SUPPORTING INFORMATION

Straightforward synthesis of [Au(NHC)X] (NHC = *N*-heterocyclic carbene, X = Cl, Br, I) complexes

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General information

- All reactions were carried under air and technical grade solvent were used unless otherwise stated.
- K_2CO_3, Na_2CO_3, $NaHCO_3$, NaOAc, pyridine and NEt_3 were used as received without further purification.
- ^1H, and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker-400 MHz or 300 MHz spectrometer at ambient temperature in CD_2Cl_2. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks.
- Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB.
- Crystals of **3** and (Au(SITb)Cl were grown by slow diffusion of pentane into a saturated dochloromethane solution.

Screening of the reaction conditions:solvents, base, and temperature: Unless otherwise stated, all the reactions were conducted under air, and using technical grade solvents.

entry	base	equiv. of base	solvent	T (°C)	t (h)	conversion (%)[a]
1	NaOAc	2	CH_3CN	25	24	70
2	K_2CO_3	2	CH_3CN	25	24	85
3	$NaHCO_3$	2	CH_3CN	25	24	25
4	Na_2CO_3	2	CH_3CN	25	24	63
5	NEt_3	2	CH_3CN	25	24	89
6	K_2CO_3	2	Acetone	25	24	>99
7	K_2CO_3	2	^{i}PrOH	25	24	87
8	K_2CO_3	2	CH_3CN	40	24	>99
9	K_2CO_3	2	Acetone	40	24	>99
10	**K_2CO_3**	**1**	**Acetone**	**60**	**1**	**>99**
11[b]	**K_2CO_3**	**1**	**Acetone**	**60**	**1**	**>99**
12[c]	**K_2CO_3**	**1**	**Acetone**	**60**	**1**	**>99**
13	K_2CO_3	1	THF	60	1	23
14	K_2CO_3	1	Me-THF	60	1	25
15	K_2CO_3	1	^{i}PrOH	60	1	90
16	NEt_3	1	Acetone	60	1	80
17	Pyridine	1	Acetone	60	24	0

a) Conversion given by ^{1}HNMR analysis of an aliquot of the reaction mixture .b) Dry acetone was used.
c) The reaction was conducted under argon, using dry acetone

General procedure for the synthesis of [Au(NHC)Cl] complexes:

Small scale:A vial was charged, under air, with the corresponding NHC·HCl (100 mg,

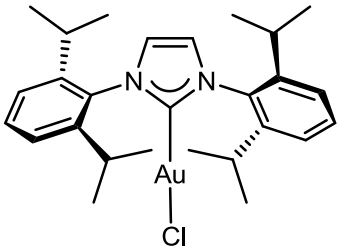
1 equiv), [Au(DMS)Cl] (1 equiv) and K_2CO_3 (1 equiv). The resulting mixture was suspended in acetone (1.0 mL) and stirred for 1-24 h at 60 ºC. After this time the solvent was removed in vacuo and dichloromethane was added (2 mL). The mixture was filtered through silica. The pad of silica was washed with dichloromethane (3 x 1 mL). The solvent was concentrated and pentane (3 mL) was added, affording a white solid that was washed with further portions of pentane (3 x 1 mL) and dried under vacuum.

Large scale: A round bottom flask equipped with a condenser was charges under air with the corresponding NHC·HCl (1 equiv), [Au(DMS)Cl] (1 equiv) and K_2CO_3 (3 equiv). The resulting mixture was dissolved in acetone and stirred for 3-24 h at 60 ºC. The same work up was carried out affording white solids in high yields.

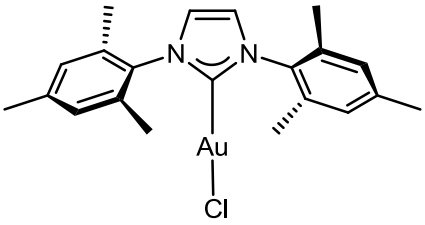
Preparation of [Au(IPr)Cl].[1]A vial was charged, under air, with IPr·HCl (100 mg, 0.235 mmol), [Au(DMS)Cl] (69.3 mg, 0.235 mmol) and finely ground K_2CO_3 (32.5 mg, 0.235 mmol). The resulting mixture was dissolved in acetone (1.0 mL) and stirred for 1 h at 60 ºC. After this time the solvent was removed in vacuo and dichloromethane was added. The mixture was filtered through silica. The pad of silica was washed with dichloromethane(3 x 1 mL). The solvent was concentrated and pentane (3 mL) was added, affording a white solid which was washed with further portions of pentane (3 x 1 mL)and driedunder vacuum. Yield: 143 mg (97%). Anal. Calcd. for $C_{27}H_{36}AuClN_2$: C 52.22; N 4.51; H 5.84. Found: C 52.33; N 4.60; H 5.91.^{1}H NMR(300 MHz, CD_2Cl_2, 293 K): δ7.57 (t, $J_{H\text{-}H}$ = 7.8, 2H, CH_{Ar}), 7.35 (d, $J_{H\text{-}H}$ = 7.8, 4H, CH_{Ar}), 7.24 (s, 2H, CH_{imid}), 2.56 (sept, $J_{H\text{-}H}$ = 6.9, 4H, C*H*$(CH_3)_2$), 1.34 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 1.23 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR(75.4 MHz, CD_2Cl_2,293 K): δ175.7

[1]Fuctos, M. R.; Belderrain, T. R.; de Frémont, P.; Scott, N. M.; Nolan, S. P., Díaz-Requejo, M. M.; Pérez, P. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 5284.

(s, C-Au), 146.4 (s, C_{Ar}), 134.6 (s,C_{Ar}),131.2 (s, C_{Ar}), 124.8 (s, C_{Ar}), 123.9 (s, C_{imid}), 29.4 (s, *C*H(CH_3)$_2$), 24.7 (s, CH(*C*H_3)$_2$), 24.3 (s, CH(*C*H_3)$_2$).



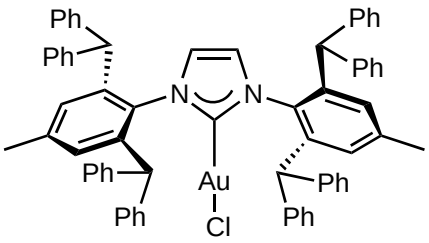
Preparation of[Au(IMes)Cl].[2]This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of IMes·HCl (100 mg, 0.294 mmol), [Au(DMS)Cl] (86.6 mg, 0.294 mmol) and K_2CO_3 (40.6 mg, 0.294 mmol) in acetone (1 mL) was stirred for 4 h at 60 ºC. A white solid was obtained. Yield: 124 mg (79%). ^{1}H NMR(300 MHz, CD_2Cl_2, 293 K): δ7.16 (s, 2H, CH_{imid}),7.07 (s,4H, CH_{Ar}), 2.38 (s, 6H, CH_3),2.13(s, 12H, CH_3). ^{13}C{^{1}H} NMR(75.4 MHz, CD_2Cl_2, 293 K): δ173.5 (s, C-Au), 140.5 (s, C_{Ar}), 135.4 (s, C_{Ar}), 135.3 (s, C_{Ar}), 129.9 (s, CH_{Ar}),123.0 (s, CH_{imid}), 21.5 (s, CH_3), 18.1 (s, CH_3).



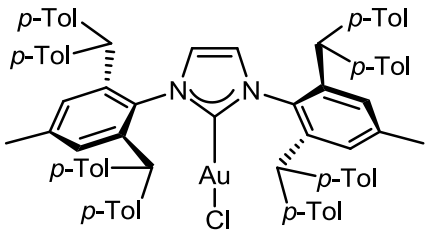
Preparation of [Au(IPr*)Cl]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of IPr*·HCl (100 mg, 0.105 mmol), [Au(DMS)Cl] (31.0 mg, 0.105 mmol) and K_2CO_3 (13.5 mg, 0.105 mmol) in acetone (1.0 mL) was stirred for 4 h at 60 ºC. A white solid was obtained. Yield: 91.4mg (76%).^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.17 (m, 24H, CH_{Ar}), 7.12-7.10

[2]de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics*, **2005**, *24*, 2411.

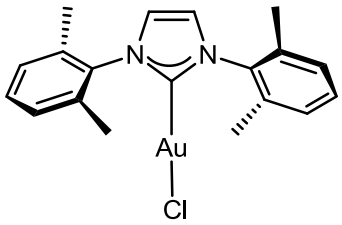
(m, 8H, CH_{Ar}), 6.93 (s, 4H, CH_{Ar}), 6.89-6.87 (m, 8H, CH_{Ar}), 5.85 (s, 2H, CH_{imid}), 5.26 (s, 4H, $CHPh_2$), 2.25 (s, 6H, CH_3).$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 293 K): δ 175.6 (s, C-Au), 143.1 (C_{Ar}), 142.9 (C_{Ar}), 141.3 (C_{Ar}), 140.8 (C_{Ar}), 134.1 (C_{Ar}), 130.6 (CH_{Ar}), 130.1 (CH_{Ar}), 129.7 (CH_{Ar}), 128.8 (CH_{Ar}), 127.1 (CH_{Ar}), 127.0 (CH_{Ar}), 123.6 (CH_{imid}), 51.6 ($CHPh_2$), 21.9 (s, CH_3).



Preparation of [Au(IPr*^{Tol})Cl].This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of IPr*$^{-Tol}$·HCl (100 mg, 0.094 mmol), [Au(DMS)Cl] (27.7 mg, 0.094 mmol) and K_2CO_3 (13.0 mg, 0.094 mmol) in acetone (1 mL) was stirred for 2 h at 60 ºC. A white solid was obtained. Yield: 104 mg (88%).Anal. Calcd. for $C_{77}H_{72}AuClN_2$: C 73.53; N 2.23; H 5.77.Found: C 73.34; N2.34; H 5.64.^{1}H-NMR (300 MHz; CD_2Cl_2, 293 K): δ 7.00 (s, 14H), 6.97 (d, J_{H-H}= 7.8 Hz, 8H), 6.92 (s, 4H, $CH_{m\text{-}Ar}$), 6.74 (d, J_{H-H}= 8.0 Hz, 8H), 5.88 (s, 2H, $CH_{2\text{-}imid}$), 5.18 (s, 4H, CH), 2.28 (s, 24H, $CH_{3p\text{-}Tol}$), 2.25 (s, 6H, $CH_{3p\text{-}Ar}$). $^{13}C\{^1H\}$ NMR (75.4 MHz; CD_2Cl_2,293 K): δ 175.4 (s, C-Au), 141.6 (s, C_{Ar}), 140.5(s, C_{Ar}), 140.3 (s, C_{Tol}), 140.2 (s, C_{Tol}), 136.65 (s, C_{Tol}), 136.48 (s, C_{Tol}), 134.1(s, C_{Ar}), 130.3 (s, CH_{Ar}), 129.8 (s, CH_{Ar}), 129.49 (s, CH_{Tol}), 129.37 (s, CH_{Tol}), 123.6 (s, $CH_{2\text{-}imid}$), 50.8 (s, *C*H), 21.9 (s, $CH_{3\ p\text{-}Ar}$), 21.12 (s, $CH_{3\ p\text{-}Tol}$), 21.08 (s, $CH_{3\ p\text{-}Tol}$).

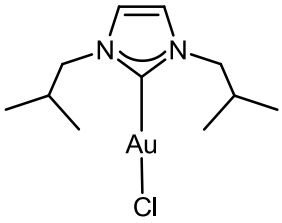


Preparation of [Au(IXy)Cl]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of IXy·HCl (100 mg, 0.320 mmol), [Au(DMS)Cl] (94.4 mg, 0.320 mmol) and K_2CO_3 (44.3 mg, 0.320 mmol) in acetone (1 mL) was stirred for 1 h at 60 ºC. A white solid was obtained. Yield: 156 mg (97%). Anal. Calcd. for $C_{19}H_{20}AuClN_2$: C 44.85; N 5.51; H 3.96. Found: C 44.75; N 5.47;H 3.87.^{1}H NMR(300 MHz, CD_2Cl_2 , 293 K): δ7.39 (m, 2H, CH_{Ar}), 7.27 (d, J_{H-H} = 7.6, 4H, CH_{Ar}),7.20 (s, 2H, CH_{imid}), 2.18 (s,12H, CH_3).^{13}C{^{1}H} NMR(75.4 MHz, CD_2Cl_2, 293 K): δ 173.5 (s, C-Au), 137.8 (s, C_{Ar}), 135.9 (s, C_{Ar}), 130.4 (s, CH_{Ar}), 129.3 (s, CH_{Ar}), 122.9 (s, CH_{imid}), 18.2 (s, CH_3).

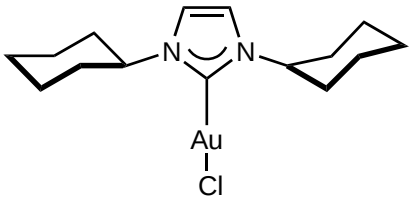


Preparation of [Au(IsB)Cl]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of IsB·HCl (100 mg, 0.461 mmol), [Au(DMS)Cl] (135.9 mg, 0.461 mmol) and K_2CO_3 (63.8 mg, 0.461 mmol) in acetone (1 mL) was stirred for 1 h at 60 ºC. A white solid was obtained. Yield: 168 mg (88%).Anal. Calcd. for $C_{11}H_{20}AuClN_2$: C 32.01; N 6.79; H 4.88. Found: C 31.97; N6.79; H 4.92.^{1}H NMR(300 MHz, CD_2Cl_2, 293 K): δ6.95 (s, 2H, CH_{imid}), 3.97 (d,J_{H-H} = 7.5 Hz,4H, CH_2), 2.23 (m, 2H, CH), 0.95(d, J_{H-H} = 6.7 Hz, 12H, CH_3). ^{13}C{^{1}H}

NMR(75.4 MHz, CD_2Cl_2, 293 K): δ 171.2 (s, C-Au), 121.3 (s, CH_{imid}), 59.1 (s, CH_2), 30.7 (s, CH), 20.1(s, CH_3).

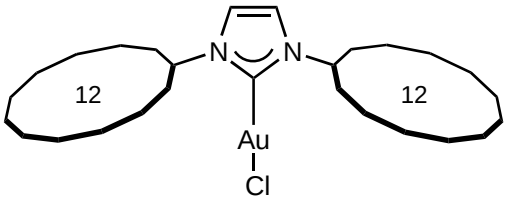


Preparation of [Au(ICy)Cl]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of ICy·HCl (100 mg, 0.371 mmol), [Au(DMS)Cl] (109.5 mg, 0.371 mmol) and K_2CO_3 (51.4 mg, 0.371 mmol) in acetone (1.0 mL) was stirred for 2 h at 60 ºC. A white solid was obtained. Yield: 129.3 mg (75%).^{1}H NMR (400 MHz; CD_2Cl_2, 293 K): δ7.00 (s, 2H, CH_{imid}), 4.56 (tt, J_{H-H}= 11.9, 3.9 Hz, 2H, CH), 2.08 (dd, J_{H-H}= 12.7, 2.0 Hz, 4H, CH_2), 1.89-1.86 (m, 4H, CH_2), 1.76-1.73 (m, 2H, CH_2), 1.61 (qd, J_{H-H}= 12.4, 3.4 Hz, 4H, CH_2), 1.47 (qt, J_{H-H}= 13.1, 3.2 Hz, 4H, CH_2), 1.22 (qt, J_{H-H}= 12.9, 3.7 Hz, 2H, CH_2).^{13}C{^{1}H} NMR (101 MHz; CD_2Cl_2, 298 K): δ 168.7 (s, C-Au), 117.6 (s, *C*H_{imid}), 61.4 (s, CH), 34.4 (s, CH_2), 25.8 (s, CH_2), 25.5 (s, CH_2).

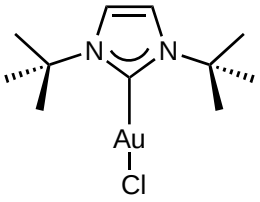


Preparation of [Au(IDD)Cl]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of IDD·HCl (100 mg, 0.228 mmol), [Au(DMS)Cl] (67.2 mg, 0.228 mmol) and K_2CO_3 (31.6 mg, 0.228 mmol) in acetone (1.0 mL) was stirred for 3 h at 60 ºC. A white solid was obtained. Yield: 101 mg (70%).^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 6.97 (s, 2H, CH_{imid}), 4.87 (quintet,

$J_{H\text{-}H}$= 6.5 Hz, 2H, $CH_{cyclododecanyl}$), 2.06-1.95 (m, 4H, CH_2), 1.66-1.48 (m, 10H, CH_2), 1.48-1.28 (m, 30H, CH_2). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 293 K): δ 170.0 (s, C-Au), 118.1 (s, CH_{imid}), 58.1 (s, $CH_{cyclododecanyl}$), 31.5 (s, CH_2), 24.2 (s, CH_2), 23.9 (s, CH_2), 23.7 (s, CH_2), 23.4 (s, CH_2), 22.0 (s, CH_2).



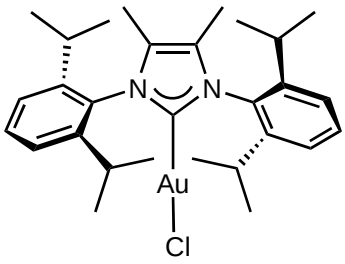
Preparation of [Au(I^{t}Bu)Cl]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of I^{t}Bu·HCl (100 mg, 0.461 mmol), [Au(DMS)Cl] (135.8 mg, 0.461 mmol) and K_2CO_3 (63.8 mg, 0.461 mmol) in acetone (1.0 mL) was stirred for 2 h at 60 ºC. A white solid was obtained. Yield: 114 mg (60%).^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.12 (s, 2H, CH_{imid}), 1.86 (s, 18H, CH_3).$^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 168.4 (s, C-Au), 116.8 (s, CH_{imid}), 59.22 (s, C_{tBu}), 31.9 (s, CH_3).



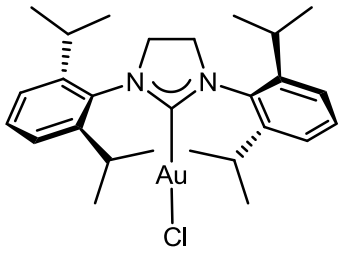
Preparation of [Au(IPr^{Me})Cl][3]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of IPr^{Me}·HCl (100 mg, 0.221 mmol), [Au(DMS)Cl] (65.0 mg, 0.221 mmol) and K_2CO_3 (30.5 mg, 0.221 mmol) in acetone (1.0 mL) was stirred for 5 h at 60 ºC. A white solid was obtained. Yield: 76 mg (53%). When the reaction was run using 2 equiv of K_2CO_3(61.0 mg, 0.442 mmol) the isolated yield was 78%.^{1}H NMR (400 MHz, CD_2Cl_2, 293 K): δ 7.57 (t, $J_{H\text{-}H}$= 7.8 Hz, 2H, CH_{Ar}), 7.36 (d, $J_{H\text{-}H}$= 7.8 Hz, 4H, CH_{Ar}), 2.47 (sept, $J_{H\text{-}H}$= 6.9 Hz, 4H, CH(CH_3)$_2$),

[3] Gaillard, S.; Bantreil, X.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans*. **2009**, *68*, 7949-7955

1.95 (s, 6H, CH_3), 1.34 (d, J_{H-H} = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.25 (d, J_{H-H} = 6.9 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (101 MHz; CD_2Cl_2, 293 K): δ 171.3 (s, C-Au), 146.4 (s, C_{Ar}), 132.9 (s, C_{Ar}), 130.9 (s, CH_{Ar}), 126.8 (s, $C_{2\text{-imid}}$), 124.7 (s, CH_{Ar}), 29.0 (s, CH(CH$_3$)$_2$), 25.2 (s, CH(CH$_3$)$_2$), 23.5 (s, CH(CH$_3$)$_2$), 9.9 (s, CH$_3$).

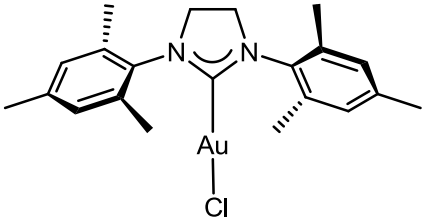


Preparation of [Au(SIPr)Cl].[2] This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of SIPr·HCl (100 mg, 0.234 mmol), [Au(DMS)Cl] (69.0 mg, 0.234 mmol) and K_2CO_3 (32.9 mg, 0.234 mmol) in acetone (1.0 mL) was stirred for 24 h at 60 ºC. A white solid was obtained. Yield: 114 mg (78%). ^{1}H NMR(300 MHz, CD_2Cl_2 , 293 K): δ 7.48 (t, J_{H-H} = 7.7, 2H, CH_{Ar}), 7.29 (d, J_{H-H} = 7.7, 4H, CH_{Ar}), 4.06 (s, 4H, $CH_{2\text{-imid}}$), 3.07 (sept, J_{H-H} = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 1.40 (d, J_{H-H} = 6.9, 12H, CH(CH_3)$_2$), 1.34 (d, J_{H-H} = 6.9, 12H, CH(CH_3)$_2$).^{13}C{^{1}H} NMR(75.4 MHz, CD_2Cl_2, 293 K): δ 196.4 (s, C-Au), 147.3 (s, C_{Ar}), 134.7 (s, C_{Ar}), 130.5 (s, C_{Ar}), 125.2 (s, C_{Ar}), 54.1 (s, $CH_{2\text{-imid}}$), 29.5 (s, CH(CH$_3$)$_2$), 25.4 (s, CH(CH$_3$)$_2$), 24.4 (s, CH(CH$_3$)$_2$).

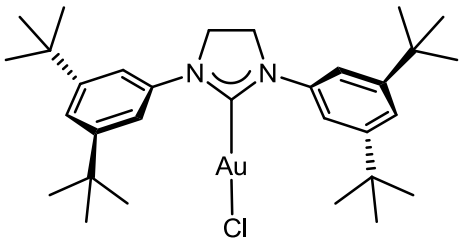


Preparation of [Au(SIMes)Cl].[2]This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of SIMes·HCl (100 mg, 0.292

mmol), [Au(DMS)Cl] (86.1 mg, 0.292 mmol) and K_2CO_3 (40.4 mg, 0.292 mmol) in acetone (1.0 mL) was stirred for 24 h at 60 ºC. A white solid was obtained. Yield: 129 mg(82%). ^{1}H NMR(300 MHz, CD_2Cl_2 , 293 K): δ7.02 (s,4H, CH_{Ar}), 4.00 (s, 4H, $CH_{2\text{-}imid}$), 2.33 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ195.1 (s, C-Au), 139.5 (s, C_{Ar}), 136.2 (s, C_{Ar}), 135.1 (s, C_{Ar}), 130.0 (s, CH_{Ar}), 51.1 (s, $CH_{2\text{-}imid}$), 21.3 (s, CH_3), 18.2 (s, CH_3).

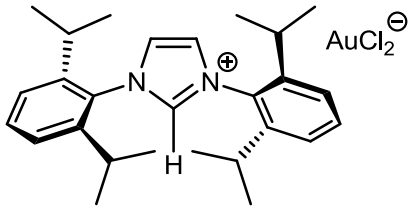


Preparation of [Au(SITb)Cl]. This complex was prepared following the same procedure as for the synthesis of [Au(IPr)Cl]. A mixture of SITb·HCl (100 mg, 0.207 mmol), [Au(DMS)Cl] (61.1 mg, 0.207 mmol) and K_2CO_3 (28.7 mg, 0.207 mmol) in acetone (1.0 mL) was stirred for 24 h at 60 ºC. A white solid was obtained. Yield: 96 mg (68%). Anal. Calcd. for $C_{31}H_{16}AuClN_2$: C 54.82; N 4.12; H 6.83. Found: C 54.75; N 4.23;H 6.88. ^{1}H NMR(300 MHz, CD_2Cl_2 ,293 K): δ 7.56 (d, $J_{H\text{-}H}$ = 1.7, 4H, CH_{Ar}), 7.41 (t, $J_{H\text{-}H}$ = 1.7, 2H, CH_{Ar}), 4.31 (s, 4H, CH_{imid}), 1.37(s, 36H, CH_3).$^{13}C\{^1H\}$ NMR(75.4 MHz, CD_2Cl_2, 293 K): δ190.5 (s, C-Au),152.7(s, C_{Ar}), 140.8 (s, C_{Ar}), 121.9 (s, CH_{Ar}), 118.0 (s, CH_{Ar}), 51.7 (s, $CH_{2\text{-}imid}$), 35.6 (s, $C(CH_3)_3$), 31.6 (s, $C(CH_3)_3$).



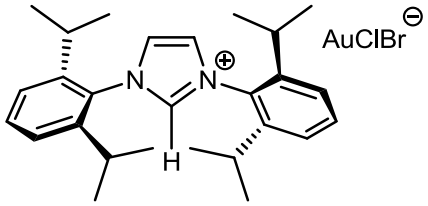
Preparation of[IPrH][$AuCl_2$] (3).A vial was charged, under air, with IPr·HCl (100 mg, 0.235 mmol), and [Au(DMS)Cl] (69.3 mg, 0.235 mmol). The resulting mixture was

dissolved in acetone (1.0 mL) and stirred for 10 min at r.t. After this time the mixture was filtered through Celite. The solvent was concentrated and pentane (3 mL) was added, affording a white solid which was washed with further portions of pentane (3 x 1 mL)and dried under vacuum. Yield: 141 mg (91%). Anal. Calcd. for $C_{27}H_{37}AuCl_2N_2$: C 49.32; N 4.26; H 5.67. Found: C 49.27; N 4.30; H 5.69. ^{1}H NMR(300 MHz, CD_2Cl_2, 293 K): δ8.89 (t, J_{H-H} = 1.5, 1H, CH_{NCN}), 7.79 (d, J_{H-H} = 1.5, 2H, CH_{imid}), 7.66 (t, J_{H-H} = 7.9, 2H, CH_{Ar}), 7.42 (d, J_{H-H} = 7.9, 4H, CH_{Ar}), 2.41 (sept, J_{H-H} = 6.9, 4H, C*H*$(CH_3)_2$), 1.31 (d, J_{H-H} = 6.9, 12H, CH(C*H*$_3)_2$), 1.24 (d, J_{H-H} = 6.9, 12H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR(75.4 MHz, CD_2Cl_2, 293 K): δ145.4 (s, C_{Ar}), 137.7 (s, CH_{NCN}), 133.2 (s, C_{Ar}), 129.9 (s, C_{Ar}), 126.7 (s, CH_{imid}), 125.6 (s, CH_{Ar}), 29.8 (s, *C*H$(CH_3)_2$), 25.0 (s, CH(*C*H$_3)_2$), 24.1 (s, CH(*C*H$_3)_2$).

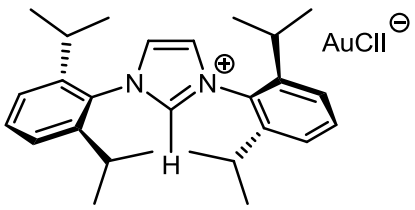


Preparation of [IPrH][AuClBr] (6).A vial was charged, under air, with IPr·HBr (50 mg, 0.106 mmol), and [Au(DMS)Cl] (31.4 mg, 0.106 mmol). The resulting mixture was dissolved in acetone (0.5 mL) and stirred for 10 min at r.t. After this time the mixture was filtered through Celite. The solvent was concentrated and pentane (3 mL) was added, affording a white solid which was washed with further portions of pentane (3 x 1 mL)and dried under vacuum. Yield: 73 mg (98%). Anal. Calcd. for $C_{27}H_{37}AuBrClN_2$: C 46.20; N 3.99; H 5.31. Found: C 46.34; N 4.14; H 5.45. ^{1}H NMR(300 MHz, CD_2Cl_2, 293 K): δ8.98 (t, J_{H-H} = 1.5, 1H, CH_{NCN}), 7.80 (d, J_{H-H} = 1.5, 2H, CH_{imid}), 7.65 (t, J_{H-H} = 7.8, 2H, CH_{Ar}), 7.42 (d, J_{H-H} = 7.8, 4H, CH_{Ar}), 2.41 (sept, J_{H-H} = 6.9, 4H, C*H*$(CH_3)_2$), 1.30 (d, J_{H-H} = 6.9, 12H, CH(C*H*$_3)_2$), 1.24 (d, J_{H-H} = 6.8, 12H, CH(C*H*$_3)_2$). ^{13}C{^{1}H}

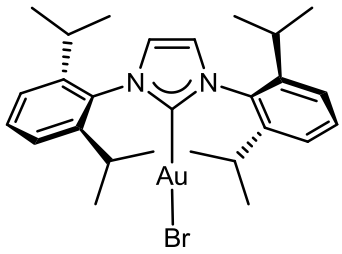
NMR(75.4 MHz, CD_2Cl_2, 293 K): δ145.5 (s, C_{Ar}), 137.6 (s, CH_{NCN}), 133.1 (s, C_{Ar}), 129.9 (s, C_{Ar}), 126.7 (s, CH_{imid}), 125.6 (s, CH_{Ar}), 29.7 (s, *C*H(CH_3)$_2$), 25.0 (s, CH(*C*H_3)$_2$), 24.2 (s, CH(*C*H_3)$_2$).



Preparation of [IPrH][AuClI] (7).A vial was charged, under air, with IPr·HBr (50 mg, 0.097 mmol), and [Au(DMS)Cl] (28.6 mg, 0.097 mmol). The resulting mixture was dissolved in acetone (0.5 mL) and stirred for 10 min at r.t. After this time the mixture was filtered through Celite. The solvent was concentrated and pentane (3 mL) was added, affording a white solid which was washed with further portions of pentane (3 x 1 mL) and dried under vacuum. Yield: 71 mg (98%). Anal. Calcd. for $C_{27}H_{37}AuIClN_2$: C 43.30; N 3.74; H 4.98. Found: C 43.37; N 3.86; H 5.01. ^{1}H NMR (300 MHz, CD_2Cl_2 , 293 K): δ 8.89 (t, J_{H-H} = 1.5, 1H, CH_{NCN}), 7.81 (d, J_{H-H} = 1.6, 2H, CH_{imid}), 7.66 (t, J_{H-H} = 7.8, 2H, CH_{Ar}), 7.43 (d, J_{H-H} = 7.8, 4H, CH_{Ar}), 2.41 (sept, J_{H-H} = 6.8, 4H, C*H*(CH_3)$_2$), 1.31 (d, J_{H-H} = 6.9, 12H, CH(C*H*$_3$)$_2$), 1.24 (d, J_{H-H} = 6.8, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 145.5 (s, C_{Ar}), 137.5 (s, CH_{NCN}), 133.2 (s, C_{Ar}), 129.9 (s, C_{Ar}), 126.7 (s, CH_{imid}), 125.6 (s, CH_{Ar}), 29.7 (s, *C*H(CH_3)$_2$), 25.0 (s, CH(*C*H_3)$_2$), 24.2 (s, CH(*C*H_3)$_2$).

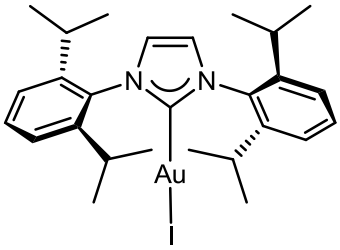


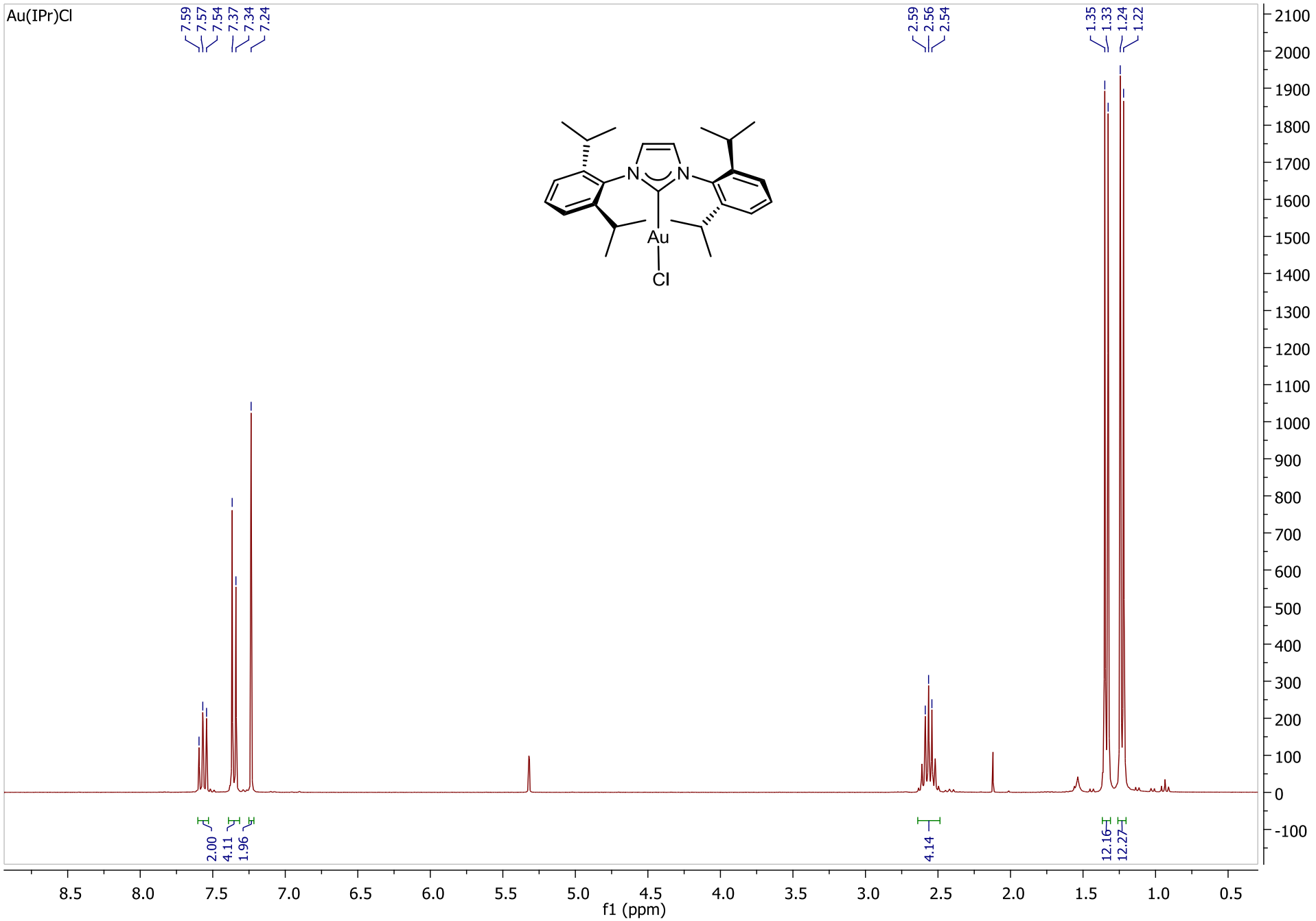
Preparation of [Au(IPr)Br] (8).A vial was charged, under air, with IPr·HBr (100 mg, 0.213 mmol), [Au(DMS)Cl] (62.7 mg, 0.213 mmol) and finely ground K_2CO_3 (29.4mg, 0.213 mmol). The resulting mixture was dissolved in acetone (1.0 mL) and stirred for 2 h at 60 ºC. After this time the solvent was removed in vacuo and dichloromethane was added. The mixture was filtered through silica. The pad of silica was washed with dichloromethane (3 x 1 mL). The solvent was concentrated and pentane (3 mL) was added, affording a white solid which was washed with further portions of pentane (3 x 1 mL) and dried under vacuum. Yield: 121 mg (85%). Anal. Calcd. for $C_{27}H_{36}AuBrN_2$: C 48.73; N 4.21; H 5.45. Found: C 48.68; N 4.19; H 5.57.^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.57 (t, J_{H-H} = 7.8, 2H, CH_{Ar}), 7.35 (d, J_{H-H} = 7.8, 4H, CH_{Ar}), 7.24 (s, 2H, CH_{imid}), 2.57 (sept, J_{H-H} = 6.9, 4H, C*H*$(CH_3)_2$), 1.34 (d, J_{H-H} = 6.9, 12H, CH(C*H*$_3)_2$), 1.23 (d, J_{H-H} = 6.9, 12H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 293 K): δ179.0 (s, C-Au), 146.3 (s, C_{Ar}), 134.6 (s,C_{Ar}), 131.2 (s, C_{Ar}), 124.8 (s, C_{Ar}), 123.8 (s, C_{imid}), 29.3 (s, *C*H$(CH_3)_2$), 24.7 (s, CH(*C*H$_3)_2$), 24.3 (s, CH(*C*H$_3)_2$).



Preparation of [Au(IPr)I] (9). A vial was charged, under air, with IPr·HBr (100 mg, 0.194 mmol), [Au(DMS)Cl] (57.1 mg, 0.194 mmol) and finely ground K_2CO_3 (26.8 mg, 0.194 mmol). The resulting mixture was dissolved in acetone (1.0 mL) and stirred for 2 h at 60 ºC. After this time the solvent was removed in vacuo and dichloromethane was added. The mixture was filtered through silica. The pad of silica was washed with dichloromethane (3 x 1 mL). The solvent was concentrated and pentane (3 mL) was

added, affording a white solid which was washed with further portions of pentane (3 x 1 mL) and dried under vacuum. Yield: 119 mg (86%). Anal. Calcd. for $C_{27}H_{36}AuIN_2$: C 45.52; N 3.93; H 5.09. Found: C 45.53; N 3.87; H 5.19.^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.57 (t, $J_{H\text{-}H}$ = 7.8, 2H, CH_{Ar}), 7.35 (d, $J_{H\text{-}H}$ = 7.8, 4H, CH_{Ar}), 7.24 (s, 2H, CH_{imid}), 2.58 (sept, $J_{H\text{-}H}$ = 6.9, 4H, C*H*$(CH_3)_2$), 1.34 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$), 1.23 (d, $J_{H\text{-}H}$ = 6.9, 12H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 185.5 (s, C-Au), 146.3 (s, C_{Ar}), 134.4 (s,C_{Ar}), 131.2 (s, C_{Ar}), 124.7 (s, C_{Ar}), 123.7 (s, C_{imid}), 29.3 (s, *C*H$(CH_3)_2$), 24.7 (s, CH(*C*H$_3)_2$), 24.3 (s, CH(*C*H$_3)_2$).

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7.54
7.37
7.34
7.24
2.59
2.56
2.54
1.35
1.33
1.24
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N
N
Au
Cl
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4.11
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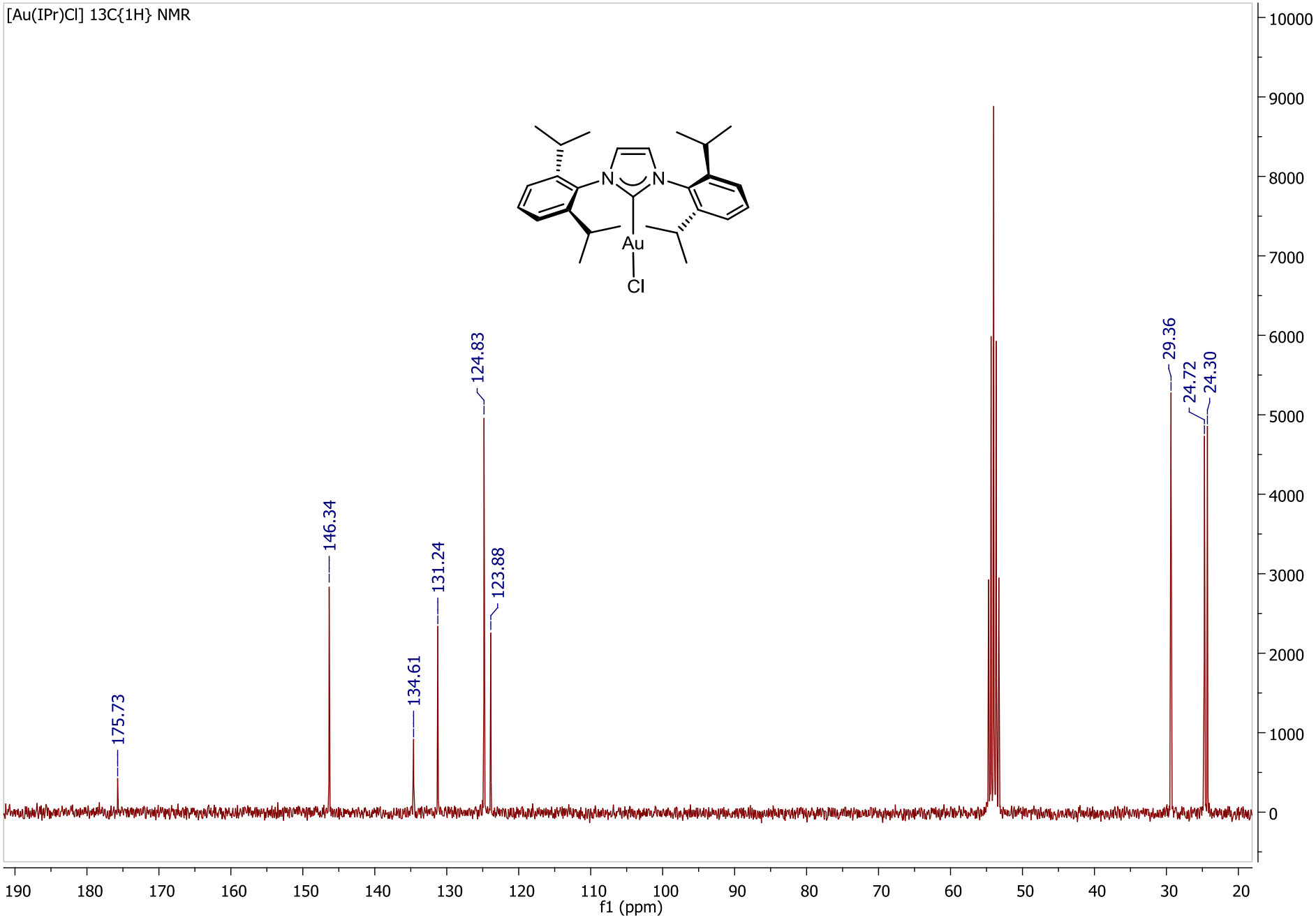
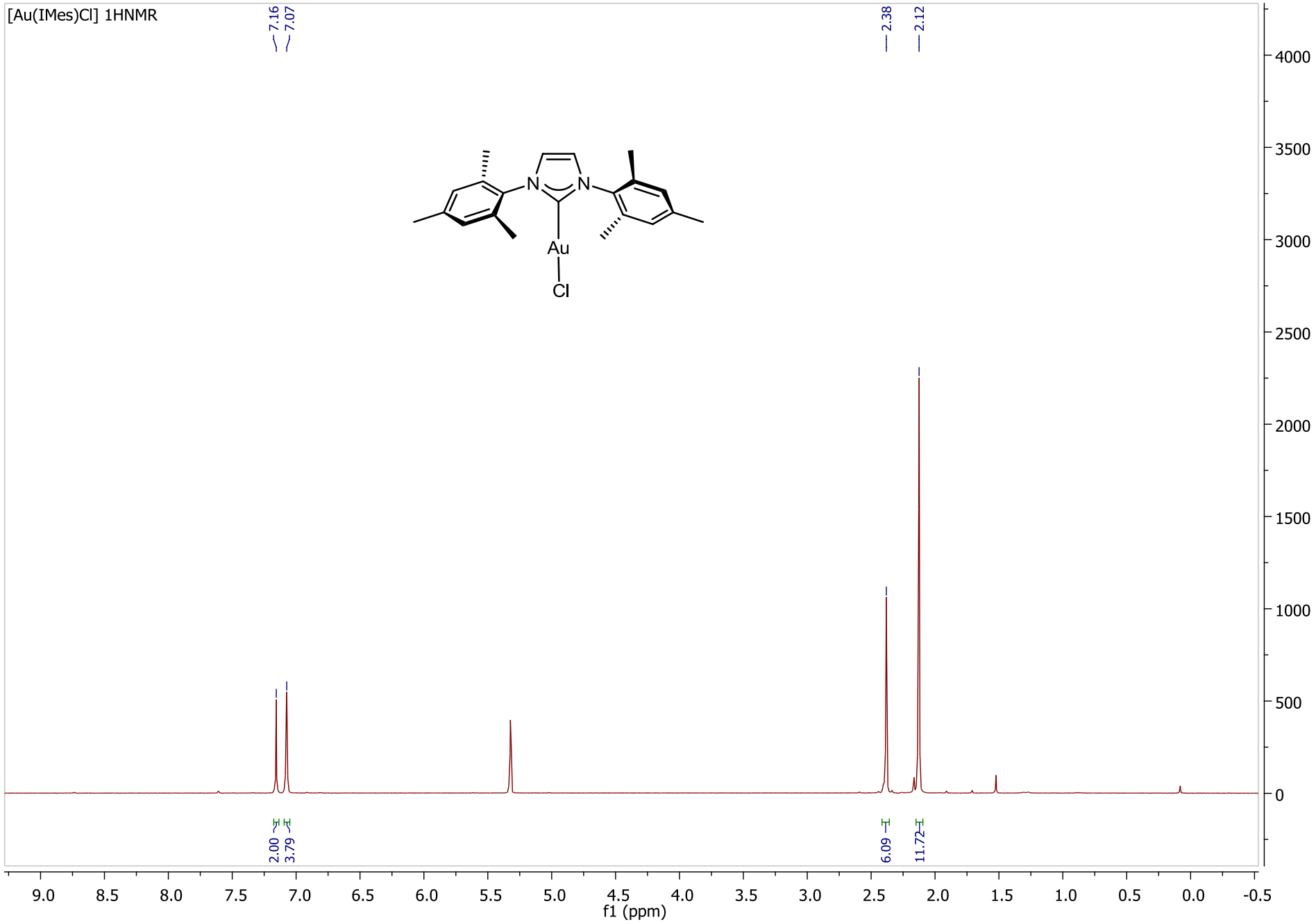
4.14
12.16
12.27
f1 (ppm)




[Au(IMes)Cl] 1HNMR
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7.07
2.38
2.12
N
N
Au
Cl
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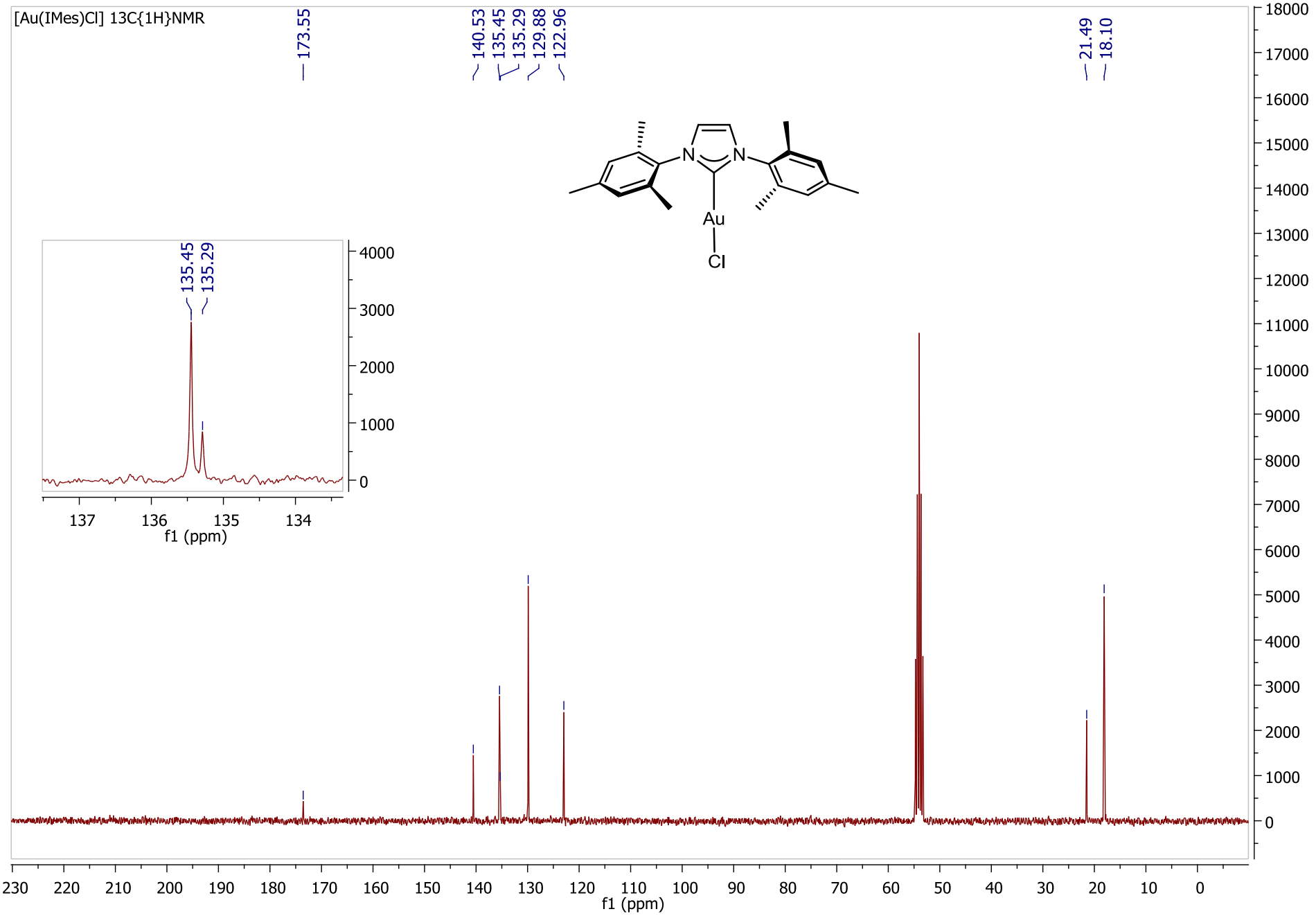
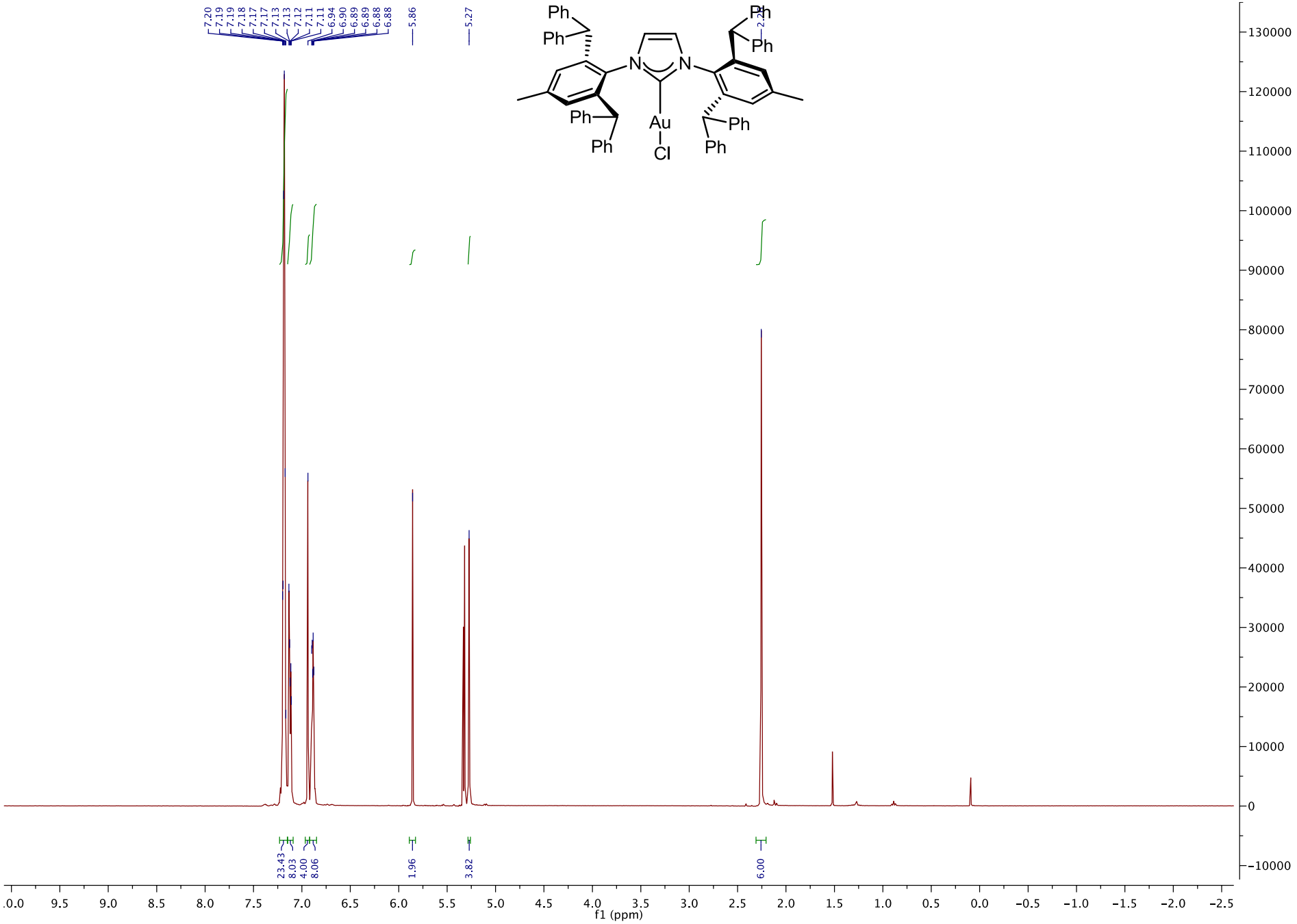
3.79
6.09
11.72
4000
3500
3000
2500
2000
1500
1000
500
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)




7.20
7.19
7.19
7.18
7.17
7.17
7.13
7.13
7.12
7.11
7.11
6.94
6.90
6.89
6.89
6.88
6.88
5.86
5.27
2.21
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
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Au
Cl
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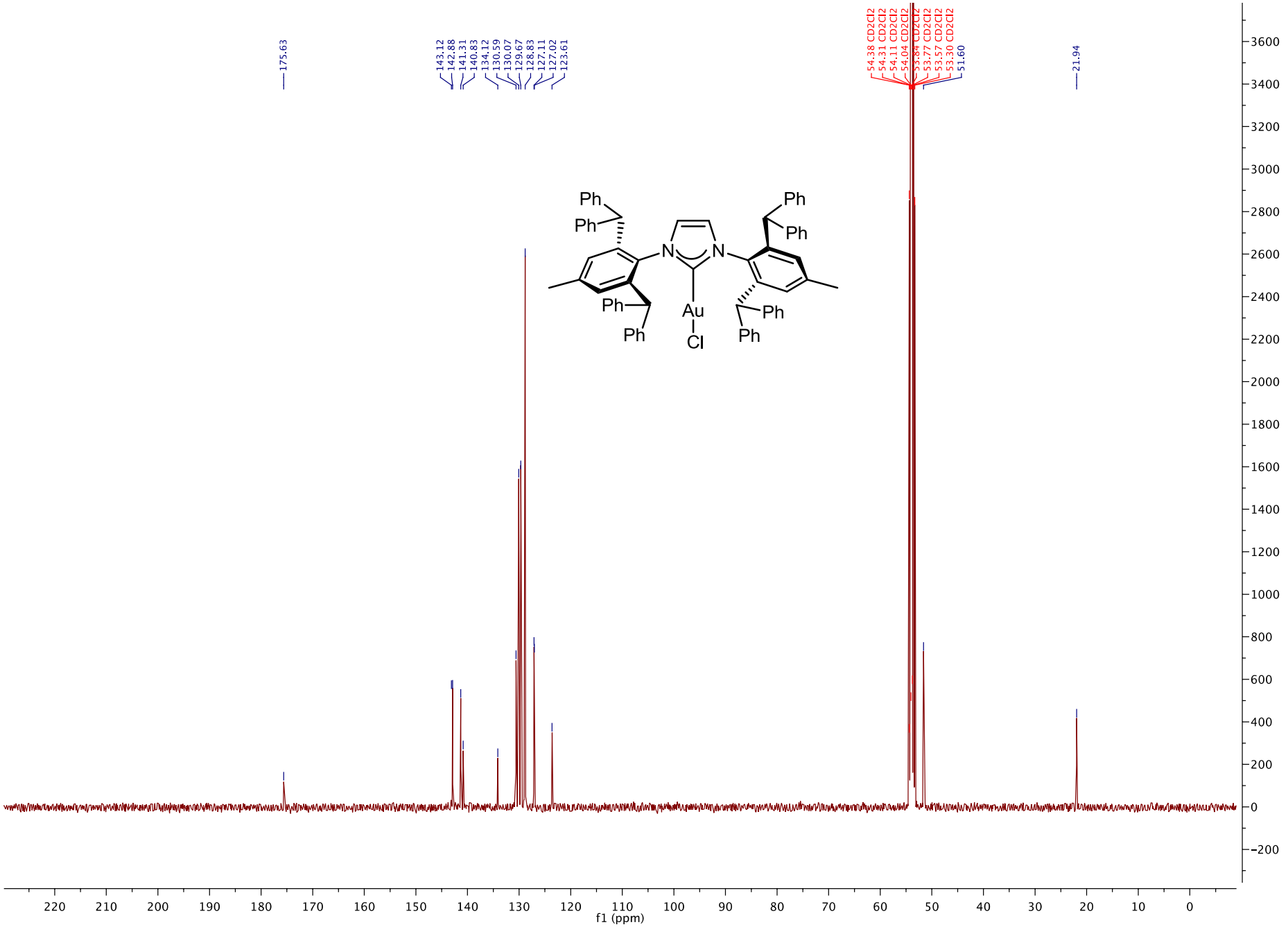
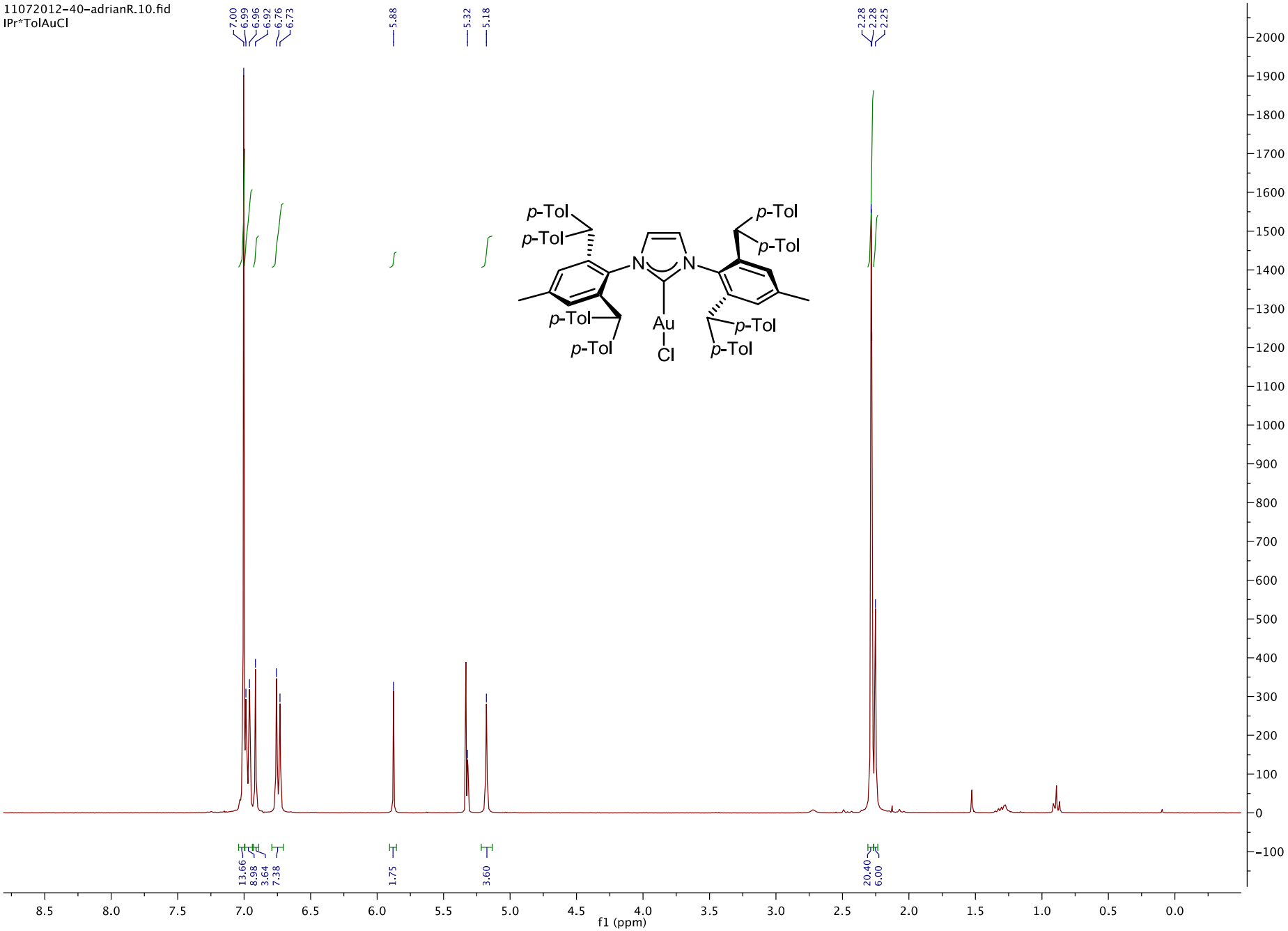
4.00
8.06
1.96
3.82
6.00
f1 (ppm)

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6.96
6.92
6.76
6.73
5.88
5.32
5.18
2.28
2.28
2.25
p-Tol
p-Tol
p-Tol
p-Tol
p-Tol
p-Tol
p-Tol
p-Tol
N
N
Au
Cl
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3.64
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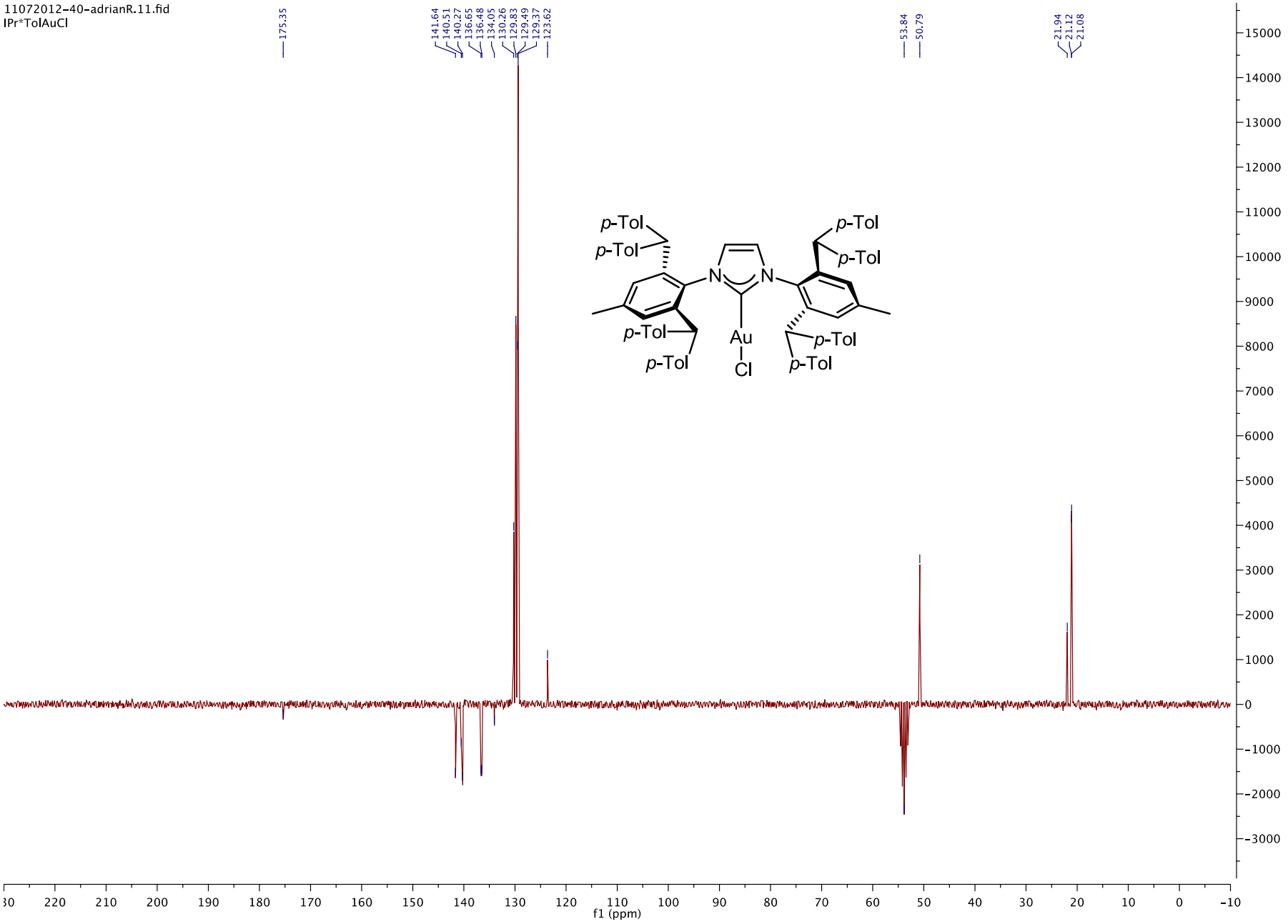
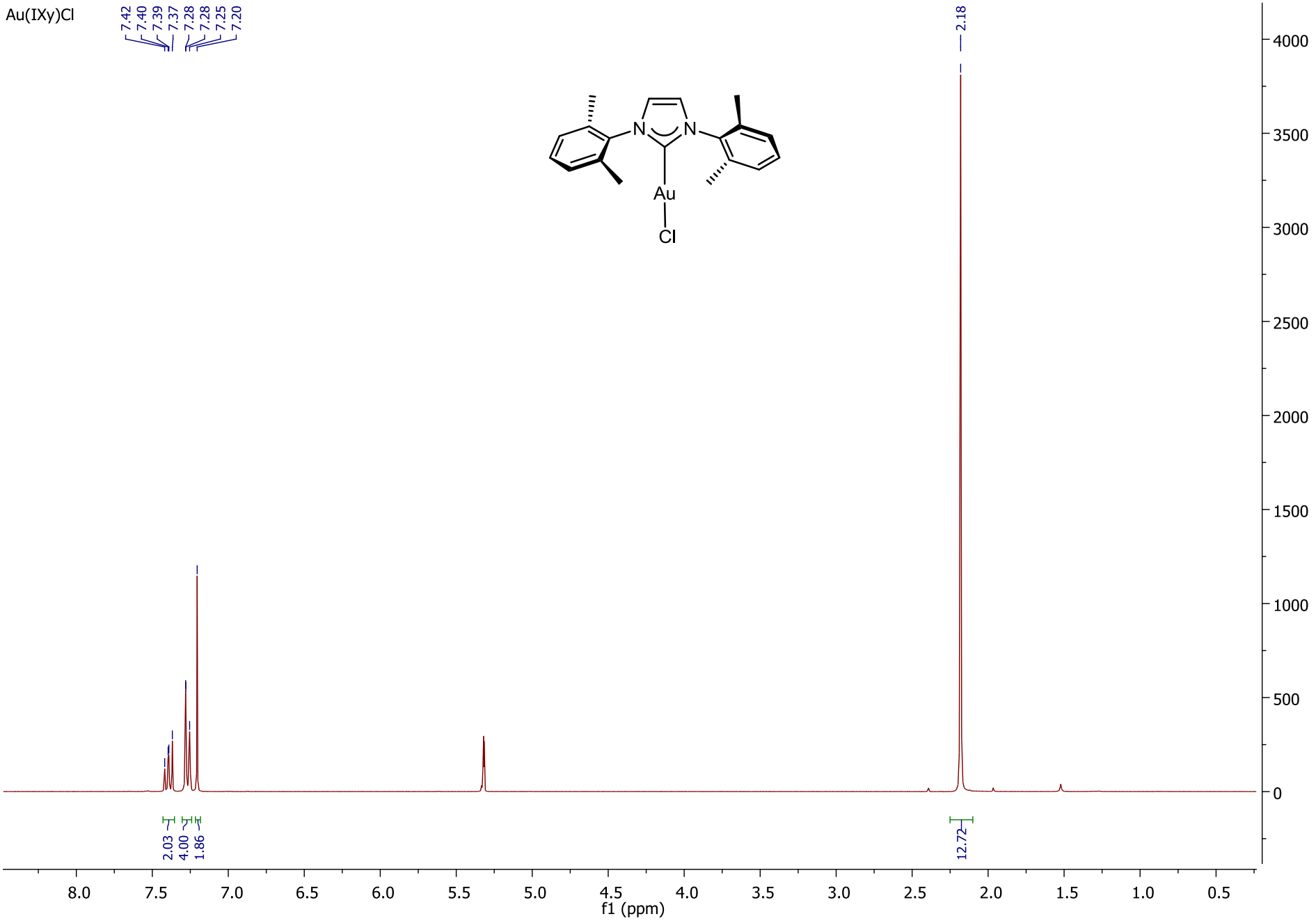
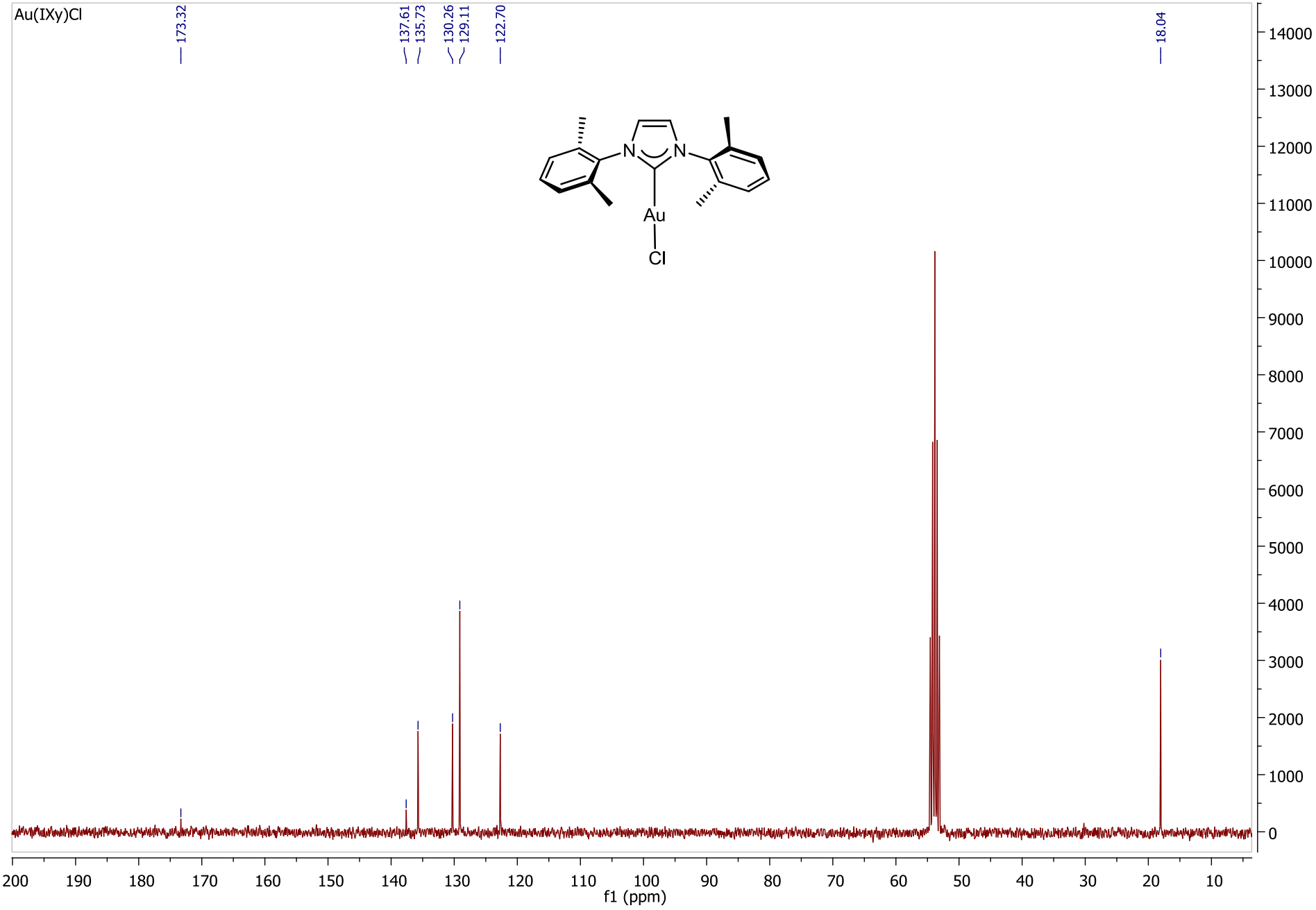
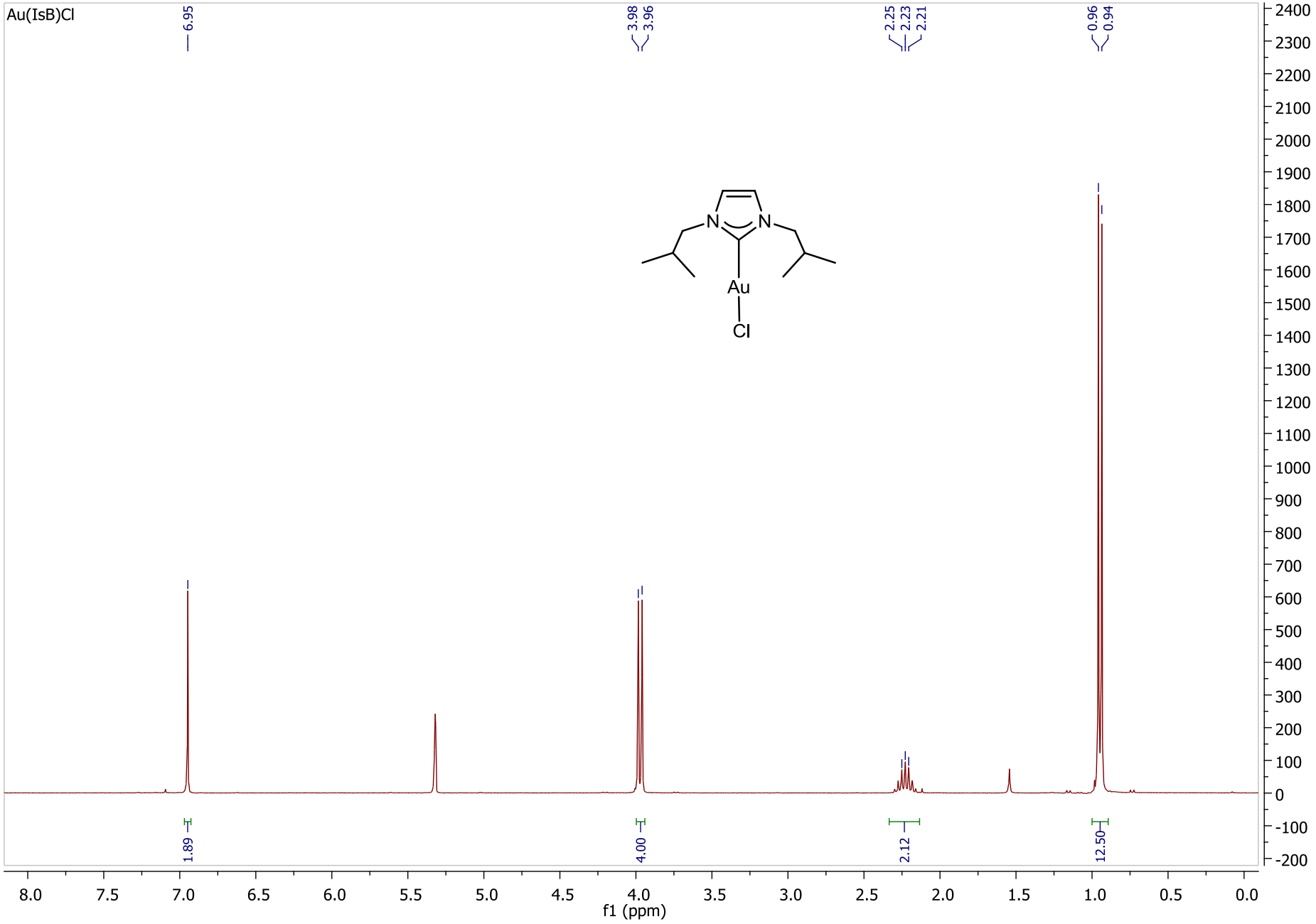
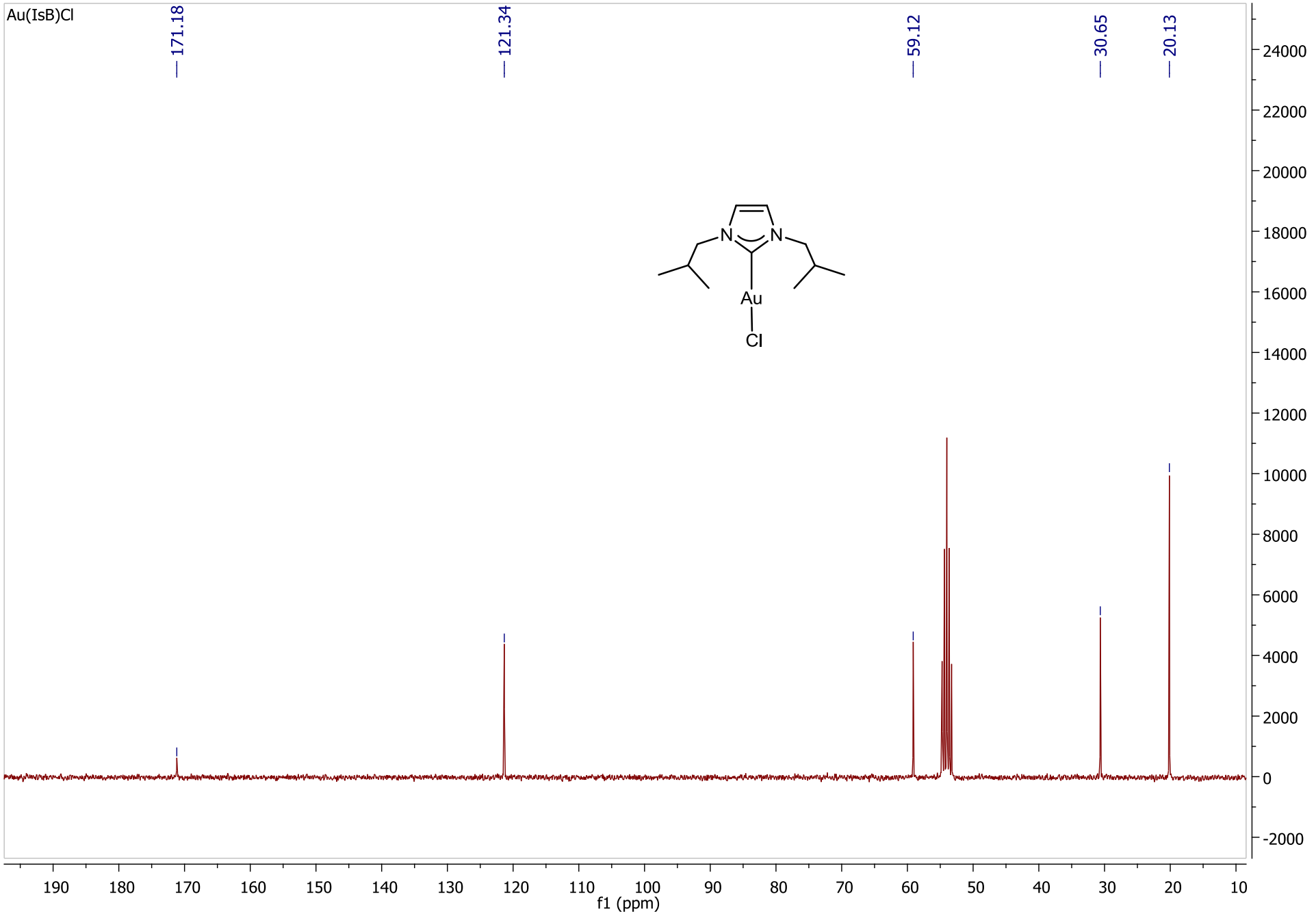
3.60
20.40
6.00
f1 (ppm)

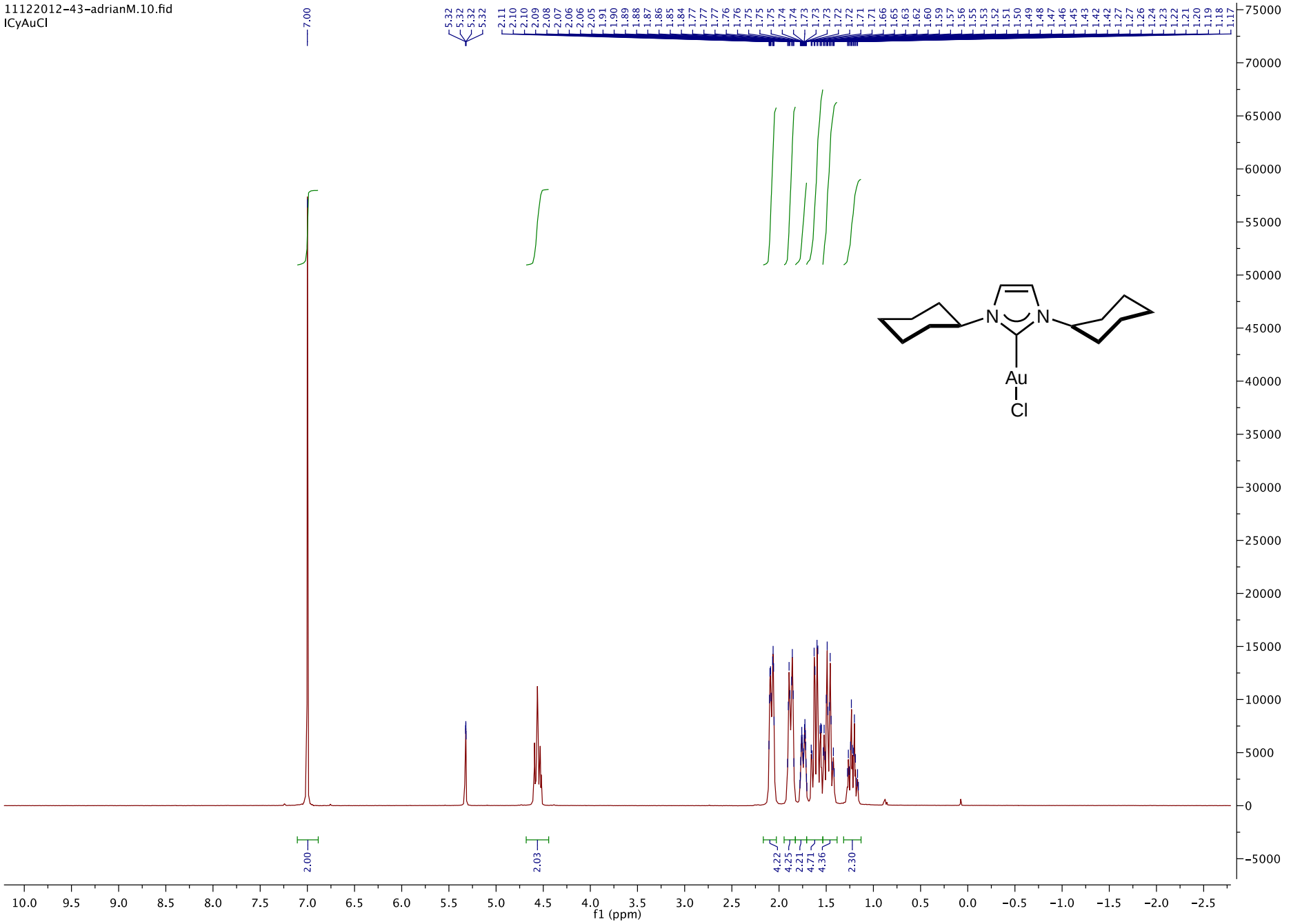


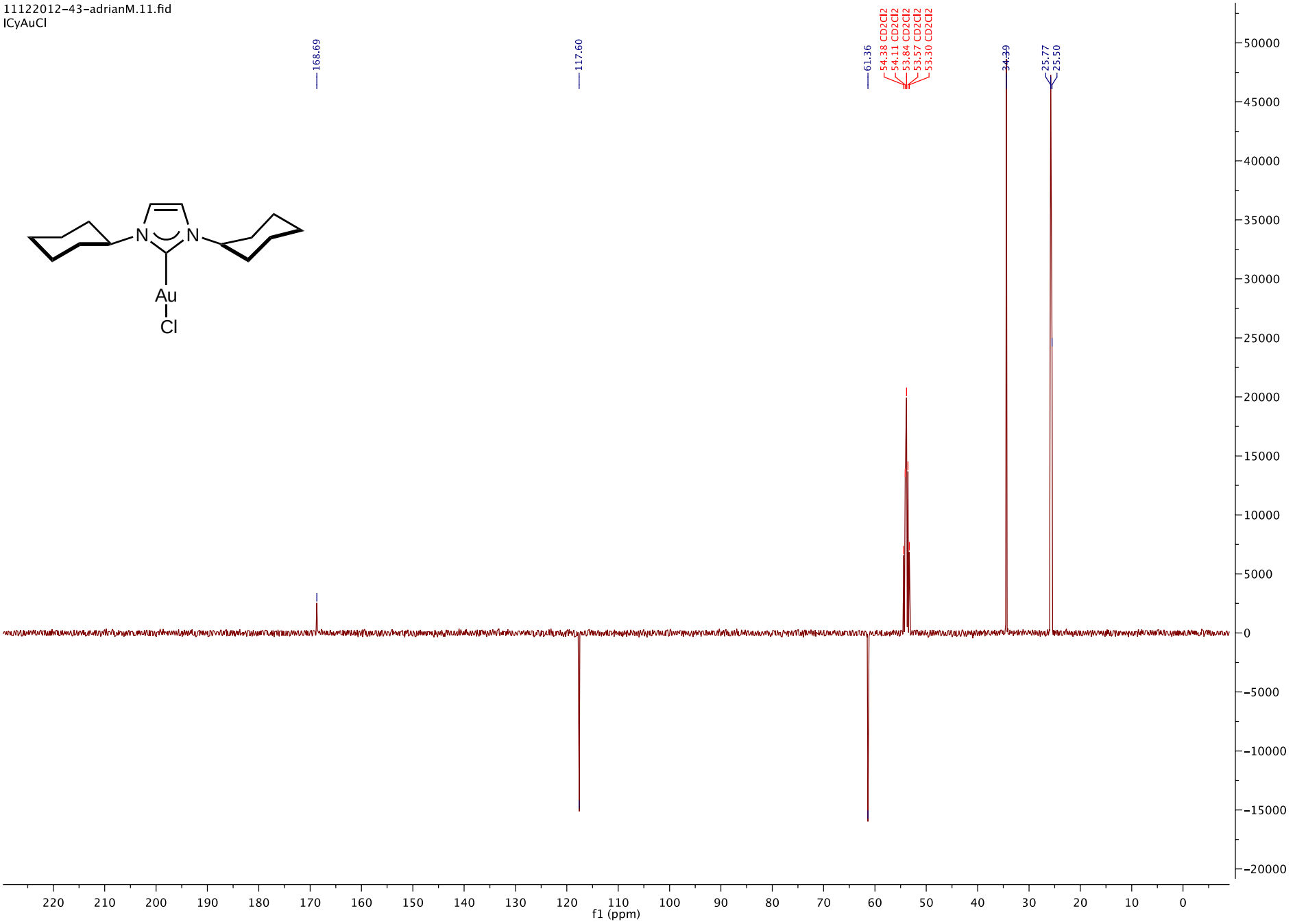


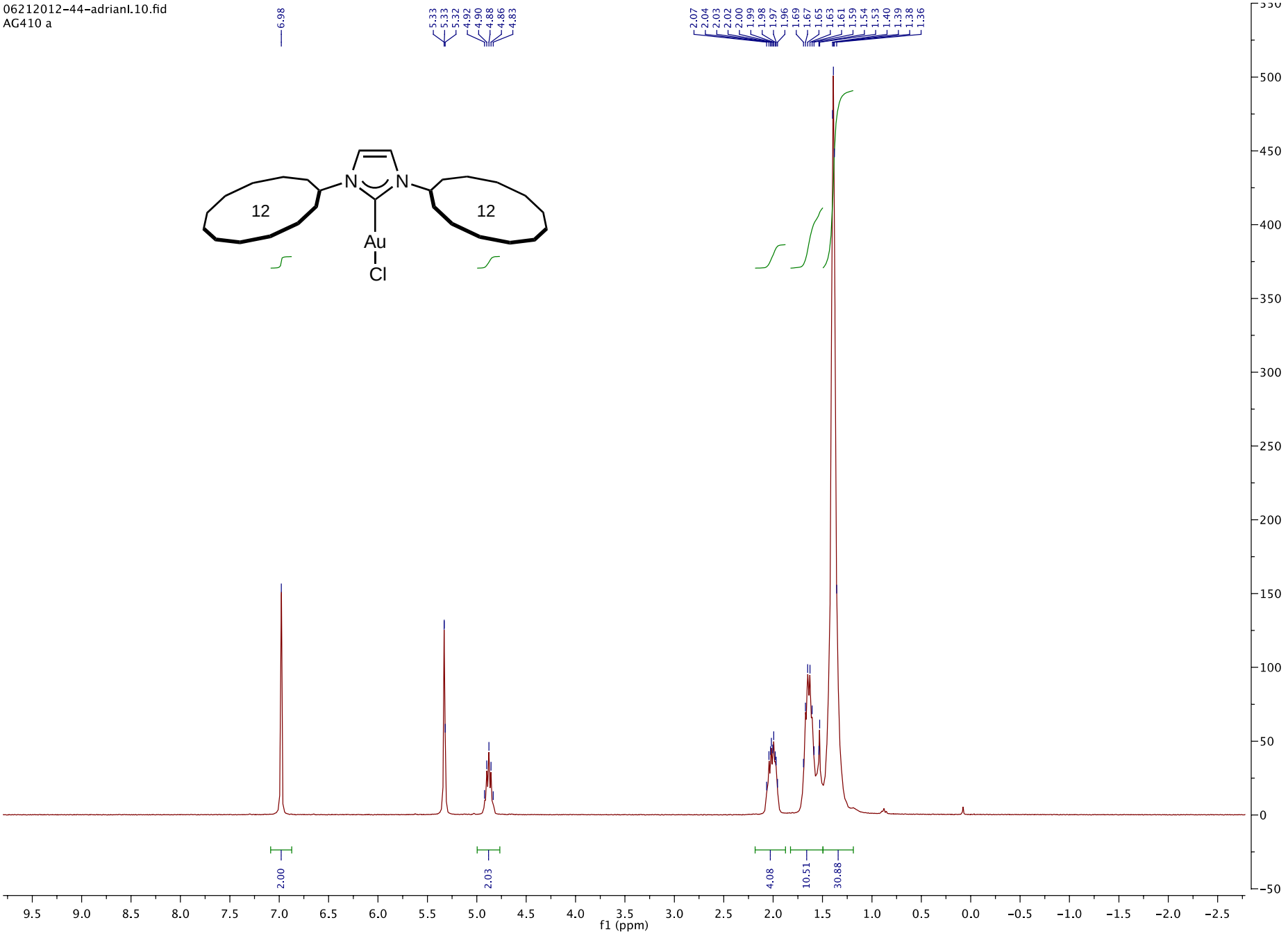








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4.88
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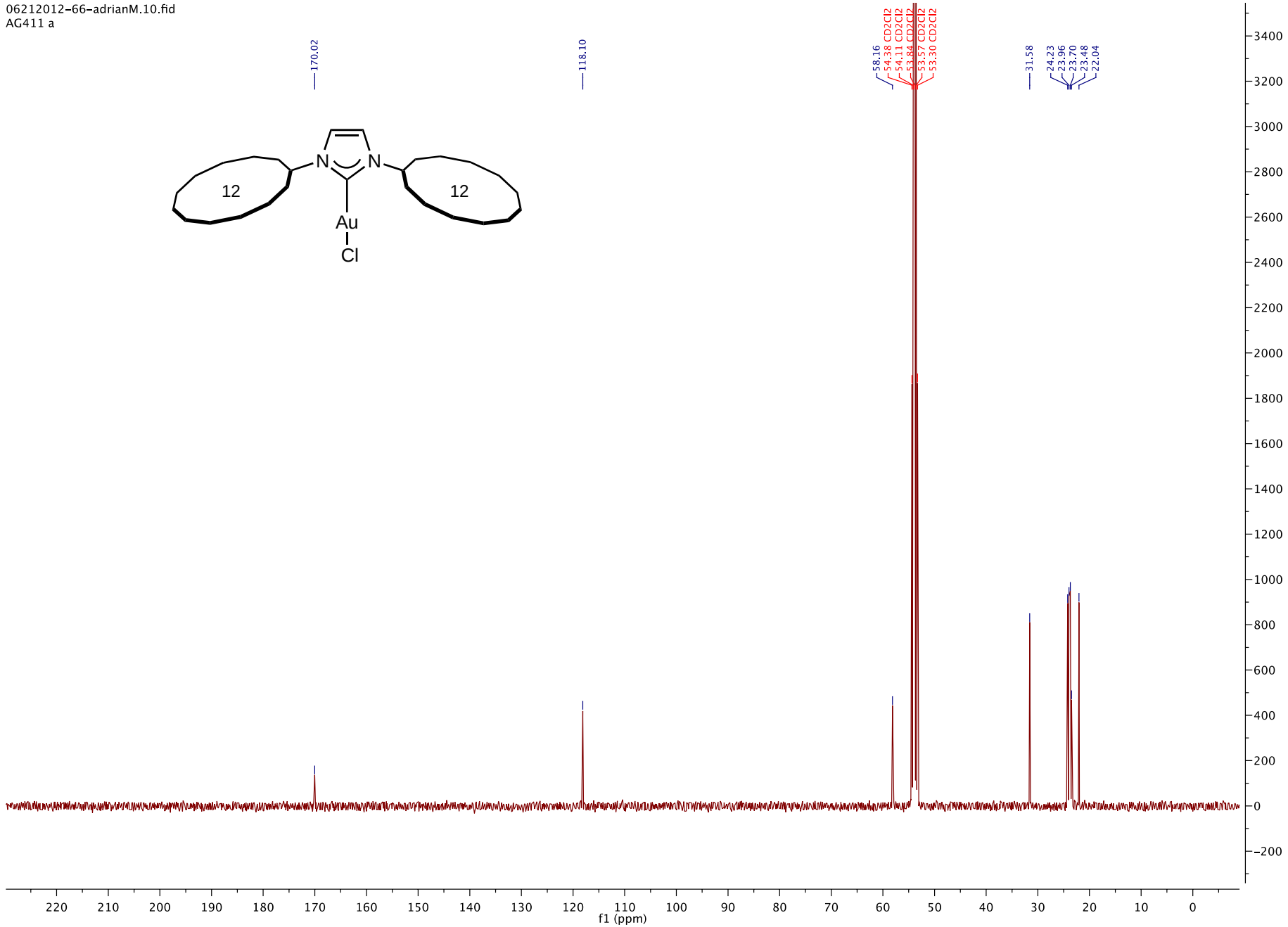
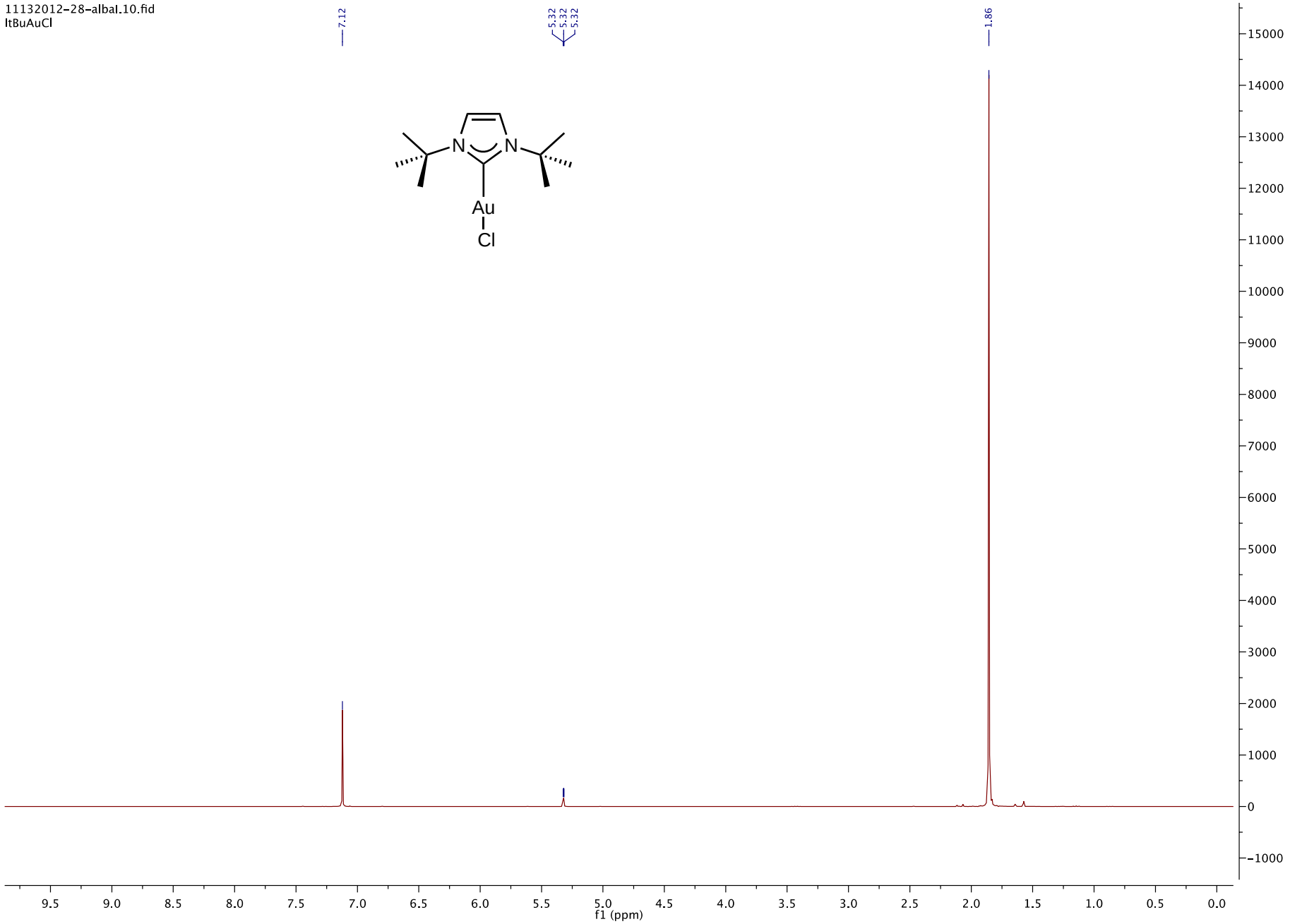
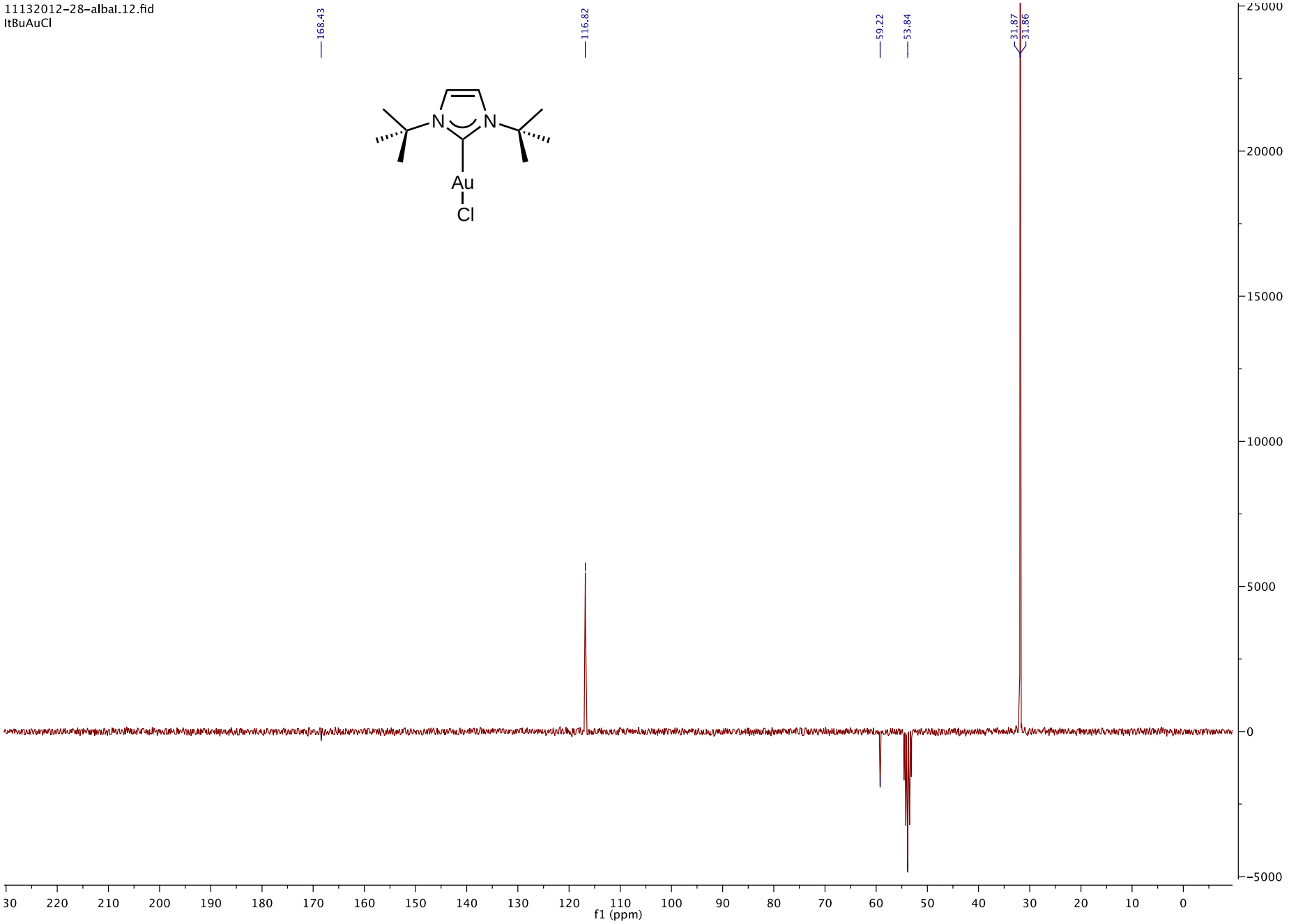
10.51
30.88
f1 (ppm)



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31.86
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Au
Cl
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15000
10000
5000
0
-5000
30
220
210
200
190
180
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120
110
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90
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50
40
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10
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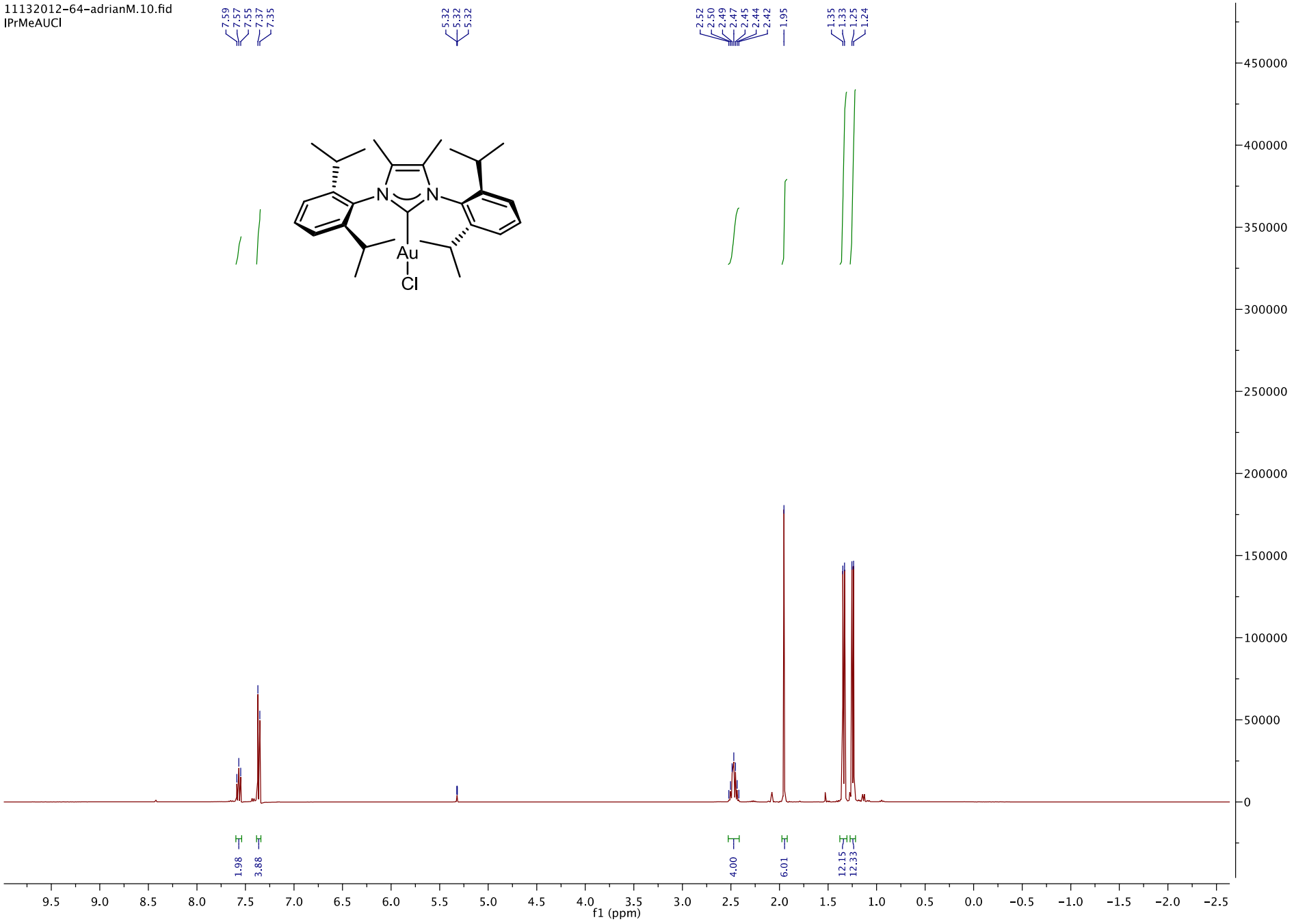
f1 (ppm)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1.33
1.25
1.24
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N
Au
Cl
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350000
300000
250000
200000
150000
100000
50000
0
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3.88
4.00
6.01
12.15
12.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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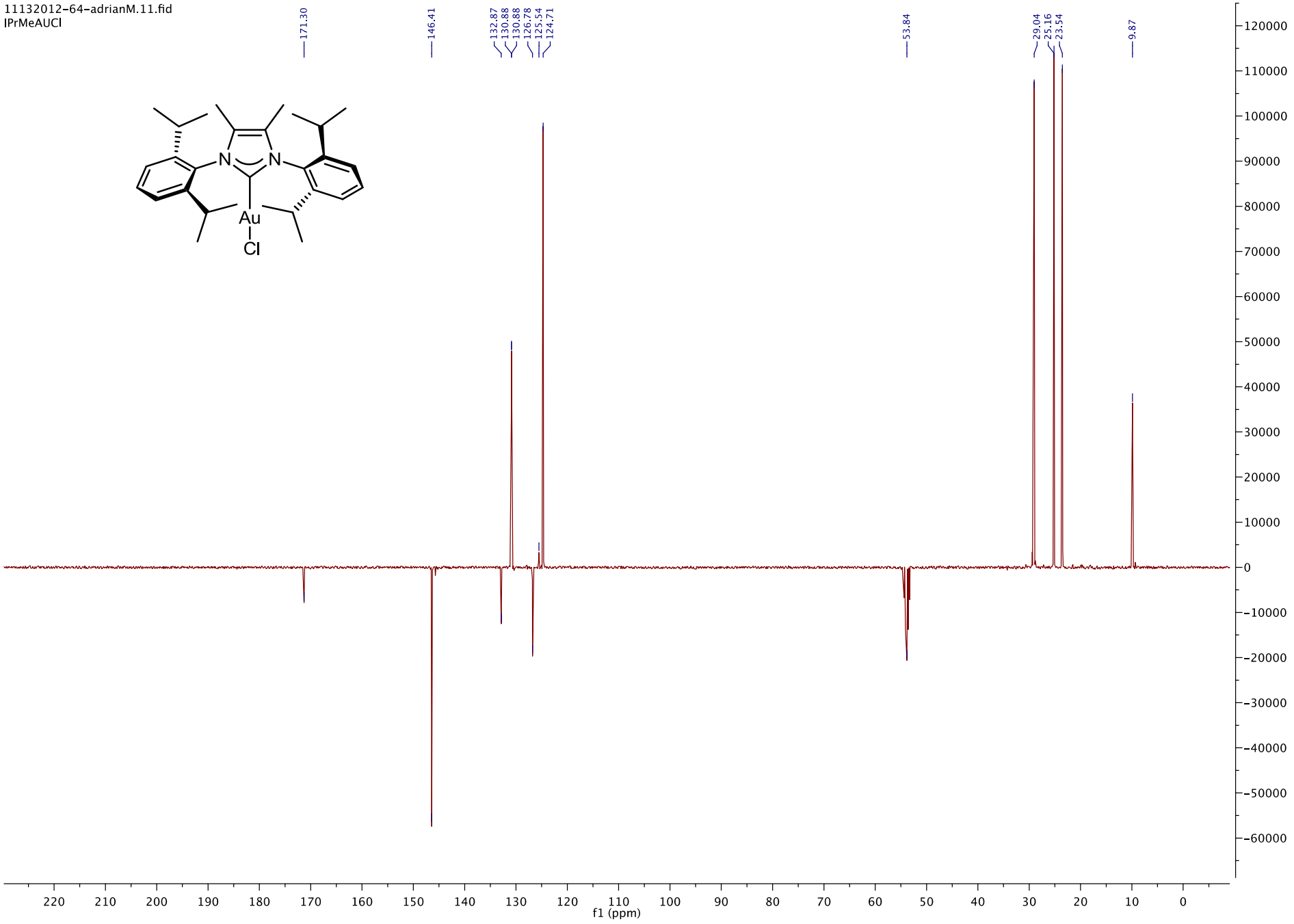
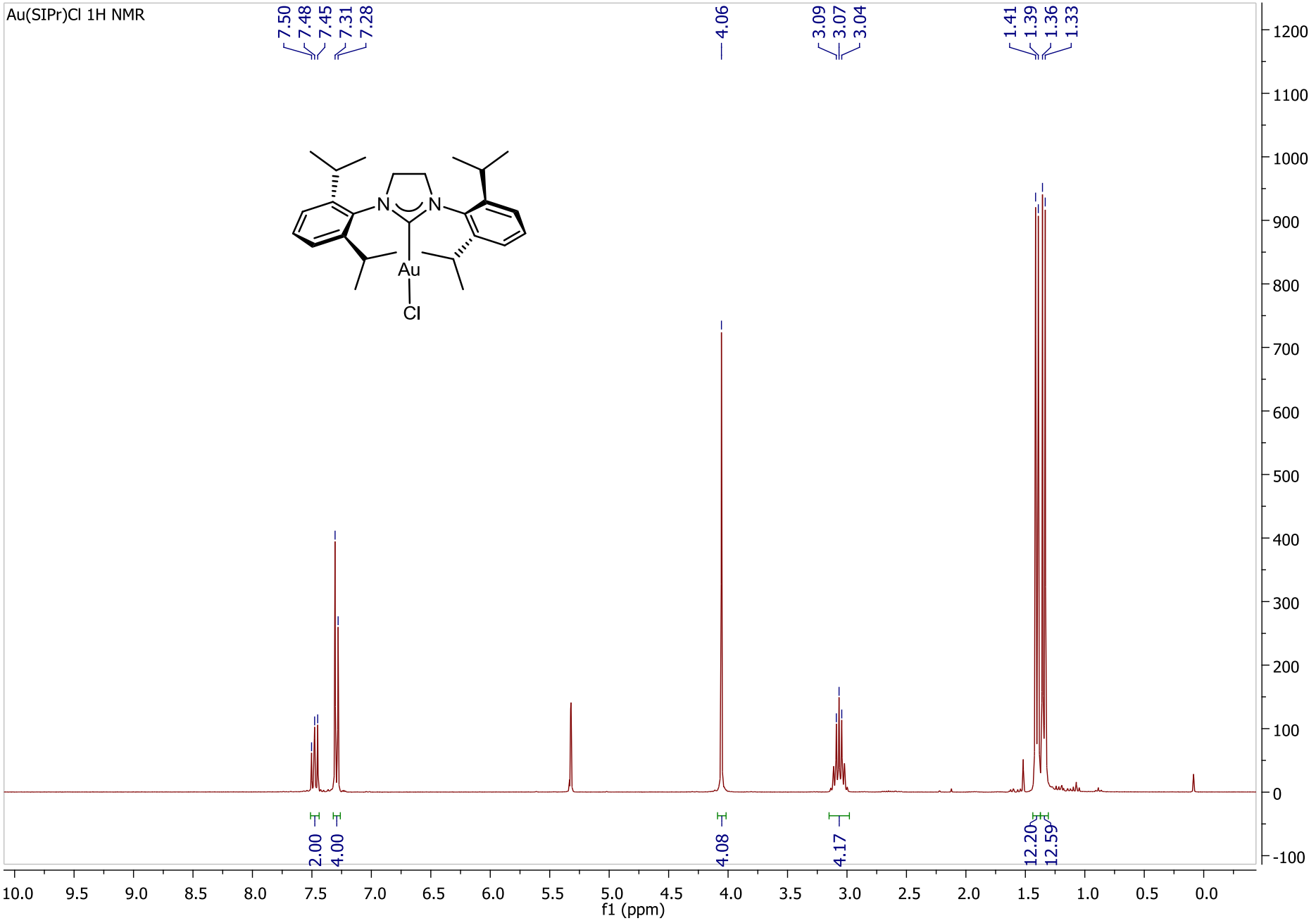
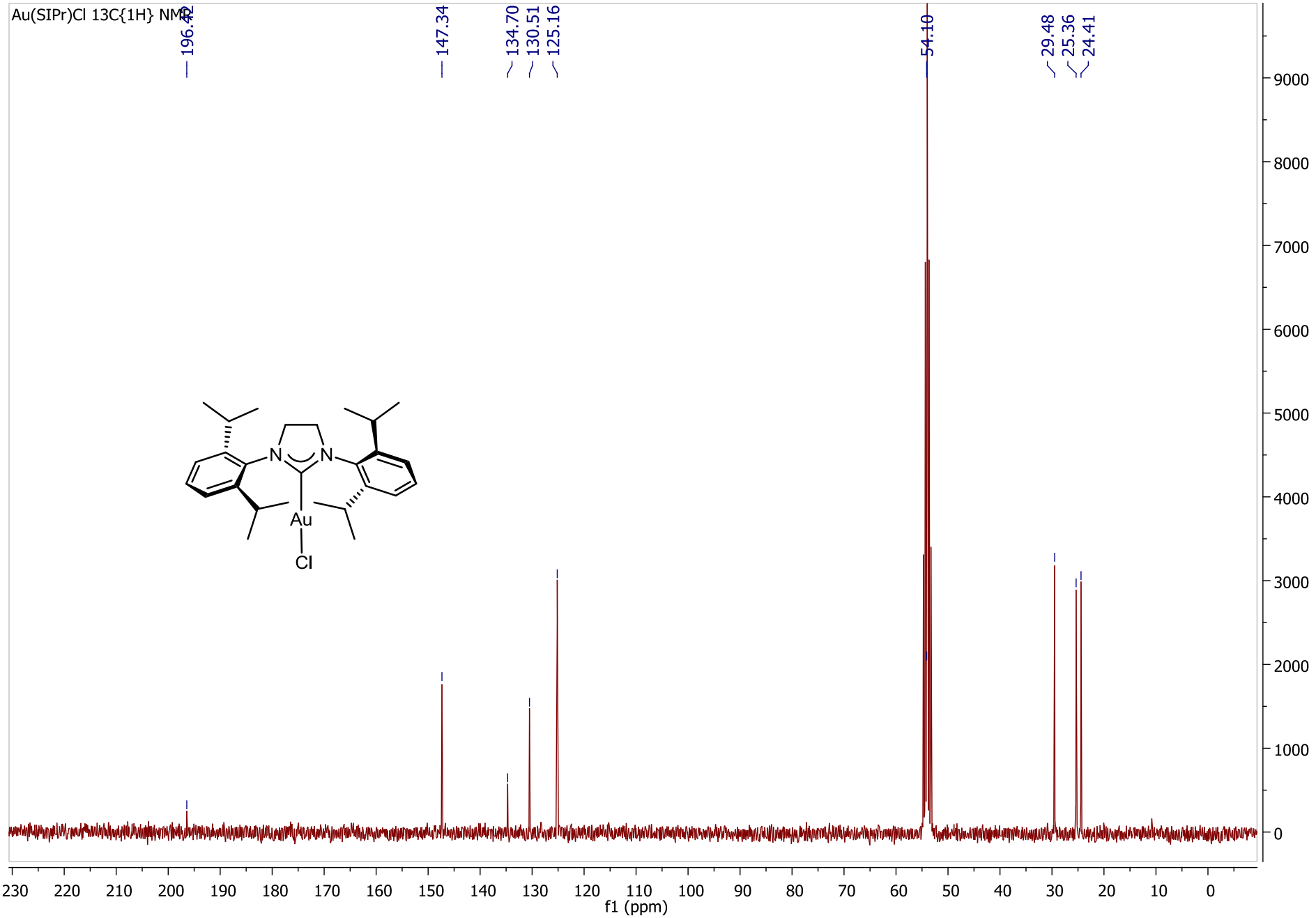
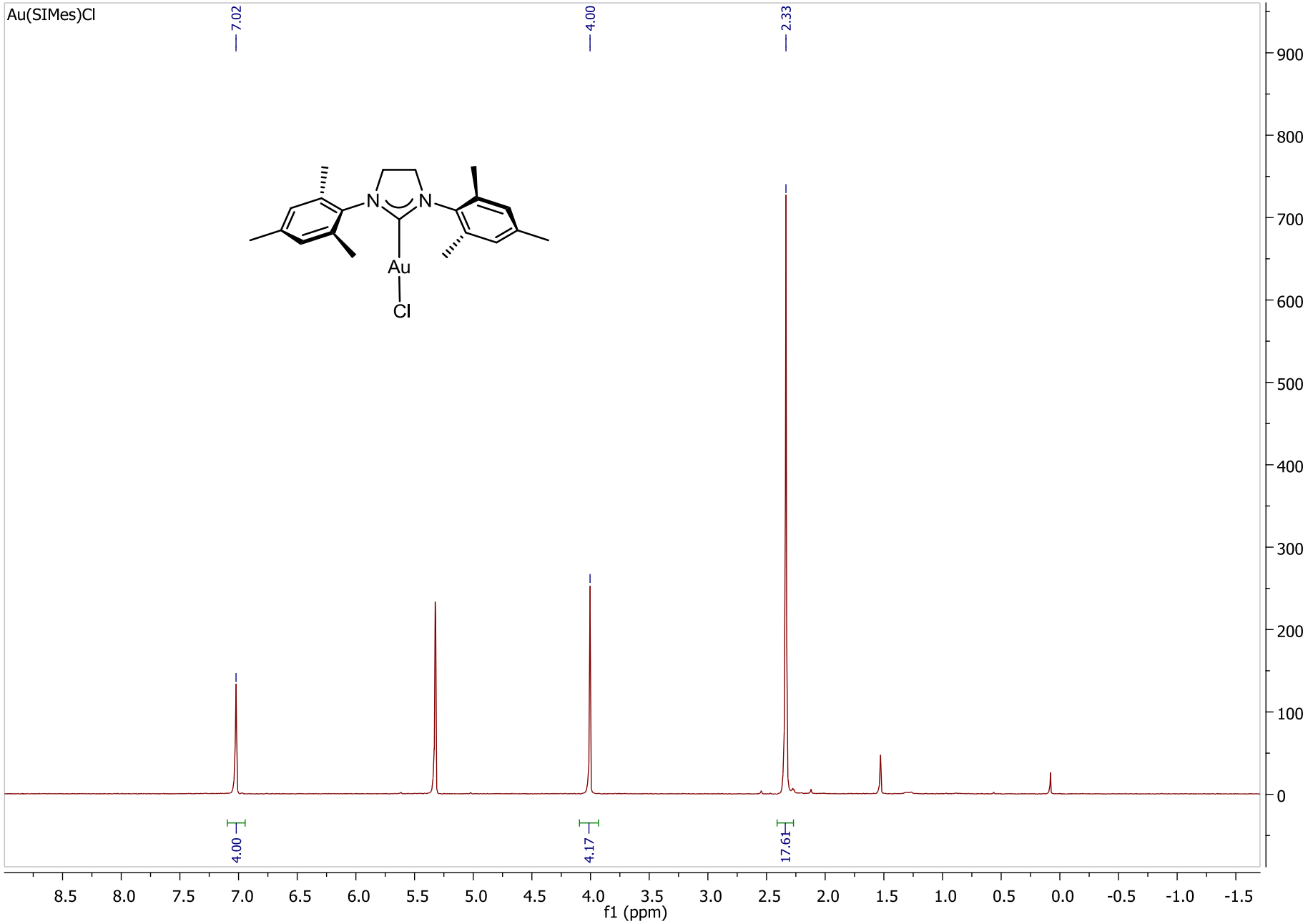
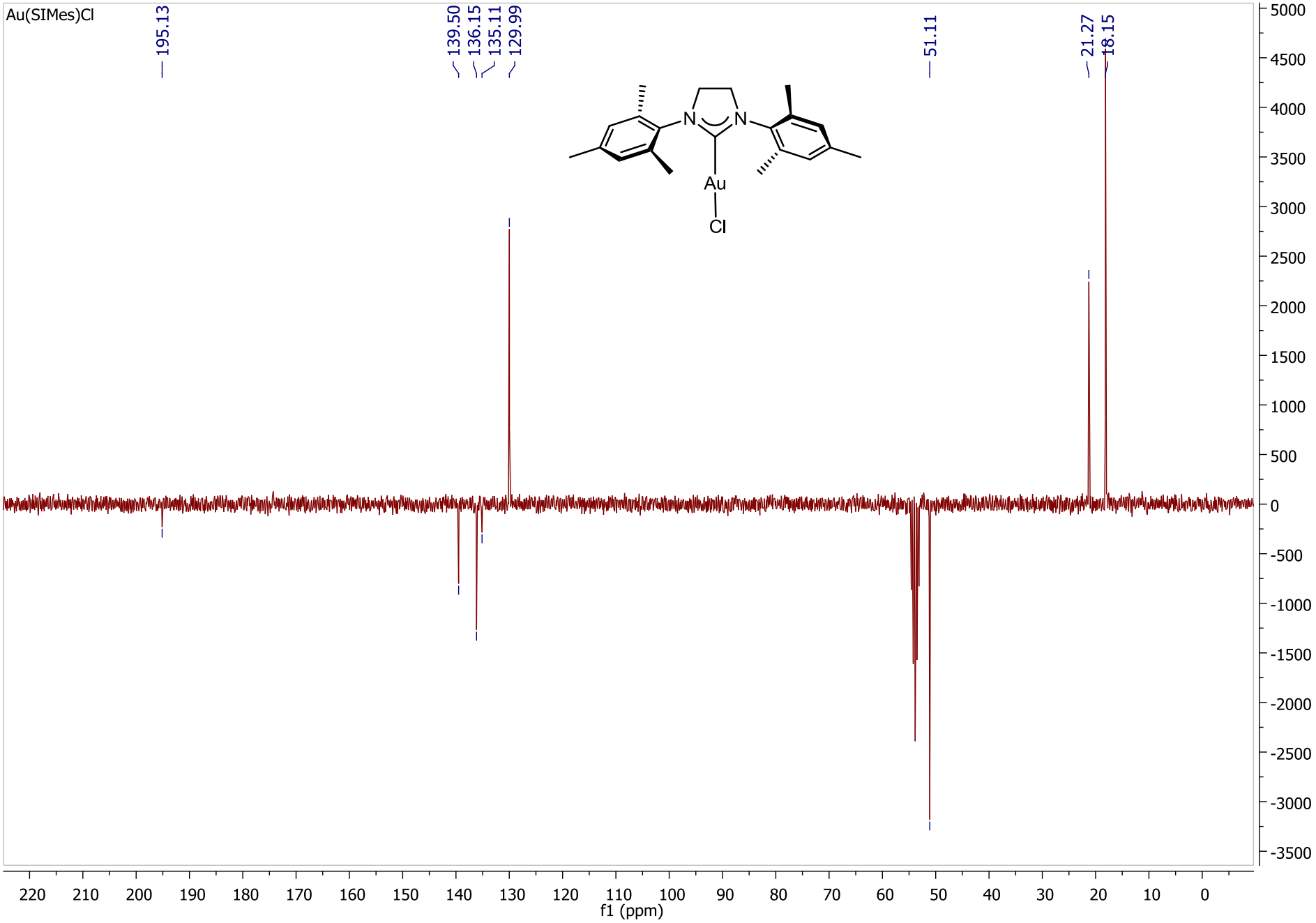
f1 (ppm)

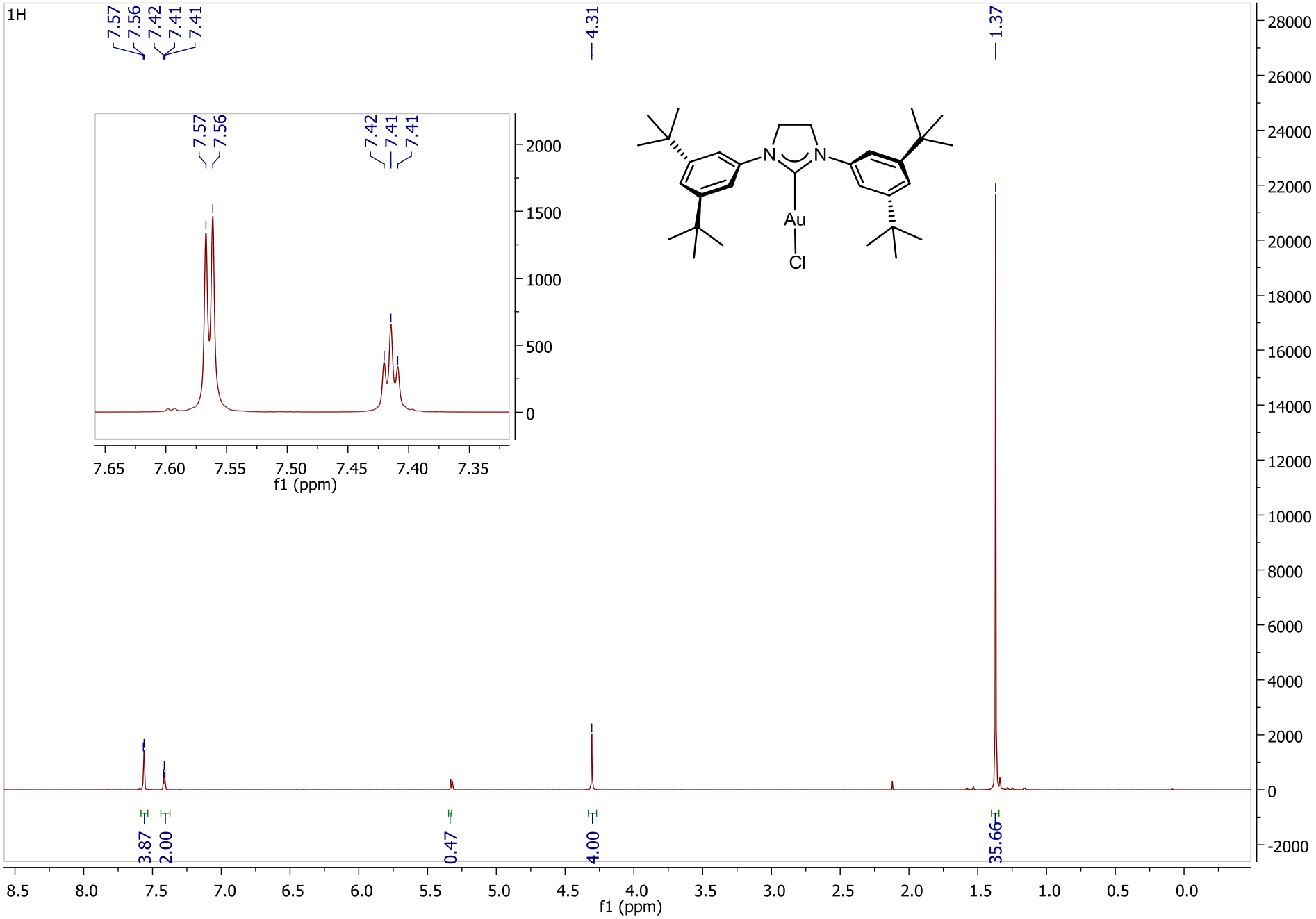

11132012-64-adrianM.11.fid
IPrMeAUCl
171.30
146.41
132.87
130.88
130.88
126.78
125.54
124.71
53.84
29.04
25.16
23.54
9.87
N
N
Au
Cl
f1 (ppm)

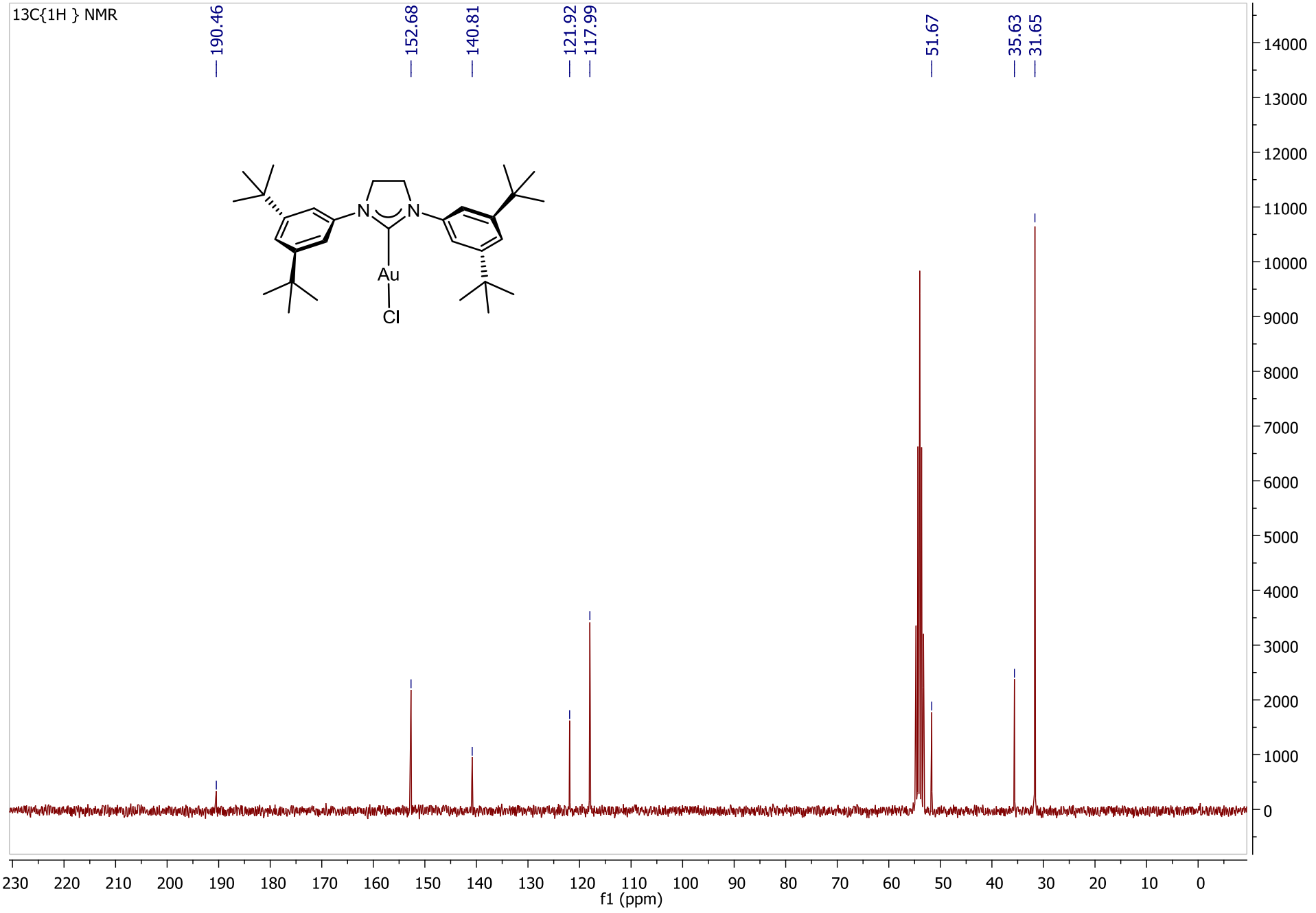


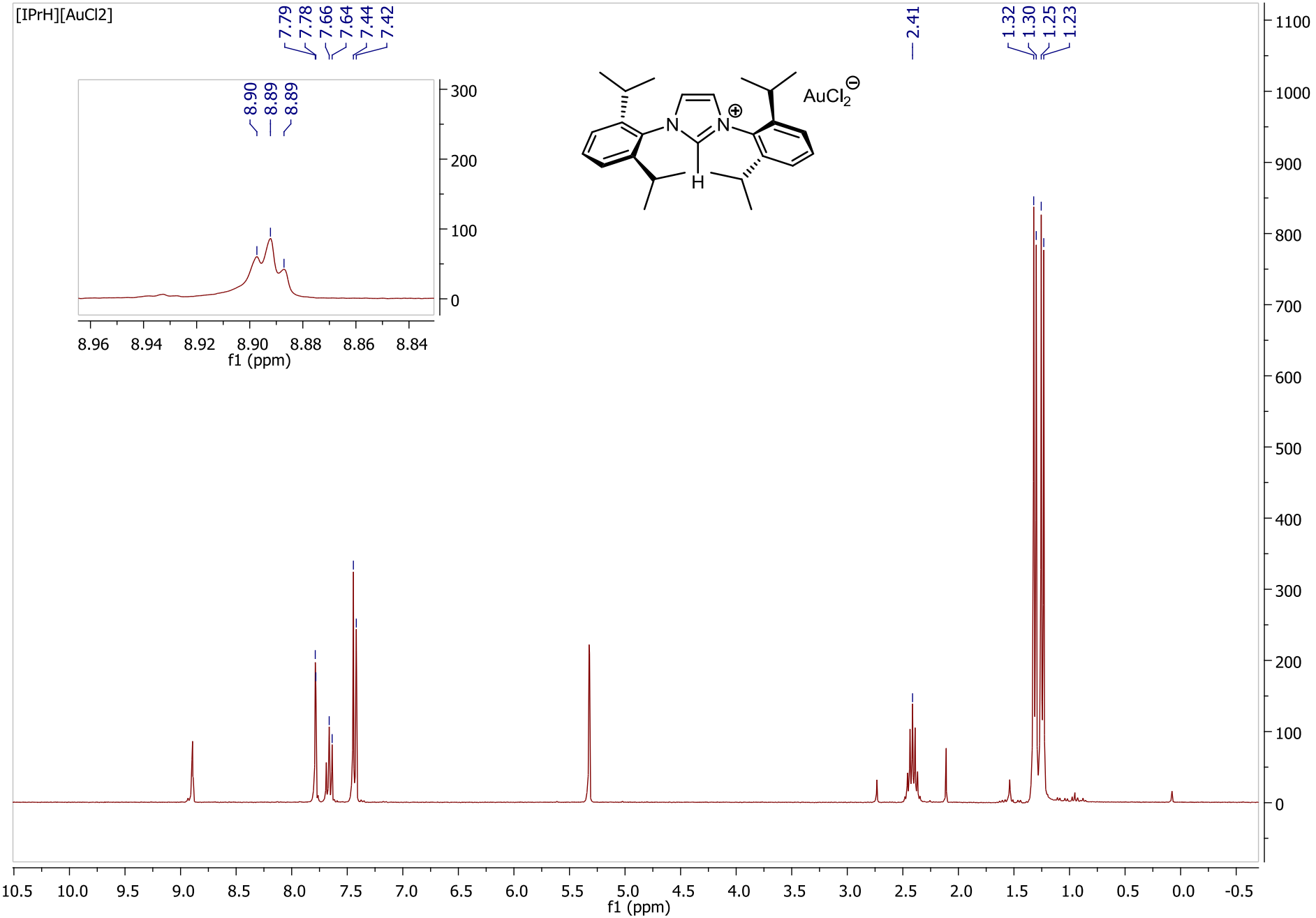

Au(SIPr)Cl 13C{1H} NMR
196.42
147.34
134.70
130.51
125.16
54.10
29.48
25.36
24.41
N
N
Au
Cl
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

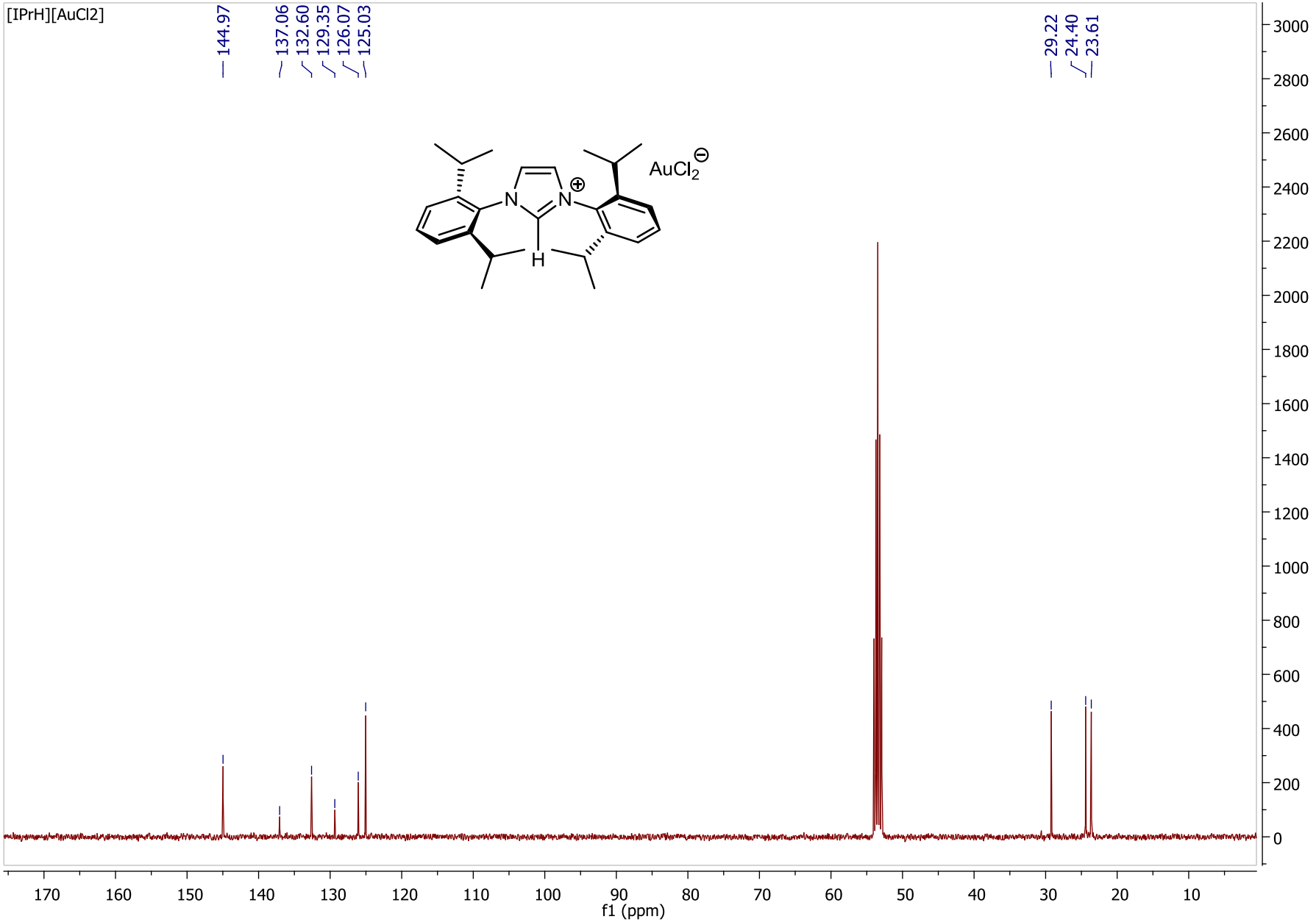


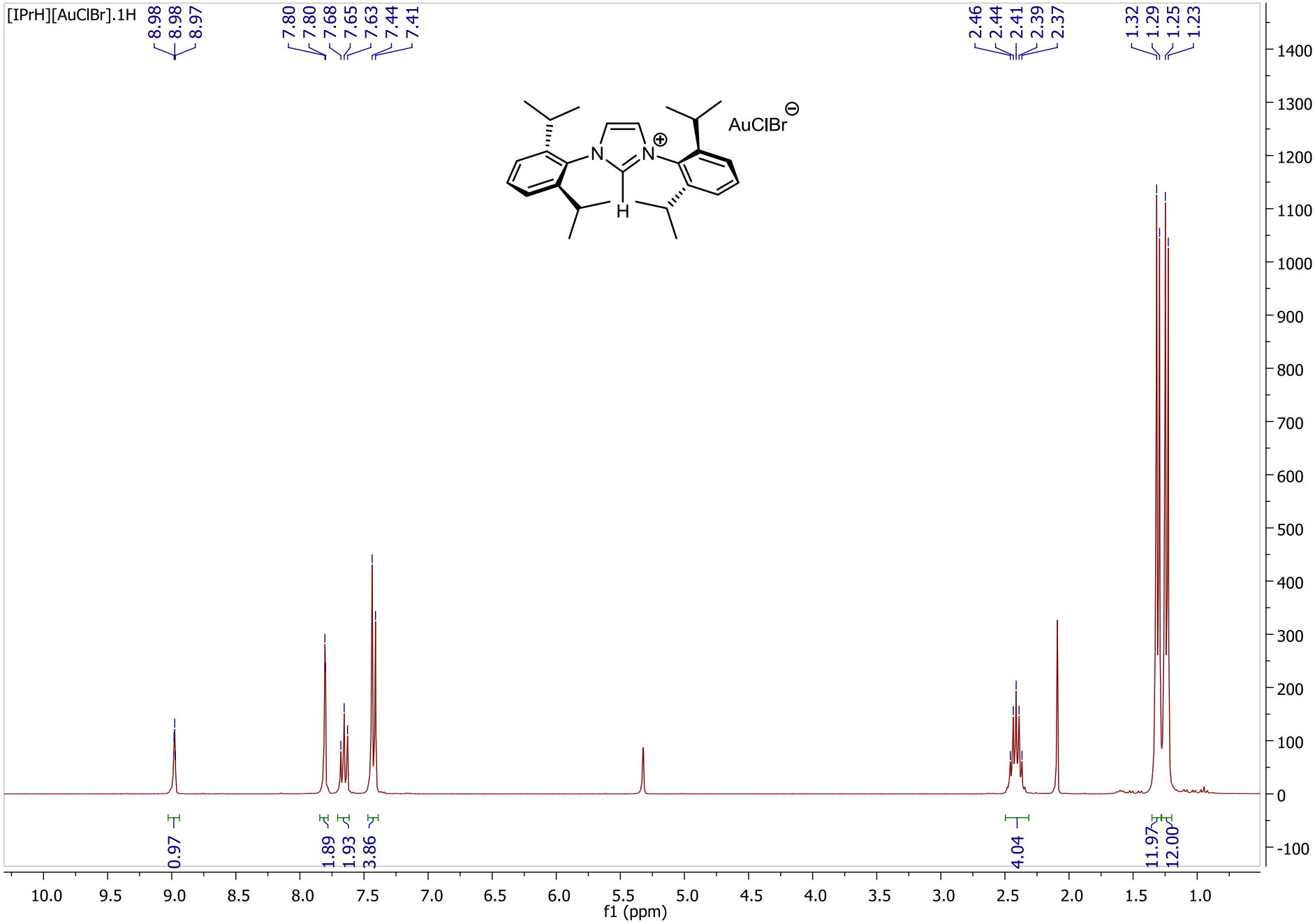


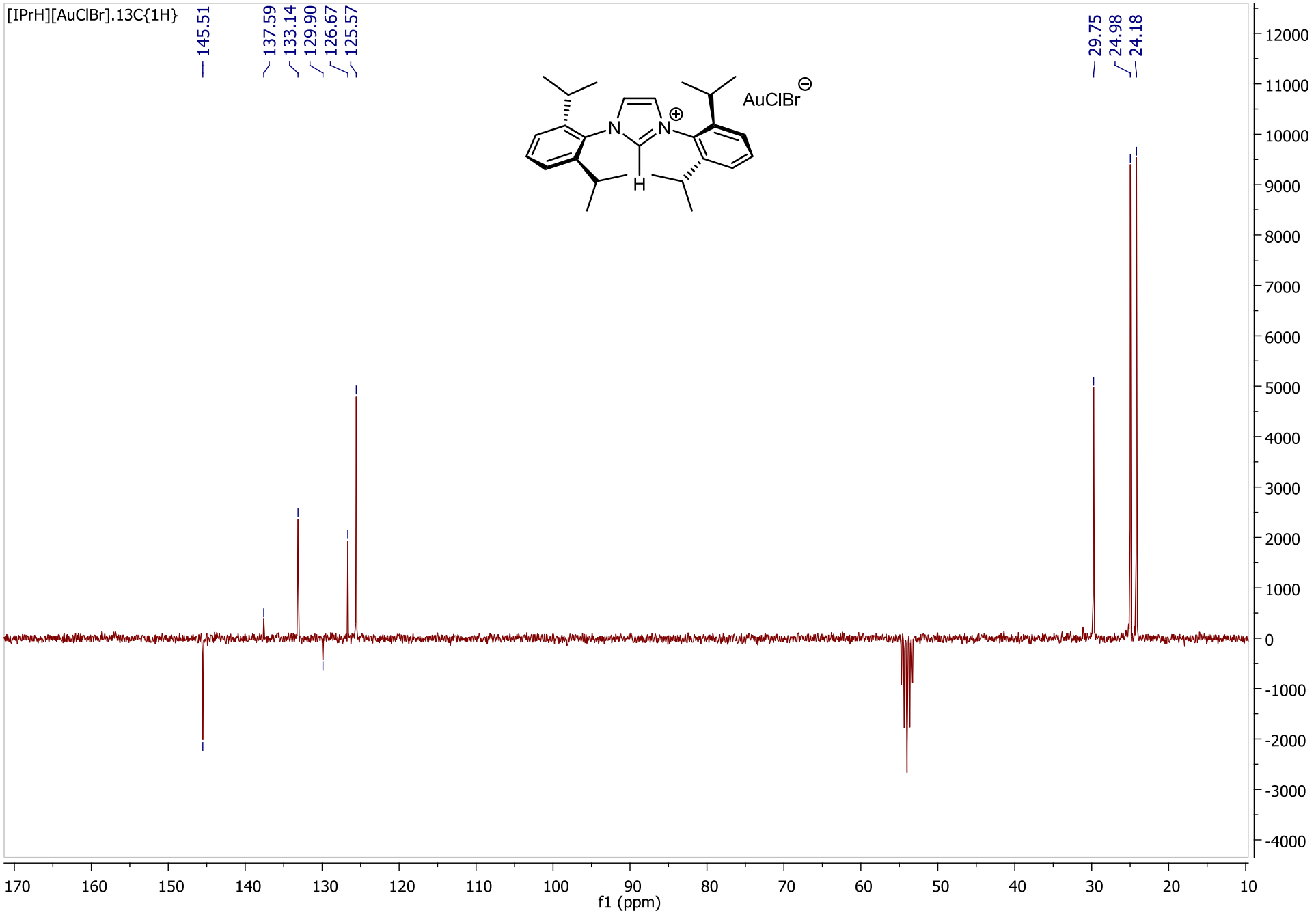


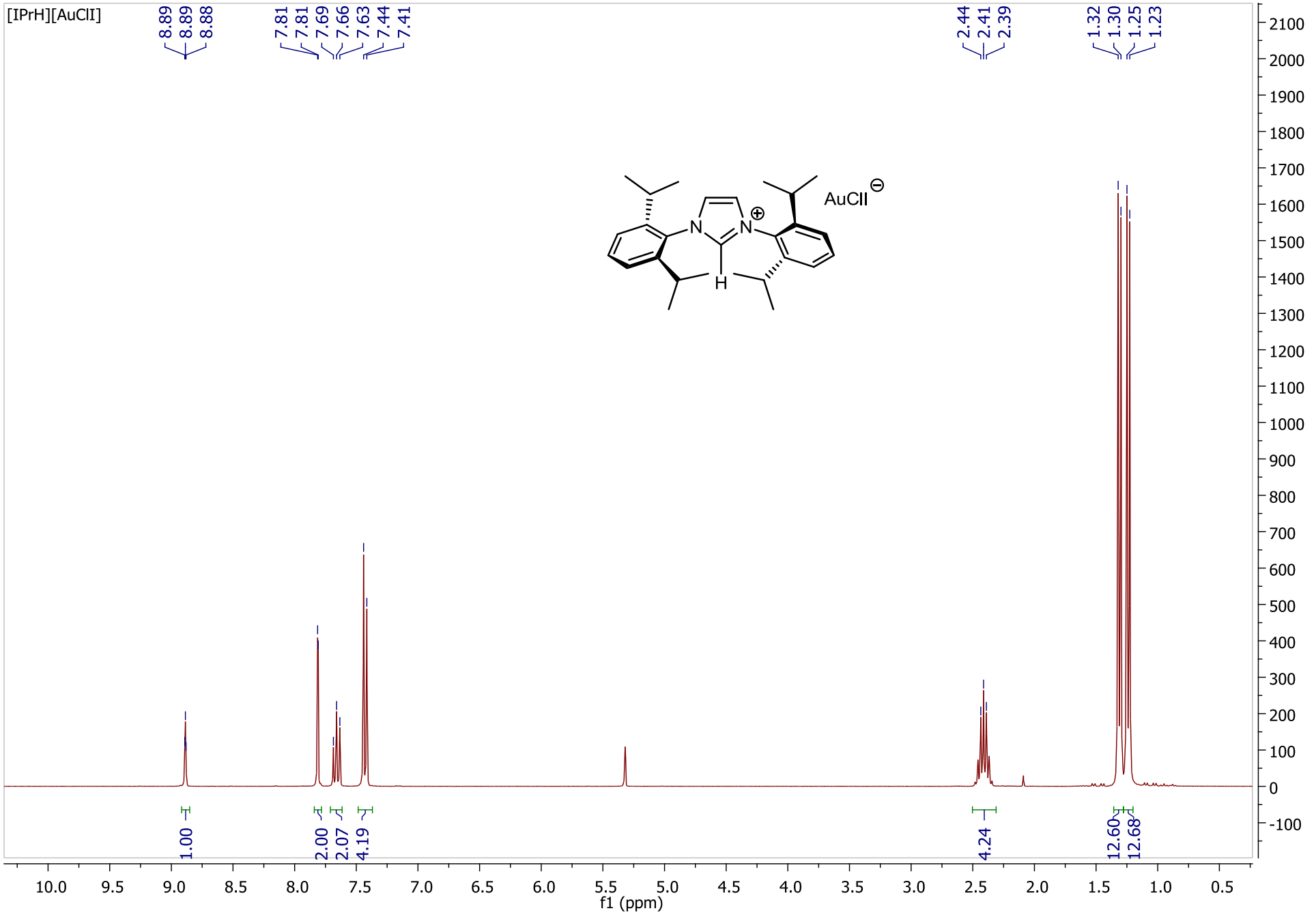

13C{1H } NMR
190.46
152.68
140.81
121.92
117.99
51.67
35.63
31.65
N
N
Au
Cl
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

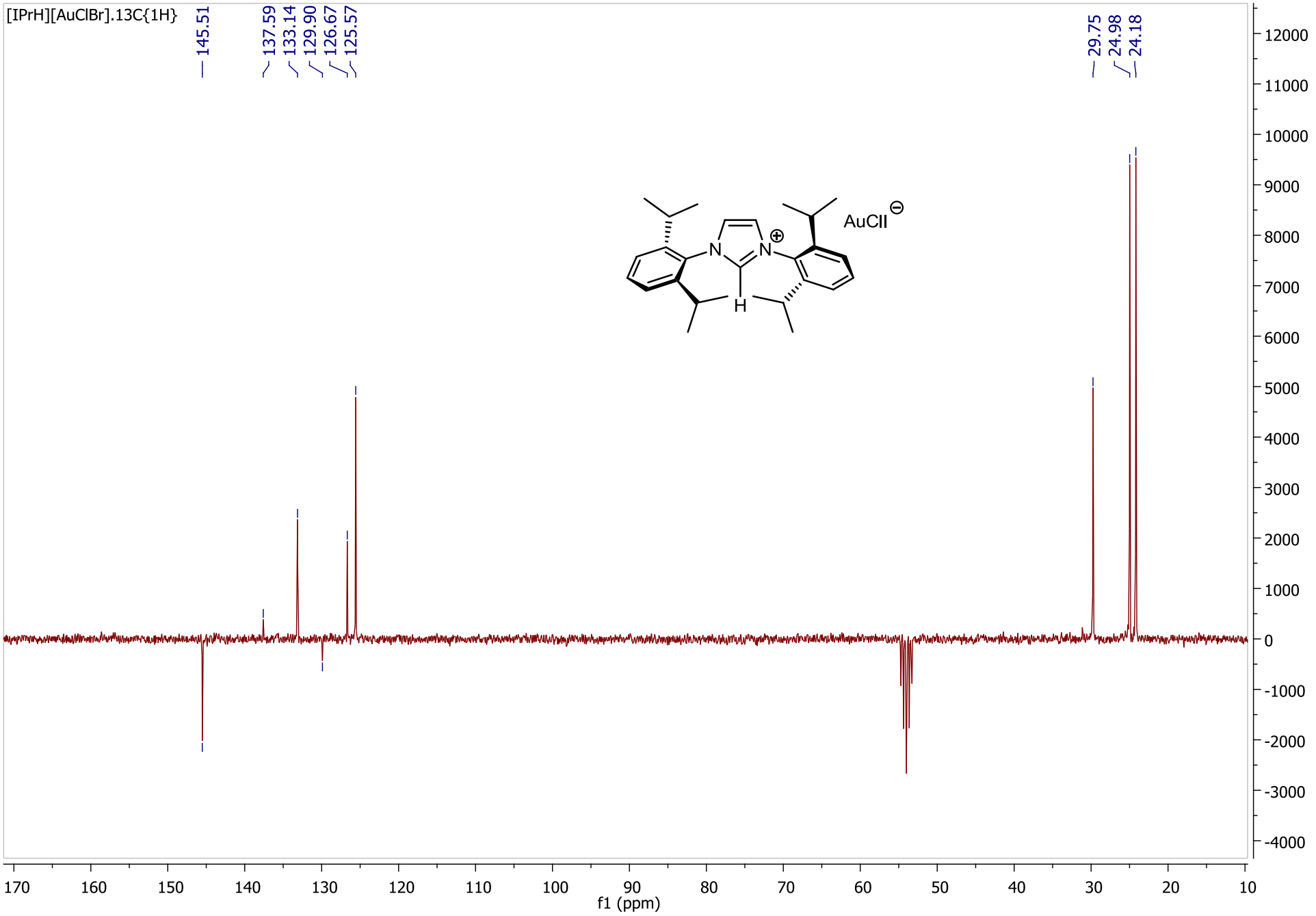


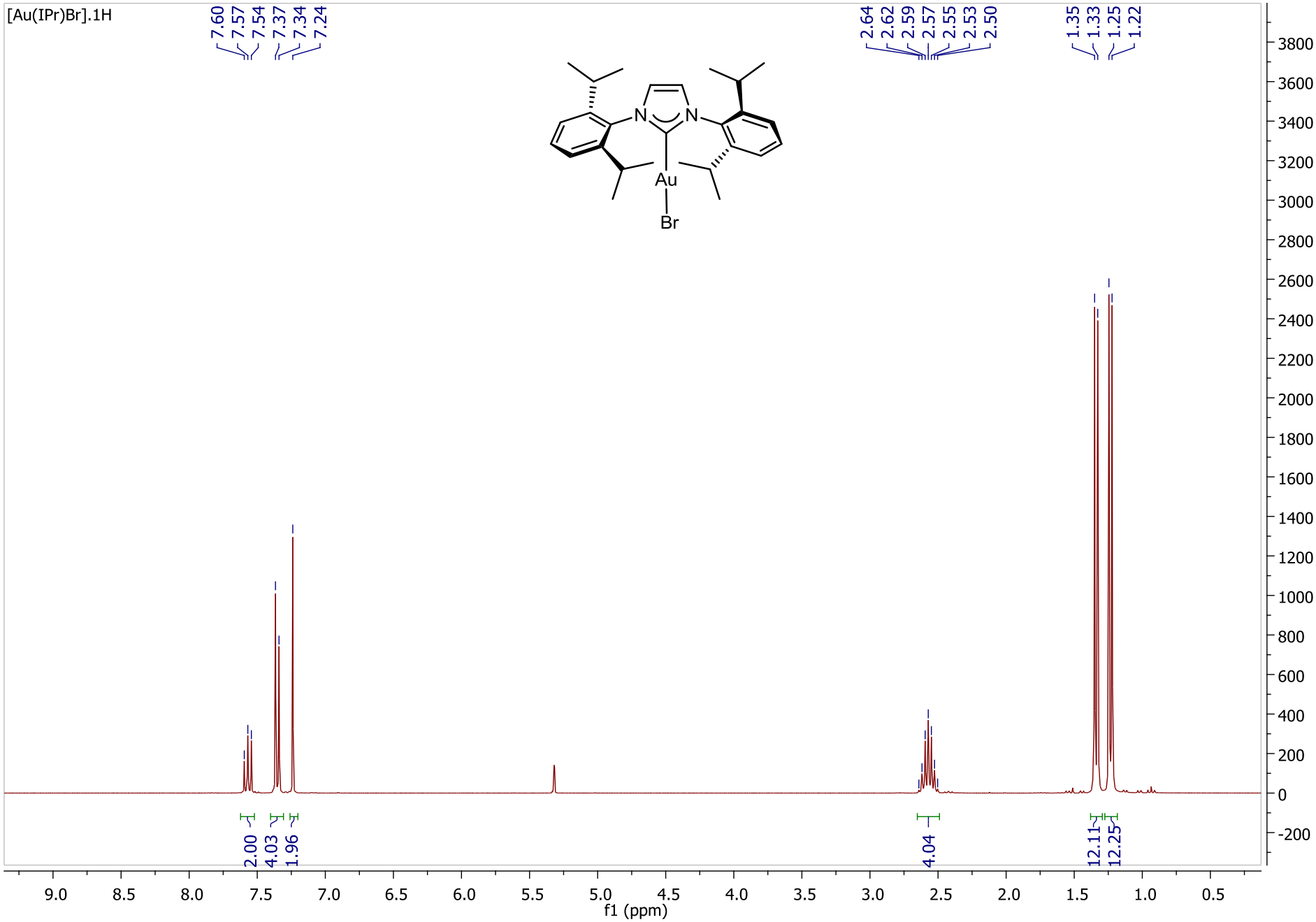

[IPrH][AuCl2]
144.97
137.06
132.60
129.35
126.07
125.03
29.22
24.40
23.61
AuCl2
N
N
H
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

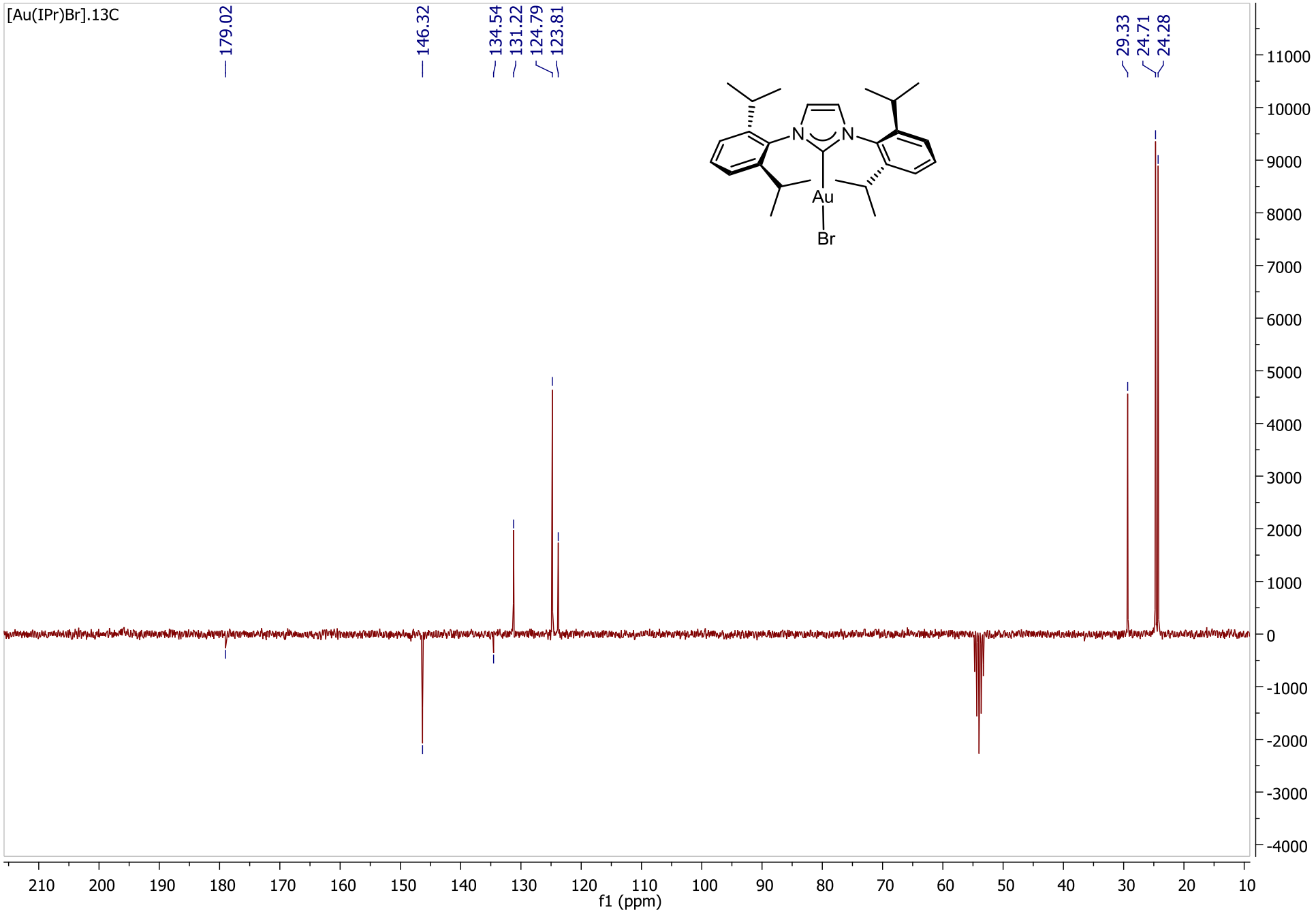


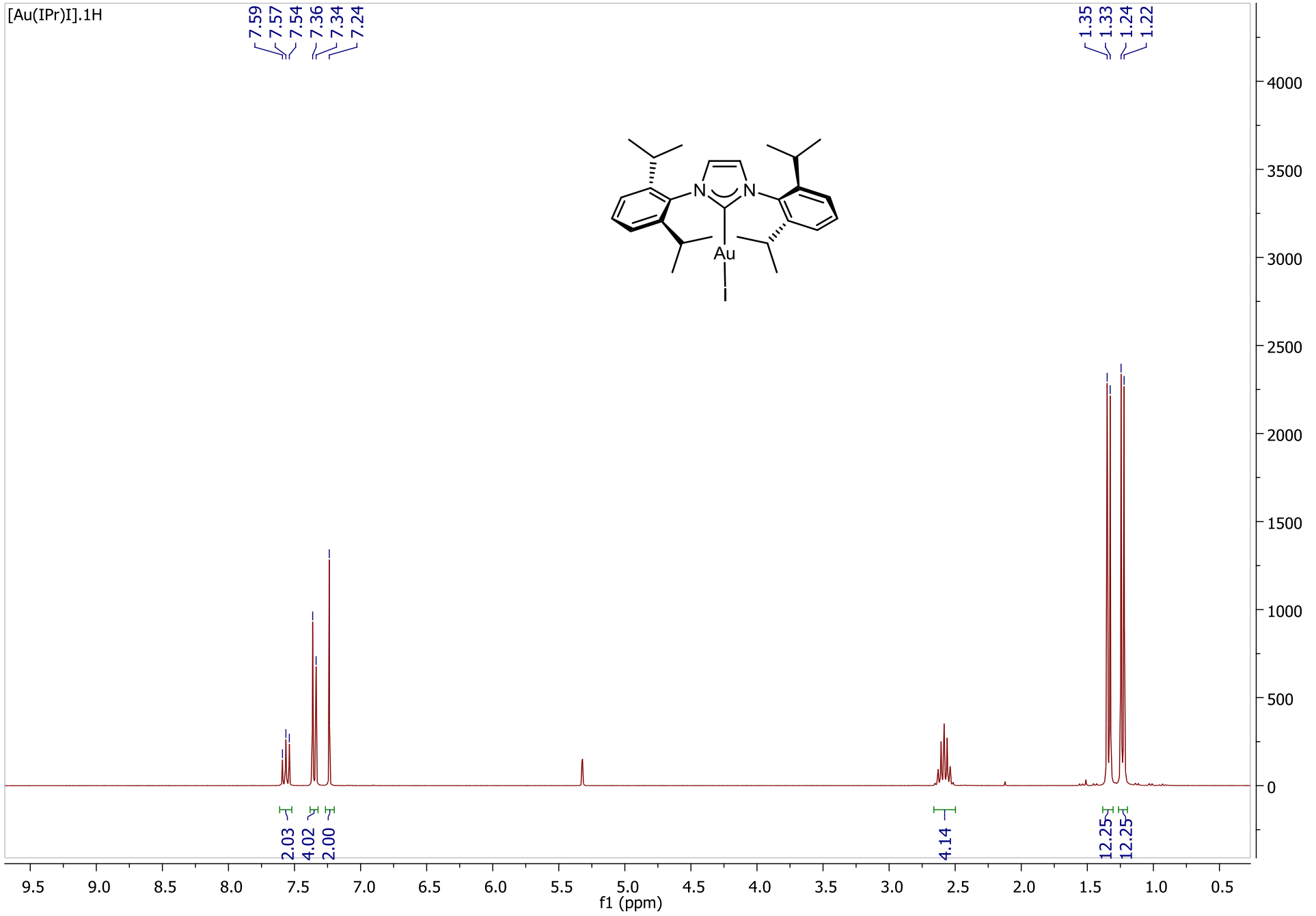

[IPrH][AuClBr].13C{1H}
145.51
137.59
133.14
129.90
126.67
125.57
29.75
24.98
24.18
AuClBr
N
N
H
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

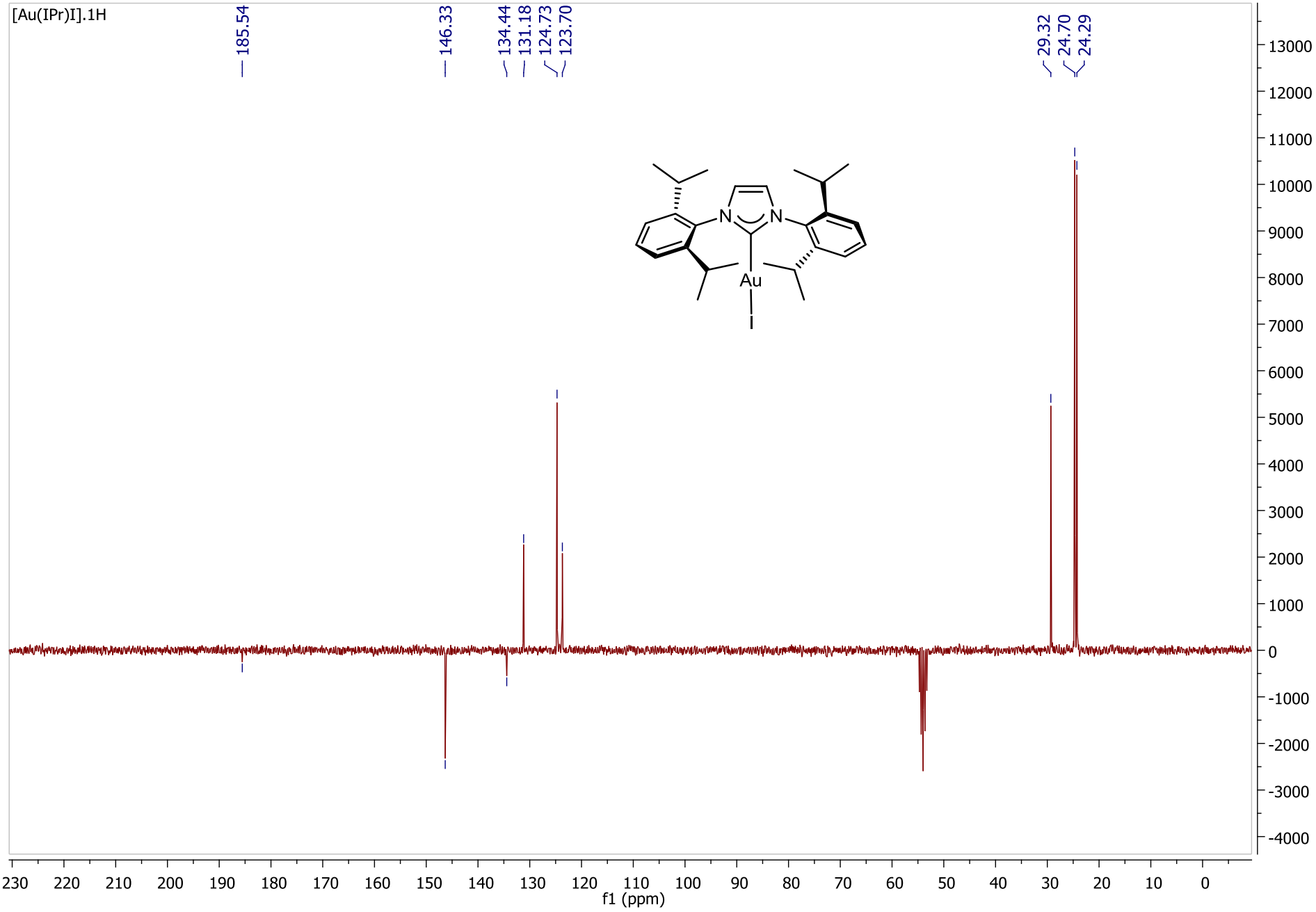



[IPrH][AuClBr].13C{1H}
145.51
137.59
133.14
129.90
126.67
125.57
29.75
24.98
24.18
AuClBr
N
N
H
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)




[Au(IPr)Br].13C
179.02
146.32
134.54
131.22
124.79
123.81
29.33
24.71
24.28
N
N
Au
Br
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


[Au(IPr)I].1H
7.59
7.57
7.54
7.36
7.34
7.24
1.35
1.33
1.24
1.22
N
N
Au
I
2.03
4.02
2.00
4.14
12.25
12.25
4000
3500
3000
2500
2000
1500
1000
500
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


[Au(IPr)I].1H
185.54
146.33
134.44
131.18
124.73
123.70
29.32
24.70
24.29
N
N
Au
I
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)