Supporting Information

for

Synthesis, reactivity and catalytic activity of Au-PAd_3 complexes

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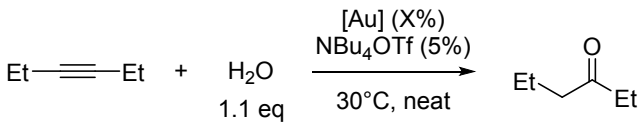
Catalytic tests

Hydration of 3-hexyne

[Au(PAd_3)X], 3-hexyne (199 μL, 1.75 mmol), H_2O (34.6 μL, 1.925 mmol) and NBu_4OTf (34.3 mg, 0.0875 mmol) were mixed in a 2 mL glass screw-top vial. Reaction mixture was stirred (rpm 1500) at 30°C. The progress of the reaction was monitored by ^1H NMR. The conversion was calculated from the integral intensities of the -CH_2- protons. The reported values are the average of two runs. NMR shifts of the product corresponded the reported values[1]

Table S1. Gold-cataysed hydration of alkynes



Entry	Catalyst	mol % of the catalyst	Conv. % (time)
1	[Au(PAd_3)OTf]	**0.05**	<5 (24h)
2	[Au(PAd_3)OTf]	**0.1**	<5 (24h)[a]
3	[Au(PAd_3)OTf]	**0.25**	<5 (24h)
4	[Au(PAd_3)NTf_2]	**0.1**	<5 (24h)
5	[Au(PAd_3)(CH_3CN)]BF_4	**0.1**	<5 (24h)

[a] Reaction was also performed at 60 °C with no difference in conversion

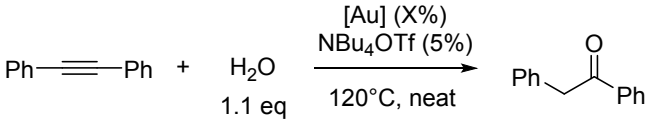
Hydration of diphenylacetylene

[Au(PAd_3)X], diphenylacetylene (312 mg, 1.75 mmol), H_2O (34.6 μL, 1.925 mmol) and NBu_4OTf (34.3 mg, 0.0875 mmol) were mixed in a 4 mL glass screw-top vial. Reaction mixture was stirred (rpm 1500) at 120°C. The progress of the reaction was monitored by ^1H NMR. The conversion was calculated from the integral intensities of suitable aromatic protons.

^1H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H, CH_{Ar}), 7.60 – 7.52 (m, 1H, CH_{Ar}), 7.50 – 7.42 (m, 2H, CH_{Ar}), 7.38 – 7.21 (m, 5H, CH_{Ar}), 4.29 (s, 2H, C*H*CO).

NMR shifts of the product corresponded the reported values[1]

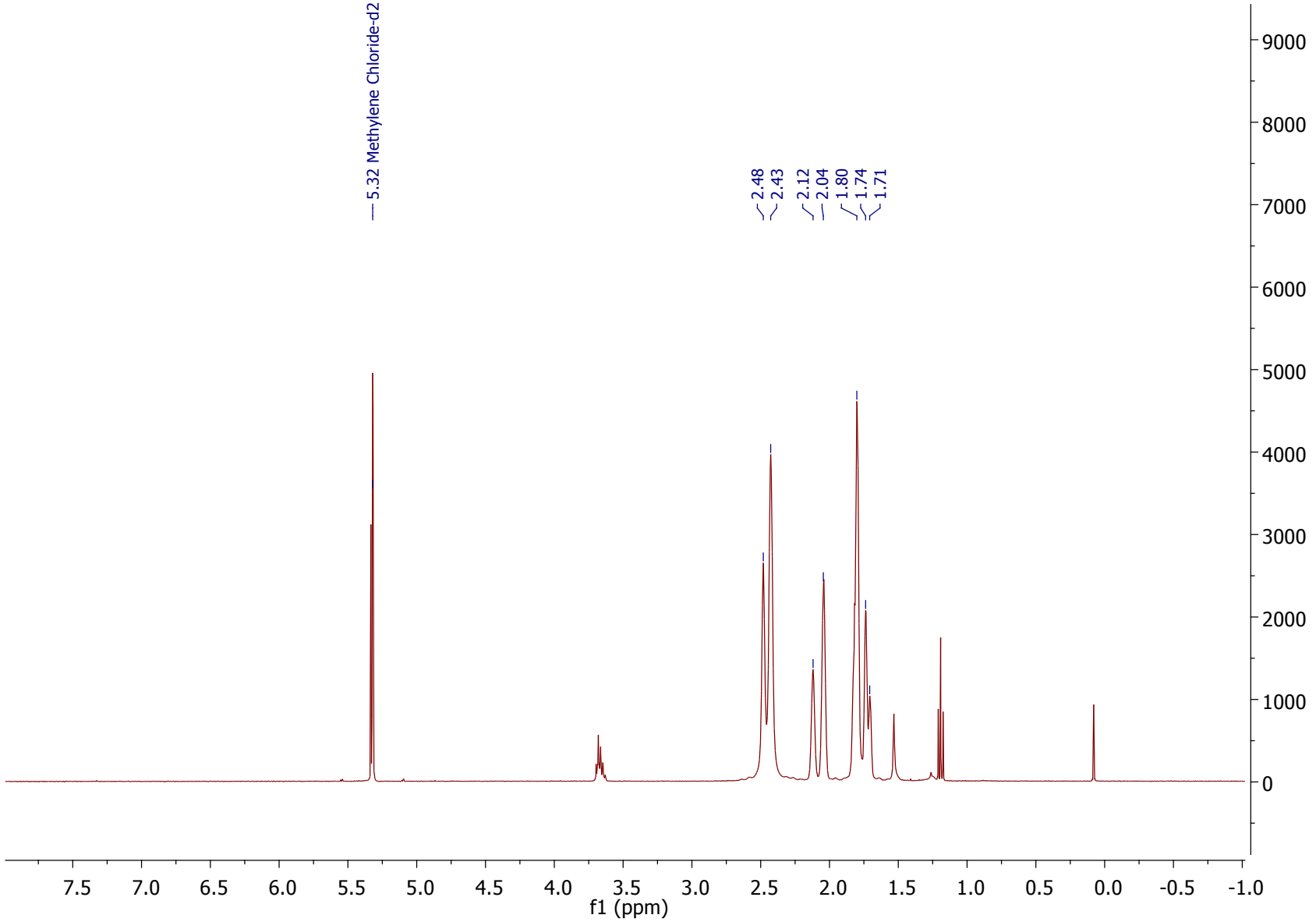
Table S2. Gold-cataysed hydration of diphenylacetylene



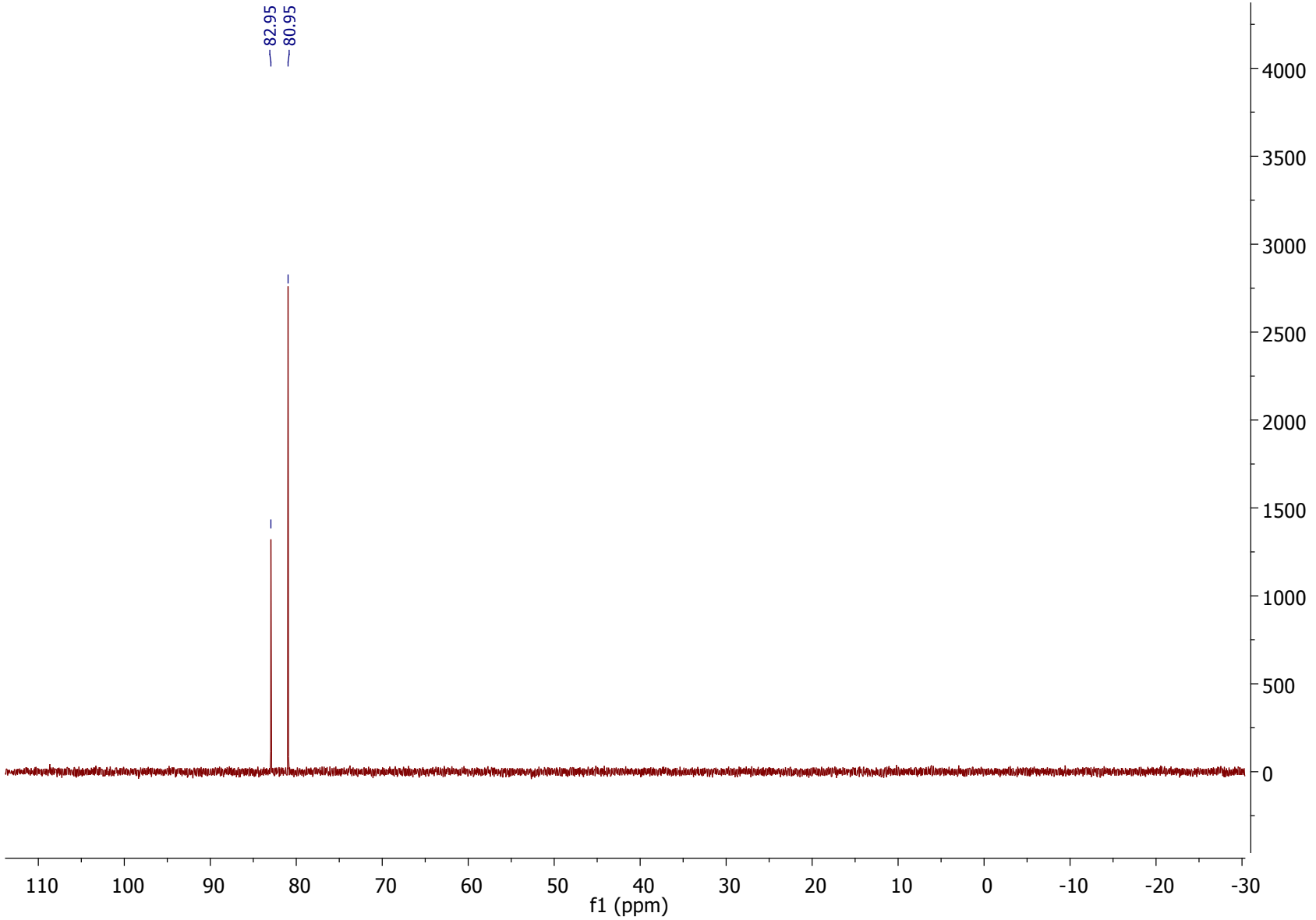
Entry	Catalyst	mol % of the catalyst	Conv. % (time)
1	[Au(PAd_3)OTf]	**0.05**	29 (15h)
2	[Au(PAd_3)OTf]	**0.1**	62 (4h) 78 (8h) 88 (15h)
3	[Au(PAd_3)OTf]	**0.2**	90 (4h) 96 (8h) 96 (15h)
4	[Au(PAd_3)NTf_2]	**0.1**	80 (4h) 91 (8h) 95 (15h)
5	[Au(PAd_3)NTf_2]	**0.2**	94 (4h) 96 (8h) 96 (15h)
6	[Au(JohnPhos)OTf]	**0.2**	86 (4h) 91 (8h)
7	-	**-**	0 (8h)

The reported values are the average of two runs.

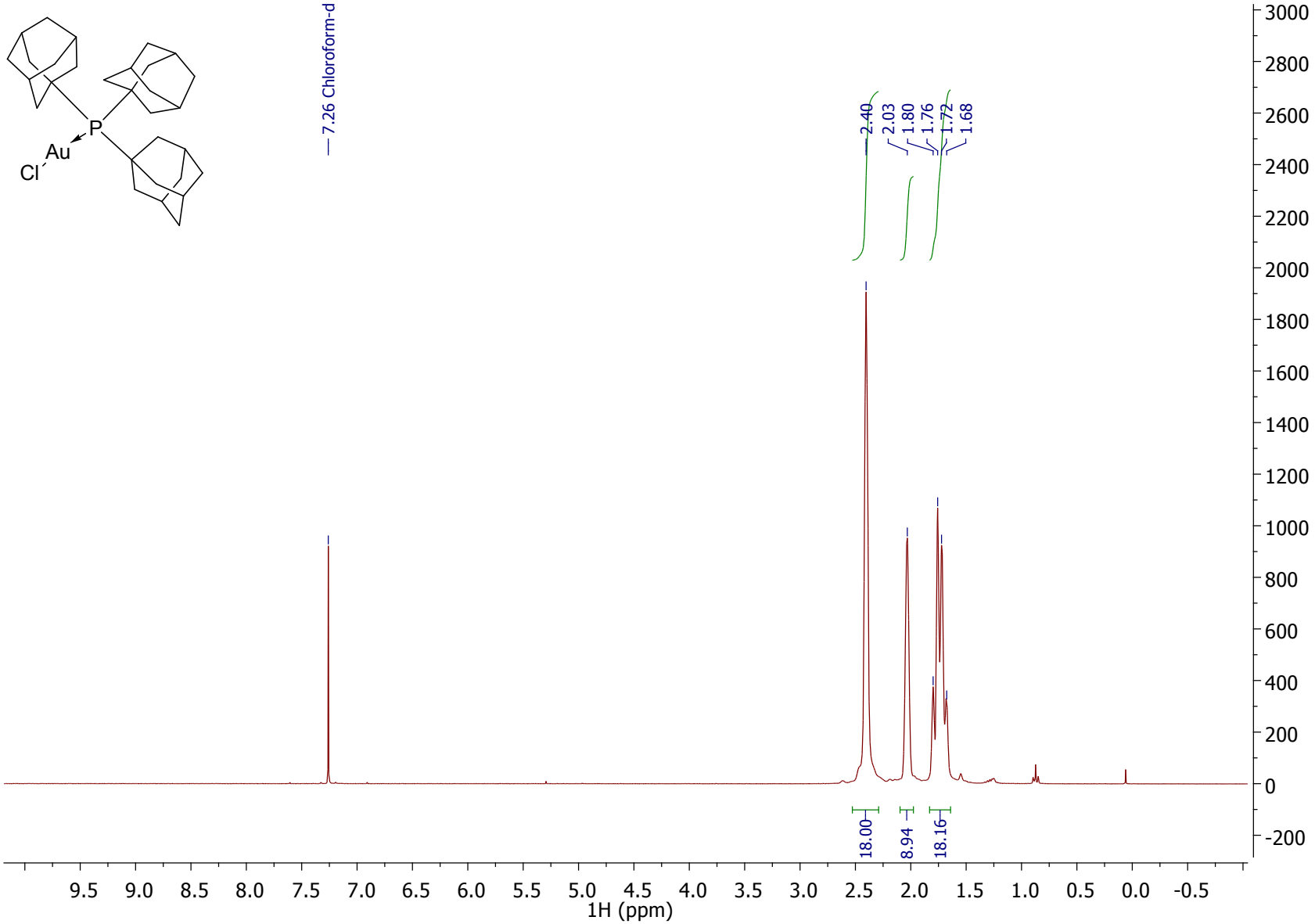
^{1}H NMR spectrum of solid obtained with **Procedure A** for complex **1**



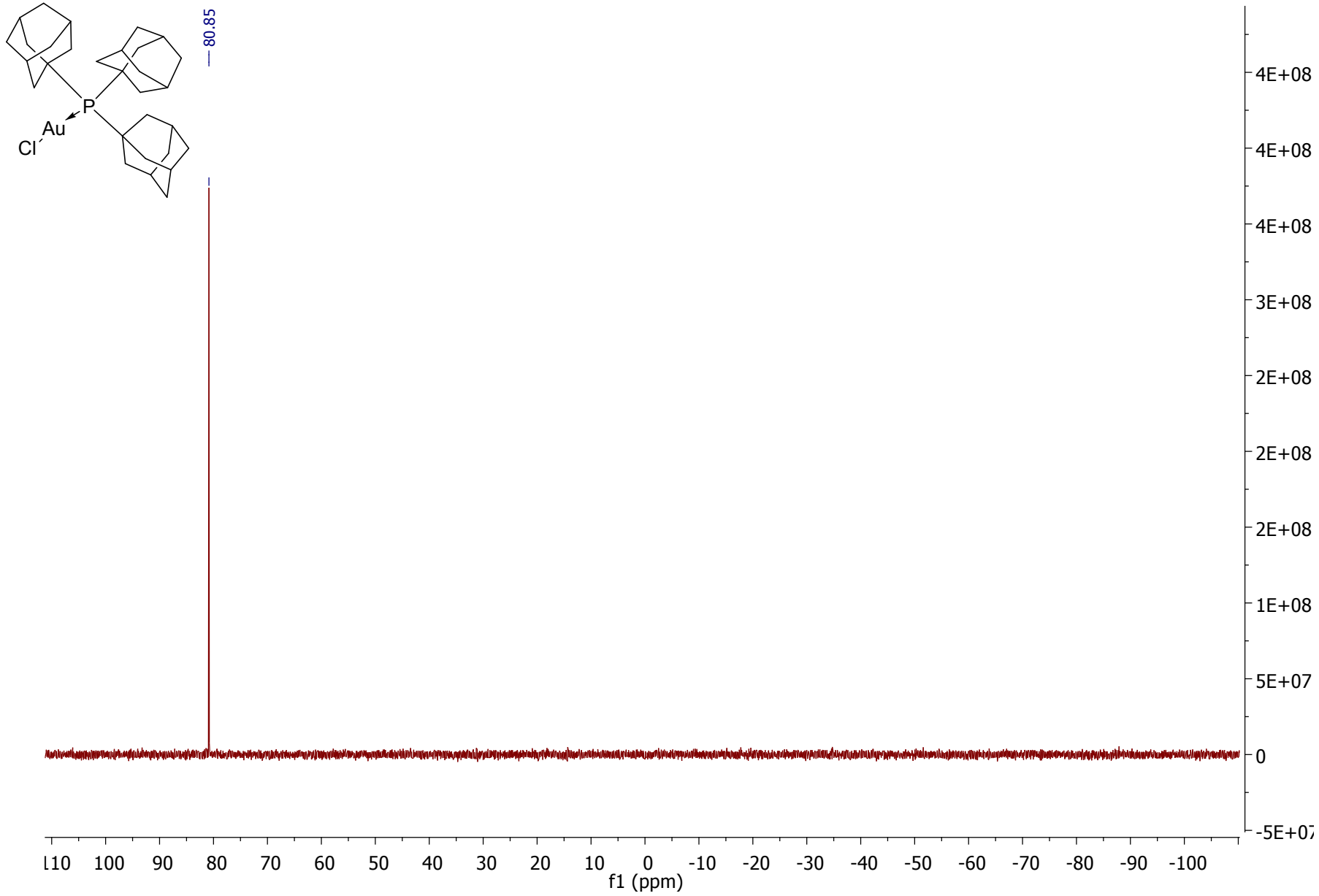
^{31}P NMR spectrum of solid obtained with **Procedure A** for complex **1**



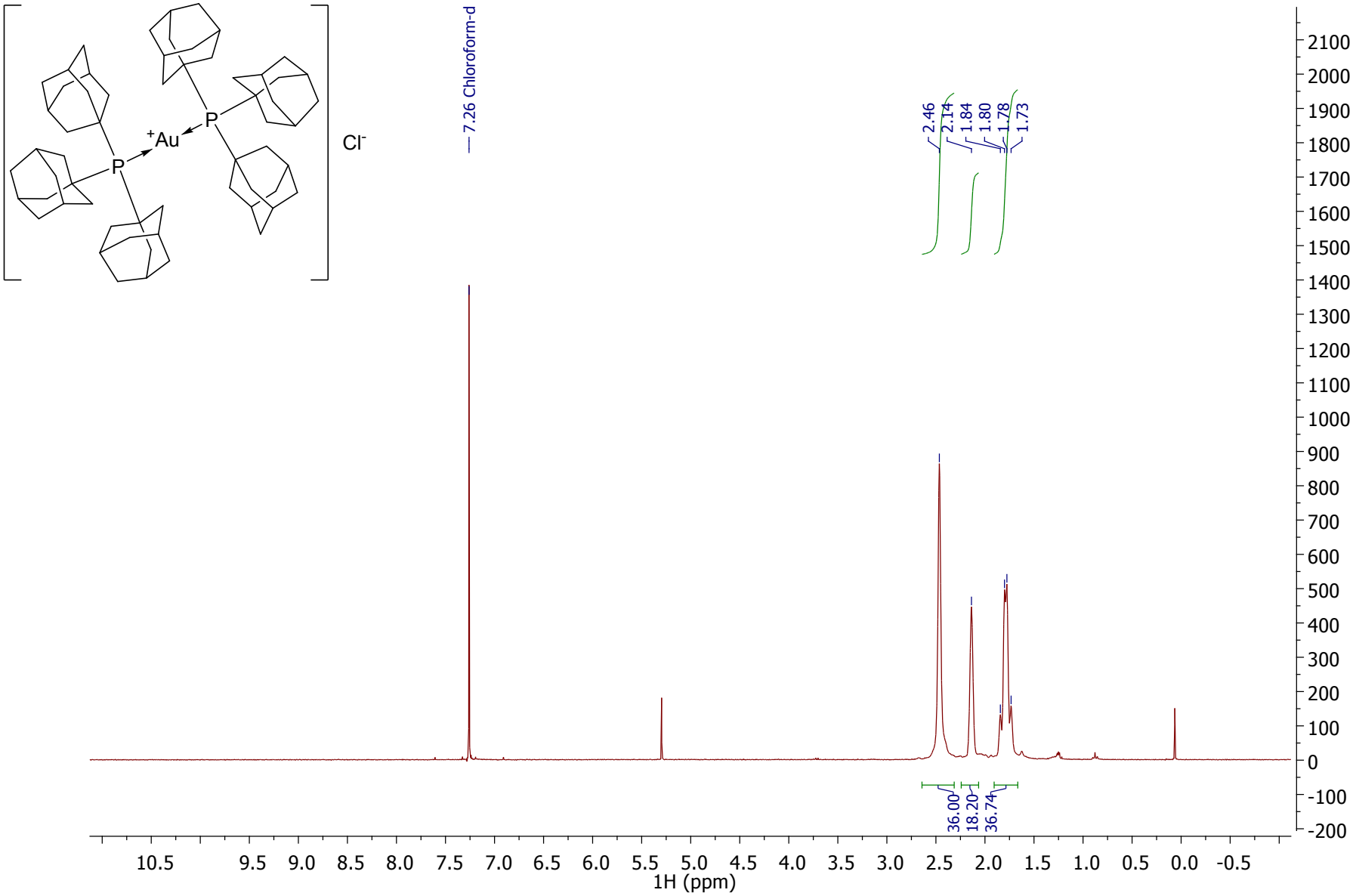
[Au(PAd$_3$)Cl] (**1**) ^{1}H NMR spectrum



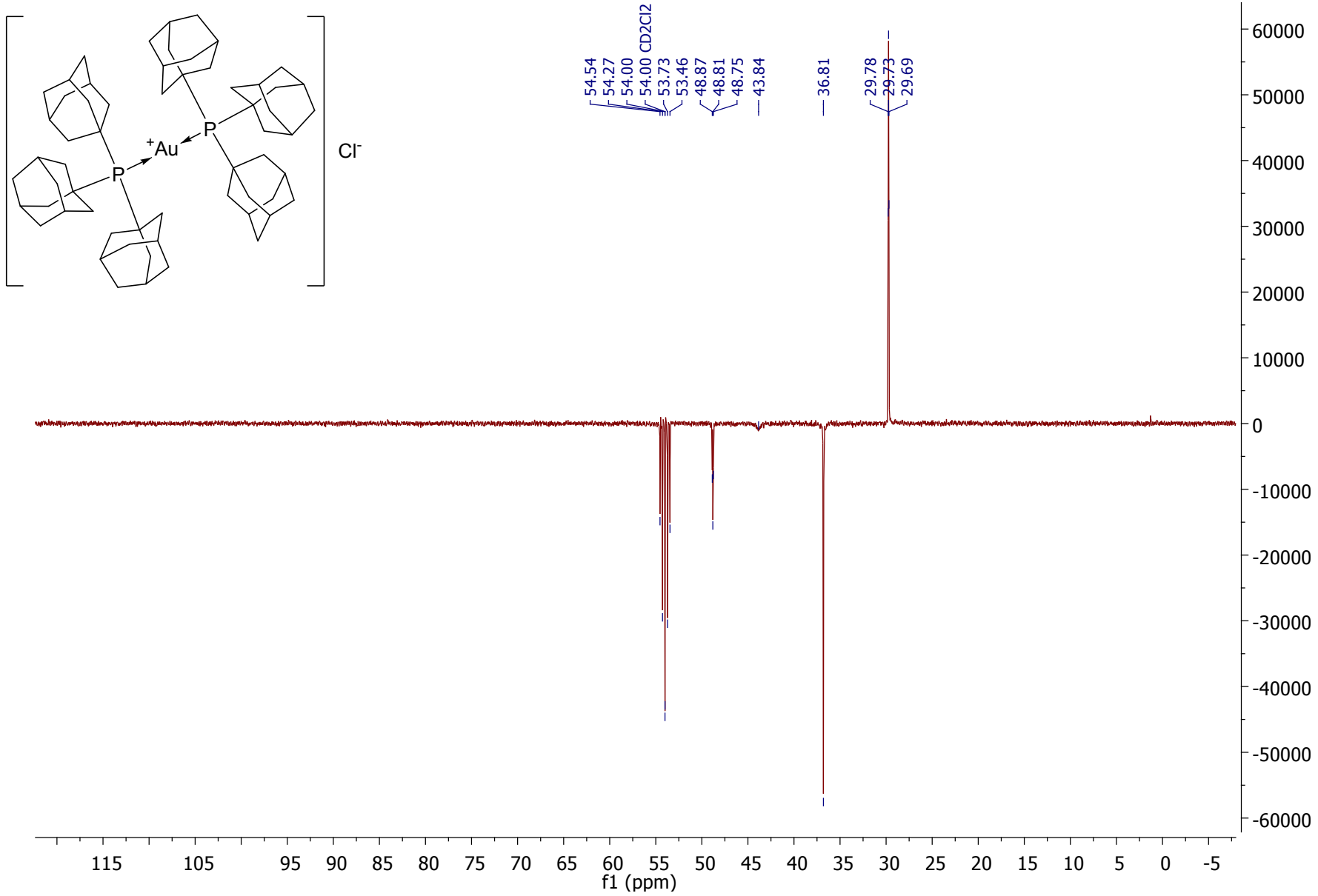
[Au(PAd$_3$)Cl] (**1**) ^{31}P NMR spectrum



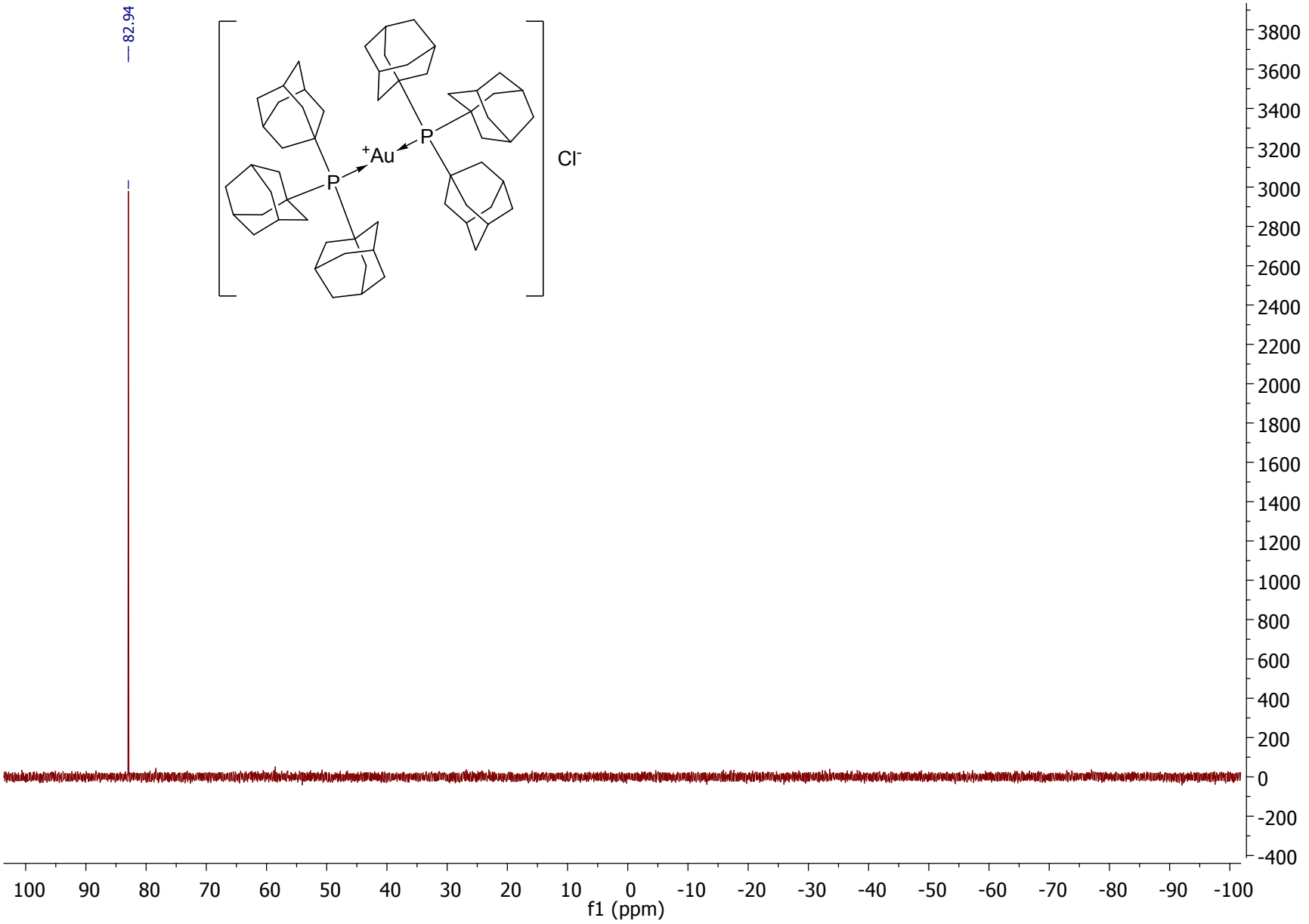
[Au(PAd$_3$)$_2$]Cl (**2**) ^{1}H NMR spectrum



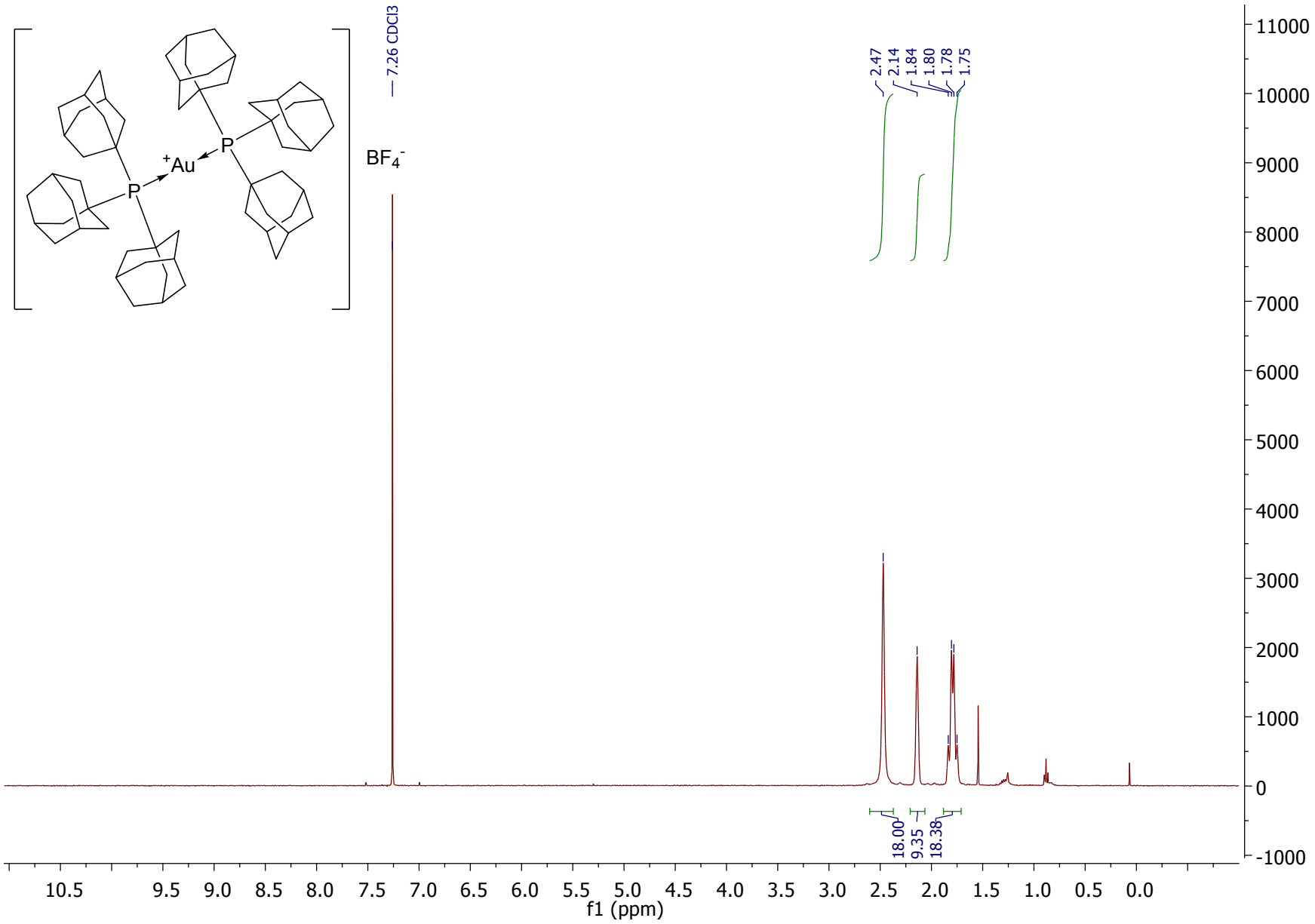
[Au(PAd$_3$)$_2$]Cl (**2**) ^{13}C APT NMR spectrum



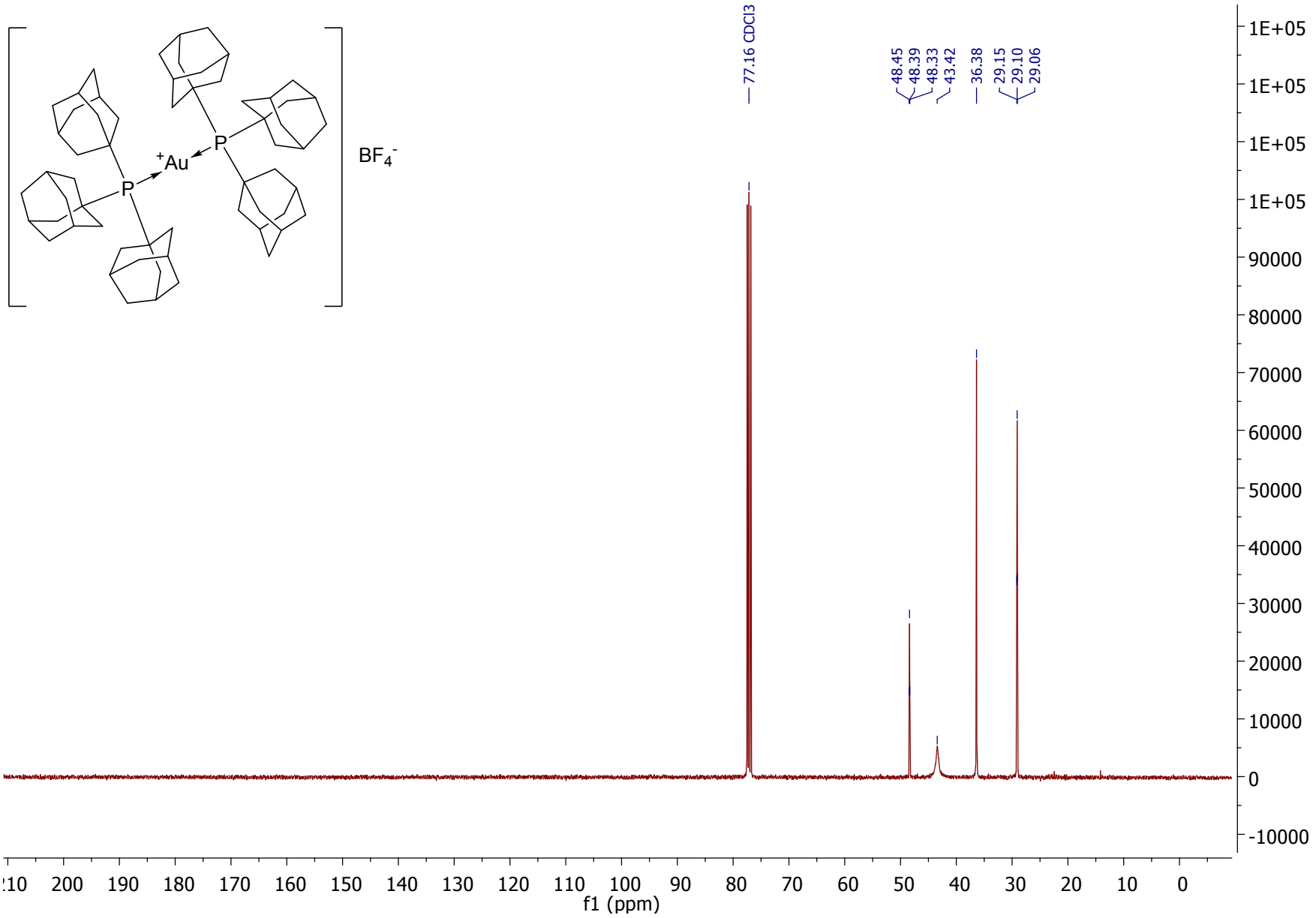
[Au(PAd$_3$)$_2$]Cl (**2**) ^{31}P NMR spectrum



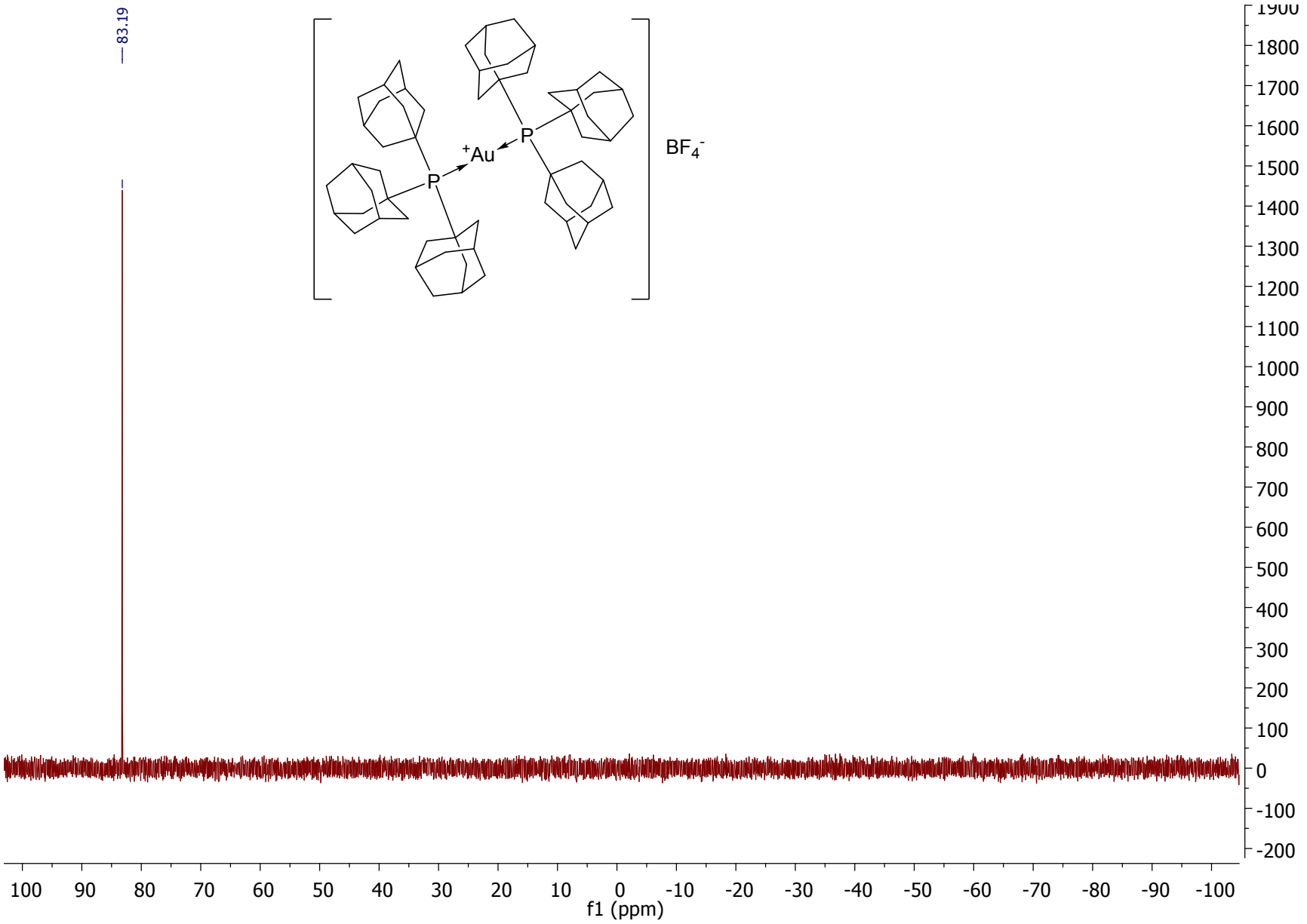
[$Au(PAd_3)_2$]BF_4 (**3**) ^{1}H NMR spectrum



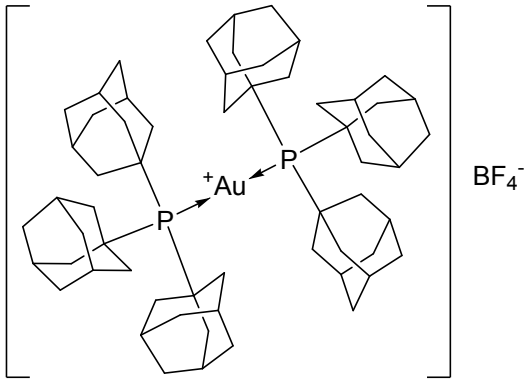
$[Au(PAd_3)_2]BF_4$ (**3**) ^{13}C NMR spectrum



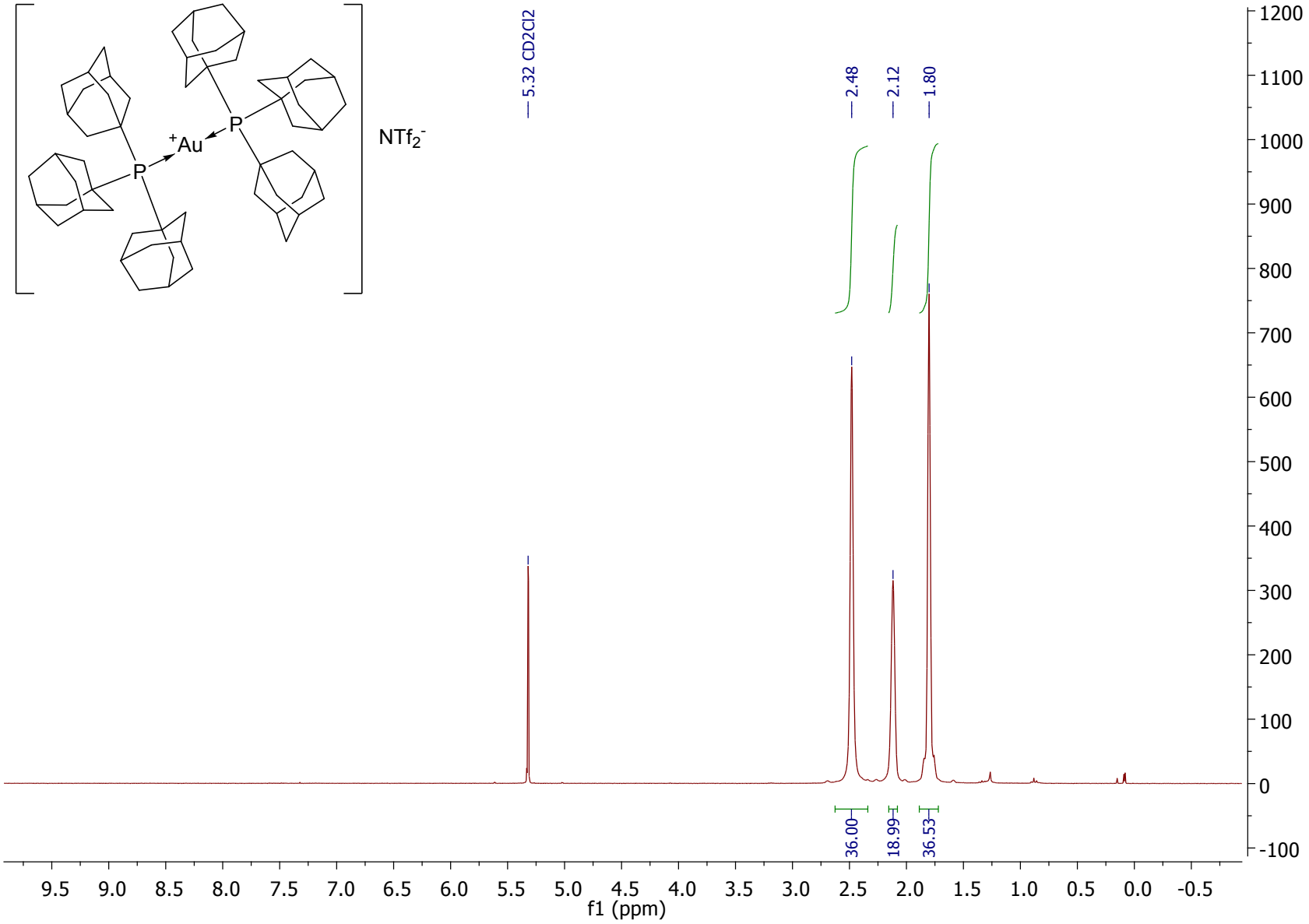
[$Au(PAd_3)_2$]BF_4 (**3**) ^{31}P NMR spectrum



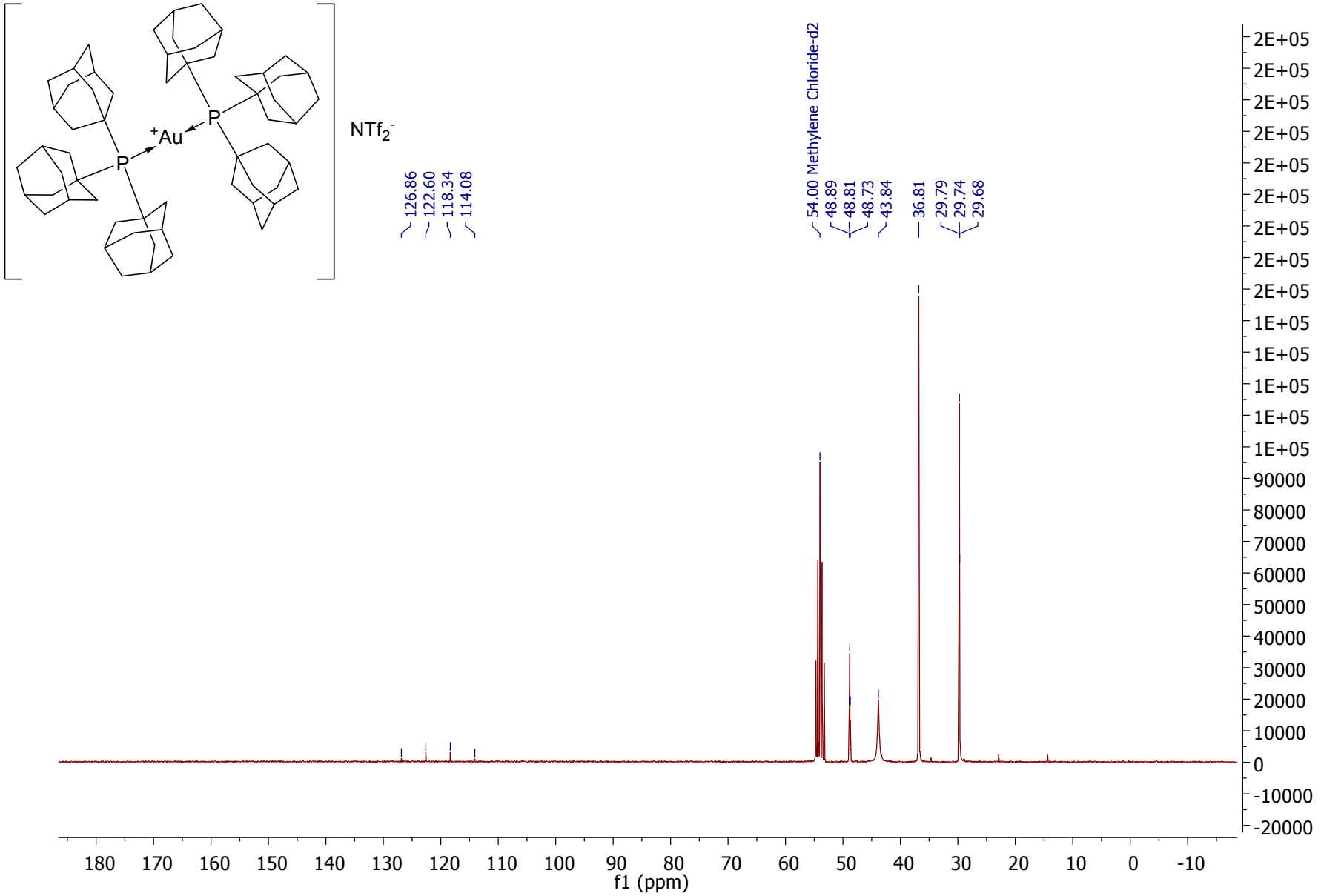
[Au(PAd$_3$)$_2$]BF$_4$ (**3**) ^{19}F NMR spectrum



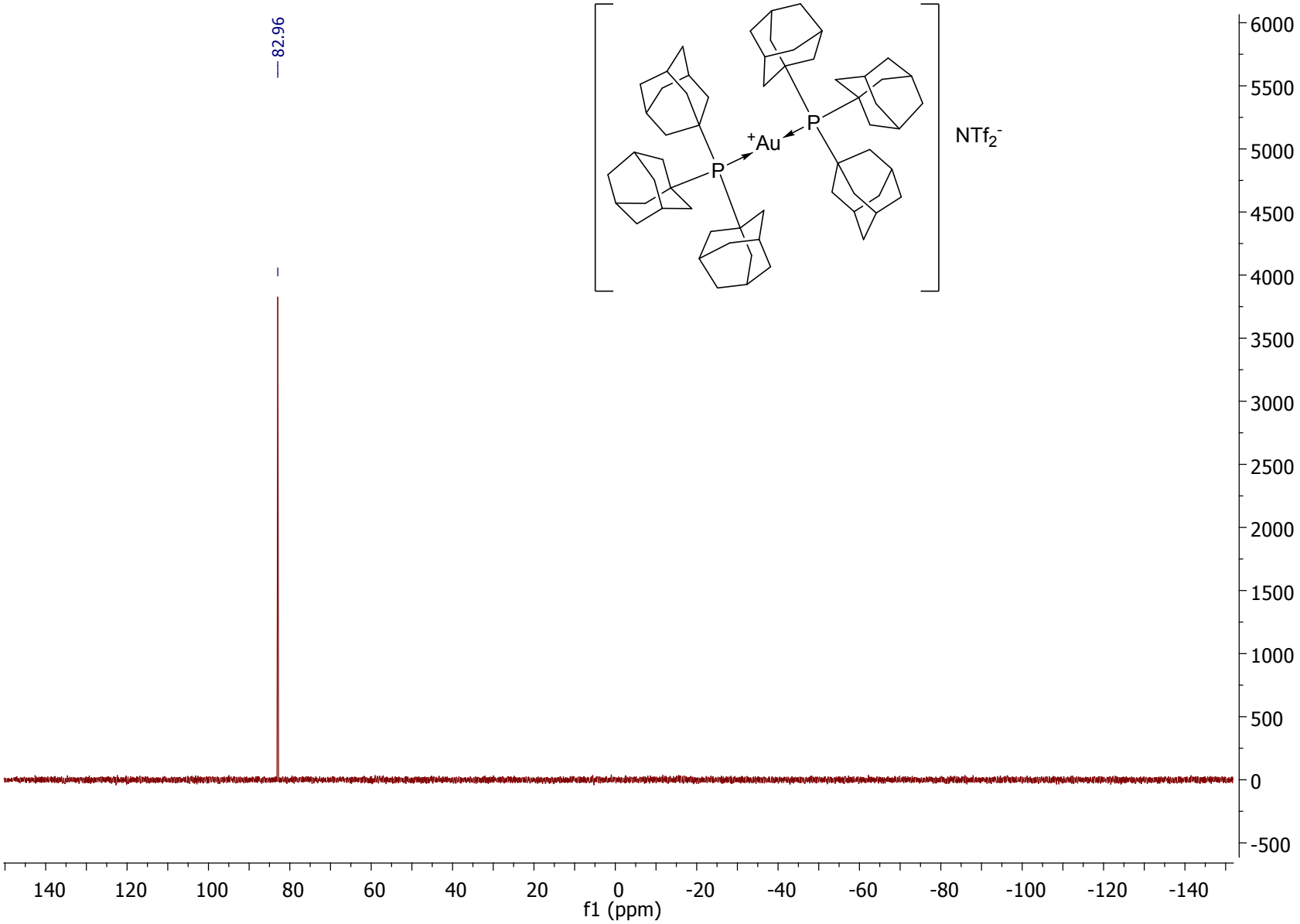
[$Au(PAd_3)_2$]NTf_2 (**4**) ^{1}H NMR spectrum



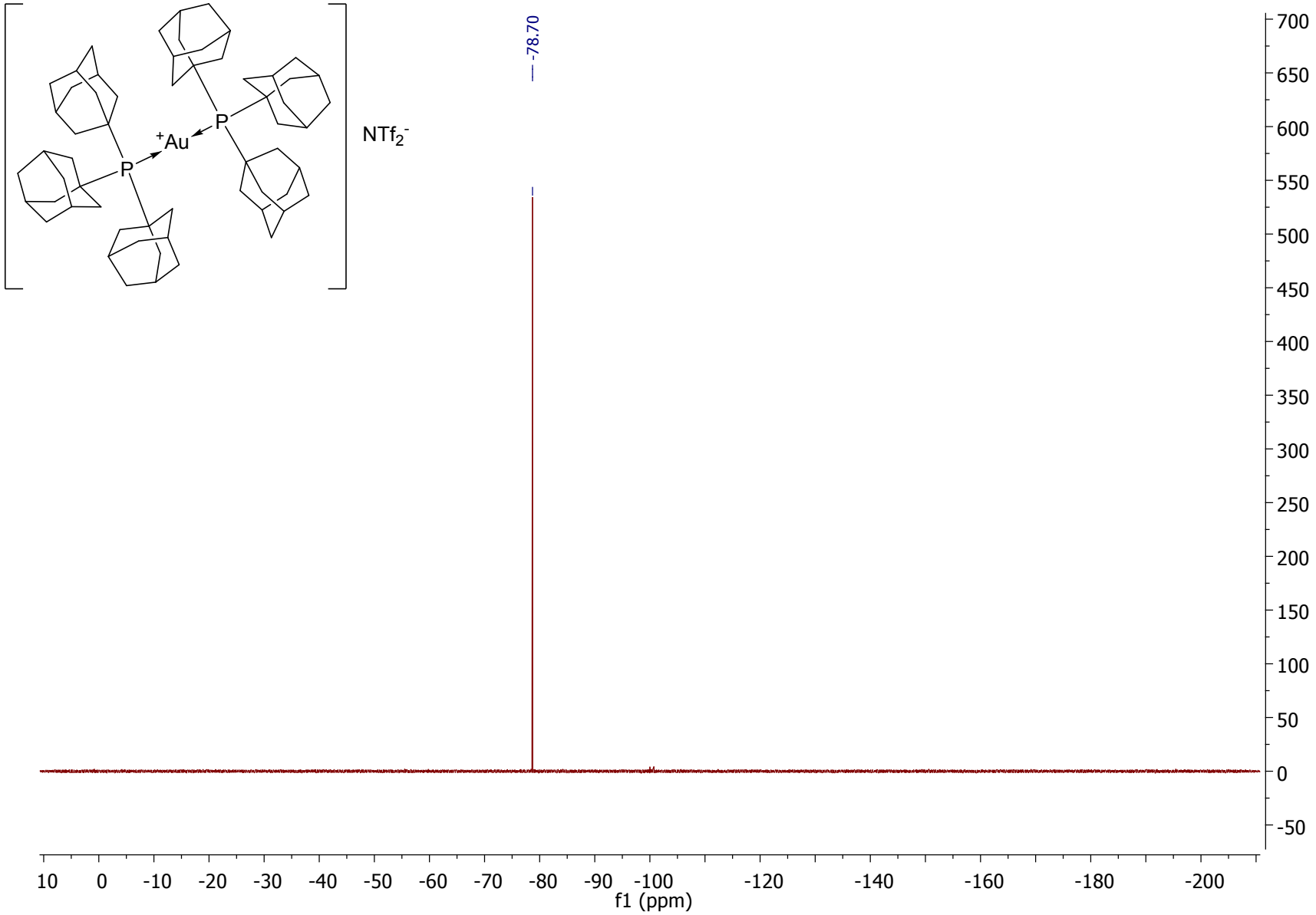
[Au(PAd$_3$)$_2$]NTf$_2$ (**4**) ^{13}C NMR spectrum



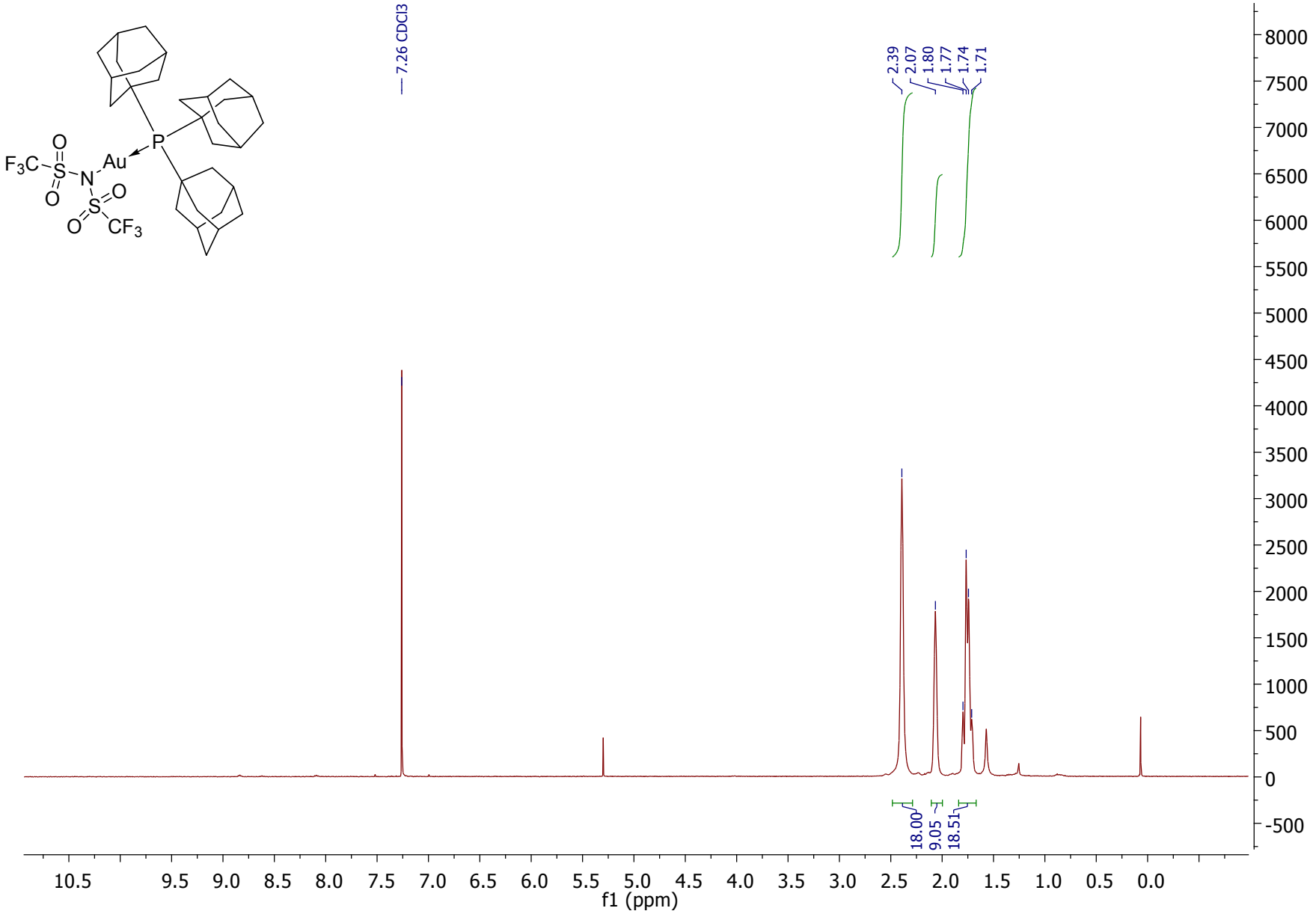
[$Au(PAd_3)_2$]NTf_2 (**4**) ^{31}P NMR spectrum



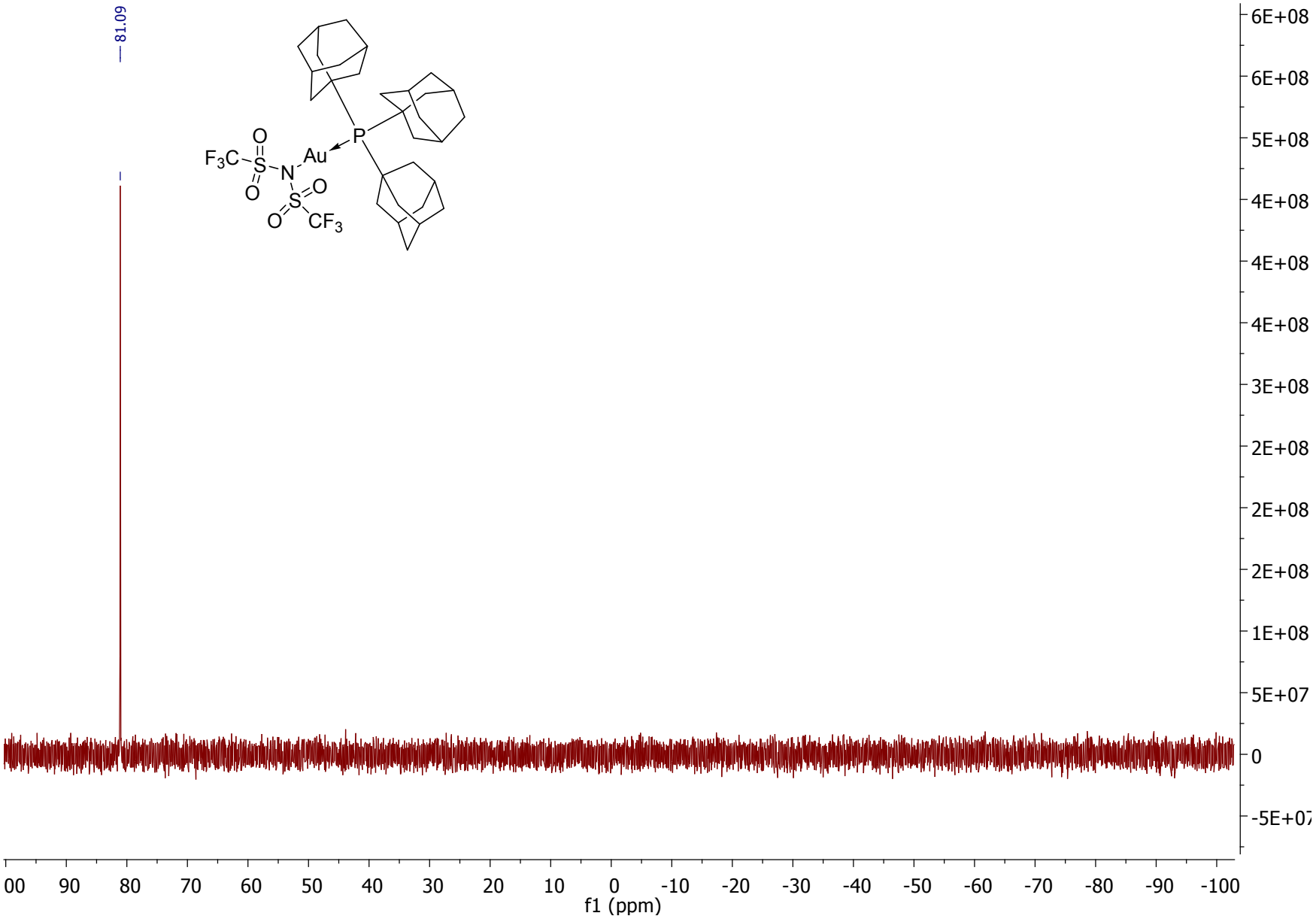
$[Au(PAd_3)_2]NTf_2$ (**4**) ^{19}F NMR spectrum



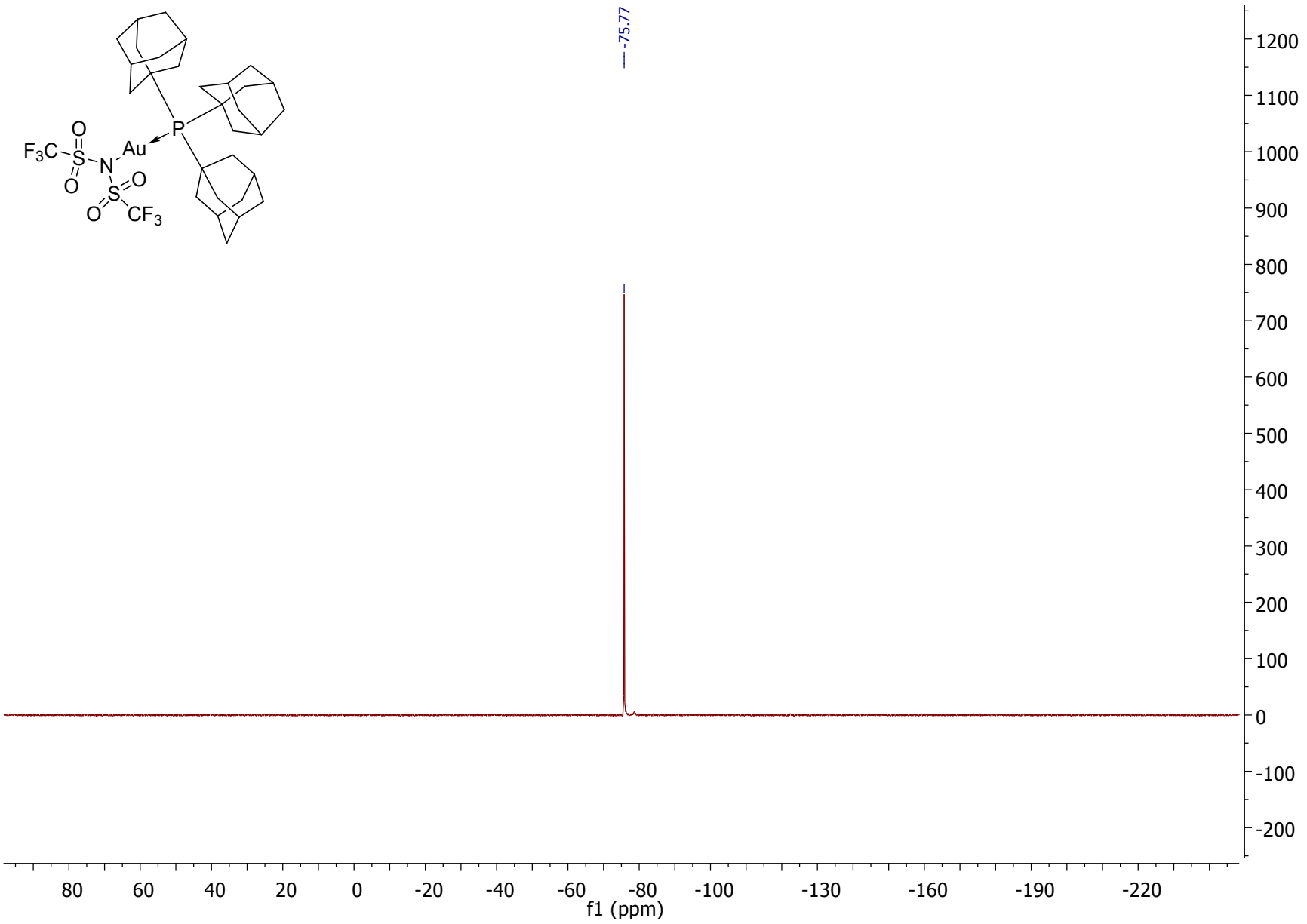
[Au(PAd$_3$)(NTf$_2$)] (**5**) ^{1}H NMR spectrum



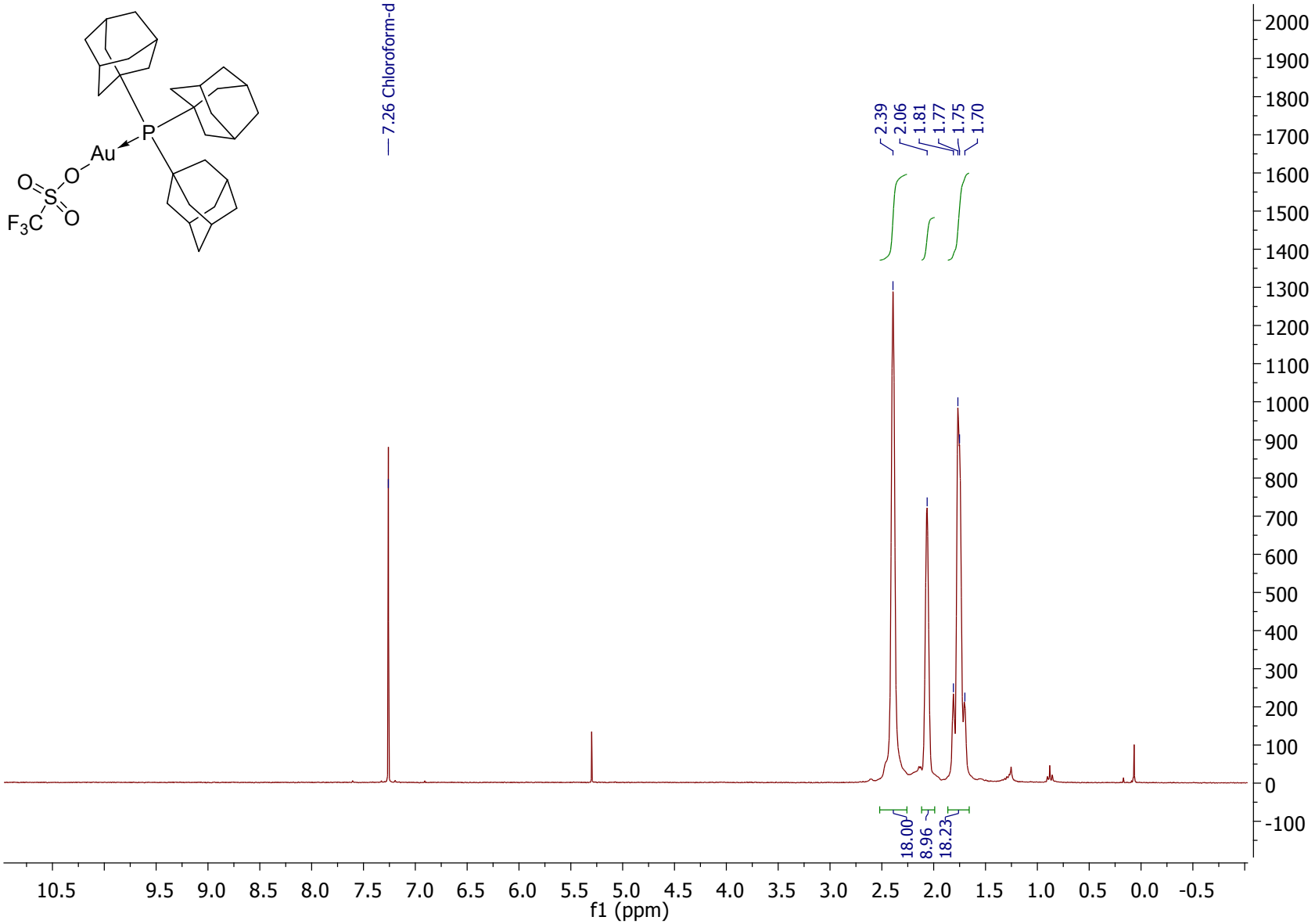
[Au(PAd$_3$)(NTf$_2$)] (**5**) ^{31}P NMR spectrum



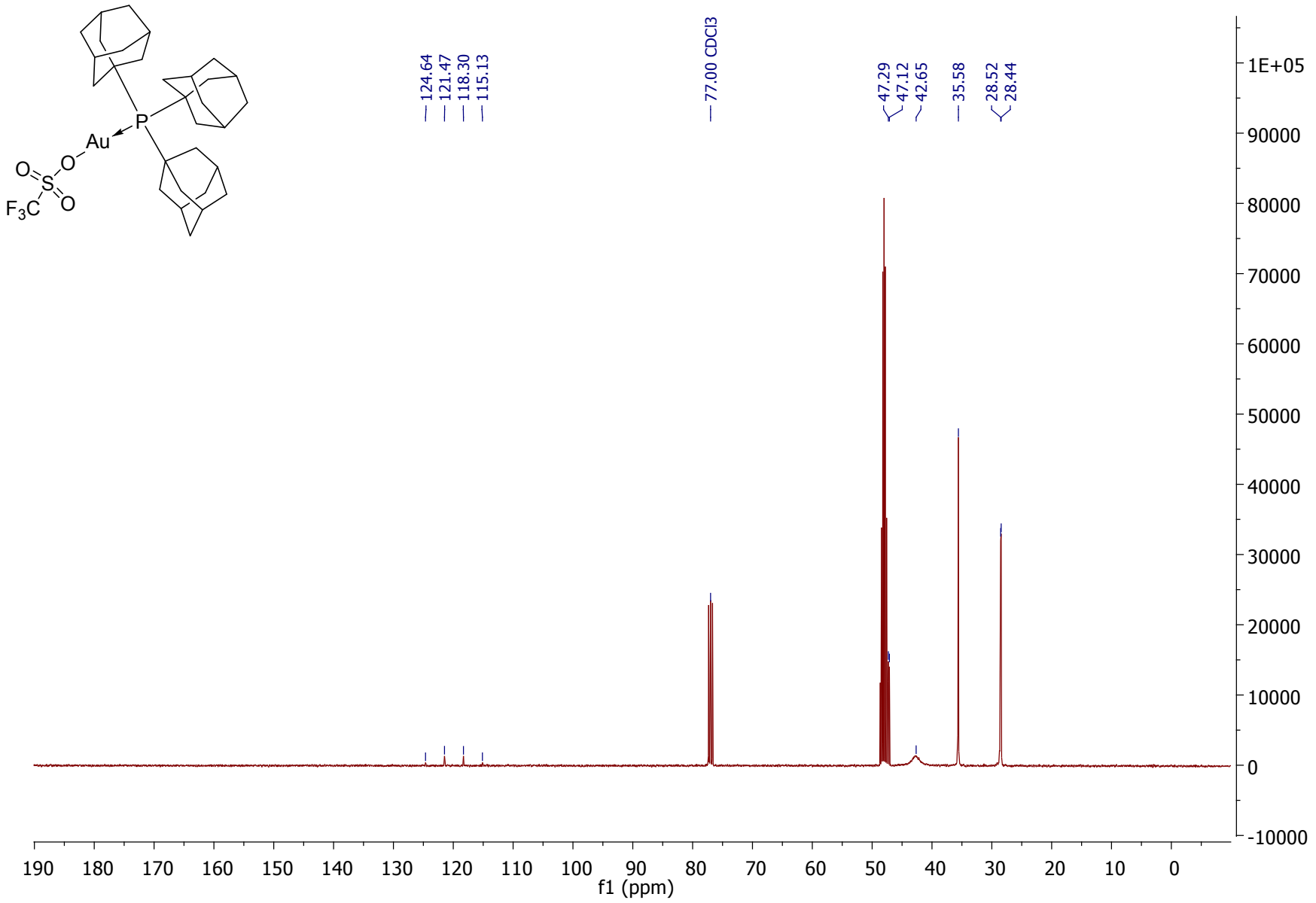
[Au(PAd$_3$)(NTf$_2$)] (**5**) ^{19}F NMR spectrum



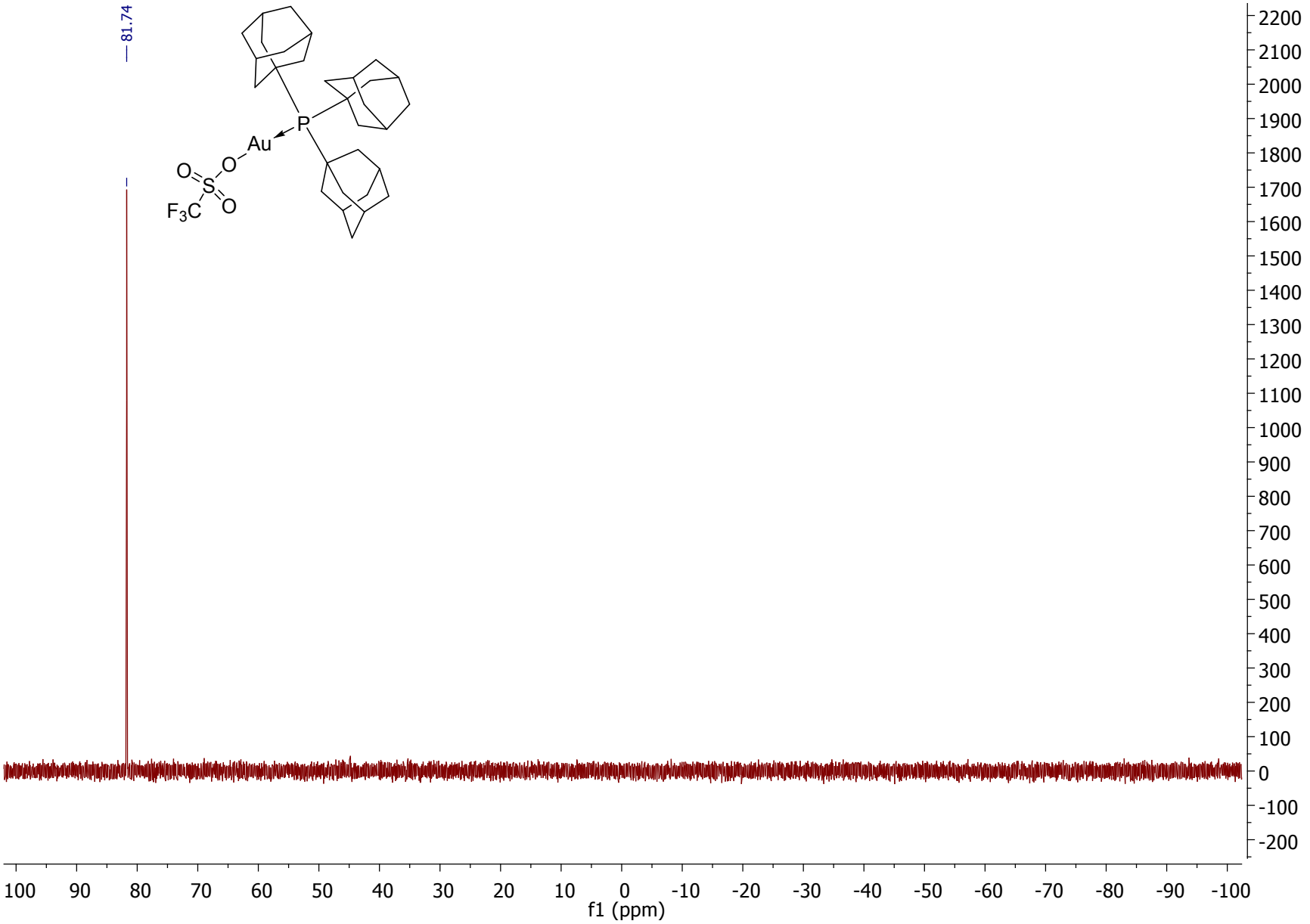
[Au(PAd$_3$)OTf] (**6**) ^{1}H NMR spectrum



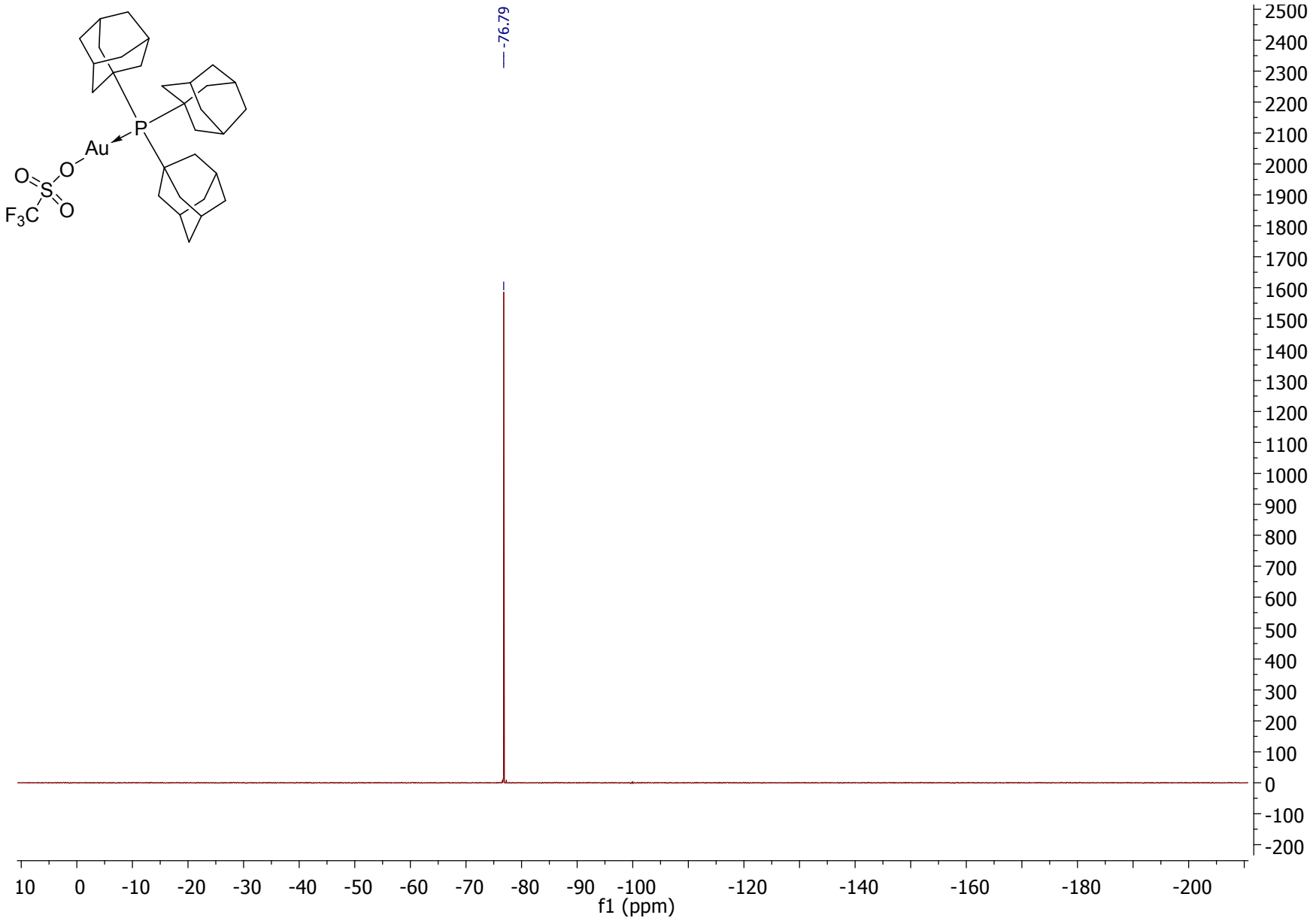
[Au(PAd$_3$)OTf] (**6**) ^{13}C NMR spectrum



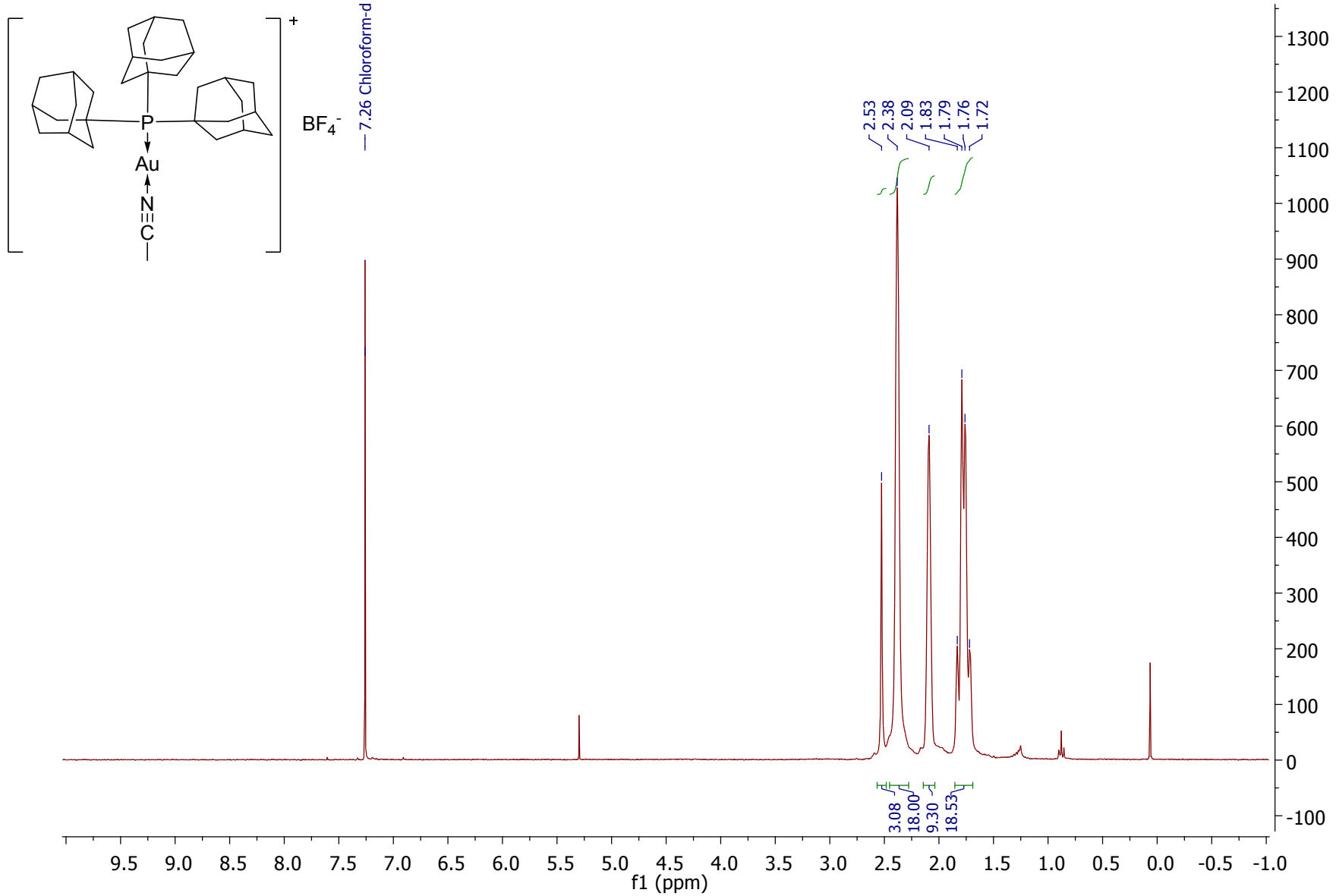
[Au(PAd$_3$)OTf] (**6**) ^{31}P NMR spectrum



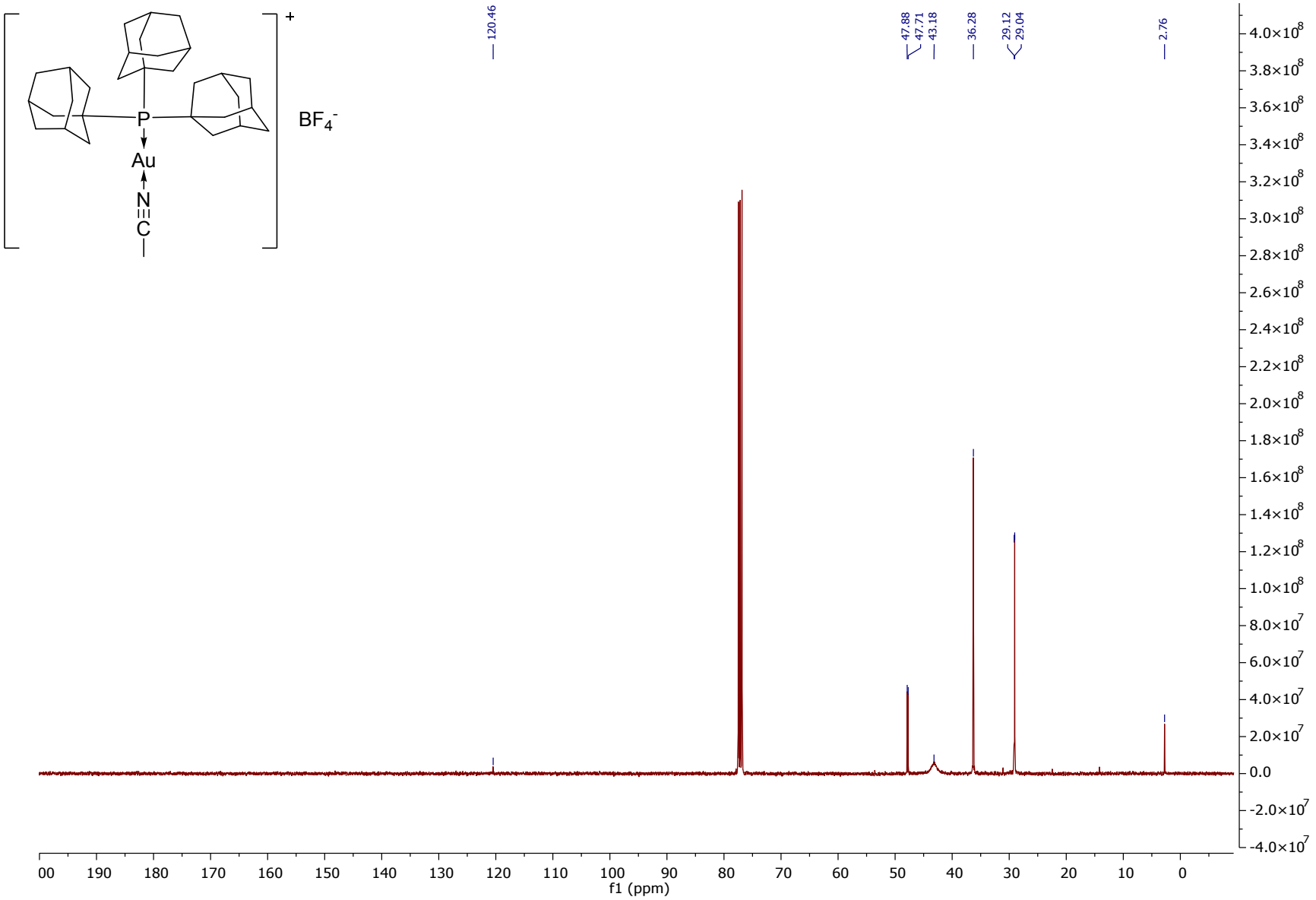
[Au(PAd_3)OTf] (**6**) ^{19}F NMR spectrum



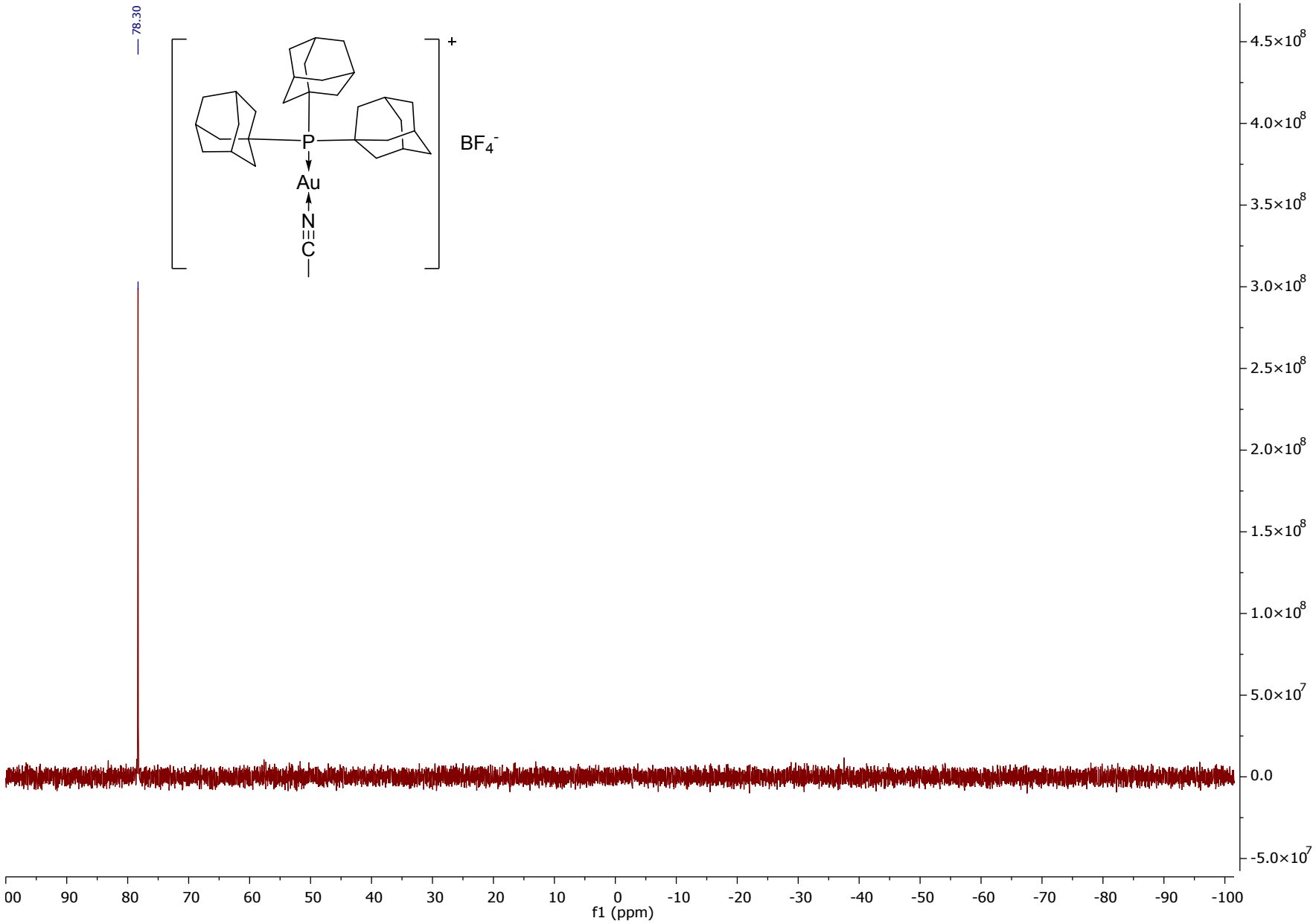
[Au(PAd$_3$)(MeCN)]BF$_4$ (**7**) ^{1}H NMR spectrum



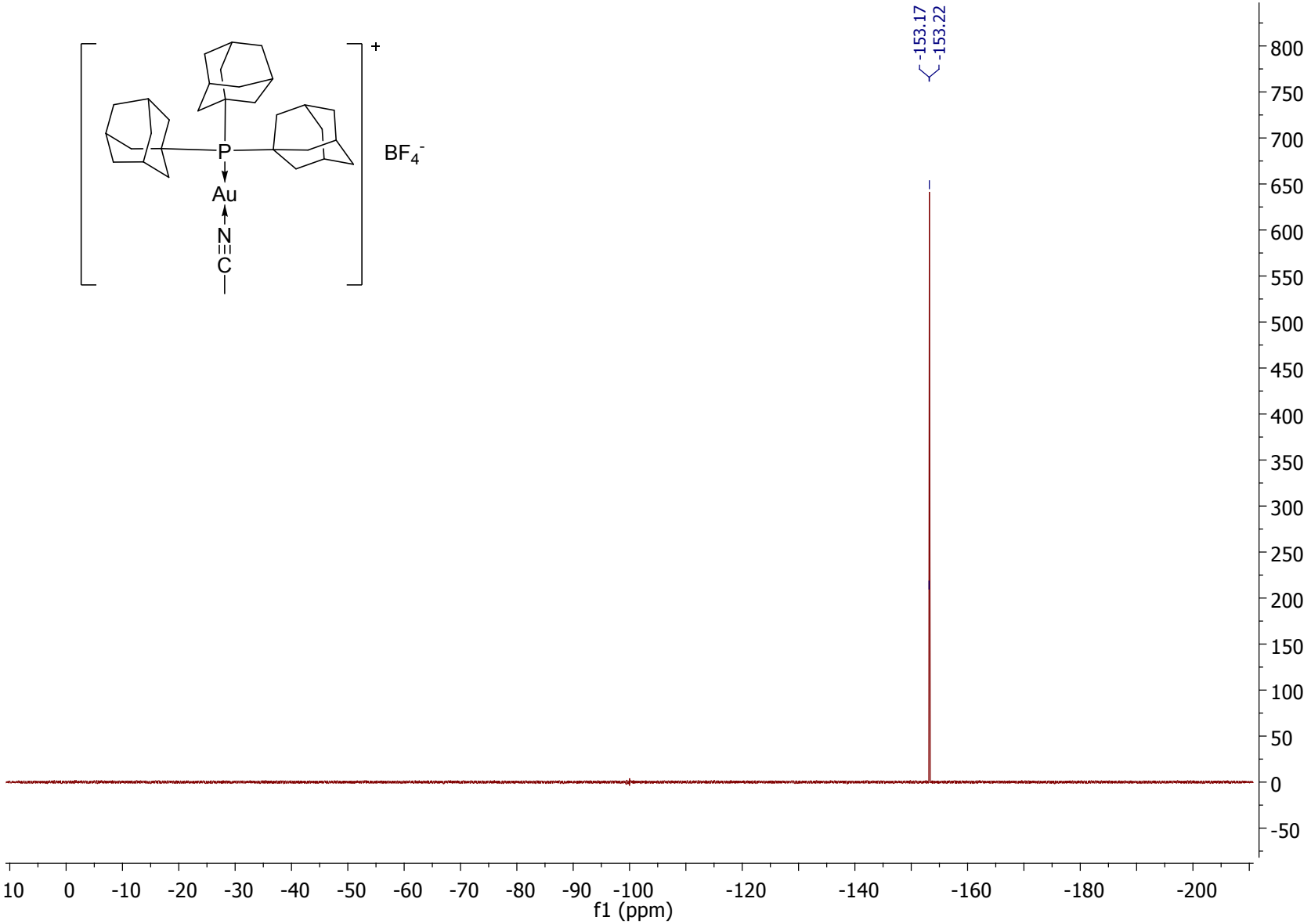
[Au(PAd$_3$)(MeCN)]BF$_4$ (**7**) ^{13}C NMR spectrum



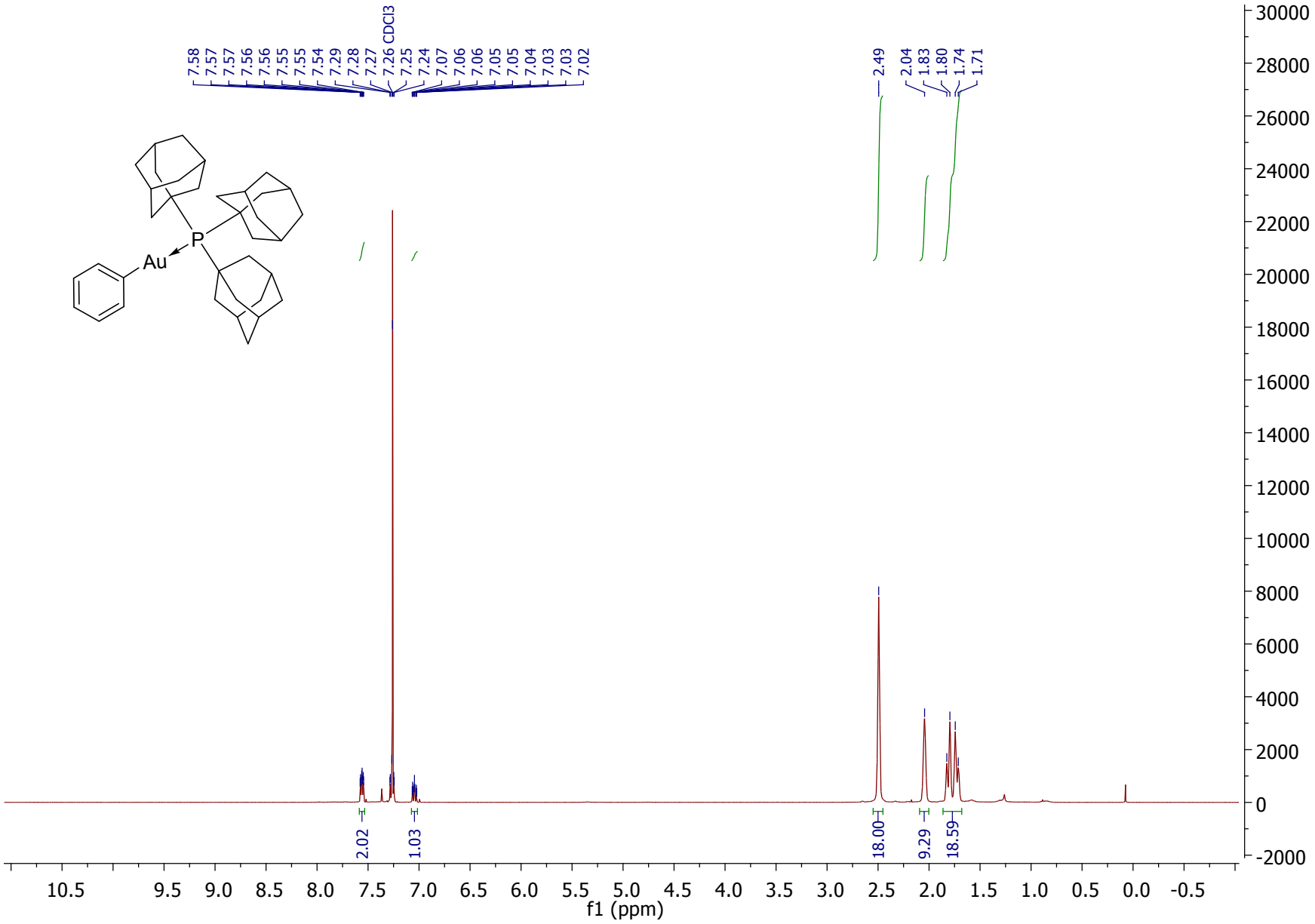
[Au(PAd$_3$)(MeCN)]BF$_4$ (**7**) ^{31}P NMR spectrum



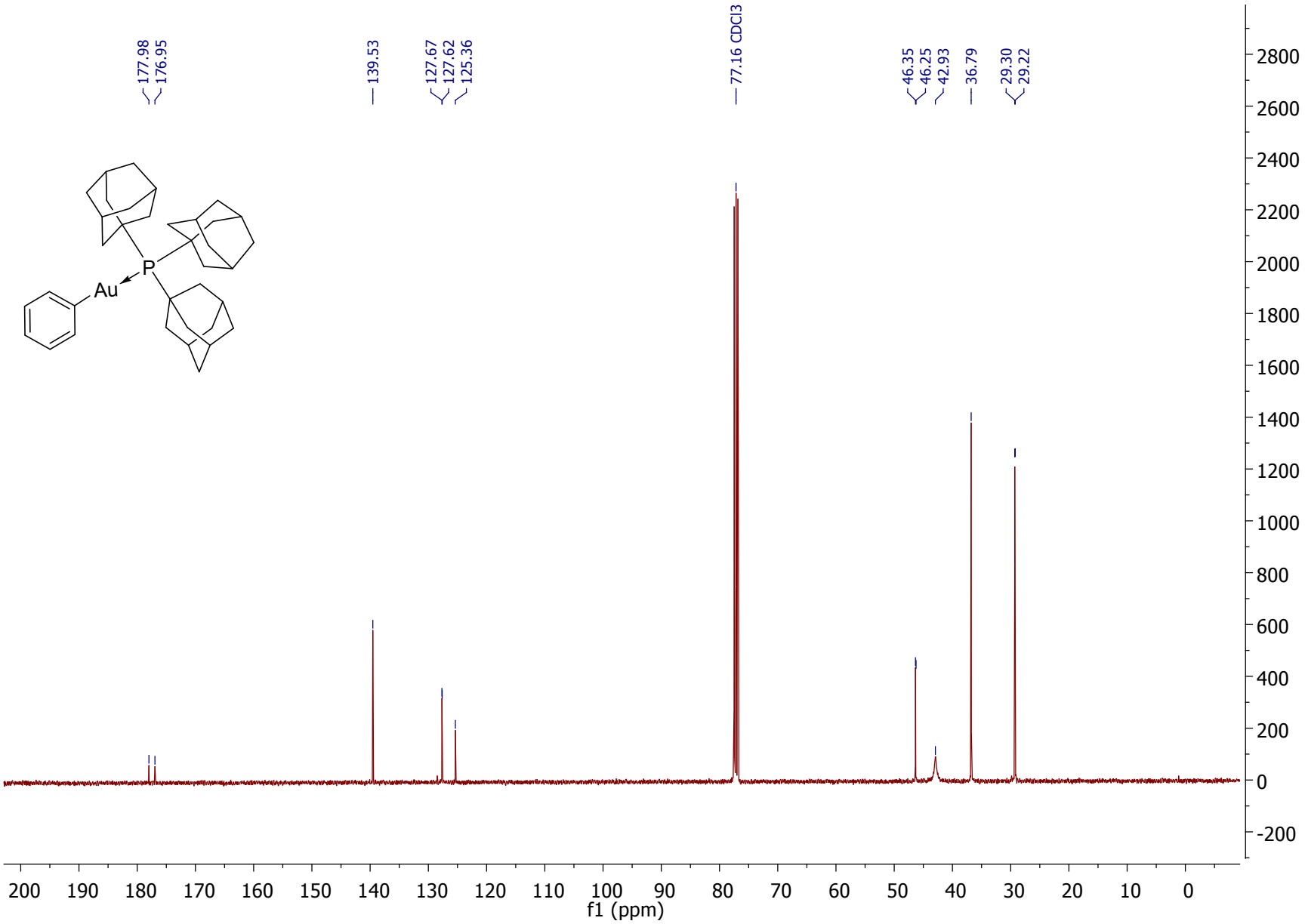
[Au(PAd$_3$)(MeCN)]BF$_4$ (**7**) ^{19}F NMR spectrum



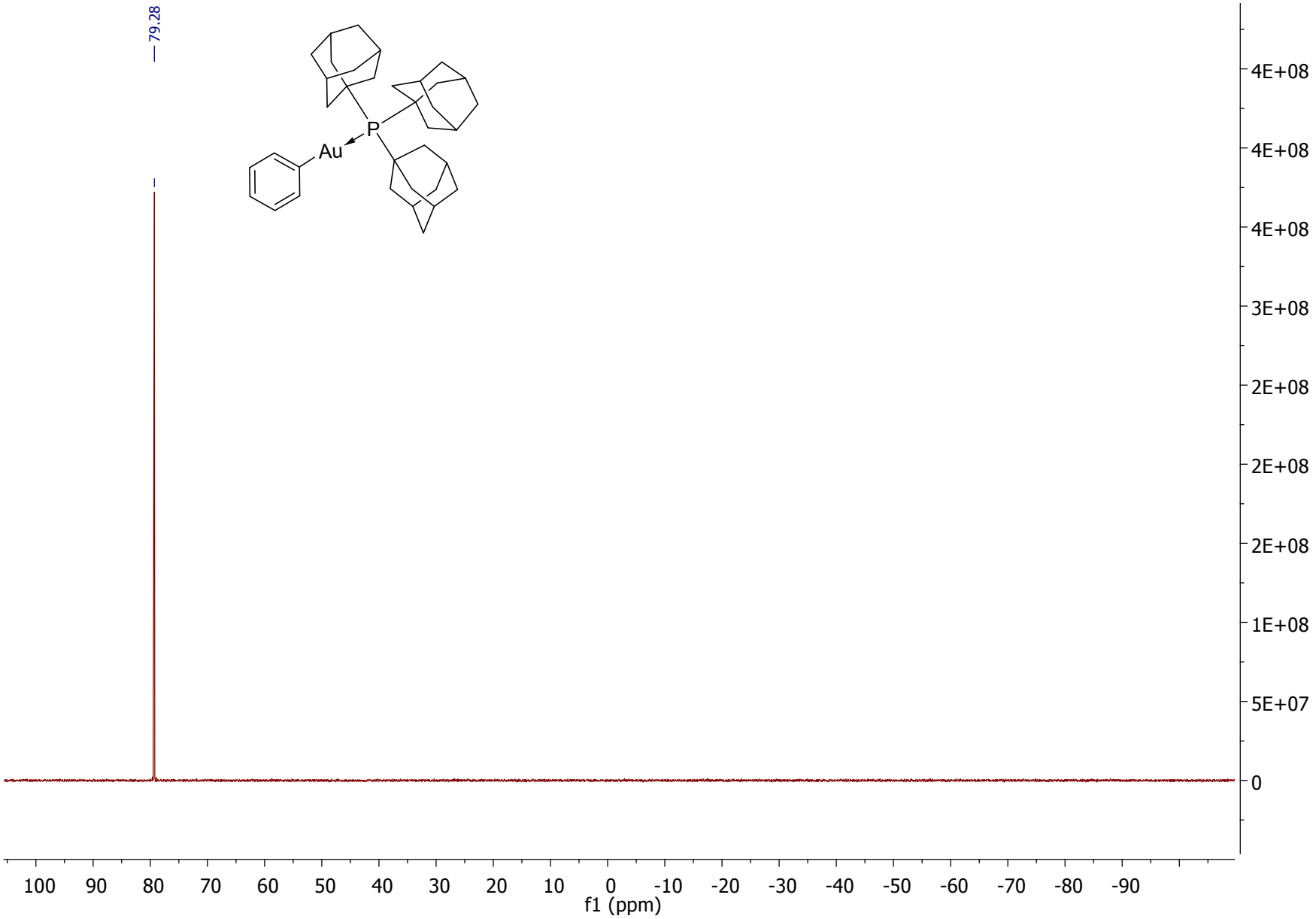
[Au(PAd$_3$)Ph] (**8**) ^{1}H NMR spectrum



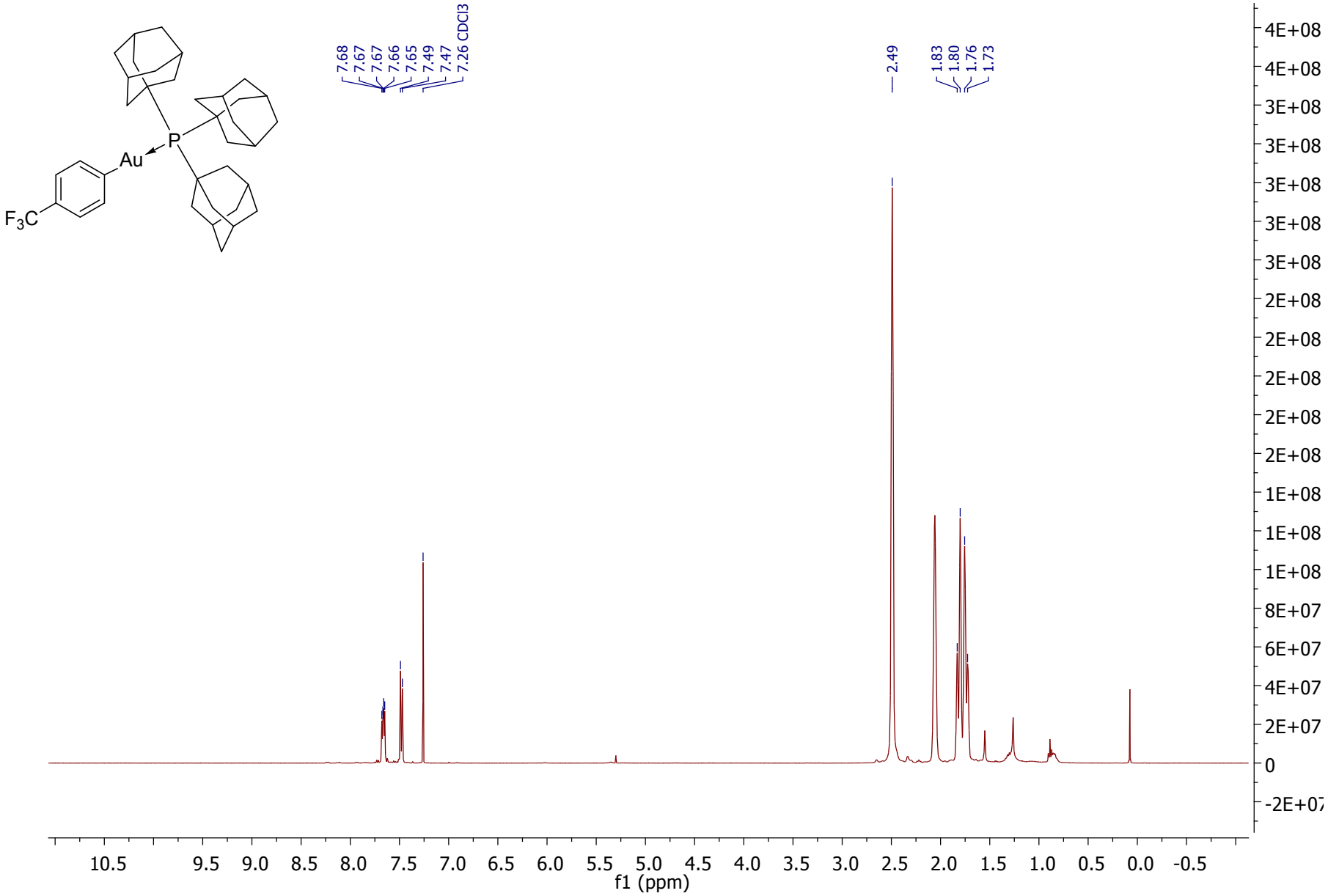
[Au(PAd$_3$)Ph] (**8**) ^{13}C NMR spectrum



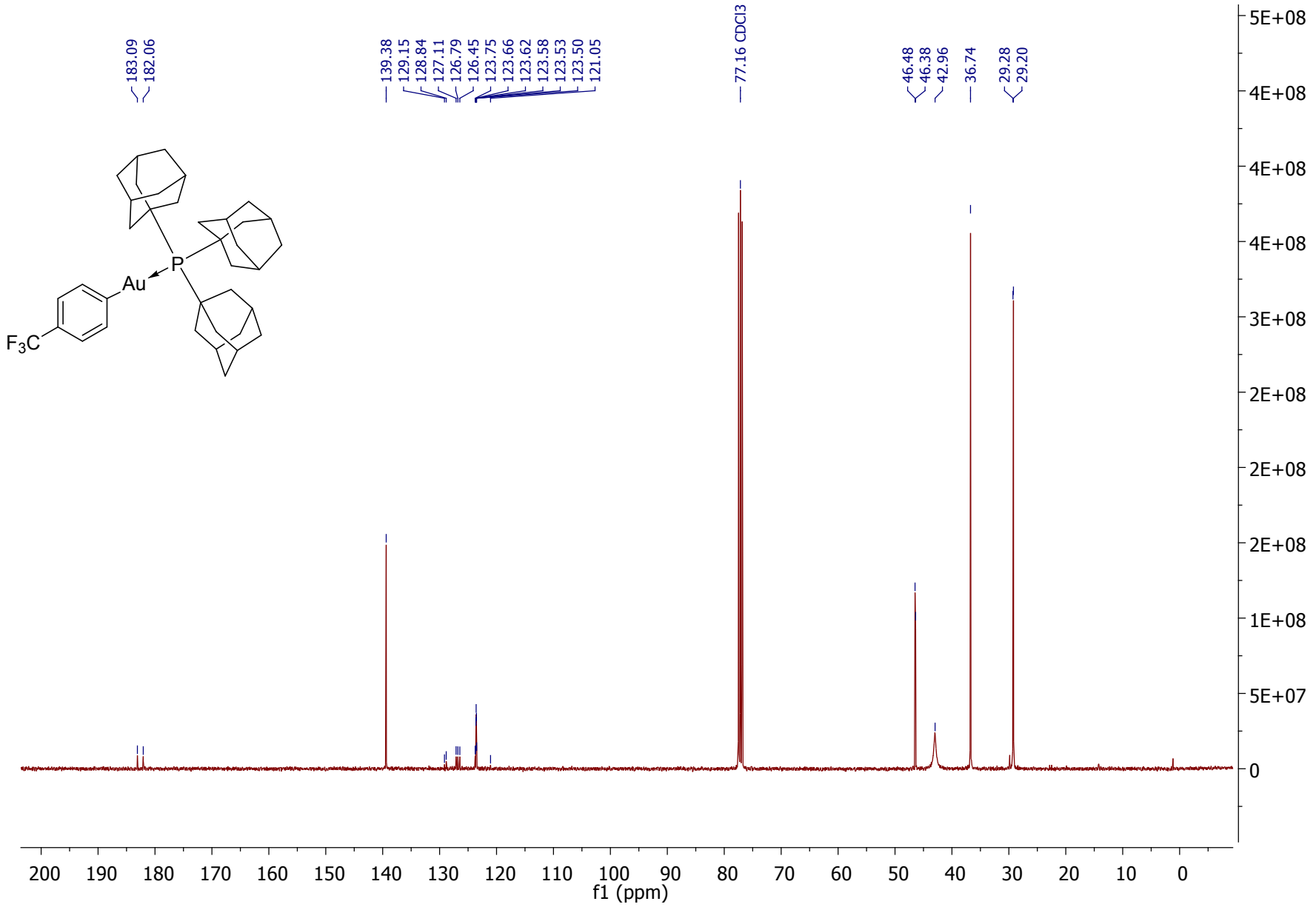
[Au(PAd$_3$)Ph] (**8**) ^{31}P NMR spectrum



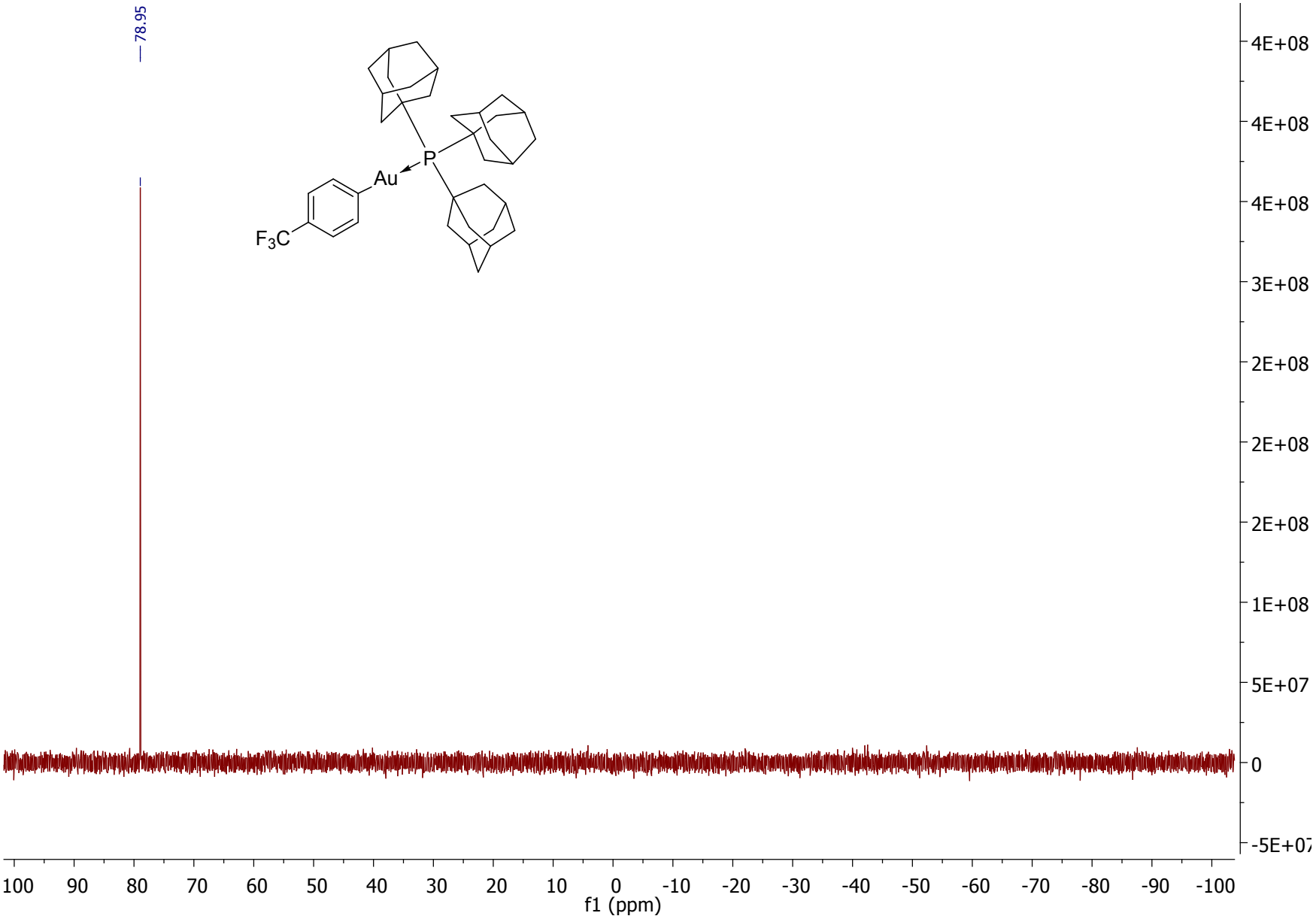
[Au(PAd$_3$)(p-CF$_3$Ph)] (**9**) ^{1}H NMR spectrum



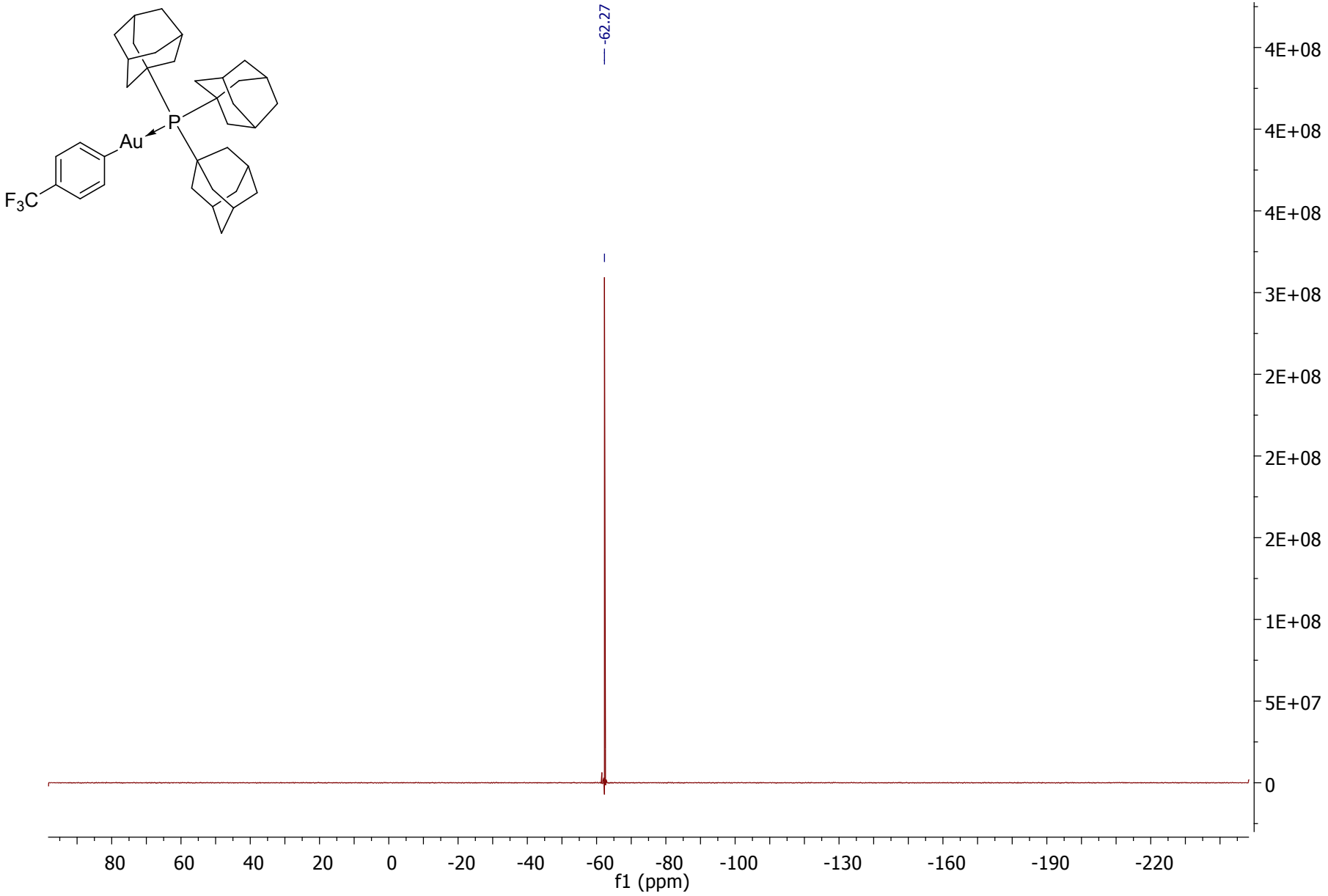
[Au(PAd$_3$)(p-CF$_3$Ph)] (**9**) ^{13}C NMR spectrum



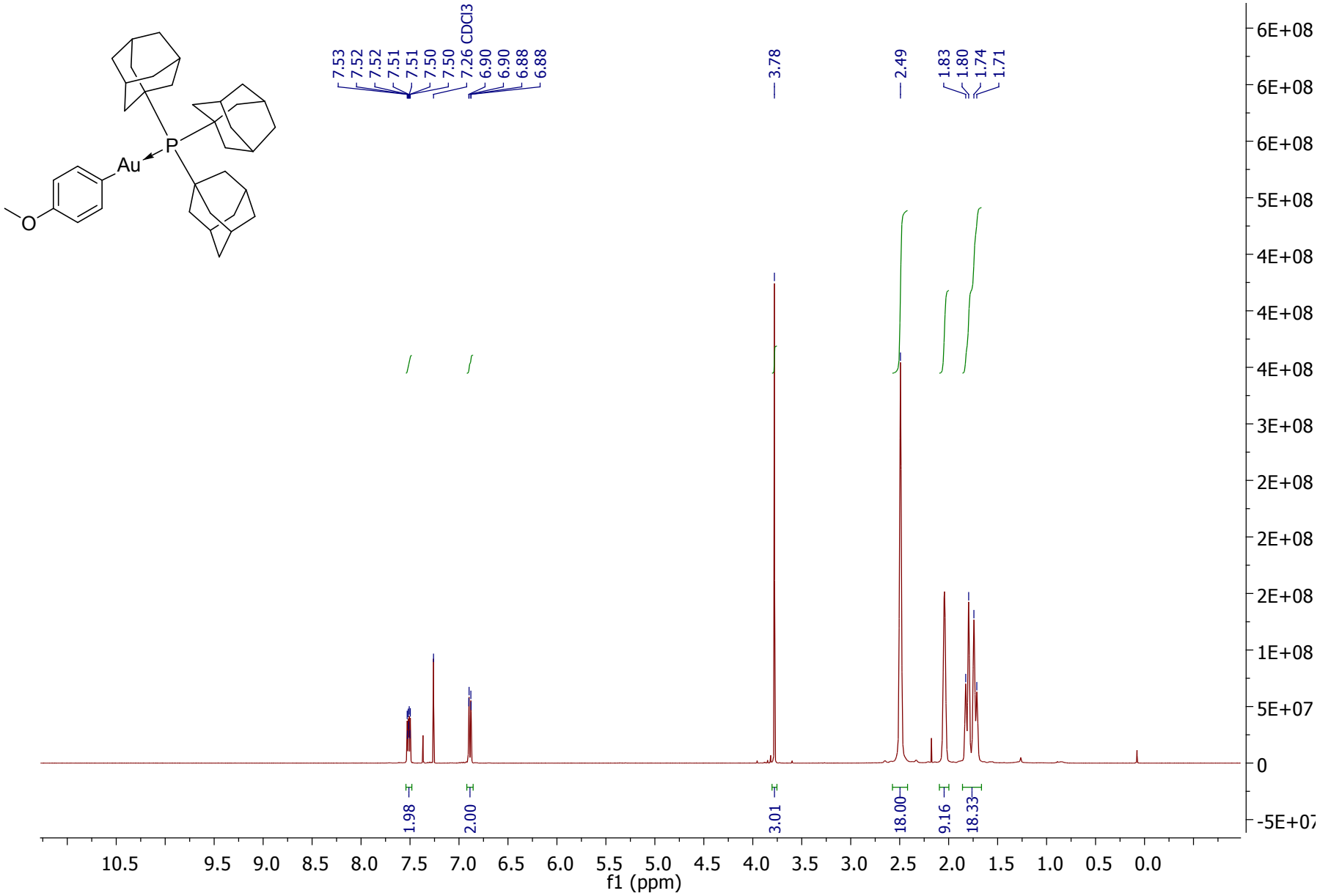
[Au(PAd$_3$)(p-CF$_3$Ph)] (**9**) ^{31}P NMR spectrum



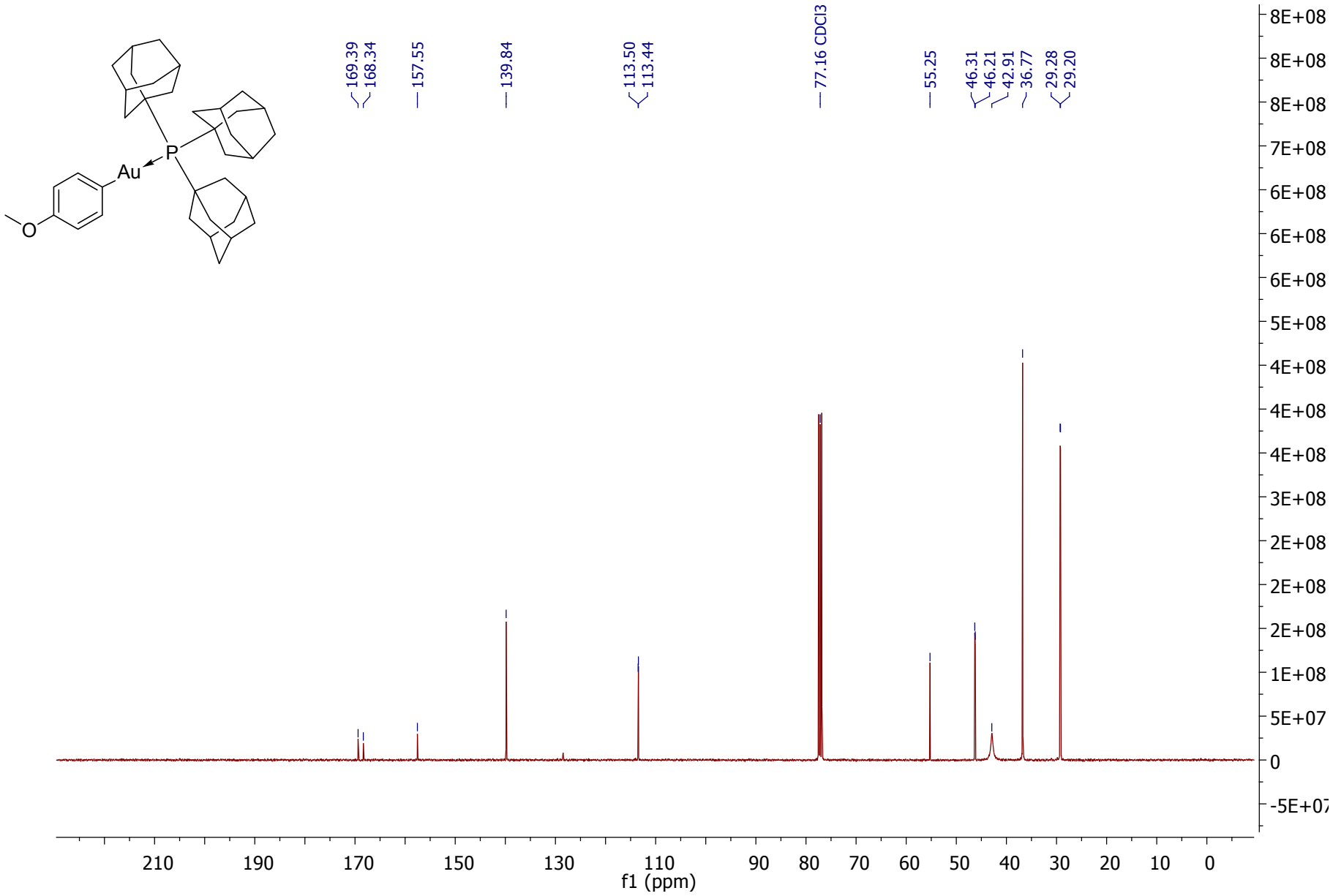
[Au(PAd$_3$)(p-CF$_3$Ph)] (**9**) ^{19}F NMR spectrum



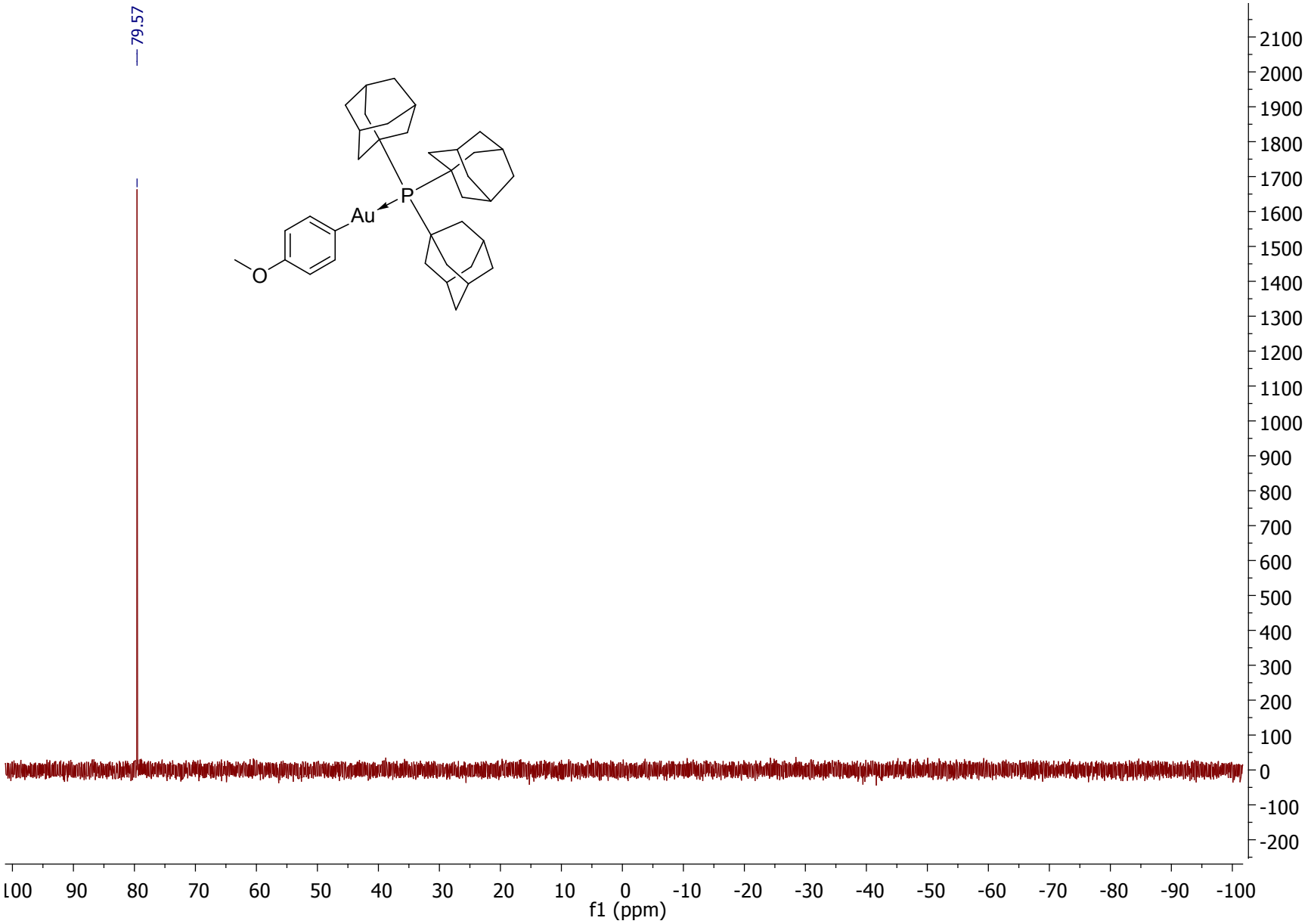
[Au(PAd$_3$)(p-OMePh)] (**10**) ^{1}H NMR spectrum



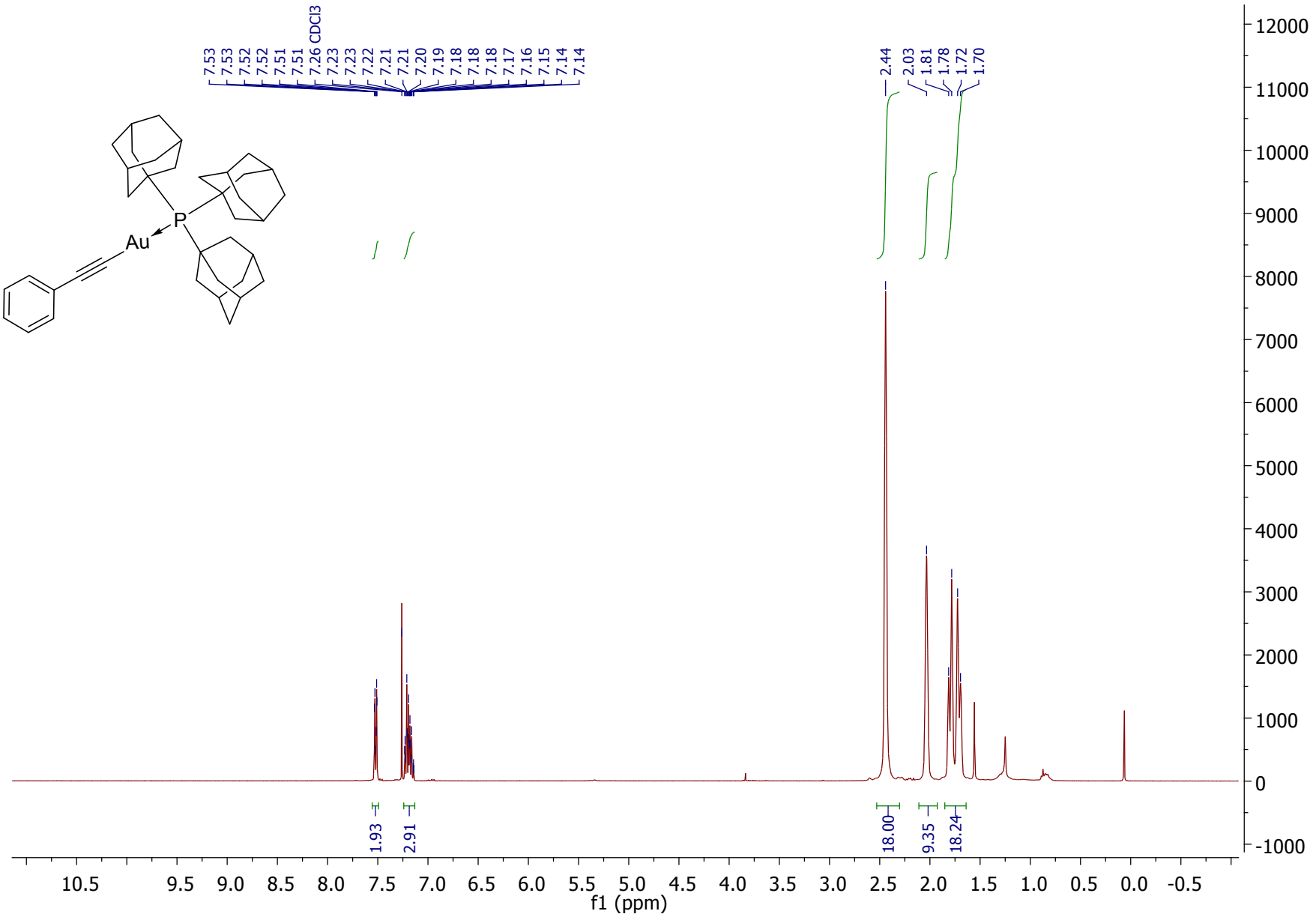
[Au(PAd$_3$)(p-OMePh)] (**10**) ^{13}C NMR spectrum



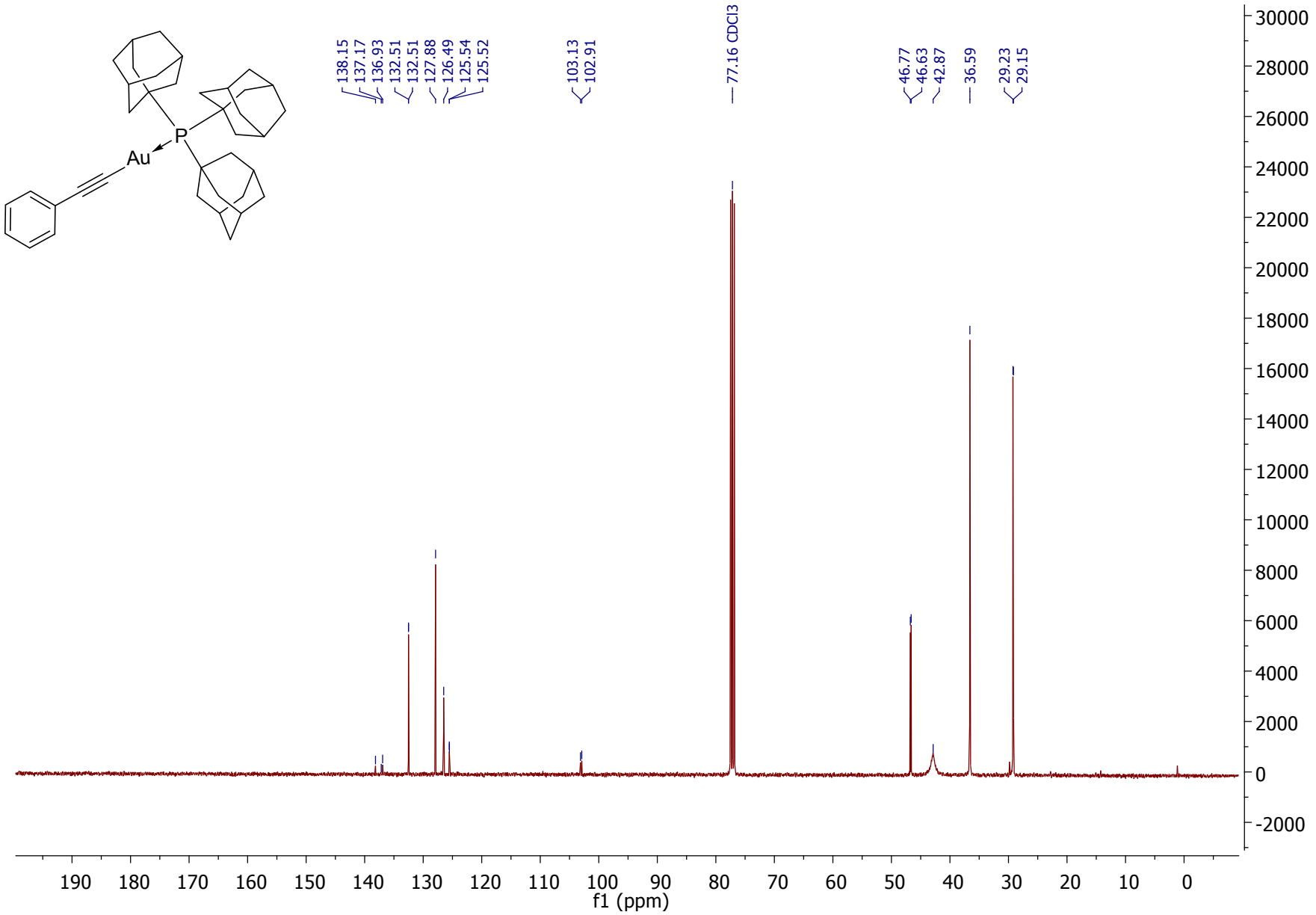
[Au(PAd$_3$)(p-OMePh)] (**10**) ^{31}P NMR spectrum



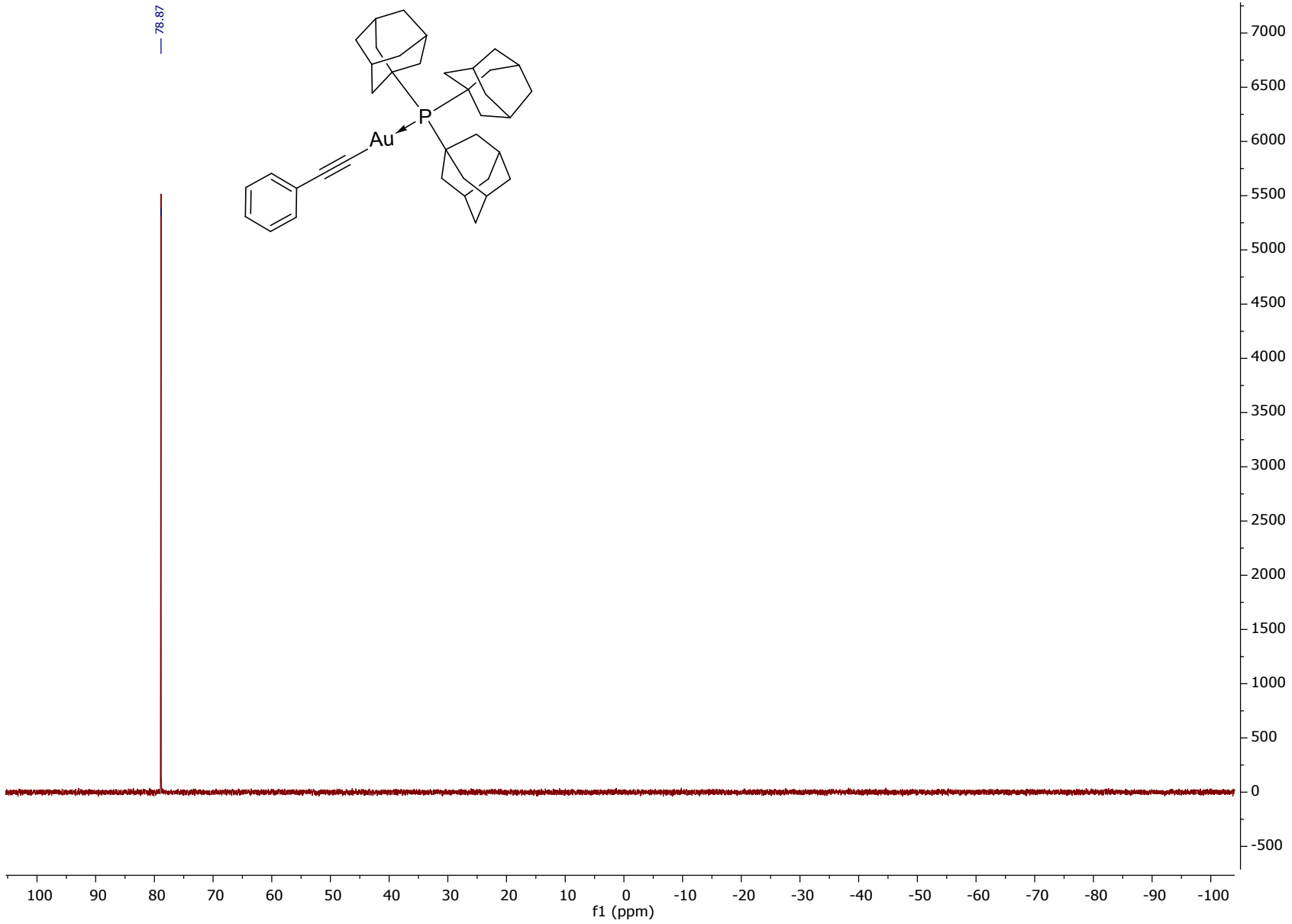
[Au(PAd$_3$)(C≡CPh)] (**11**) ^{1}H NMR spectrum



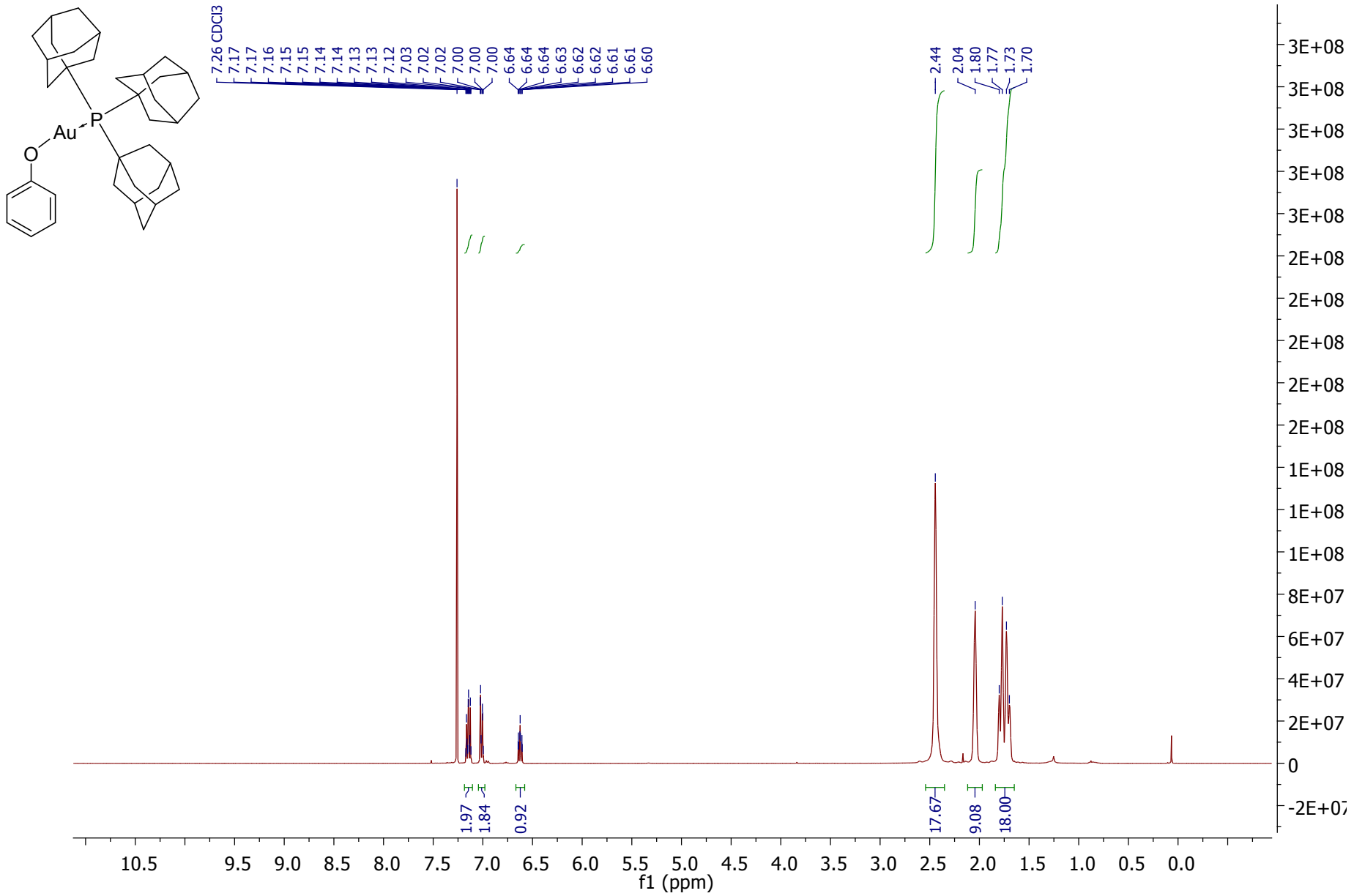
[Au(PAd$_3$)(C≡CPh)] (**11**) ^{13}C NMR spectrum



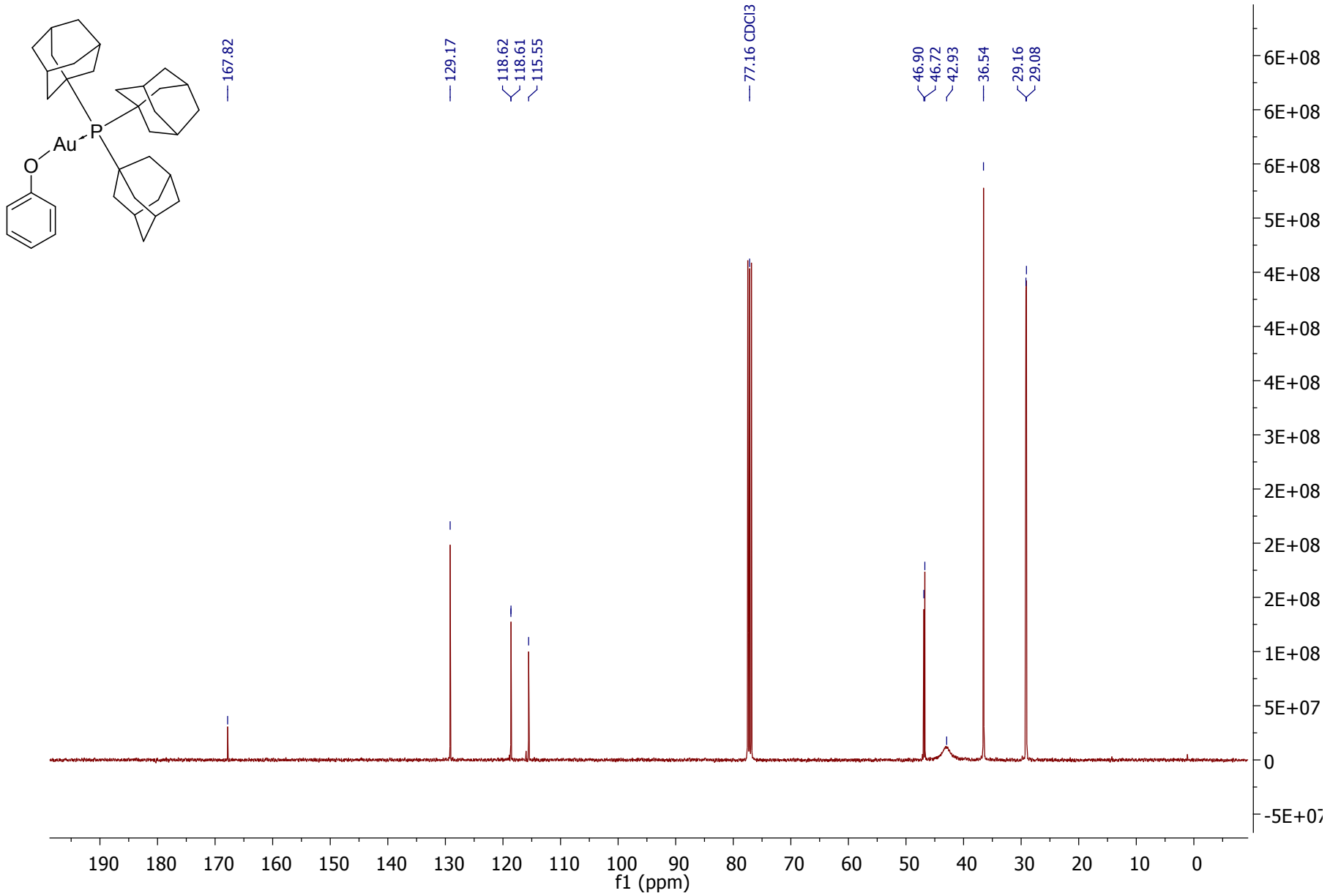
[Au(PAd$_3$)(CΞCPh)] (**11**) ^{31}P NMR spectrum



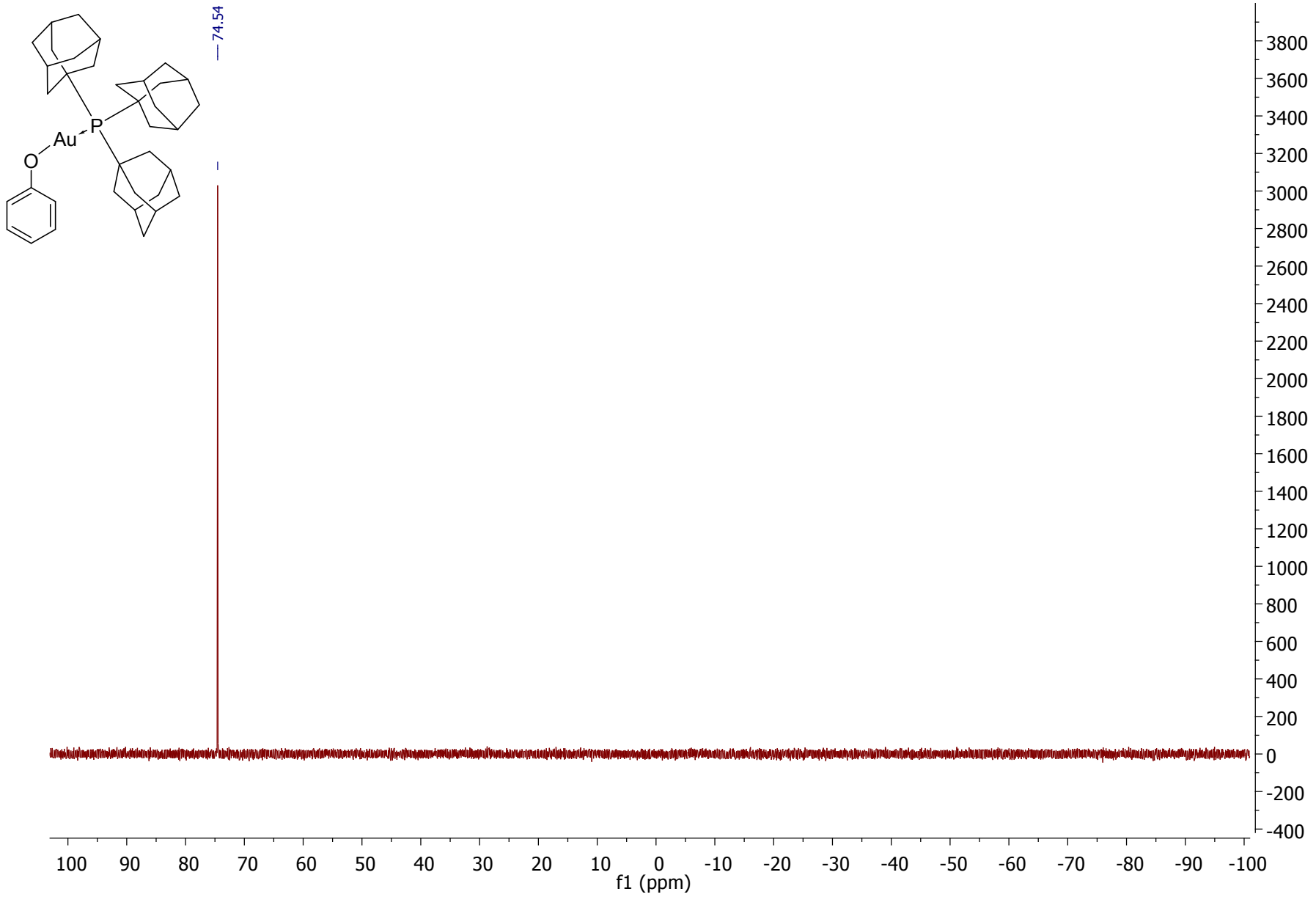
[Au(PAd$_3$)(OPh)] (**13**) ^{1}H NMR spectrum



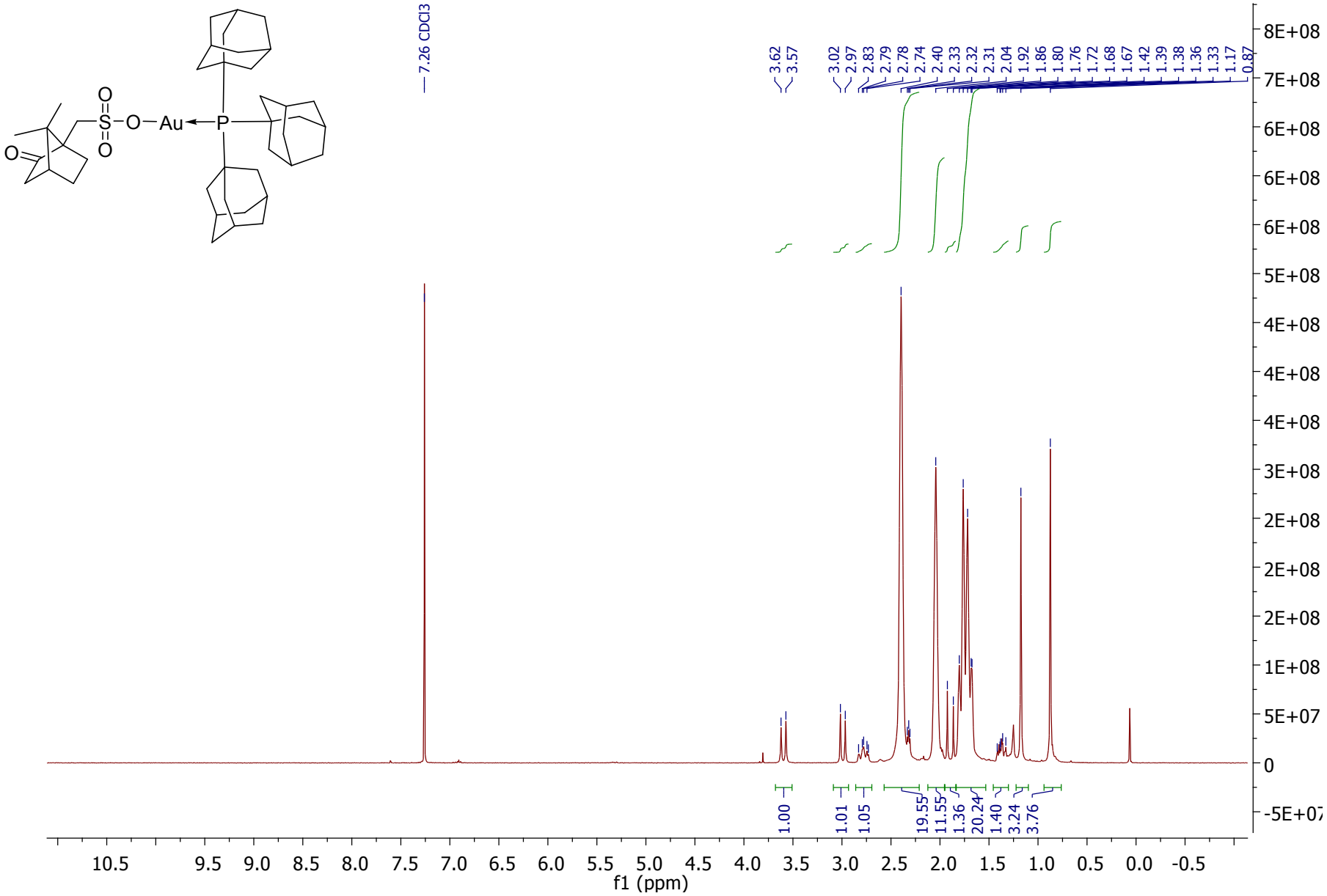
[Au(PAd$_3$)(OPh)] (**13**) ^{13}C NMR spectrum



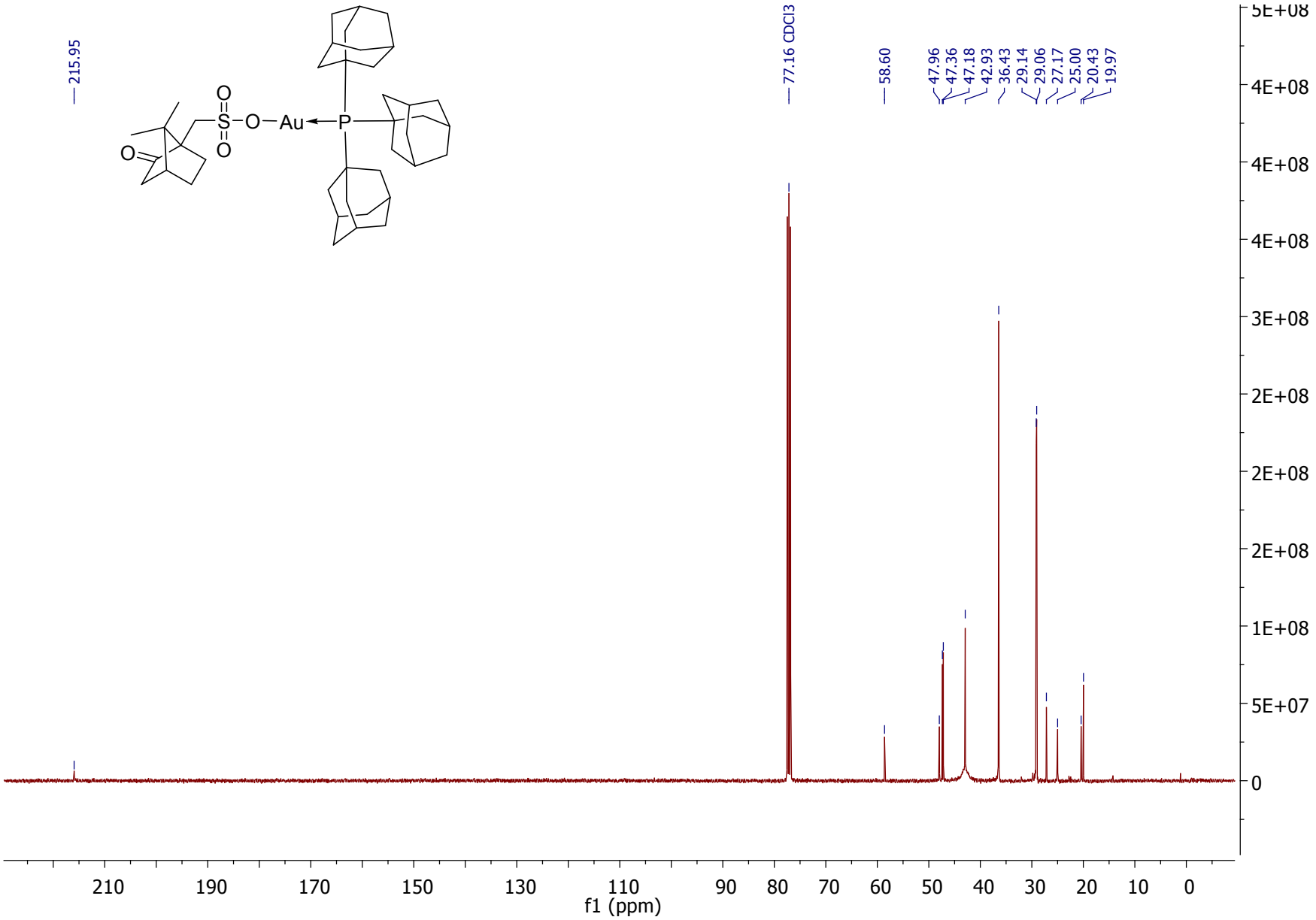
[Au(PAd$_3$)(OPh)] (**13**) ^{31}P NMR spectrum



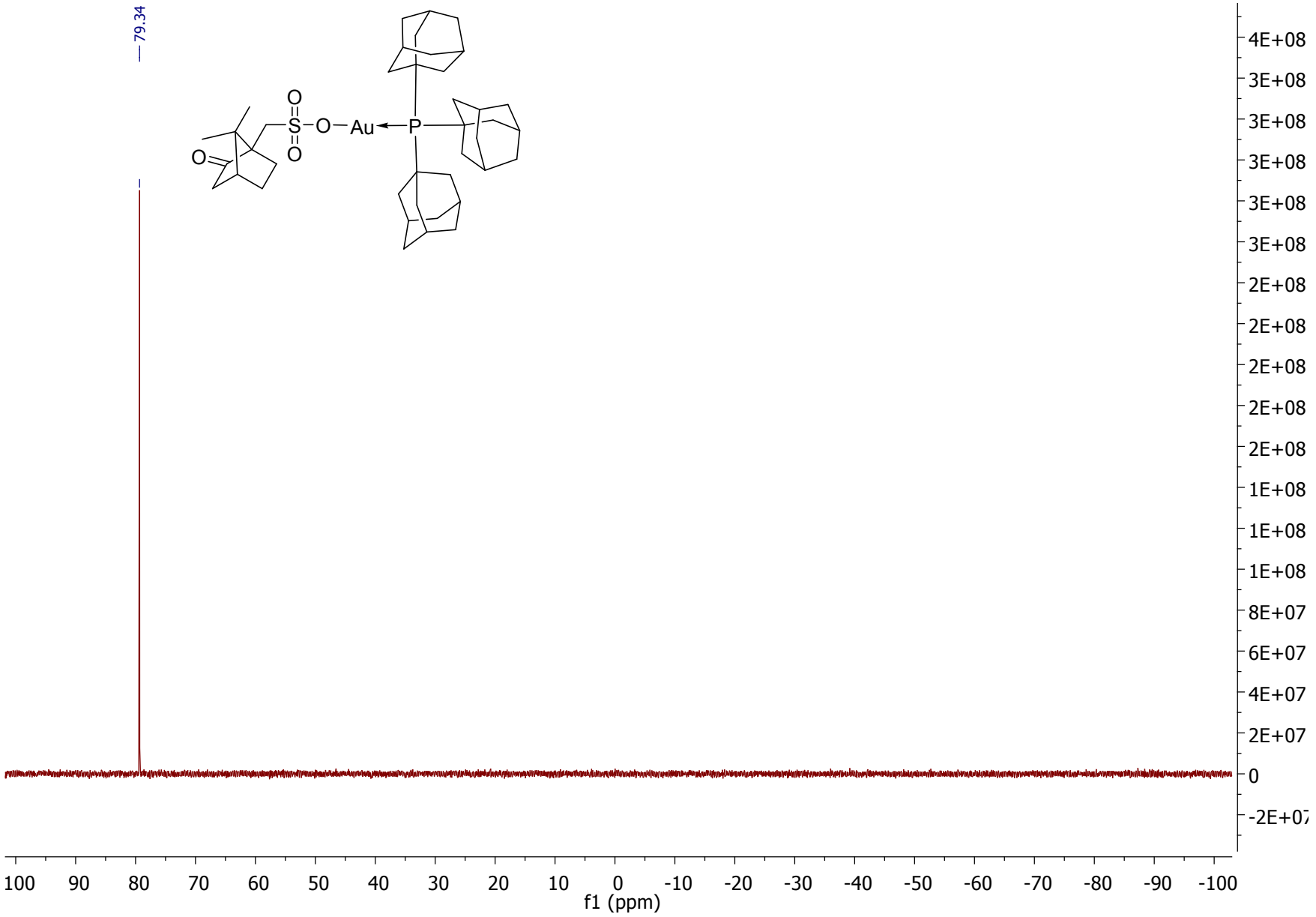
[Au(PAd$_3$(CSA)] (**12**) ^{1}H NMR spectrum



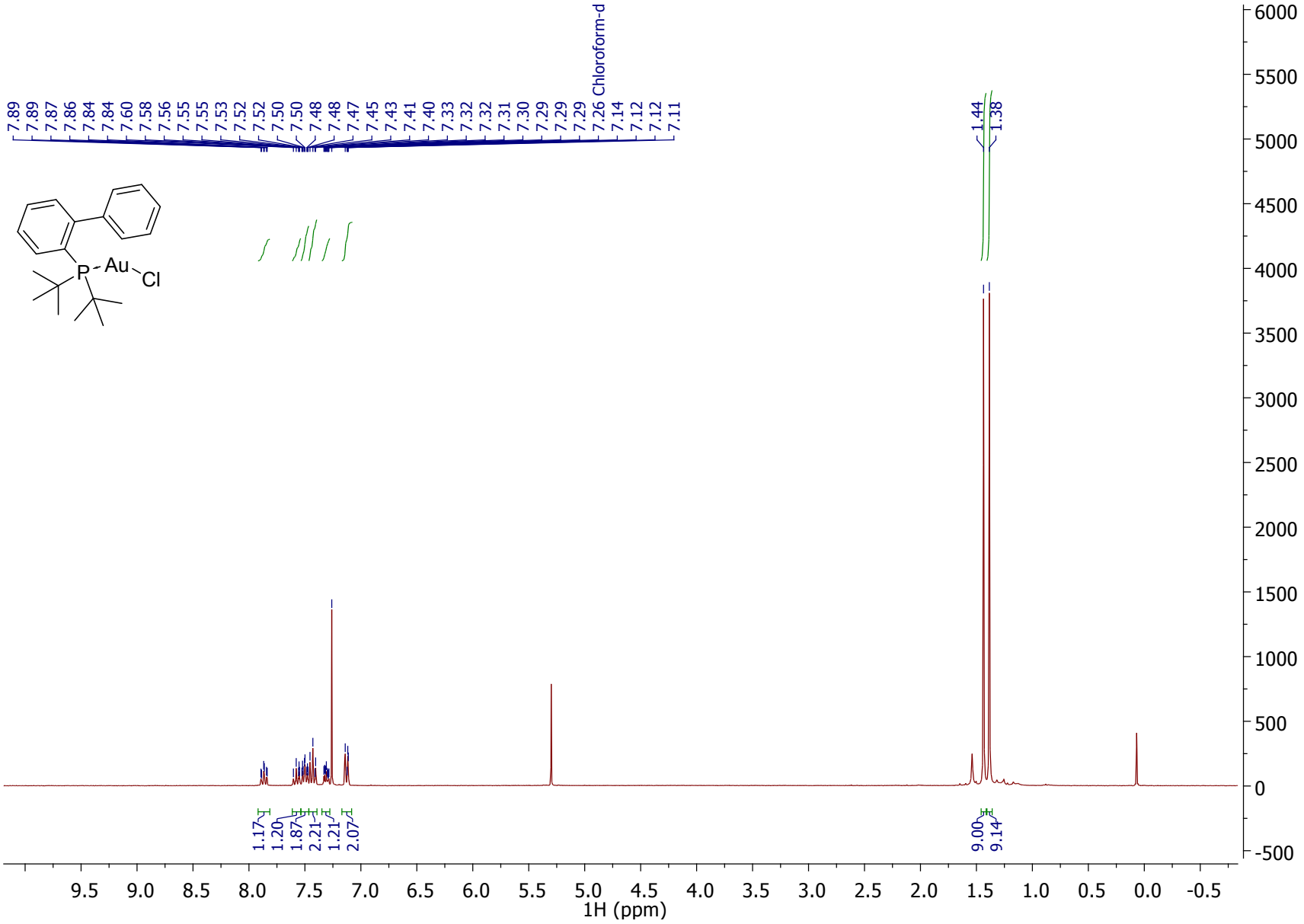
[Au(PAd$_3$(CSA)] (**12**) ^{13}C NMR spectrum



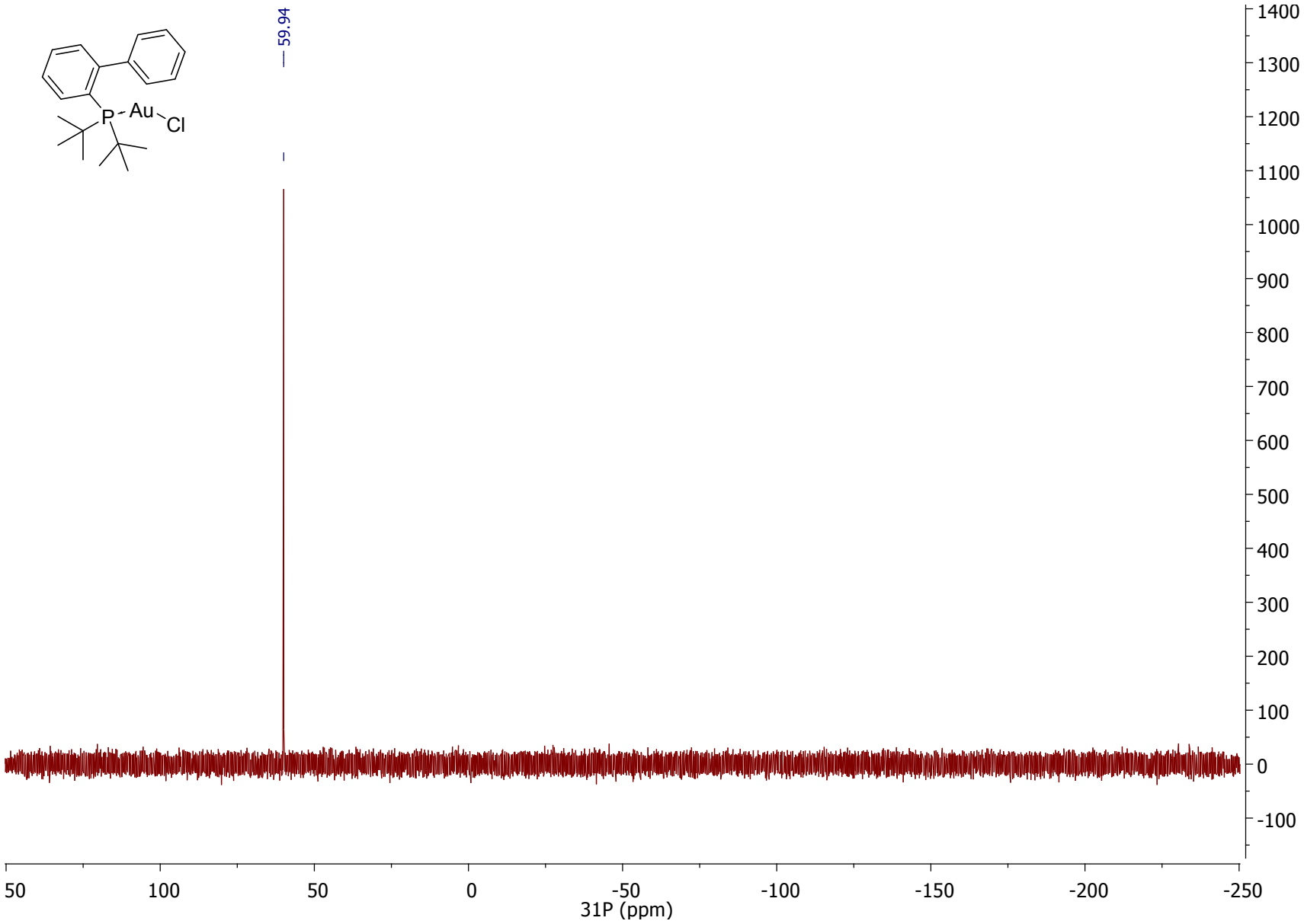
[Au(PAd_3(CSA)] (**12**) ^{31}P NMR spectrum



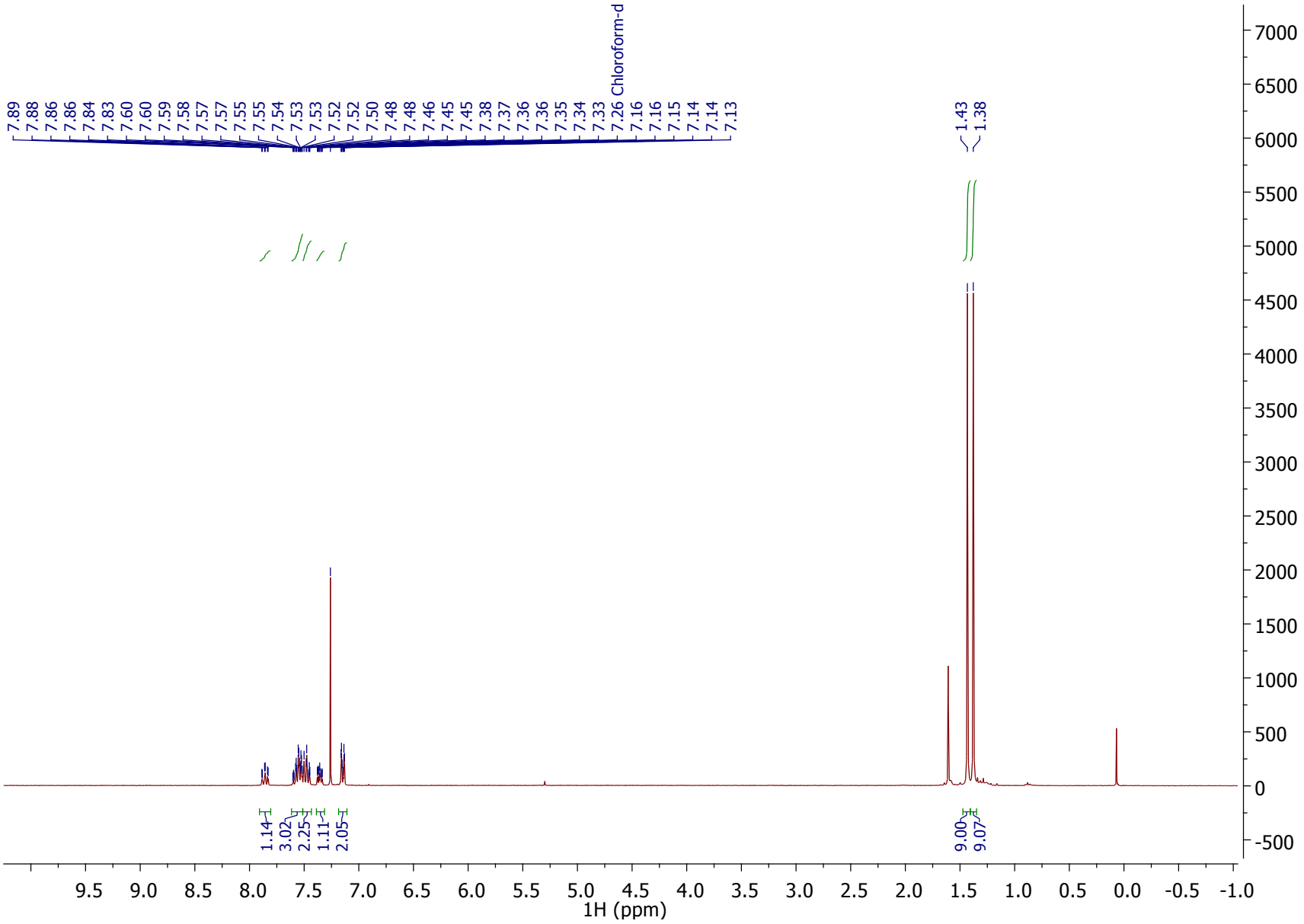
[Au(JohnPhos)Cl] ^{1}H NMR spectrum



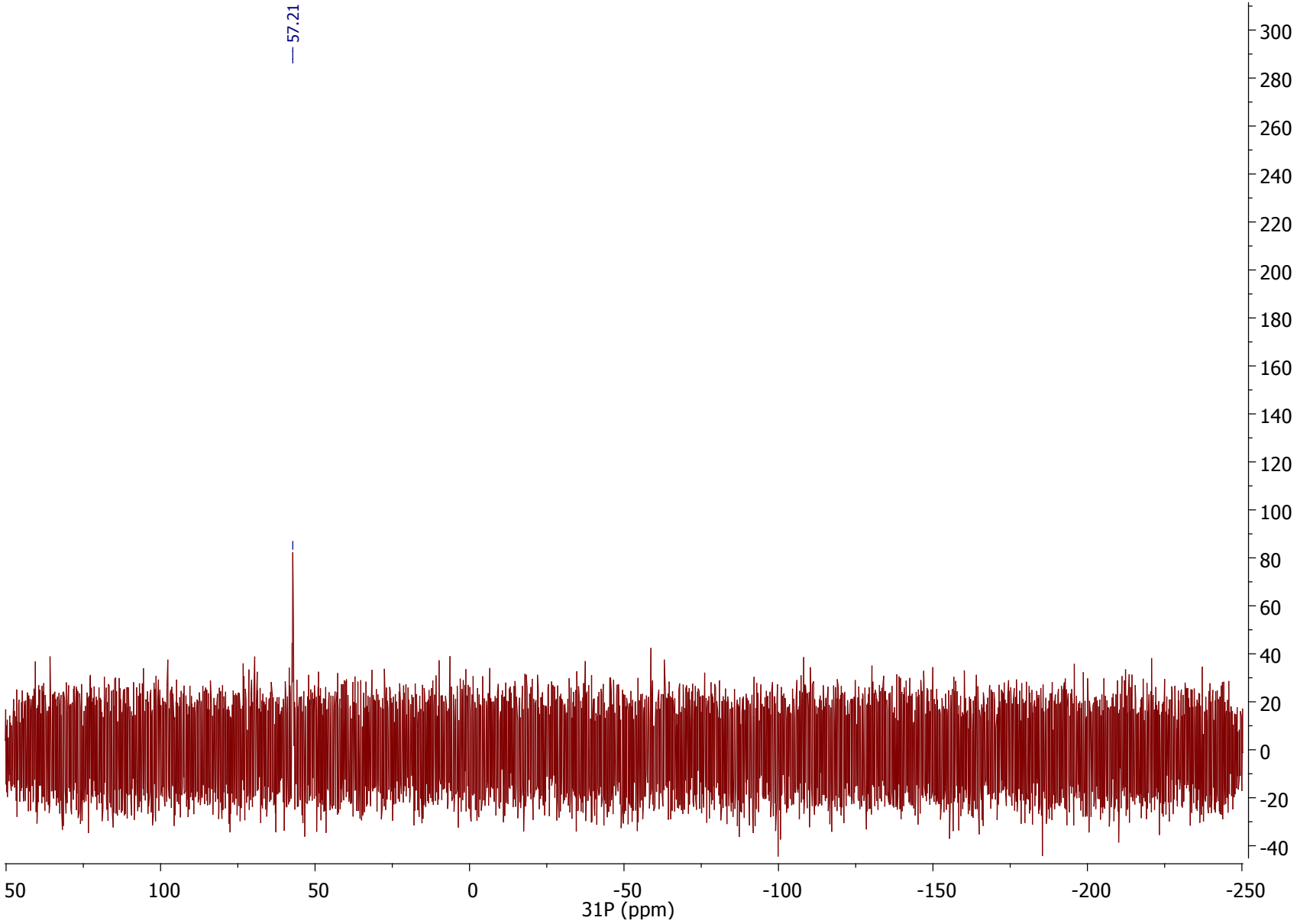
[Au(JohnPhos)Cl] ^{31}P NMR spectrum



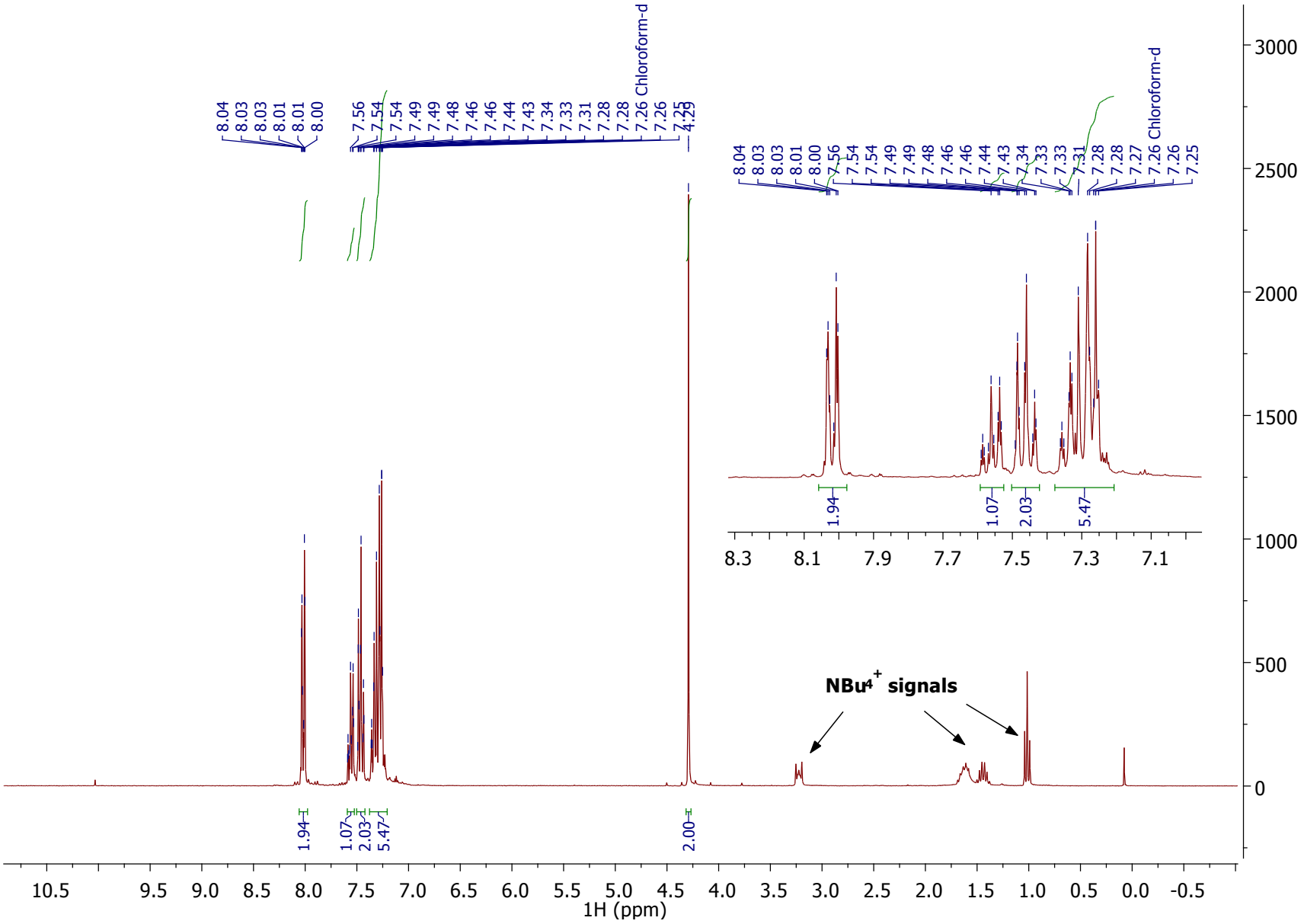
[Au(JohnPhos)OTf] ^{1}H NMR spectrum



[Au(JohnPhos)OTf] ^{31}P NMR spectrum



^{1}H NMR spectrum of sample taken from reaction mixture of diphenylacetylene hydration after 8h with 0.2 mol% of **6**



References

1 M. Gatto, A. Del Zotto, J. Segato and D. Zuccaccia, *Organometallics*, 2018, **37**, 4685–4691.