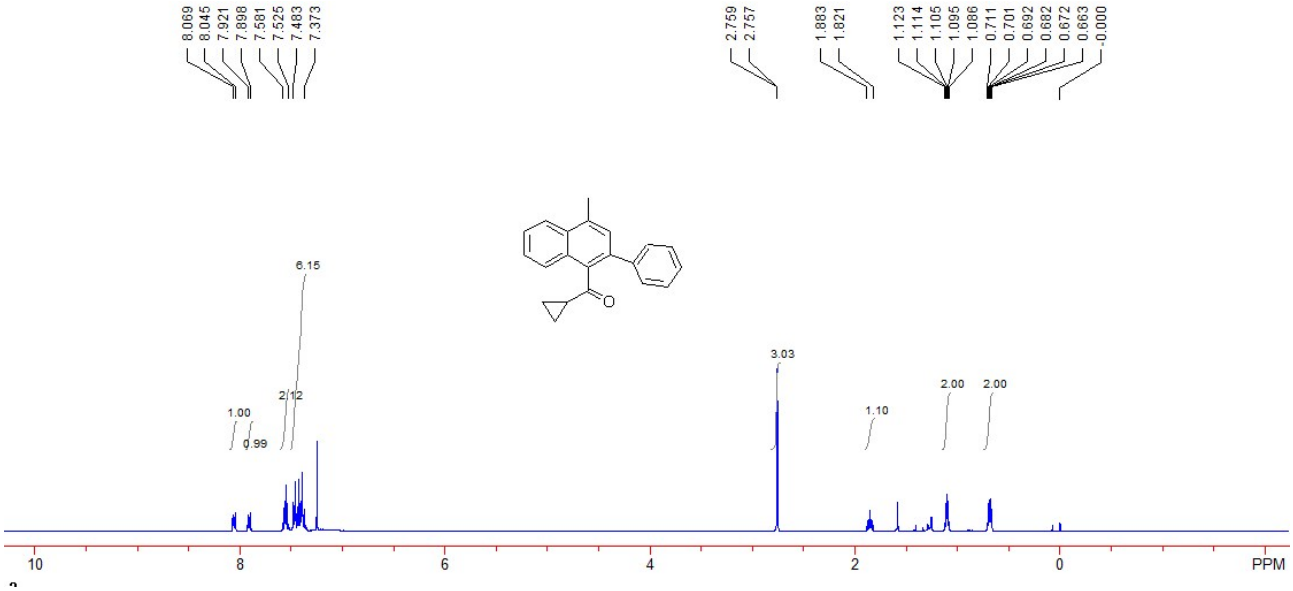


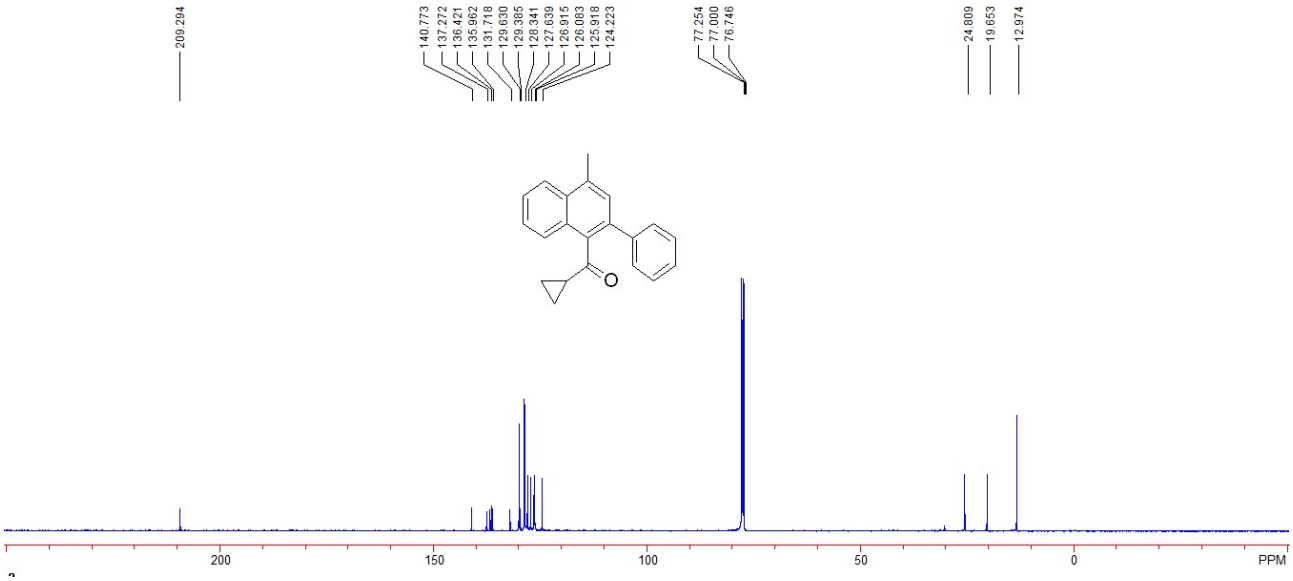


^{1}H NMR and ^{13}C NMR spectra of compound **13d**

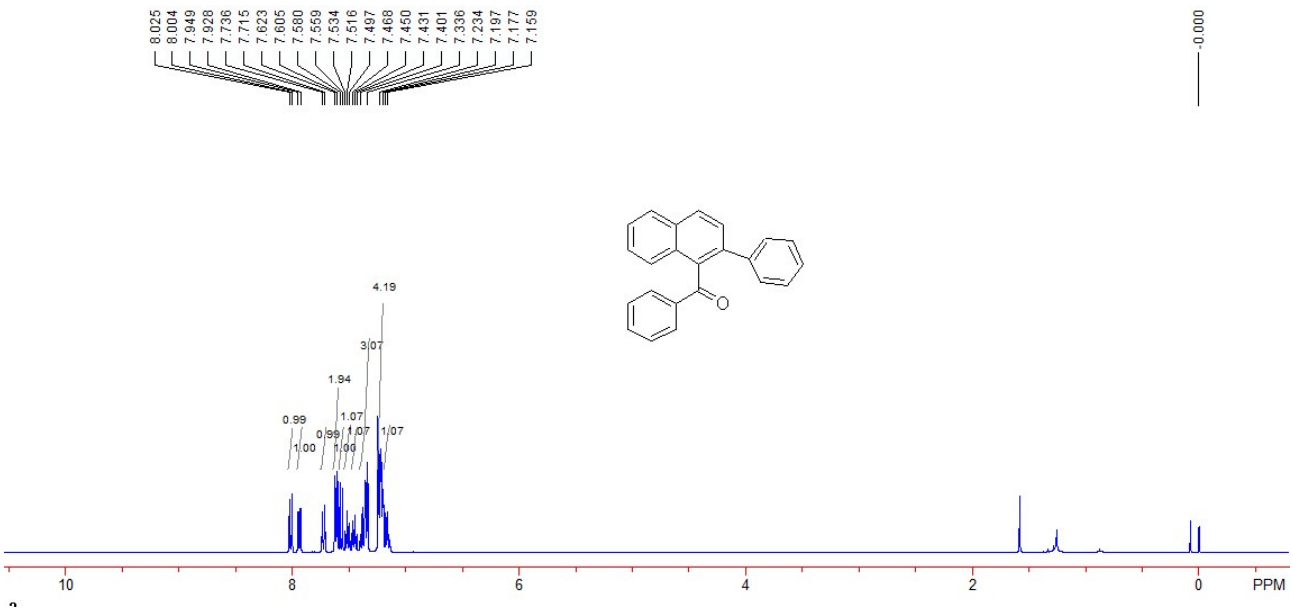


^{1}H NMR and ^{13}C NMR spectra of compound **13e**

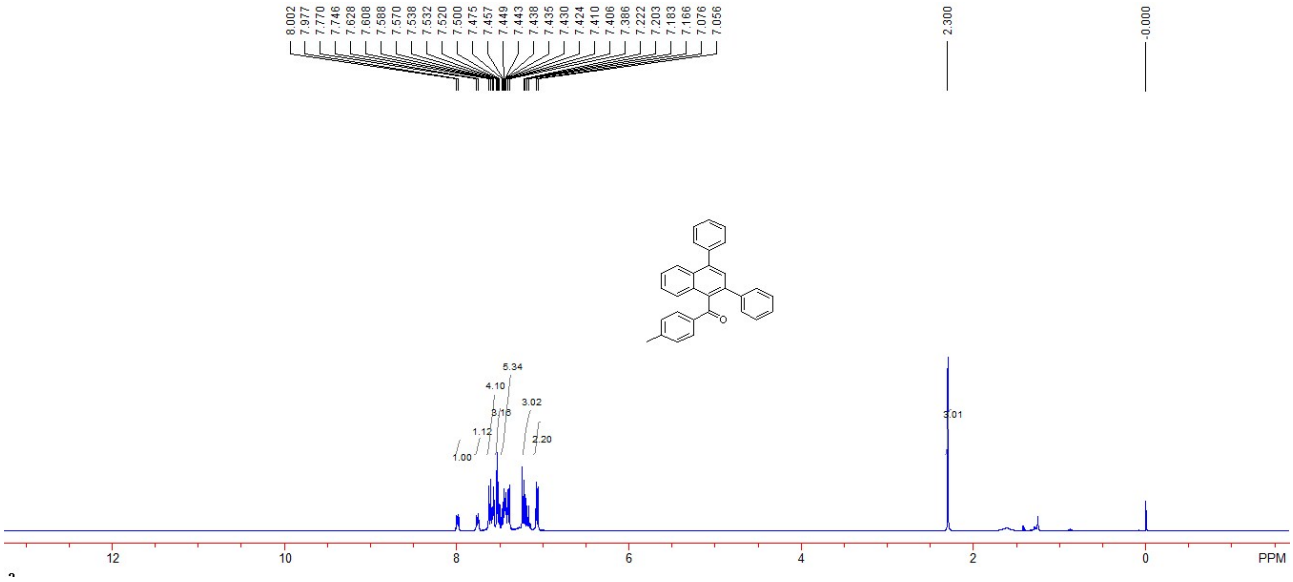


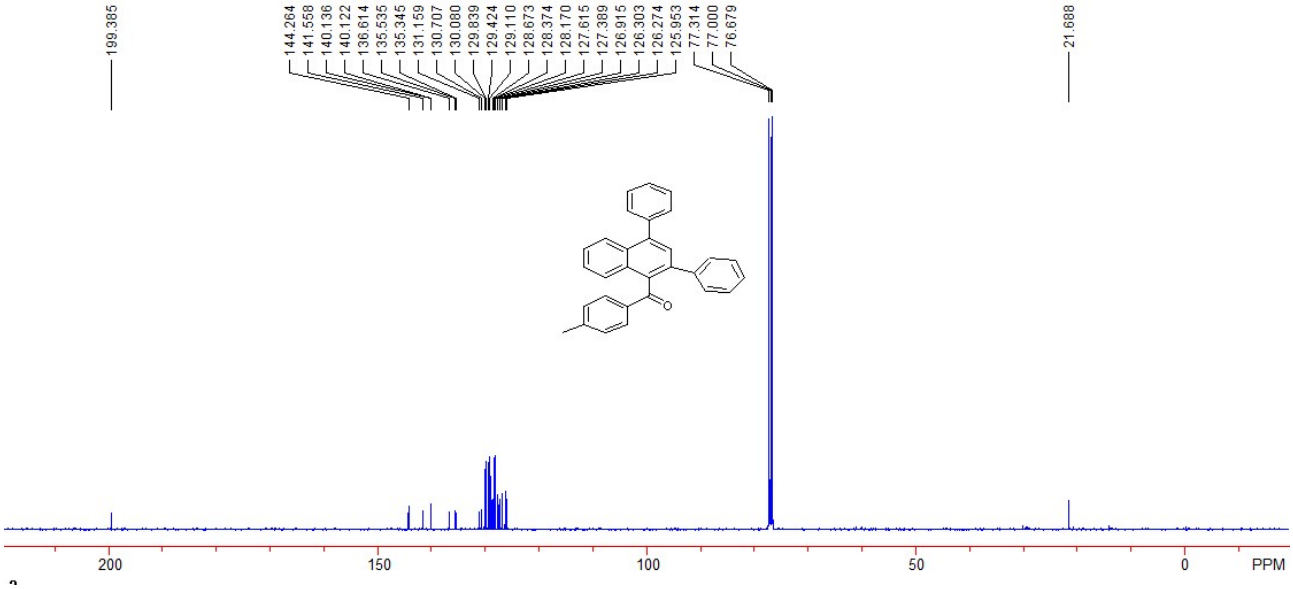


^{1}H NMR spectra of compound **13f**



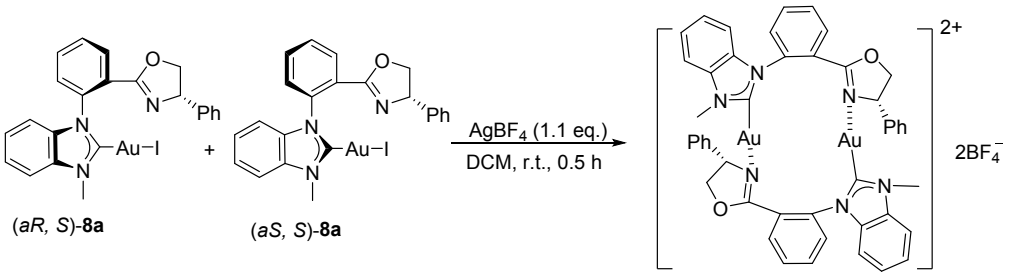
^{1}H NMR and ^{13}C NMR spectra of compound **13g**





5. Controlled experiments

A. The synthesis of active complex **14** with $AgBF_4$



HRMS (ESI)
$[M+H]^+$: $C_{23}H_{20}AuIN_3O$
Calcd: 678.0317
Found: 678.0303

14

HRMS (ESI)
$[M-2BF_4]^{2+}$: $C_{46}H_{38}Au_2N_6O_2/2$
Calcd: 550.1194
Found: 550.1196

To a solution of the NHC-oxazoline gold(I) complex **8a** in DCM at room temperature was added $AgBF_4$ (1.1 eq.) in one portions. The white precipitate was formed immediately and the mixture was stirred at that temperature for 0.5 h. After that, the mixture was filtered through the celite pad twice to remove the AgI and the excess amount of $AgBF_4$ and washed three times with DCM. The combined organic solvents were removed *in vacuo* to afford the crude chelated NHC-oxazoline gold(I) complex **14** as a white solid.

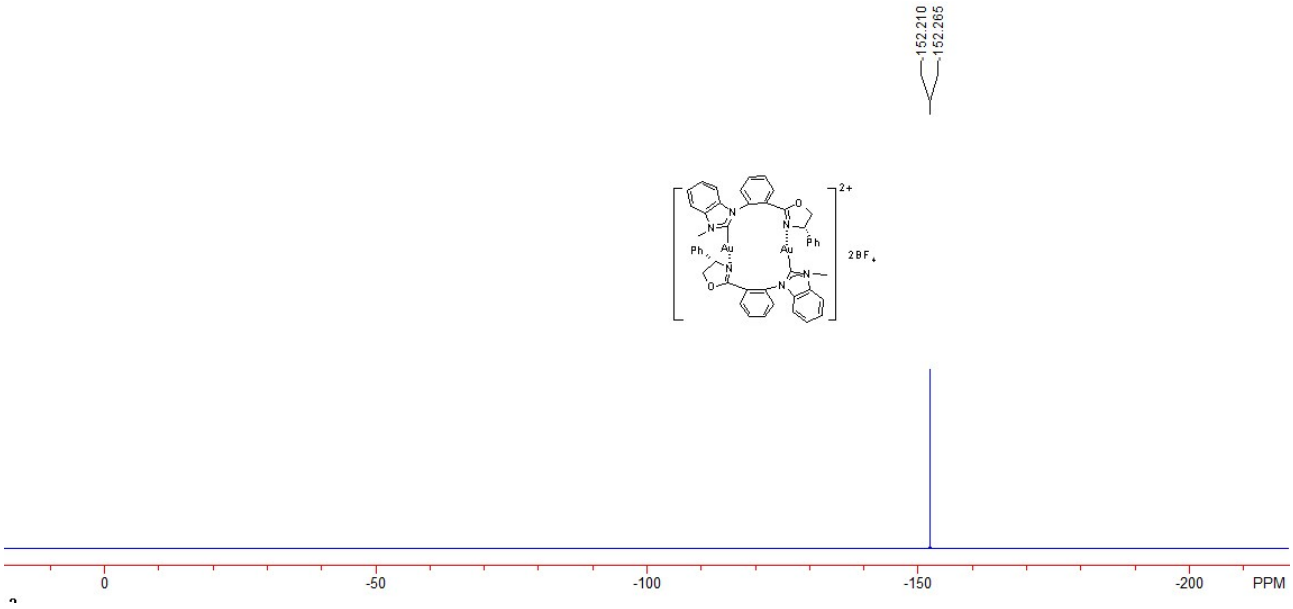


Fig. 1. The ^{19}F NMR spectra of the generated complex **14**

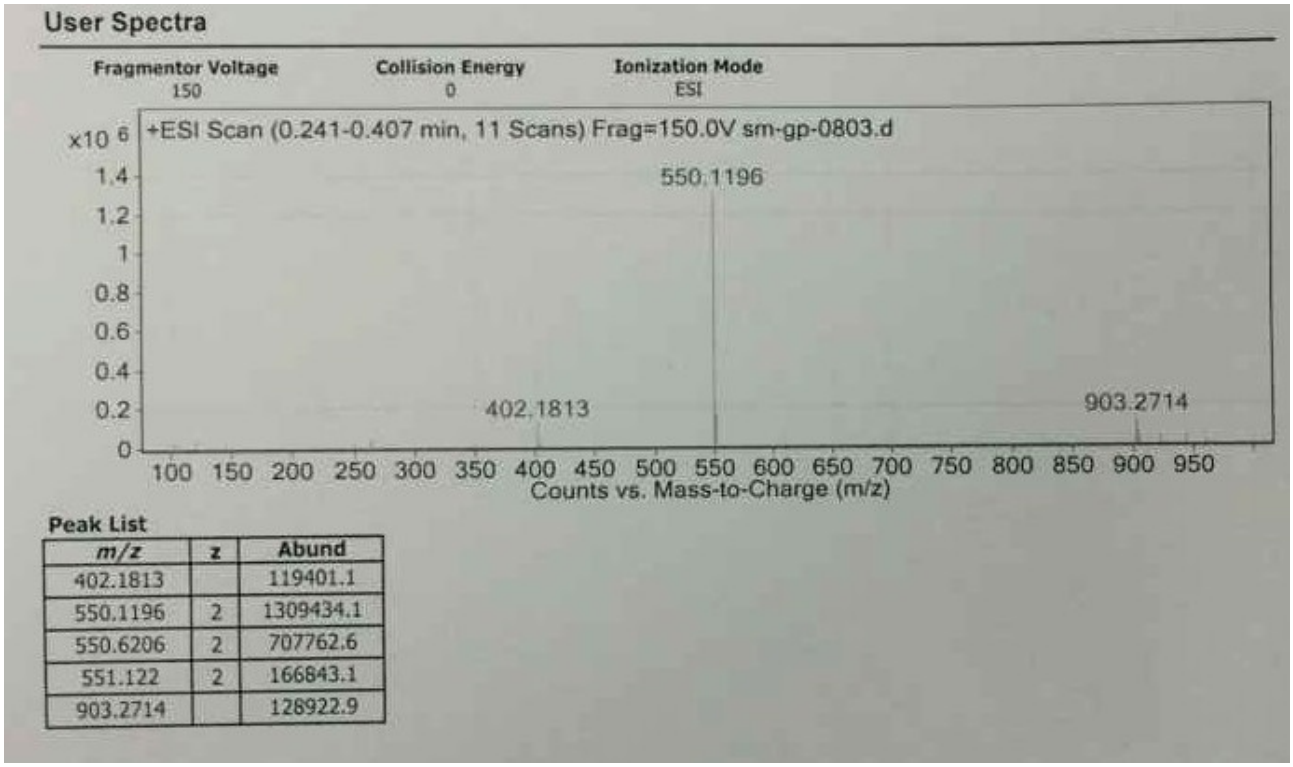
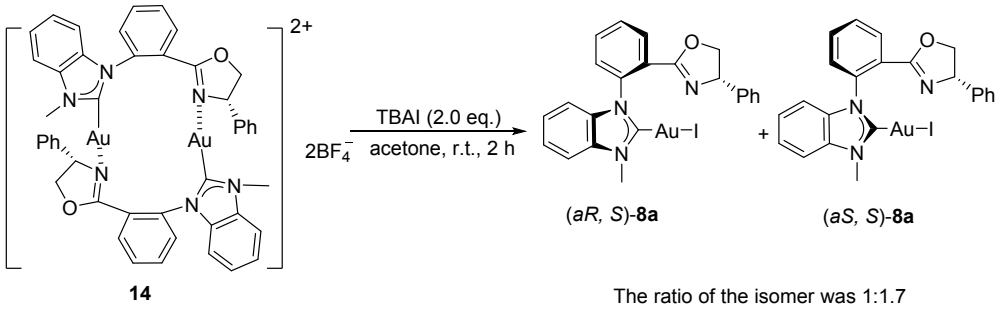


Fig. 2. The ESI-Mass spectra of the generated complex **14**

B. The reversed synthesis of NHC-oxazoline gold(I) complex **8a**



To a solution of synthesized crude ionic chelated NHC-oxazoline gold(I) complex **14** in acetone was added tetrabutylammonium iodide (2 eq.) (TBAI) in one portion. The mixture was stirred at room temperature for 2 hours. After that, the salt was filtered off and the solvent was removed under reduced pressure to afford the crude NHC-oxazoline gold(I) complex **8a**. The ratio of the isomer was changed into 1:1.7. The synthesized complex **8a** was confirmed by its ^{1}H NMR and ESI-Mass spectra.

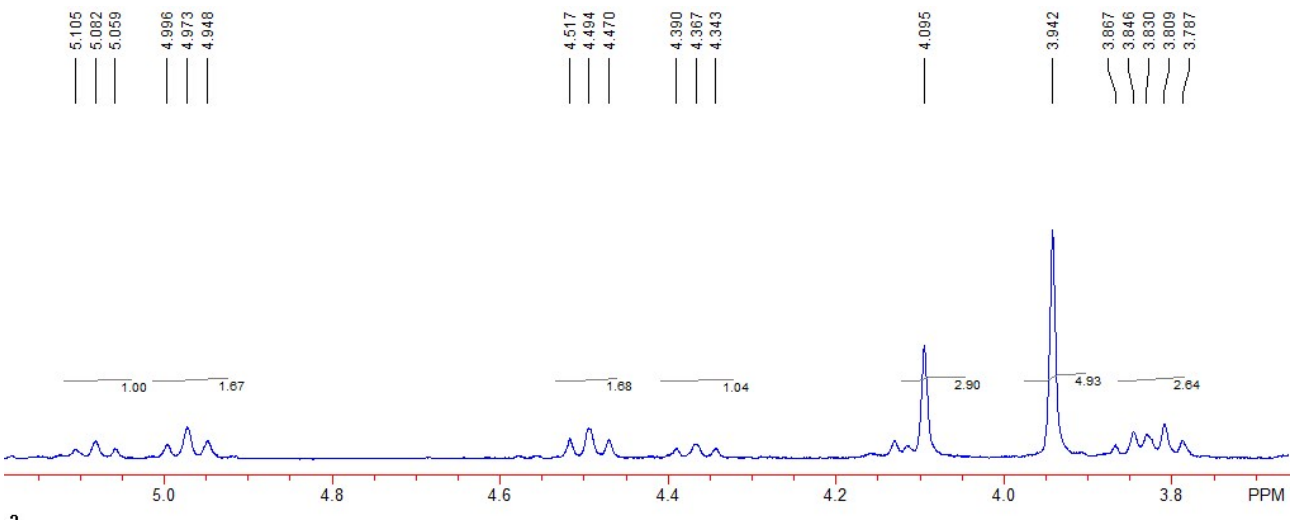
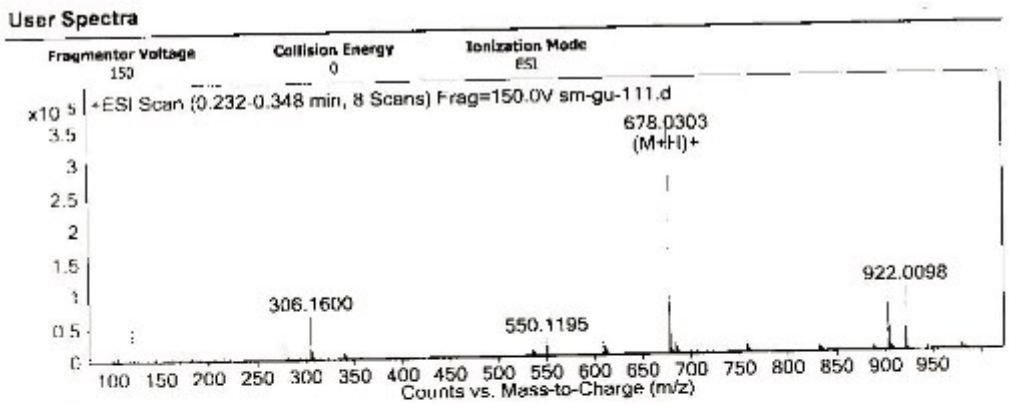


Fig. 3. The characteristic ^{1}H NMR spectra of the generated complex **8a**



Peak List

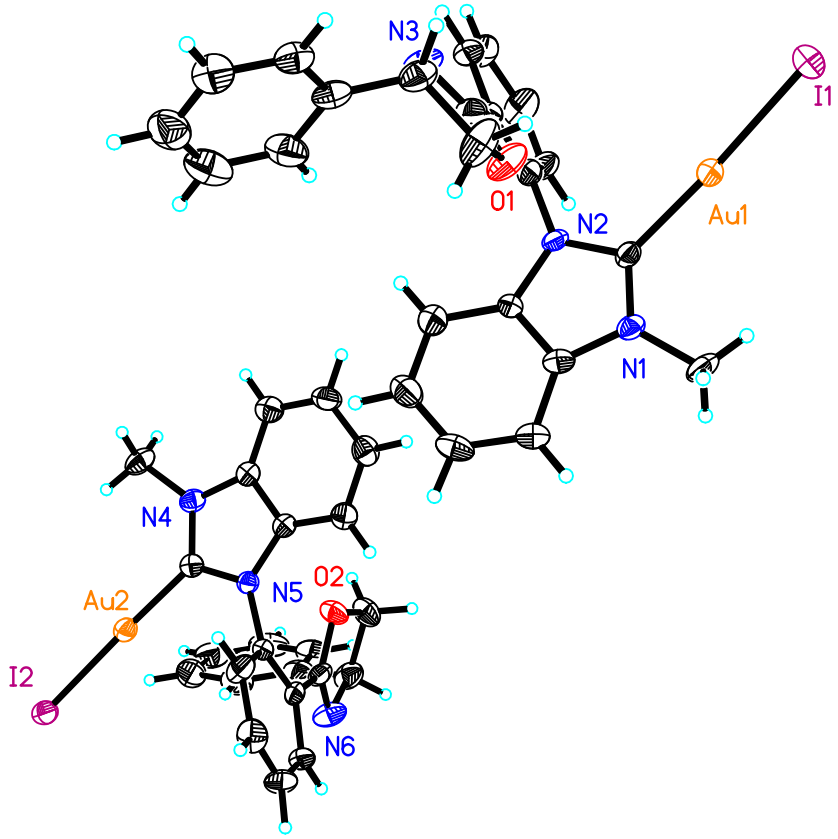
m/z	z	Abund	Formula	Ion
102.128		26275.6		
105.0176		38054.2		
121.0509		79736.8		
306.16		65163.5		
550.1195		25723.4		
678.0303	1	367149.9	C23 H20 Au 1 N3 O	(M+H)+
679.0337	1	75786.9	C23 H20 Au 1 N3 O	(M+H)+
903.2712	1	71241.9		
904.2743	1	33564.4		
922.0098		94551.3		

Formula Calculator Results

IonFormula	Measured Mass	Tgt Mass	Diff (ppm)	Score
C23 H20 Au 1 N3 O	678.0303	678.031	1.17	93.5
C18 H20 Au 1 N5 O3	678.0303	678.0271	-4.82	86.61
C11 H24 Au 1 N5 O8	678.0303	678.033	3.85	82

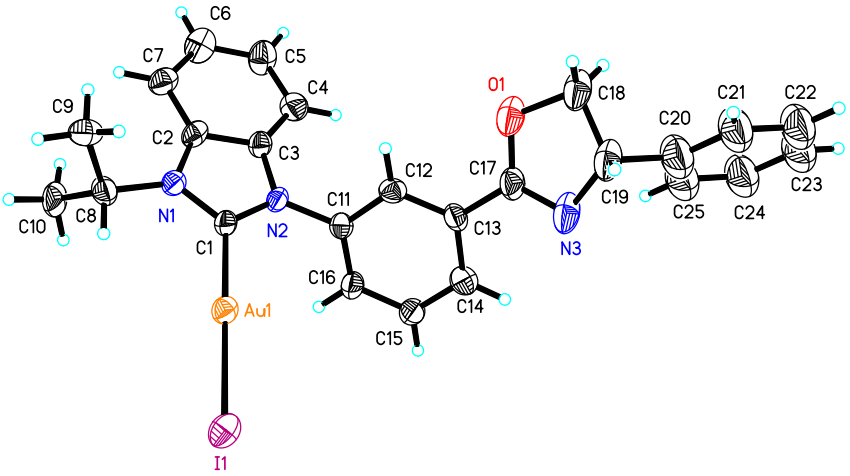
Fig. 4. The ESI-Mass spectra of the generated complex **8a**

6. Crystal structure data for complex 8a



The crystal data of **8a** have been deposited in CCDC with number 973292. Empirical Formula: $C_{23}H_{19}AuIN_3O$, Formula weight: 677.28, Temperature: 293(2) K, Crystal system, space group: Orthorhombic, P2(1)2(1)2(1), Unit cell dimensions: a = 10.3025(5) Å, alpha = 90 deg. b = 16.0231(8) Å, beta = 90 deg. c = 26.3966(14) Å, gamma = 90 deg. Volume: 4357.5(4) $Å^3$, Z, Calculated density: 8, 2.065 Mg/m^3, F(000): 2544, Crystal size: 0.176 x 0.164 x 0.112 mm^3, Final R indices [I>2sigma(I)], R1 = 0.0368, wR2 = 0.0704.

7. Crystal structure data for complex 10c



The crystal data of **10c** have been deposited in CCDC with number 950237. Empirical Formula: $C_{25}H_{23}AuIN_3O$; Formula Weight: 705.33; Crystal Color, Habit: colorless, Crystal Dimensions: 0.156 x 0.123 x 0.085 mm; Crystal System: Monoclinic; Lattice Parameters: a = 32.577(6)Å, b = 10.964(2)Å, c = 15.077(3)Å, α = 90°, β = 101.267(6)°, γ = 90°, V = 5281.1(18)Å^3; Space group: C2/c; Z = 8; D_{calc}= 1.774 g/cm^3; F_{000} = 2672; Final R indices [I>2sigma(I)] R1 = 0.0430, wR2 = 0.1081.