

Supplementary Information

New approach to the synthesis of trinuclear gold(I) imidazolate complexes and their silver(I)-induced photoluminescent behavior

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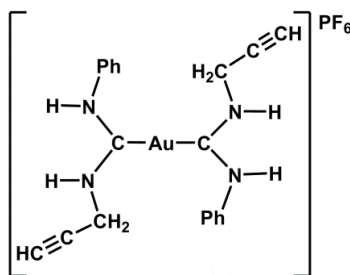
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Synthesis and characterization of the new compounds

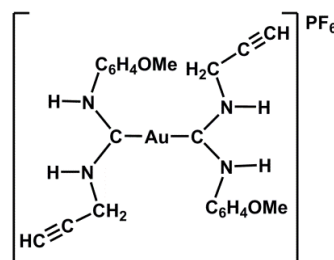
General Considerations

All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with Perkin-Elmer Spectrum 100 and Paragon 1000 spectrophotometers. Mass spectra were recorded on Bruker model Impact II (ESI and APCI) and MAT95XP (FAB) apparatus. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants J are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts of the NMR spectra were referenced to internal SiMe₄ (¹H and ¹³C) or external H₃PO₄ (³¹P). Assignments are based on ¹H, ¹H-COSY, ¹H, ¹³C-HMBC, ¹H, ¹³C-HSQC and DEPT experiments. All reagents were obtained commercially and used without further purification. Compounds [1a-c]PF₆ [1] were prepared by a slightly modified procedure of the published method.¹ Compounds [2a]PF₆, [3a]PF₆ and [4a]PF₆ were prepared as described previously by our group.

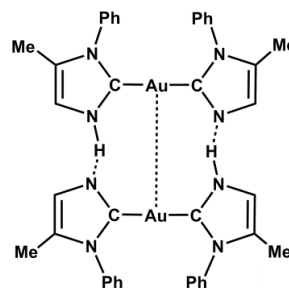
Synthesis of compound [2b]PF₆. To a solution of compound [1b]PF₆ (0.20 g, 0.36 mmol) in CH₂Cl₂ (10 mL) propargylamine (54 μL, d = 0.806 g/mL, 0.79 mmol) was added and the mixture stirred for 2 h. The solvent was then evaporated to dryness under vacuum and the remaining residue washed with hexane (2 x 10 mL) to afford a white solid. Yield: 0.214 g (89%). ¹H NMR (400 MHz, CD₂Cl₂, -80° C): δ 8.72 (s, 2H, NPh), 8.34-7.20 (12H, NHCH₂, Ph), 4.18 (br, 4H, CH₂), 2.48 (br, 2H, -C≡CH). ¹³C{¹H} NMR (150.9 MHz, CD₂Cl₂, -80° C): 205.0 (s, Ccarbene), 139.2 (s, Cipso Ph), 129.1, 123.3 (s, *o*-Ph, *m*-Ph), 126.8 (s, *p*-Ph); 78.5 (s, C≡CH), 73.1 (s, C≡CH), 38.5 (s, CH₂). MS (ESI): m/z : [M - PF₆]⁺: calcd. for C₂₀H₂₀AuN₄: 513.1348, found: 513.1344.



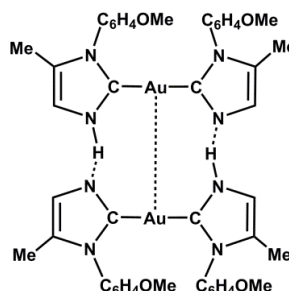
Synthesis of compound [2c]PF₆. This was similarly prepared from [1c]PF₆ (0.20 g, 0.33 mmol) dissolved in CH₂Cl₂ (10 mL) and propargylamine (50 μL, d = 0.806 g/mL, 0.73 mmol). Reaction time: 3 h. Yield: 0.205 g (87%). ¹H NMR (300 MHz, CD₂Cl₂): selected signals of the multiple conformers observed: δ 4.48, 4.44, 4.22, 4.14, 4.12, 4.08, 4.00 (CH₂), 3.84, 3.83, 3.82, 3.81, 3.80 (OMe), 2.63, 2.52, 2.48, 2.45, 2.41, 2.38, 2.34 (C≡CH). ¹³C{¹H} NMR (100.61 MHz, THF/D₂O): selected signals of the multiple conformers observed: 206.6, 205.2, 204.2, 203.4, 202.4, 201.6 (s, Ccarbene). MS (ESI): m/z : [M - PF₆]⁺: calcd. for C₂₂H₂₄AuN₄O₂: 573.1559, found: 573.1570.



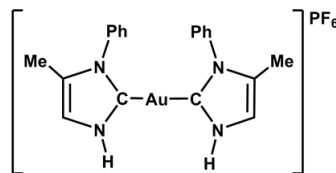
Synthesis of compound 3b. To a solution of compound [2b]PF₆ (0.10 g, 0.15 mmol) in CH₂Cl₂ (5 mL) an excess of NaH (34 mg, 1.40 mmol) was added and the mixture stirred for 2 h. The solution was then filtered and the solvent evaporated to dryness under vacuum. The remaining residue was washed with hexane (2 x 10 mL) to afford a white solid. Yield: 70 mg (90%). ¹H NMR (400 MHz, CD₂Cl₂): δ 10.52 (br, 2H, NH), 7.35-7.34 (12H, Ph), 7.22-7.20 (8H, Ph), 6.85 (s, 4H, =CH), 2.05 (s, 12H, Me). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): 185.2 (s, Ccarbene), 140.3 (s, Cipso Ph), 129.1, 127.9 (s, *o*-Ph, *m*-Ph), 128.4 (s, *p*-Ph); 127.7 (s, =CMe), 120.9 (s, =CH), 11.0 (CH₃). MS (ESI): *m/z*: [*M* + *H*]⁺: calcd. for C₄₀H₃₉Au₂N₈: 1025.2628, found: 1025.2604.



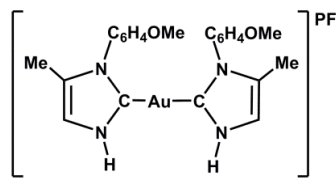
Synthesis of compound 3c. This was prepared similarly to 3b starting from compound [2c]PF₆ (0.10 g, 0.14 mmol) and NaH (34 mg, 1.40 mmol). Reaction time: 3 h. Yield: 73 mg (91%). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.09 (d, ³*J*(HH) = 8.8 Hz, 8H, C₆H₄), 6.81 (s, 4H, =CH), 6.77 (d, ³*J*(HH) = 8.8 Hz, 8H, C₆H₄), 3.81 (s, 12H, OMe), 2.03 (s, 12H, Me). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂): 183.5 (s, Ccarbene), 160.6 (s, C-OMe), 132.1, 130.5, 128.5 (s, =CH C₆H₄), 120.4 (s, =CH), 115.0 (s, =CH C₆H₄), 56.2 (s, OMe), 10.8 (CH₃). MS (ESI): *m/z*: [*M* + *H*]⁺: calcd. for C₄₄H₄₇Au₂N₈O₄: 1145.3051, found: 1145.3040.



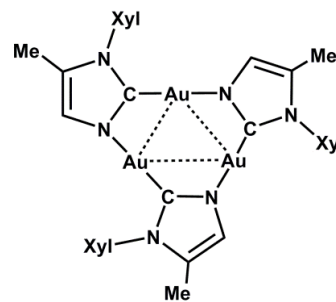
Synthesis of compound [4b]PF₆. To a solution of 3b (0.10 g, 0.10 mmol) in CH₂Cl₂ (10 mL) NH₄PF₆ (32 mg, 0.20 mmol) was added and the mixture stirred for 15 min. The solution was then filtered and the solvent evaporated to dryness under vacuum. The remaining residue was washed with hexane (2 x 10 mL) to obtain a white solid. Yield: 0.112 g (88%). ¹H NMR (400 MHz, CD₂Cl₂): δ 9.99 (br, 2H, NH), 7.49 (t, ³*J*(HH) = 7.5 Hz, 2H, *p*-Ph), 7.40 (t, ³*J*(HH) = 7.5 Hz, 4H, *m*-Ph), 7.20 (d, ³*J*(HH) = 7.3 Hz, 4H, *o*-Ph), 6.98 (d, ⁴*J*(HH) = 0.9 Hz, 2H, =CH), 2.04 (d, ⁴*J*(HH) = 0.9 Hz, s, 6H, Me). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): 181.8 (s, Ccarbene), 137.9 (s, Cipso, Ph), 130.8 (s, =C-Me), 130.0 (s, *m*-Ph), 129.8 (s, *p*-Ph), 127.4 (s, *o*-Ph), 116.5 (s, =CH), 10.6 (CH₃). MS (ESI): *m/z*: [*M* - PF₆]⁺: calcd. for C₂₀H₂₀AuN₄: 513.1348, found: 513.1342.



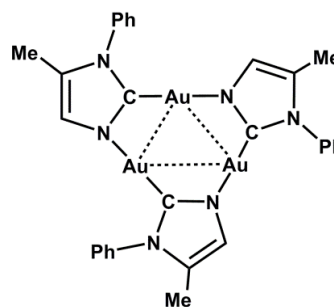
Synthesis of compound [4c]PF₆. This was prepared similarly to [4b]PF₆ starting from 3c (70 mg, 0.06 mmol) and NH₄PF₆ (20 mg, 0.12 mmol). Yield: 79 mg (90%). ¹H NMR (400 MHz, CD₂Cl₂): δ 10.20 (br, 2H, NH), 7.13 (d, ³*J*(HH) = 8.9 Hz, 4H, C₆H₄), 6.95 (s, 2H, =CH), 6.89 (d, ³*J*(HH) = 8.9 Hz, 4H, C₆H₄), 3.89 (s, 6H, OMe), 2.02 (s, 6H, Me). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): 182.1 (s, Ccarbene), 160.5 (s, C-OMe), 131.0, 130.6, 128.6 (s, =CH C₆H₄), 116.2 (s, =CH), 114.9 (s, =CH C₆H₄), 56.1 (s, OMe), 10.6 (CH₃). MS (FAB): *m/z*: [*M* - PF₆]⁺: calcd. for C₂₂H₂₄AuN₄O₂: 573.16, found: 573.6.



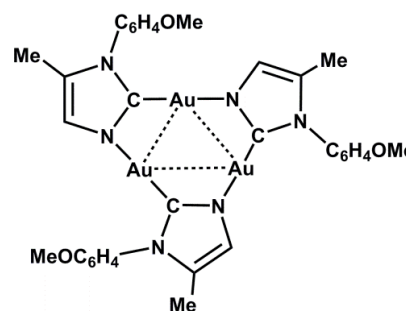
Synthesis of compound 5a. To a solution of compound **3a** (50 mg, 0.04 mmol) in THF (5 mL) [AuCl(SMe₂)] (26 mg, 0.08 mmol) and LiN(SiMe₃)₂ (97 μ L, 1 M in hexane, 0.10 mmol) were added and the mixture stirred for 45 min. The solution was then filtered and the solvent eliminated to dryness under vacuum. The remaining residue was washed with hexane (2 x 10 mL) and then extracted with toluene (2 x 10 mL). The solution was filtered and the solvent evaporated to dryness under vacuum. Hexane (10 mL) was added to the residue and the resulting mixture stirred to obtain a white solid. Colourless crystals of **5a** suitable for X-ray analysis were formed by slow diffusion of hexane into a THF solution of the compound. Yield: 49 mg (73%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.29 (dd, ³J(H,H) = 7.5 Hz, 3H, *p*-Xylyl), 7.20 (d, ³J(H,H) = 7.5 Hz, 6H, *m*-Xylyl), 6.54 (q, ⁴J(H,H) = 1.1 Hz, 1H, =CH), 2.01 ppm (s, 18H, CH₃ Xylyl), 1.80 (d, ⁴J(H,H) = 1.1 Hz, 9H, =C-CH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): δ 167.4 (s, C_{carbene}), 137.7 (s, C_{ipso} Xylyl), 137.0 (s, *o*-Xylyl), 128.7 (s, *p*-Xylyl), 128.6 (s, *m*-Xylyl), 128.2 (s, =C-CH₃), 125.7 (s, =CH), 18.3 (s, CH₃ Xylyl), 10.3 ppm (s, =C-CH₃). MS (FAB): *m/z*: [M + H]⁺: calcd. for C₃₆H₄₀Au₃N₆: 1147.2311, found: 1147.2293.



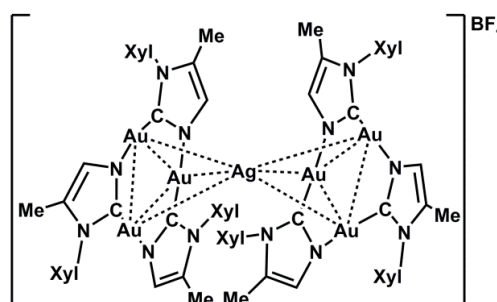
Synthesis of compound 5b. This was prepared in a similar way as **5a** from compound **3b** (50 mg, 0.05 mmol), [AuCl(SMe₂)] (28 mg, 0.10 mmol) and LiN(SiMe₃)₂ (107 μ L, 1 M in hexane, 0.11 mmol). Yield: 43 mg (62%). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.52-7.46 (m, 15H, Ph), 6.54 (q, ⁴J(H,H) = 1 Hz, 3H, =CH), 2.05 (d, ⁴J(H,H) = 1 Hz, 9H, =C-CH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): δ 168.5 (s, C_{carbene}), 139.6 (s, C_{ipso}, Ph), 129.6, 128.0 (*m*-Ph, *o*-Ph), 128.4 (s, *p*-Ph), 130.8 (s, =C-Me), 126.2 (s, =CH), 11.2 (CH₃). MS (ESI): *m/z*: [M + H]⁺: calcd. for C₃₀H₂₈Au₃N₆: 1063.1372, found: 1063.1380.



Synthesis of compound 5c. This was prepared in a similar way as **5a** from compound **3c** (50 mg, 0.04 mmol), [AuCl(SMe₂)] (26 mg, 0.08 mmol) and LiN(SiMe₃)₂ (96 μ L, 1 M in hexane, 0.10 mmol). Yield: 44 mg (66%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.37 (d, ³J(H,H) = 8.9 Hz, 6H, C₆H₄), 7.02 (d, ³J(H,H) = 8.9 Hz, 6H, C₆H₄), 6.53 (s, 3H, =CH), 3.89 (s, 9H, OMe), 2.03 (s, 9H, Me). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): δ 168.6 (s, C_{carbene}), 159.7 (s, C-OMe), 138.5, 132.5 (s), 129.0 (s, =CH, C₆H₄), 125.9 (s, =CH), 114.5 (s, =CH, C₆H₄), 56.1 (s, OMe), 11.1 (s, Me). MS (ESI): *m/z*: [M + H]⁺: calcd. for C₃₃H₃₄Au₃N₆O₃: 1153.1688, found: 1153.1668.

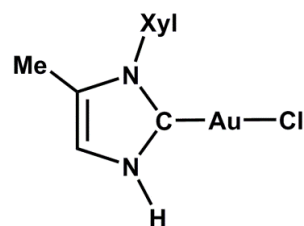


Synthesis of compound [6a]BF₄. To a solution of **5a** (32 mg, 0.028 mmol) in THF (0.5 mL) a solution of AgBF₄ (2.7 mg, 0.014 mmol) in THF (1 mL) was carefully added. After standing overnight without



stirring white crystals of the product were formed. Crystals of **[6a]BF₄** suitable for X-ray analysis were obtained by slow diffusion of hexane into a 1,3-dichloroethane solution of the compound. Yield: 28 mg (81%). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.46 (t, ³J(H,H) = 7.5 Hz, 6H, *p*-Xylyl), 7.39 (d, ³J(H,H) = 7.4 Hz, 6H, *m*-Xylyl), 7.25 (d, ³J(H,H) = 7.3 Hz, 6H, *m*-Xylyl), 6.20 (s, 6H, =CH), 1.91 (s, 36H, CH₃ Xylyl), 1.69 (s, 18H, =C-CH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): δ 163.5 (s, C_{carbene}), 137.3, 136.8, 136.6 (s, C_{ipso} Xylyl, *o*-Xylyl), 129.4, 129.3 (s, *p*-Xylyl, *m*-Xylyl, =C-Me), 128.6 (s, *m*-Xylyl), 125.4 (s, =CH), 19.0 (s, CH₃ Xylyl), 18.3 (s, CH₃ Xylyl), 9.9 (s, =C-CH₃). MS (ESI): *m/z*: [*M* - BF₄]⁺: calcd. for C₇₂H₇₈AgAu₆N₁₂: 2399.3510, found: 2399.3422.

Synthesis of compound 7a. To a solution of **5a** (80 mg, 0.07 mmol) in CH₂Cl₂ (5 mL) aqueous HCl (20 mL, d = 1.18 g/mL, 37%, 0.24 mmol) was added and the mixture stirred for 10 min. The solution was then filtered and the solvent eliminated to dryness under vacuum. The remaining residue was washed with hexane (2 x 5 mL) and then extracted with toluene (10 mL). The solution was filtered and the solvent evaporated to dryness under vacuum. Hexane (10 mL) was added to the residue and the resulting mixture stirred to obtain a white solid. Colourless crystals of **7a** suitable for X-ray analysis were formed by slow diffusion of hexane into a dichloromethane solution of the compound. Yield: 67 mg (78%). ¹H NMR (400 MHz, CD₂Cl₂): δ 11.32 (br, 1H, NH), 7.37 (t, ³J(H,H) = 7.6 Hz, 1H, *p*-Xylyl), 7.24 (d, ³J(H,H) = 7.6 Hz, 2H, *m*-Xylyl), 7.02 (s, 1H, =CH), 1.99 (s, 6H, CH₃ Xylyl), 1.89 (s, 3H, =C-CH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): δ 166.7 (s, C_{carbene}), 136.3 (s, C_{ipso} Xylyl), 136.2 (s, *o*-Xylyl), 130.1 (s, *p*-Xylyl), 129.6 (s, =C-Me), 129.1 (s, *m*-Xylyl), 115.8 (s, =CH), 18.1 (s, CH₃ Xylyl), 10.0 (s, =C-CH₃). MS (ESI): *m/z*: [*M* + H]⁺: calcd. for C₁₂H₁₅AuClN₂: 419.0589, found: 419.0583.



Photophysics of the synthesized compounds

Emission and excitation spectra were recorded in FS5 Spectrofluorometer from Edinburgh Instruments using Photomultiplier R928P (spectral coverage 200 nm - 870 nm) as detector after dispersing the photoluminescence by a Czerny-Turner monochromator. Spectra with a gate time of 100 ns and without delay are referred to as photoluminescence spectra (PL). Delayed emission spectra, PL_d, were recorded with a gate width of 1 ms and a delay of 1 μs. For solid measurements, a special SCA-1 Solid Sample Holder module was used.

Absolute photoluminescence quantum yields were measured using the FS5 Spectrofluorometer with an integrating sphere module, consisting in a hollow sphere of 150 mm diameter. QY calculations were made using Fluoracle software. Integrating sphere works by measuring all the photoluminescence emitted by the sample after a single excitation pulse of nanoseconds.

Lifetimes of photoluminescence measurements from Microseconds to Seconds (>5 μs to <10 s) were done using Multi-Channel Scaling (MCS) technique. A microsecond xenon flashlamp was used for excitation and the luminescence decay is then recorded. The experimental data are fitted using Fluoracle software, thus obtaining the lifetime evaluation. Lifetimes from picoseconds to microseconds (<10 μs) were done by Time-Correlated Single Photon Counting (TCSPC). This technique requires the excitation with picosecond-pulse diode lasers with an adequate wavelength (as close as possible to the excitation maximum). Numerical reconvolution and curve fitting using the same Fluoracle software allows determining lifetimes.

The photoluminescence emission and excitation spectra in the solid state for compound **5d** are shown in Figure 3 of the manuscript. The solid exhibits a bright red photoluminescence with a quantum yield 28.5% which can be appreciated by the naked eye when irradiated with UV light (check photo insets in Figure 3).

The emission spectrum shows four well-defined bands. The emission intensity is low when excited at 365 nm, showing two overlapped bands with maxima at 403 and 420 nm. The mean lifetime (τ) for these emissions is 0.194 ± 0.002 ns. The calculation was performed with a tri-exponential fitting, contributing this time with 80% of the decay curve. However, when the compound is excited with more energetic radiation (below 300 nm), it shows a red photoluminescence as well as an emission band at 722 nm with a lifetime in the nanoseconds range. There is also a second slower emission at 810 nm with a lifetime τ of 10.86 ± 0.02 μs and a 97% contribution to the decay curve fitted with two exponential curves. This slow and long-wavelength emission formally corresponds to a phosphorescent emission process originated from an excited triplet. The typical emission of organic monomeric molecules/ligands used to be well-structured with well-defined bands. In this case, the absence of such luminescence suggests that the emission is probably happening from dimeric units (note that the compound exists as dimers of triangular clusters as observed in the X-ray study). In fact, the diluted solution of 1 ppm **5d** in dichloromethane does not present luminescence, as the compound is as a monomeric species. It seems that the solution

process induces the loss of the molecular disposition which is responsible for the photo-emissive phenomena. Furthermore, the great Stokes shifts (more than 400 nm) imply energies too low to be ascribed to a monomeric species.

The compound **5a** does not show photo-emissive phenomena either in solid or in solution. However, when silver ions are interspersed the spectroscopic properties change drastically. Thus, the **[6a]BF₄** crystals show an intense white luminescence with 41.3% quantum yield when irradiated with light of 370 nm (inset in Figure 5 of the manuscript). In this case, the absorption/excitation band is shifted towards visible with a maximum at 370 nm and the emission is blue-shifted. The photoemission consists of two energy-degenerated short lifetime processes appearing at 492 nm with τ 3.95 ± 0.05 ns (27 %) and 49 ± 2 ns (60 %), explaining 87% of the decay curve. Moreover, the photoemission shows also three long-lifetime overlapped bands at 429 nm, 626 nm and 711 nm. Due to the overlapping of the bands, it is difficult to perform a proper fitting for estimating the lifetimes. Anyhow, with the emission at 626 nm and using two exponential curves, 97% of the decay curve is explained with lifetime 1.28 ± 0.01 μ s.

The emission at 711 nm can be fitted using three exponential curves giving raise to two lifetimes (0.89 ± 0.03 (41 %) and 1.80 ± 0.04 μ s (45 %)) explaining 86% of the decay curve. The presence of these three bands covering practically the whole visible spectrum together with the nanosecond-lasting band results in a white luminescence with a blue halo observed by the naked eye.

Opposite to the compound **5d**, the study of 10 ppm solutions in dichloromethane of **[6a]BF₄** demonstrated the presence of a blue photoemission (inset in figure S1) with a band at 475 nm and a shoulder at 430 nm and a quantum yield of 2.4%. The excitation spectrum is structured, with three bands at 260 nm, 296 nm and 360 nm, suggesting therefore that the compound is forming dimers. That is, that the presence of the solvent is not disturbing the silver ions to act as a nexus between the monomeric structures although in a small environment, thus keeping the monomer cohesion and allowing a structural regularity.

The phosphorescence lifetimes described for compounds **5d** and **[6a]BF₄**, about 0.04 μ s and 2 μ s might indicate emissions centred in the metal, since this lifetime range is quite common in Au(I) complexes showing this kind of emissions.

References

1. C. E. Briant, D. I. Gilmour, D. M. P. Mingos, *J. Chem. Soc. Dalton Trans.* 1986, 835.
2. J. Ruiz, L. García, D. Sol and M. Vivanco, *Angew. Chem. Int. Ed.*, 2016, **55**, 8386.

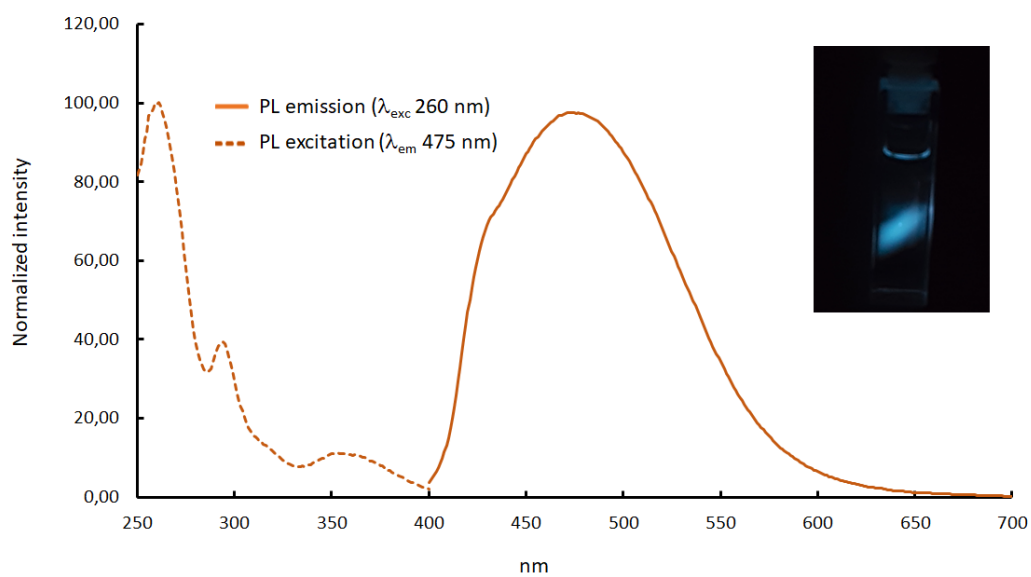
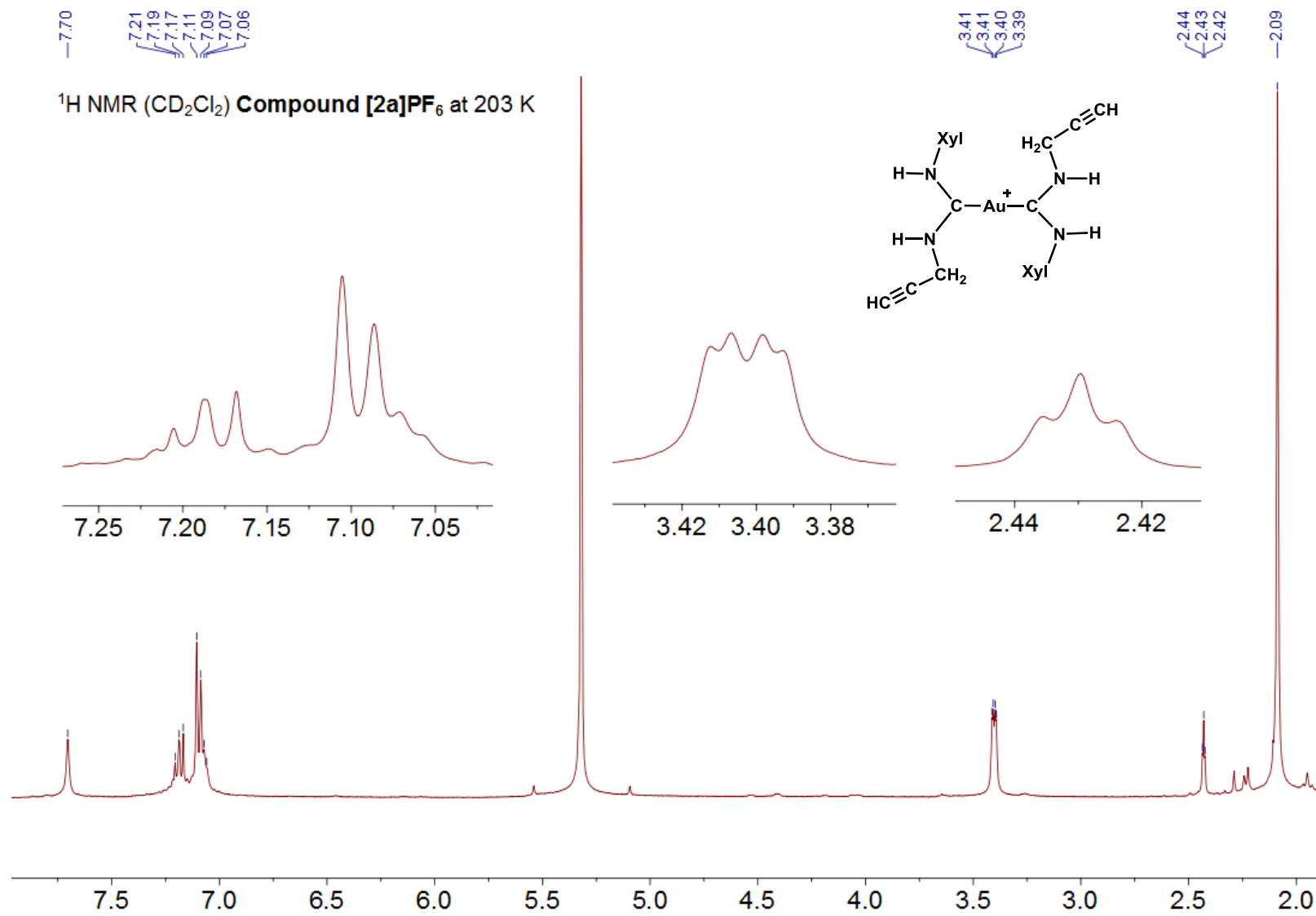


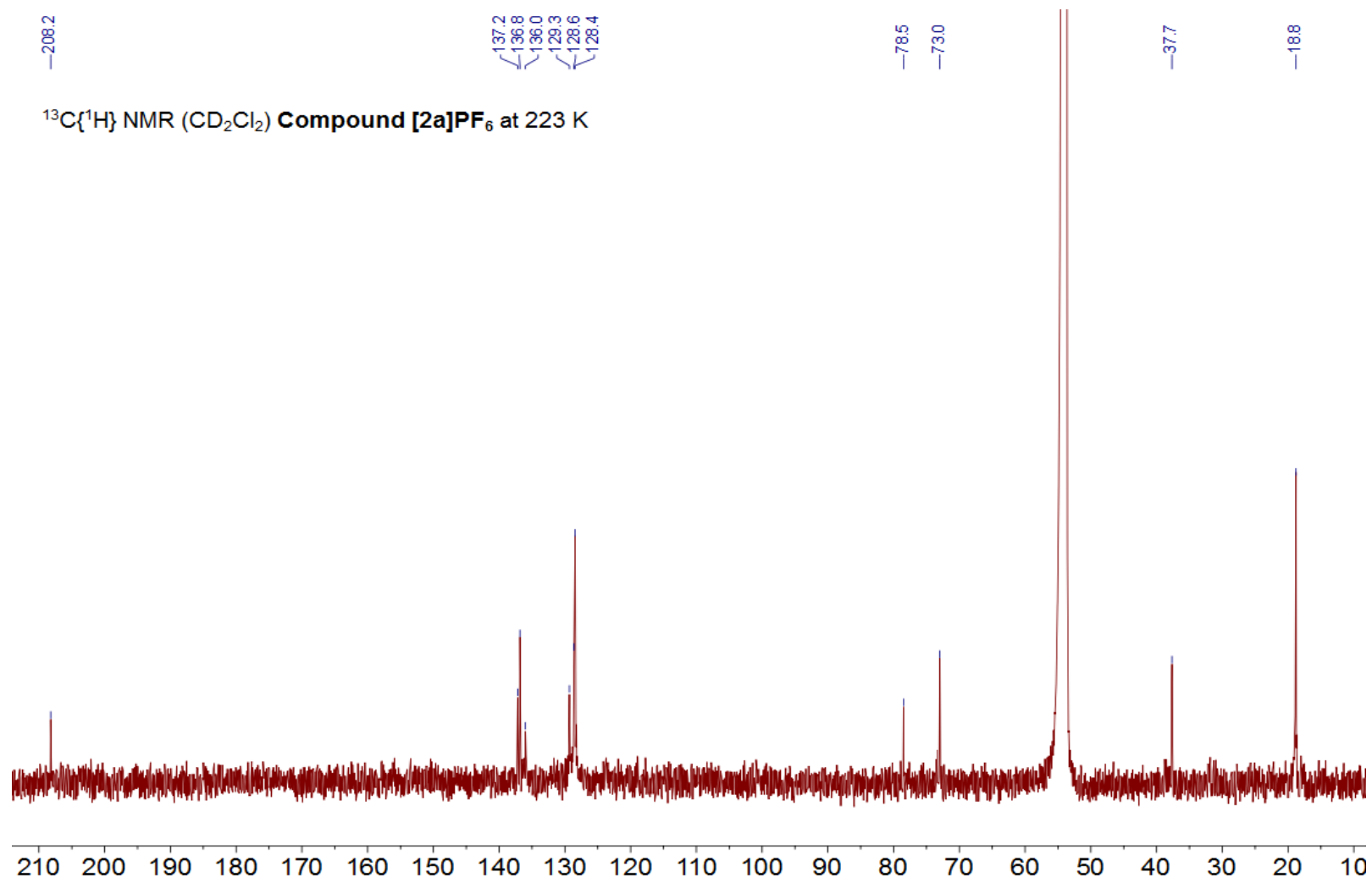
Figure S1. Photoluminescence excitation and emission spectra of a 10 ppm solution of **[6]BF₄** in dichloromethane at 20° C. The inset shows photograph of the luminescence of this solution when irradiated with a UV lamp.

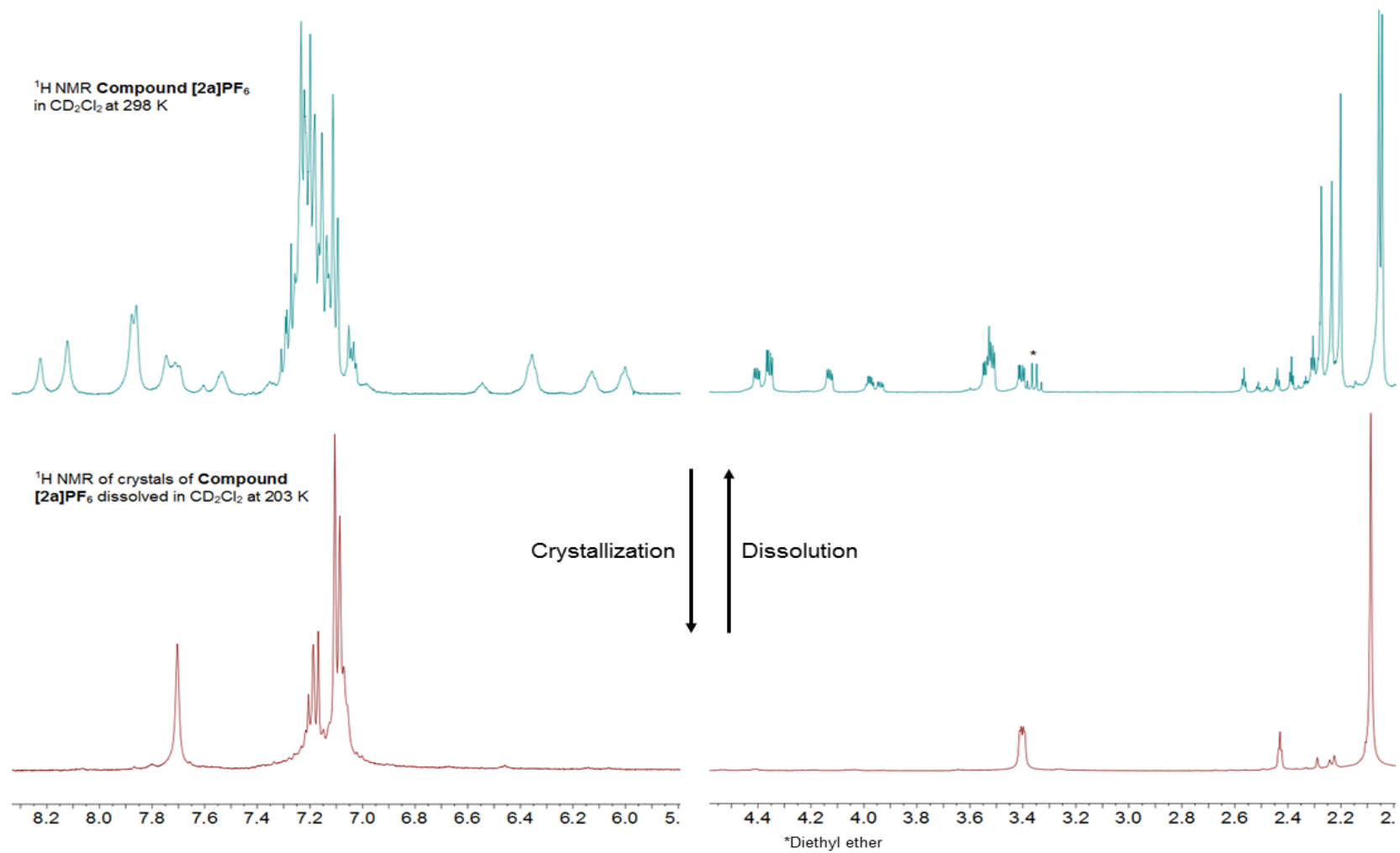
Tabla S1. Photoluminescence spectral data for selected compounds.

Compound		λ_{exc} (nm) ^b	PL	PL _d ^c	Φ^{d} (%)	$\tau \pm s^{\text{e}}$	
			λ_{em} (nm)	λ_{em} (nm)		λ_{em} (nm)	
5d	Solid	296	403		28.5		
		351 ^{sh}	420			420	0.194 ± 0.002 ns (79 %)
365		718					
		383 ^{sh}		810		810	10.86 ± 0.02 μs (97 %)
	Dichloromethane solution ^a	--	--	--	--		--
6a	Solid		492	429	41.3	492	3.95 ± 0.05 ns (27 %), 49 ± 2 ns (60 %)
		306 ^{sh}					
		334 ^{sh}		626		626	1.28 ± 0.01 μs (97 %)
		370		711		711	0.89 ± 0.03 μs (41 %) 1.80 ± 0.04 μs (45 %)
	Dichloromethane solution ^a	260 296 360	430 ^{sh} 475		2.35		---

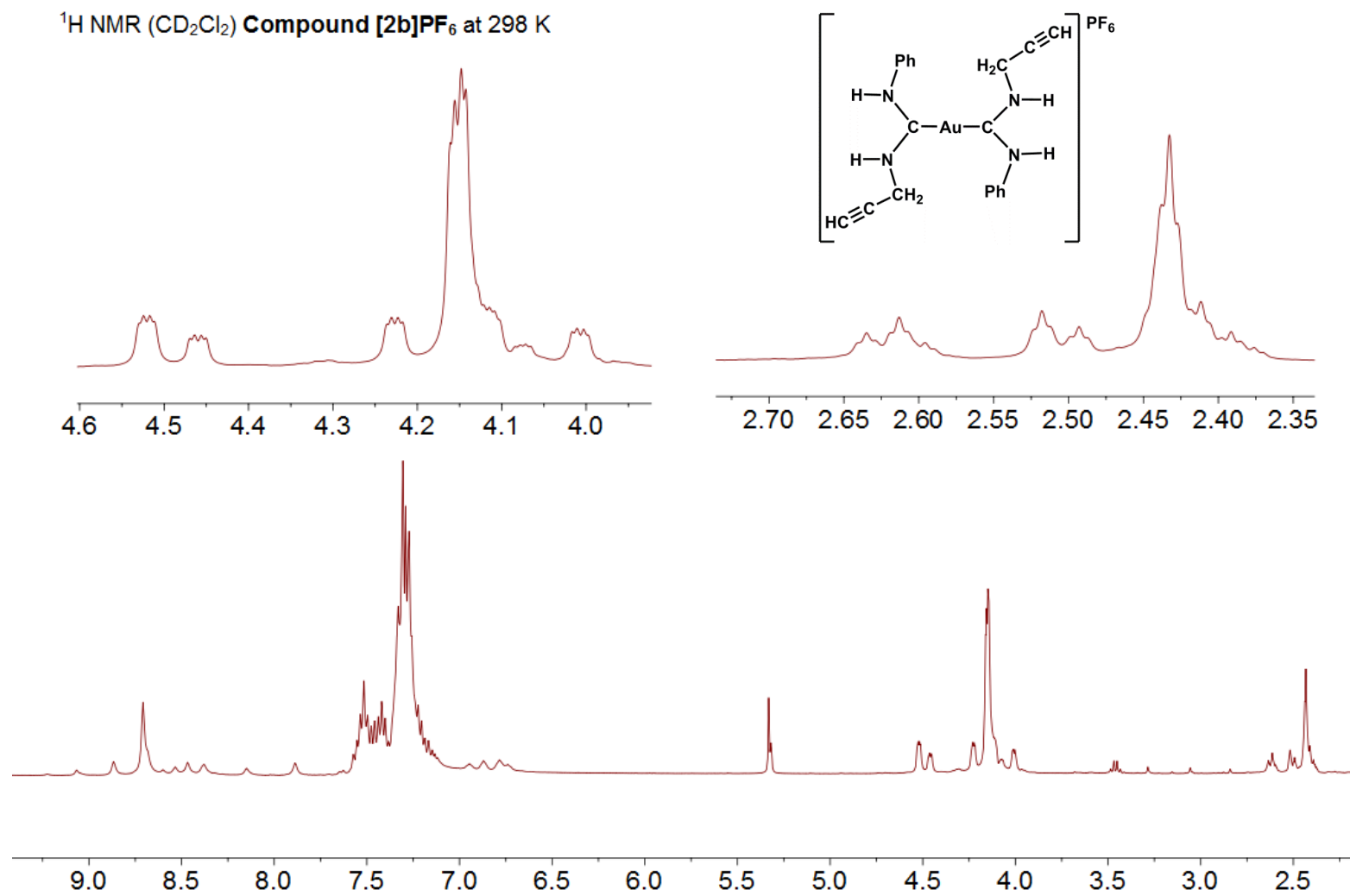
^a Measured in CH₂Cl₂ (10 ppm) at 20° C. ^b Bold values indicate the most intense bands. ^c Time delay 1 μs, time gate 1ms, ^dAbsolute photoluminescence quantum yields, ^eStandard deviation, ^{sh} shoulder.



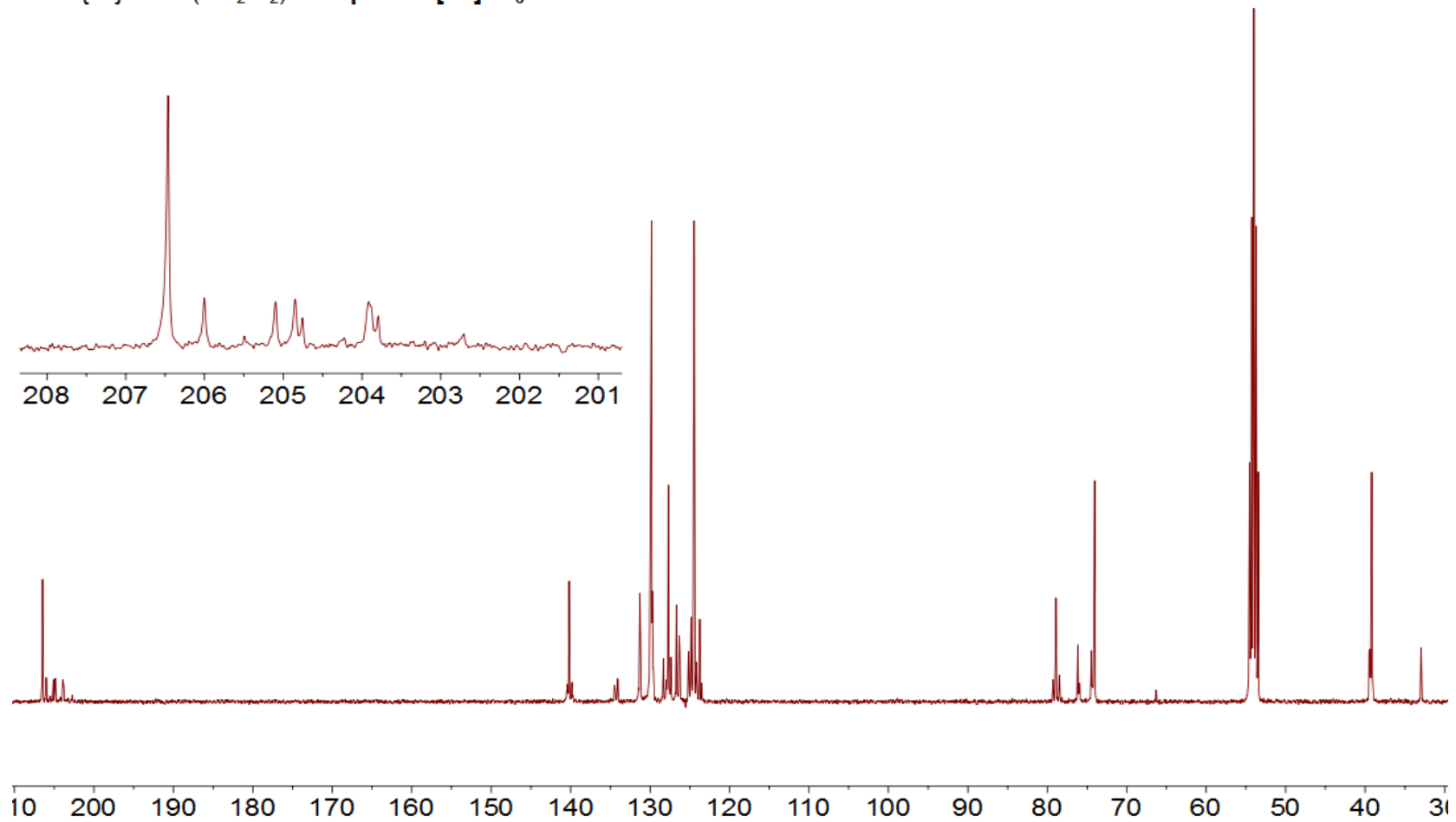




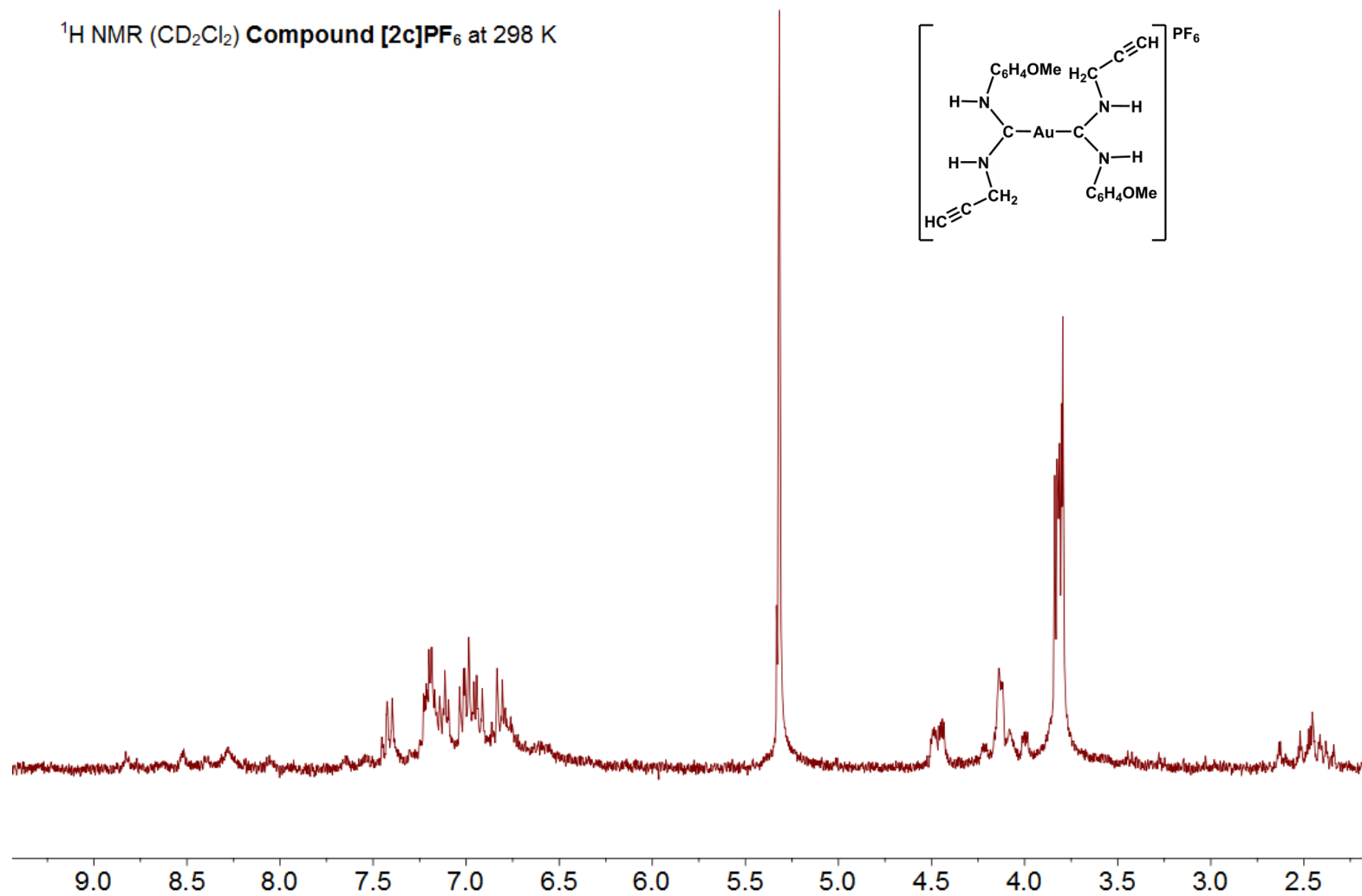
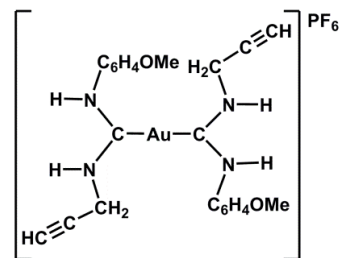
^1H NMR (CD_2Cl_2) Compound **[2b]** PF_6 at 298 K



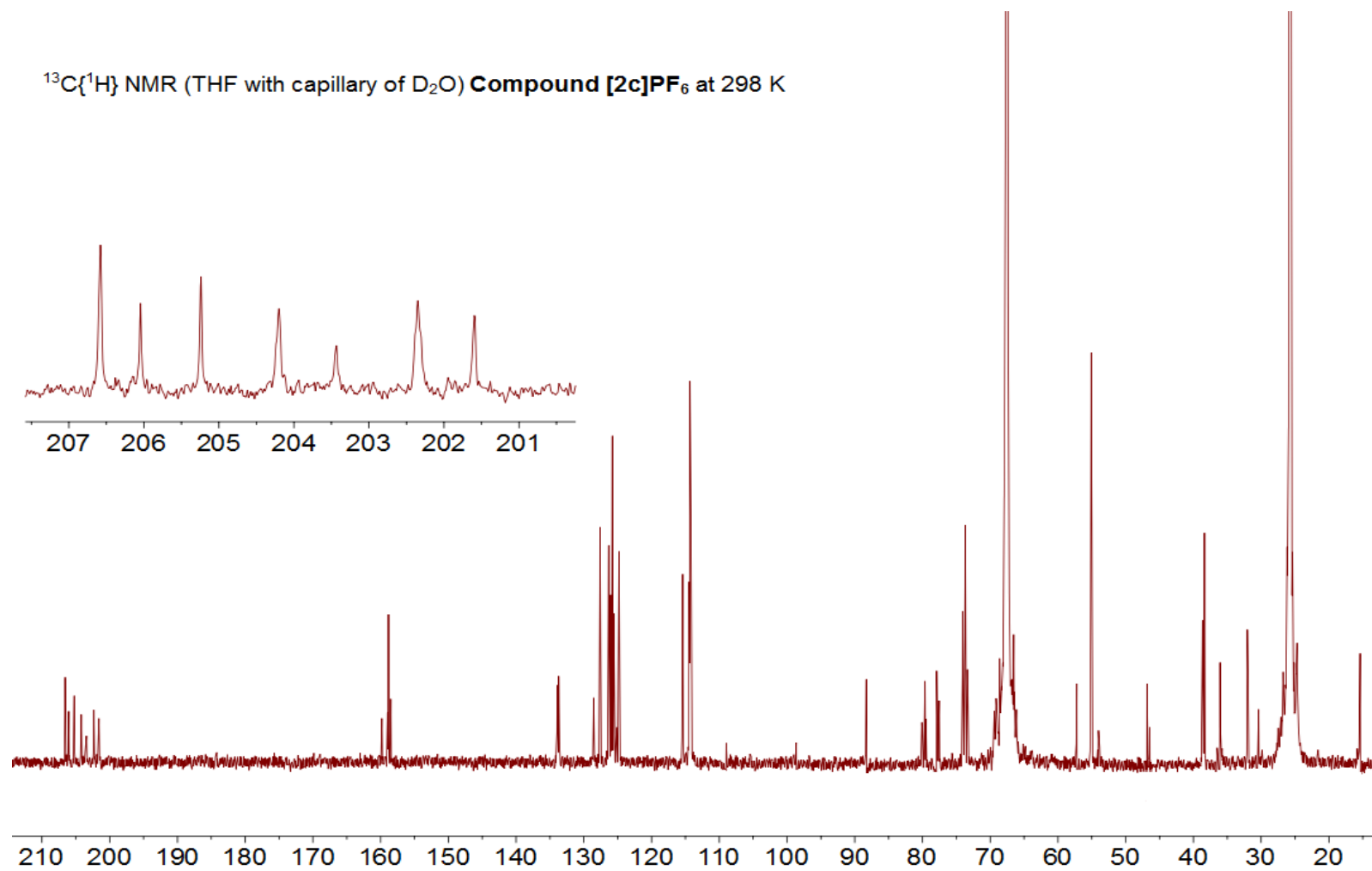
$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) Compound **[2b]** PF_6 at 298 K

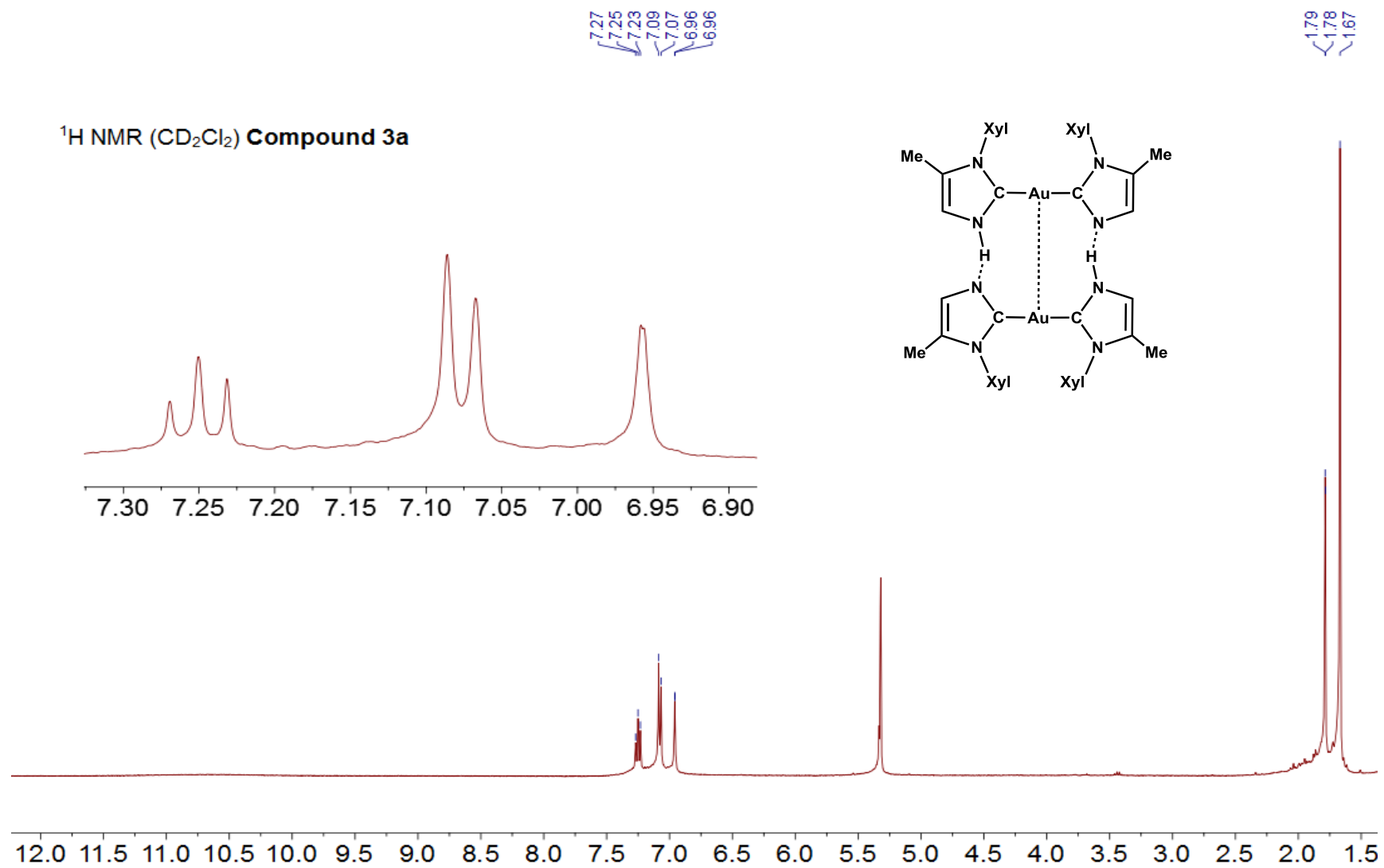


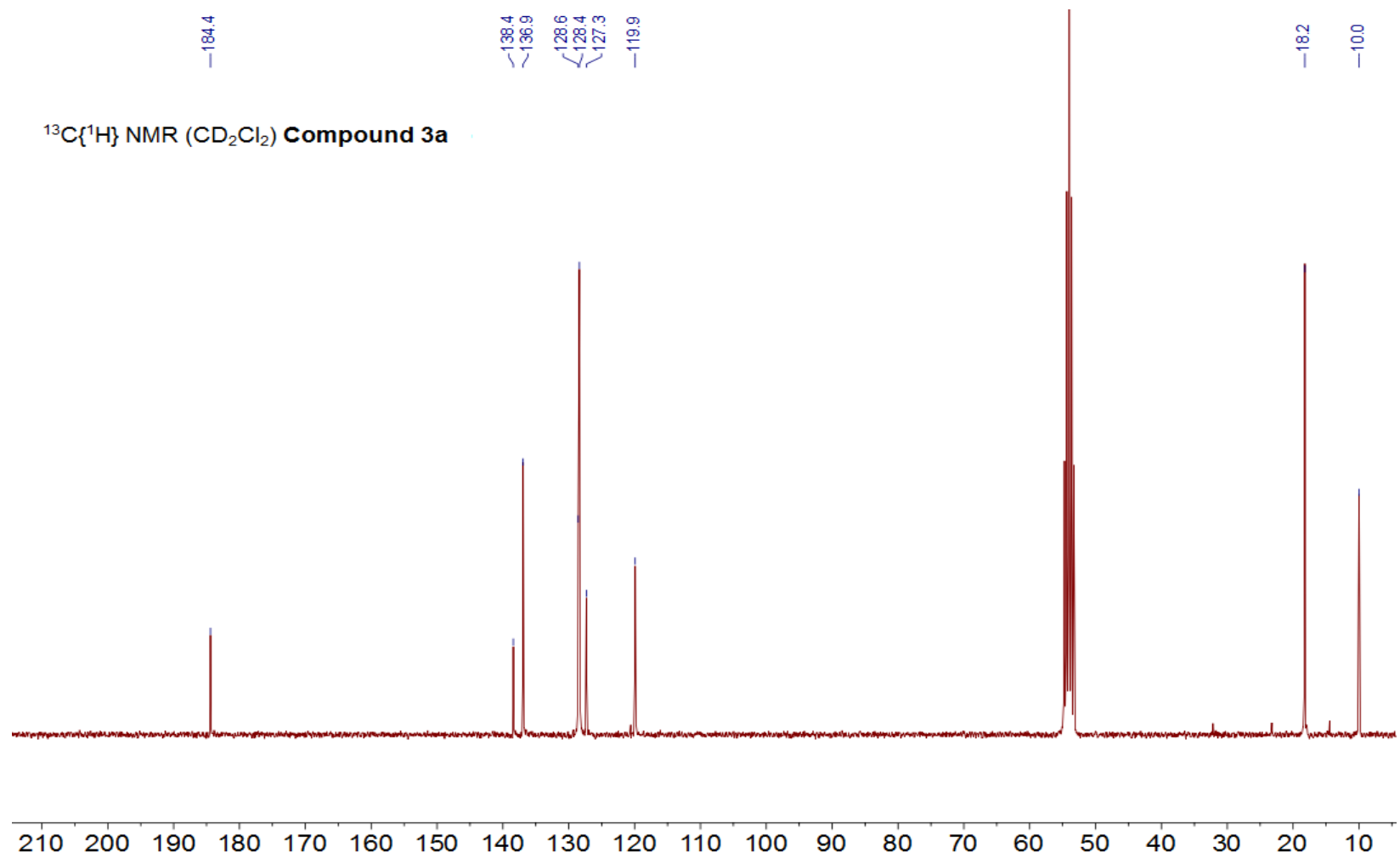
^1H NMR (CD_2Cl_2) Compound $[\mathbf{2c}]\text{PF}_6$ at 298 K



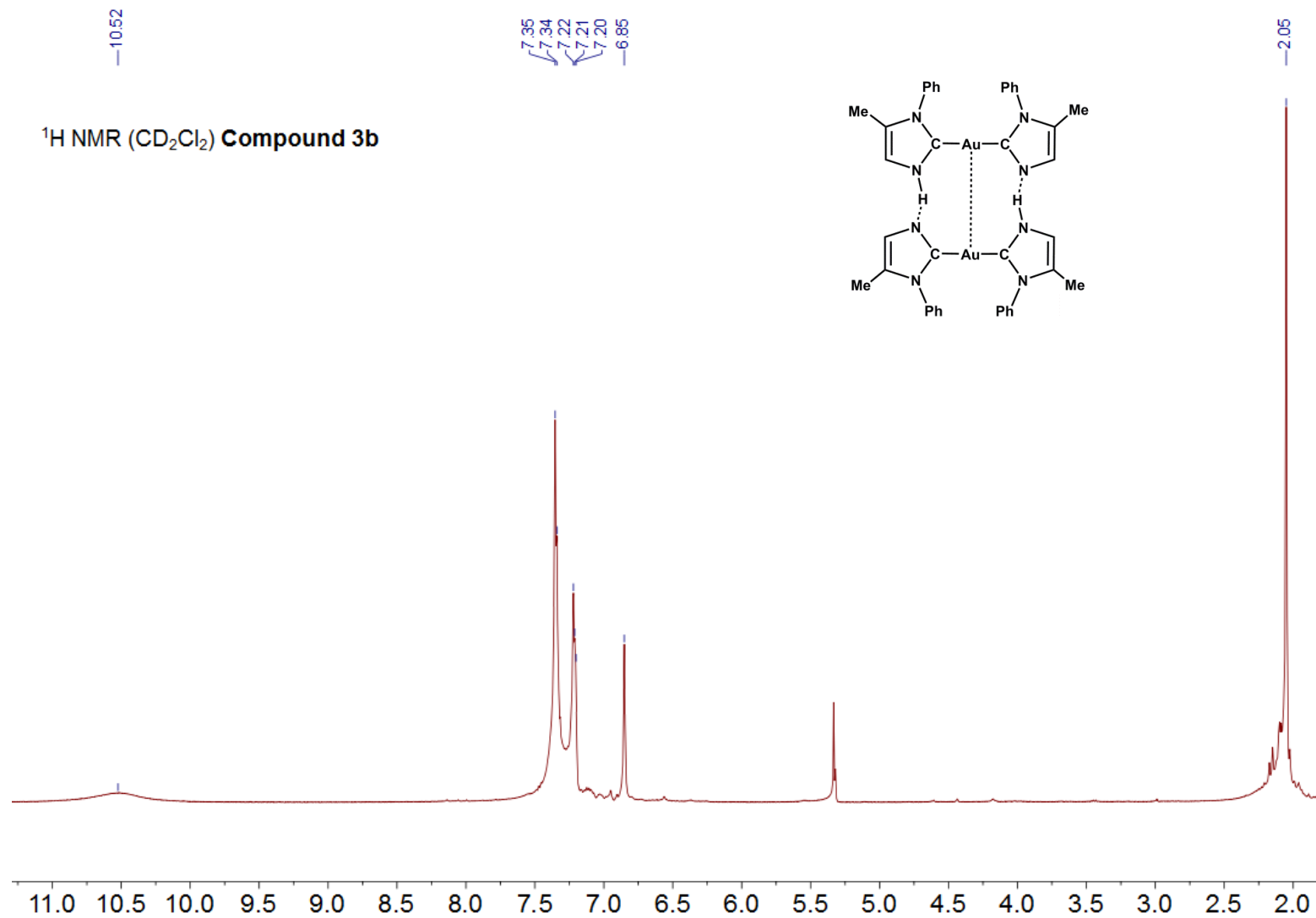
$^{13}\text{C}\{^1\text{H}\}$ NMR (THF with capillary of D_2O) **Compound [2c]PF₆** at 298 K

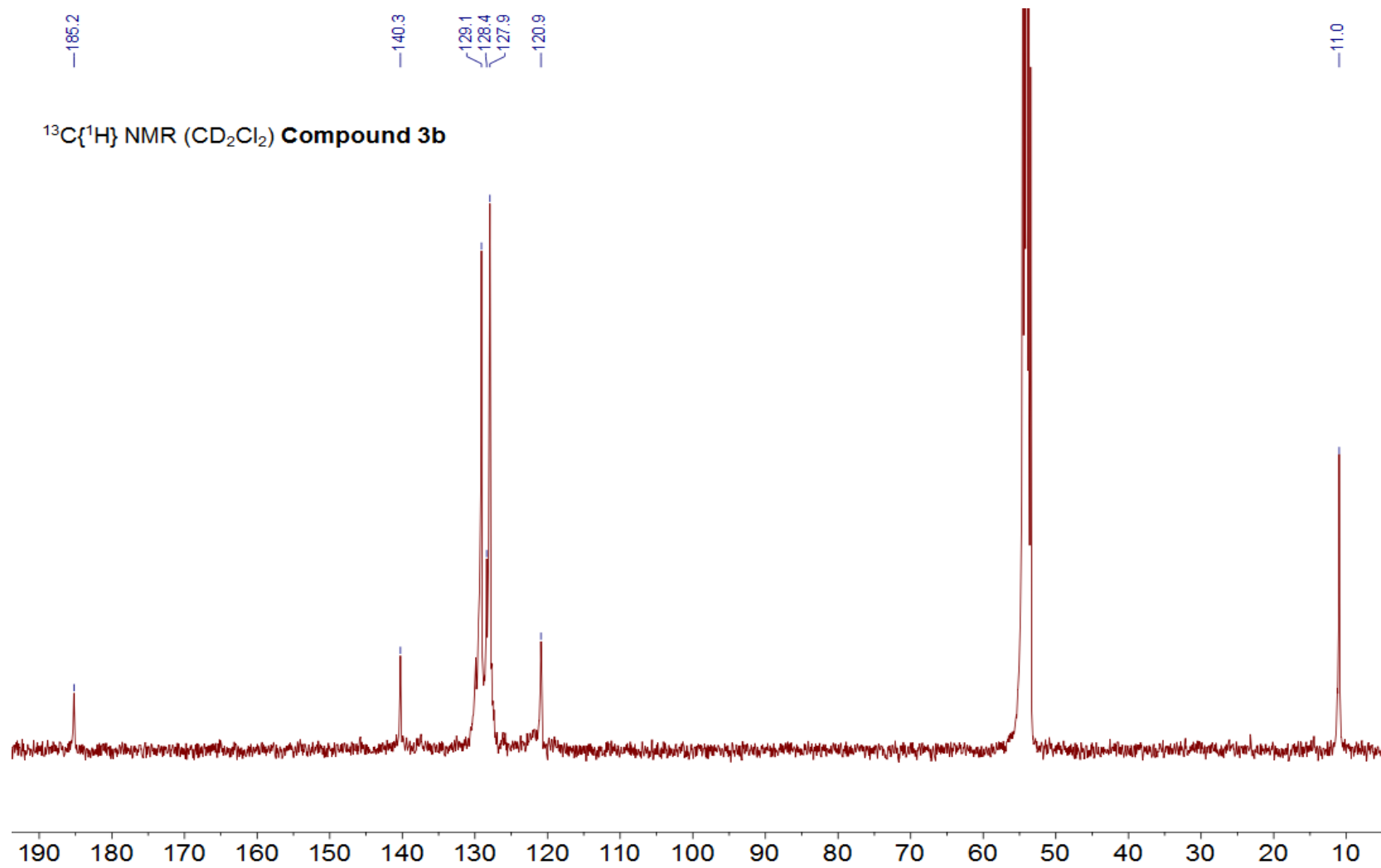


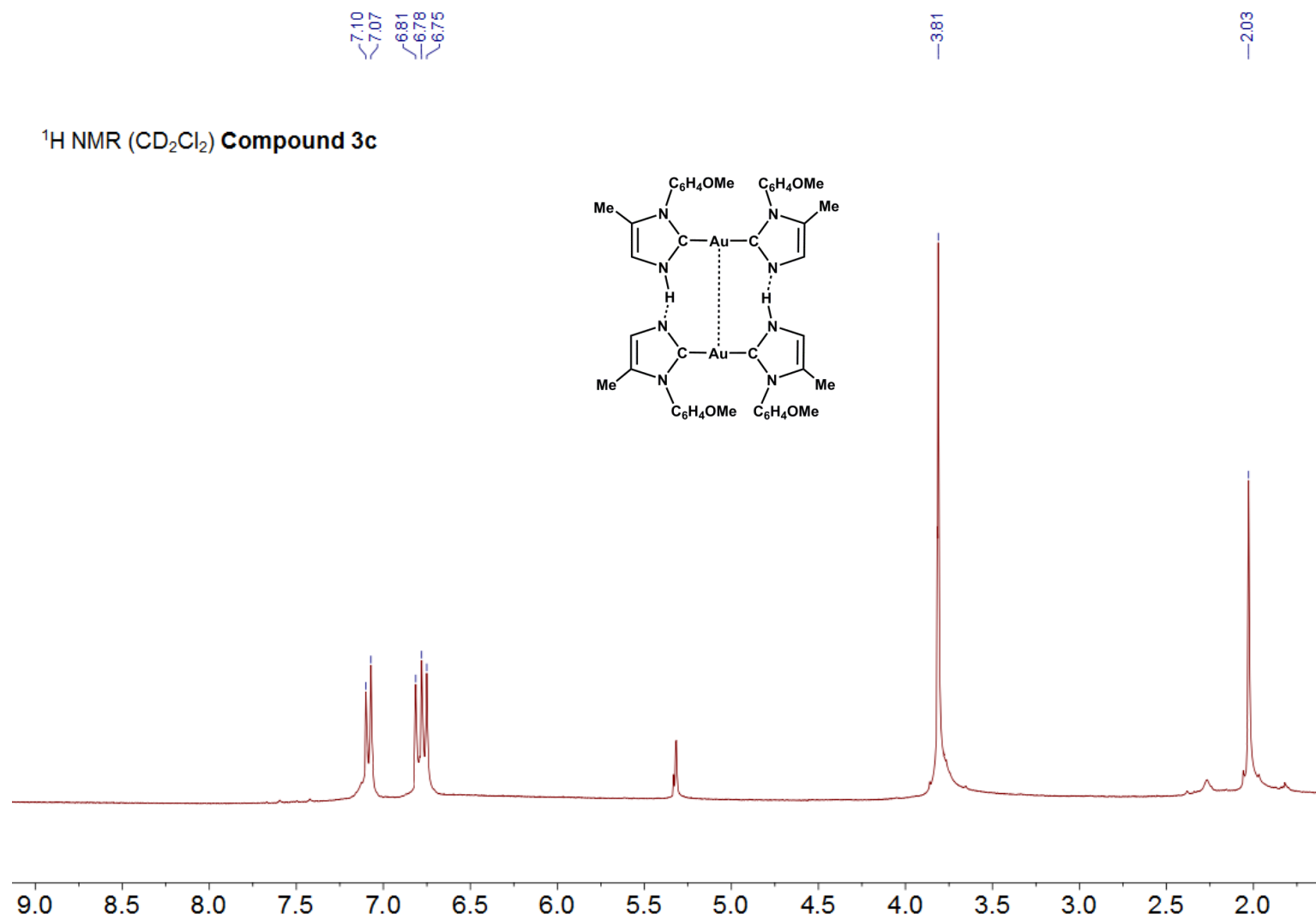


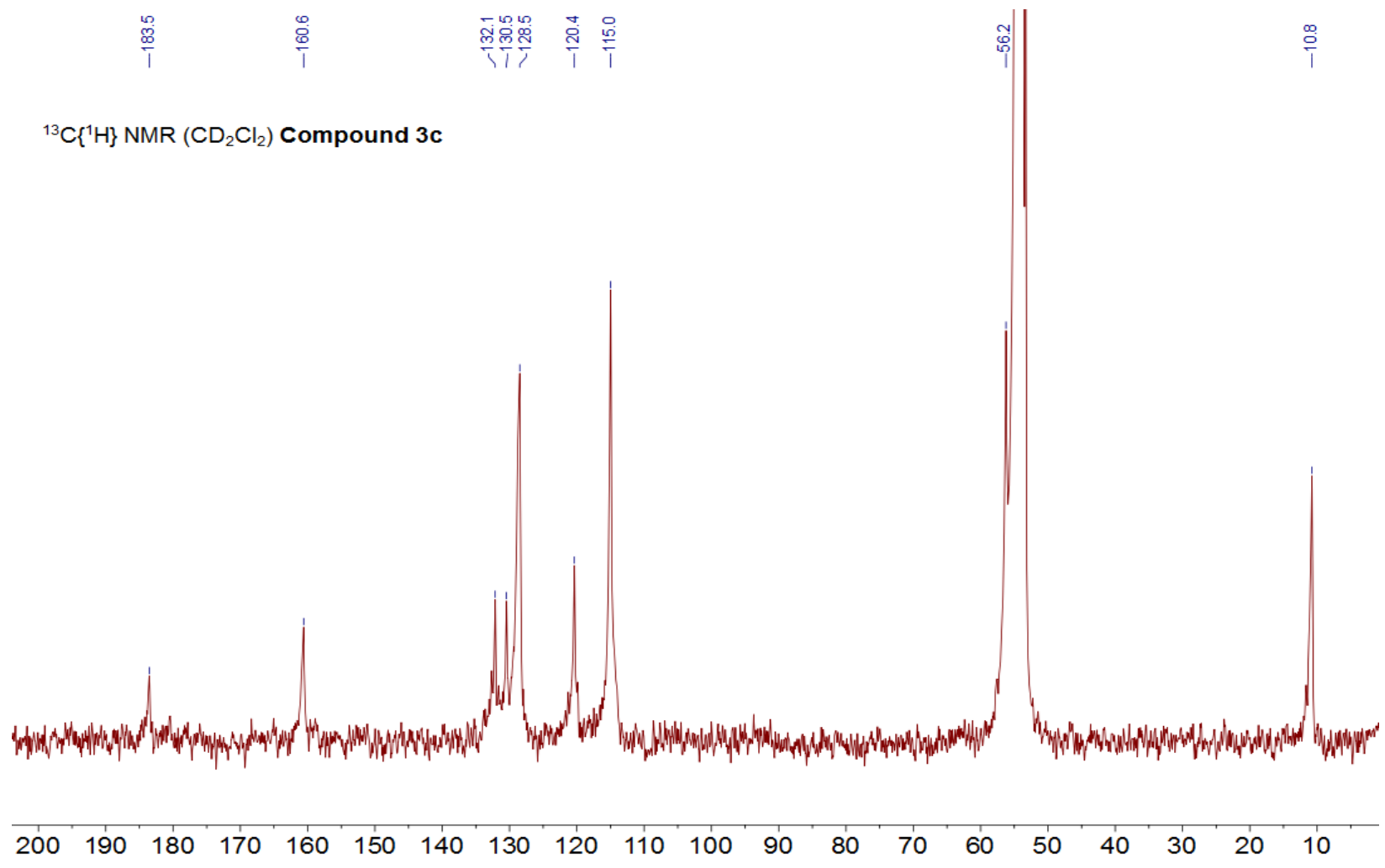


¹H NMR (CD₂Cl₂) **Compound 3b**

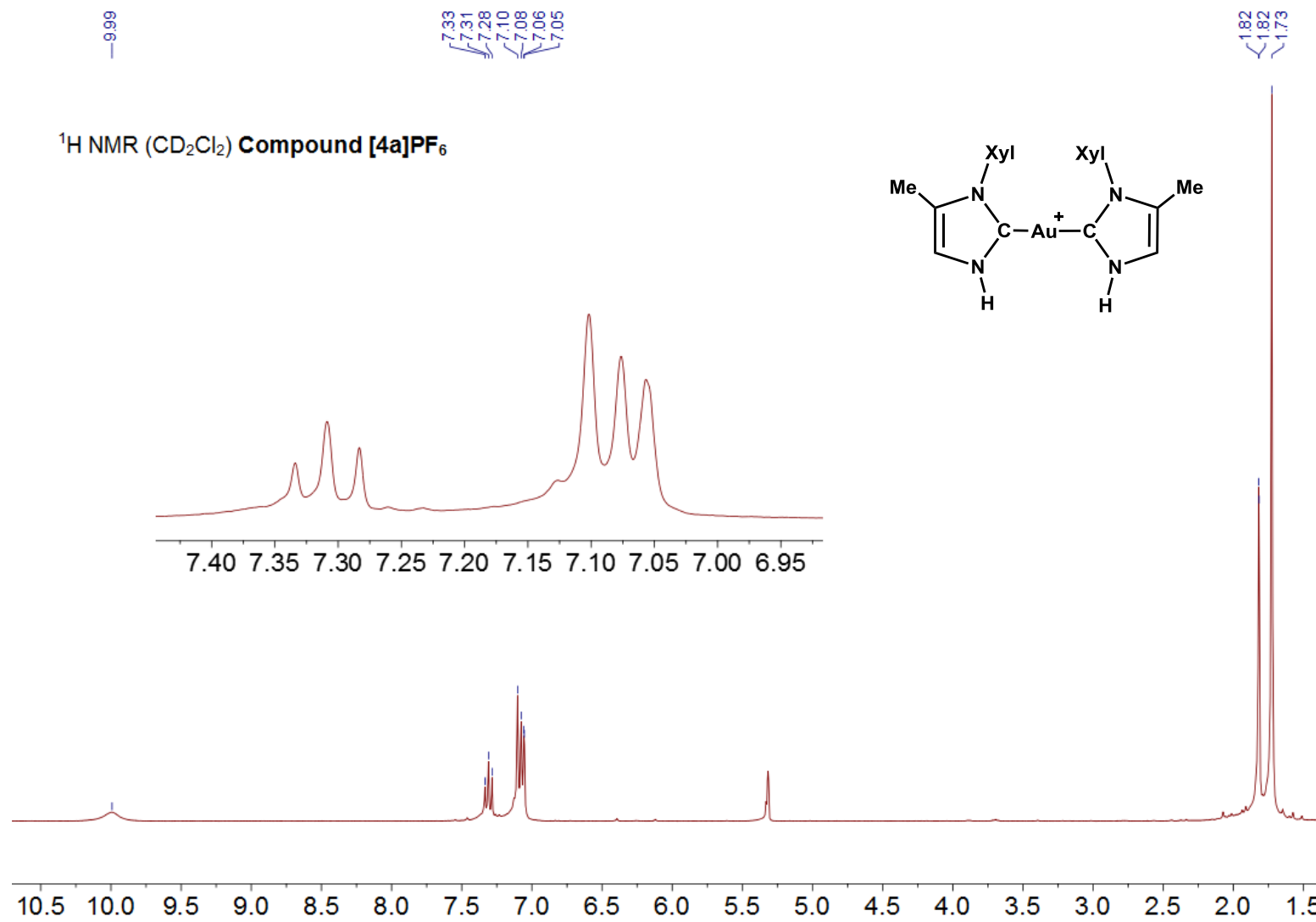


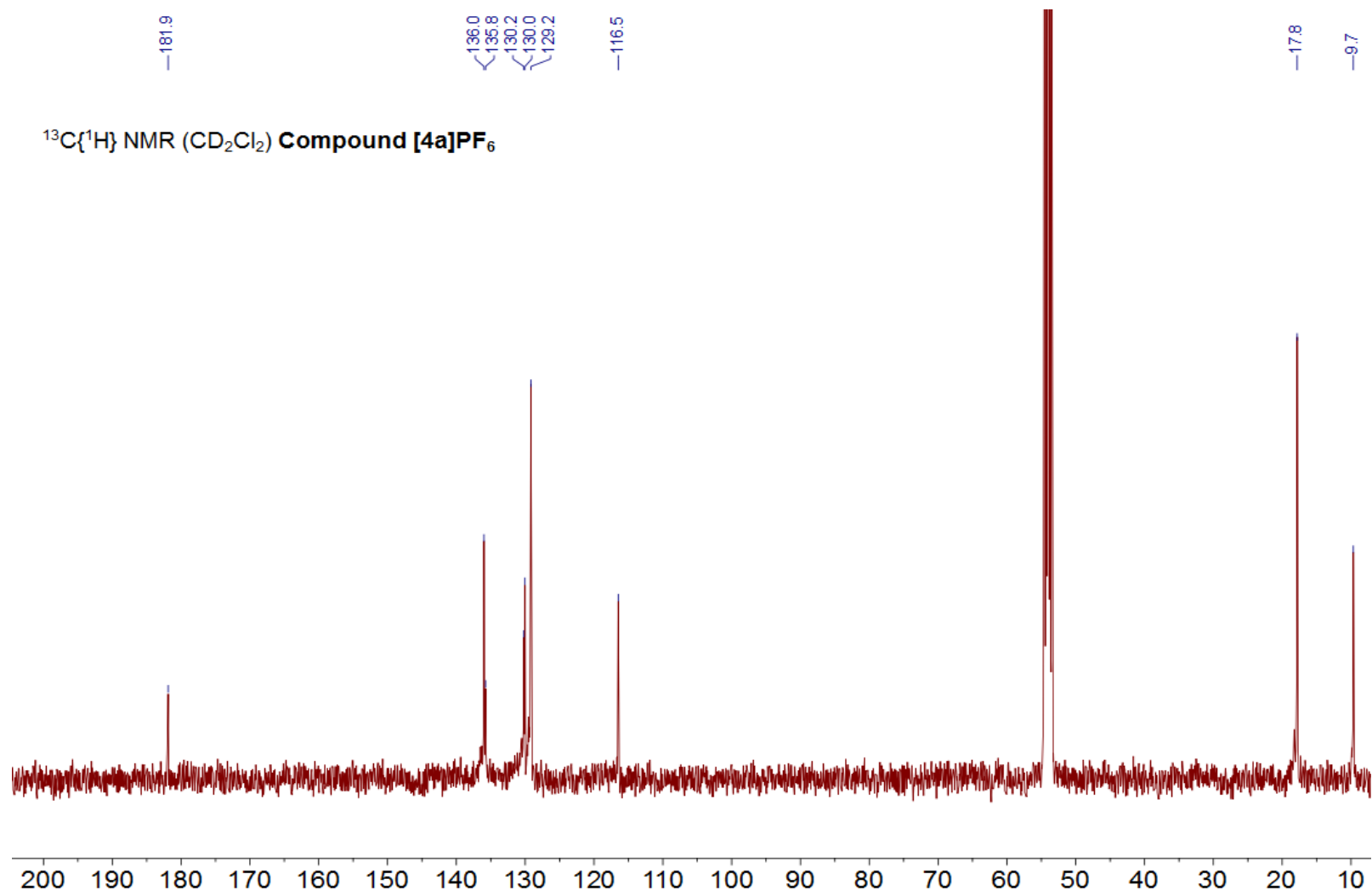


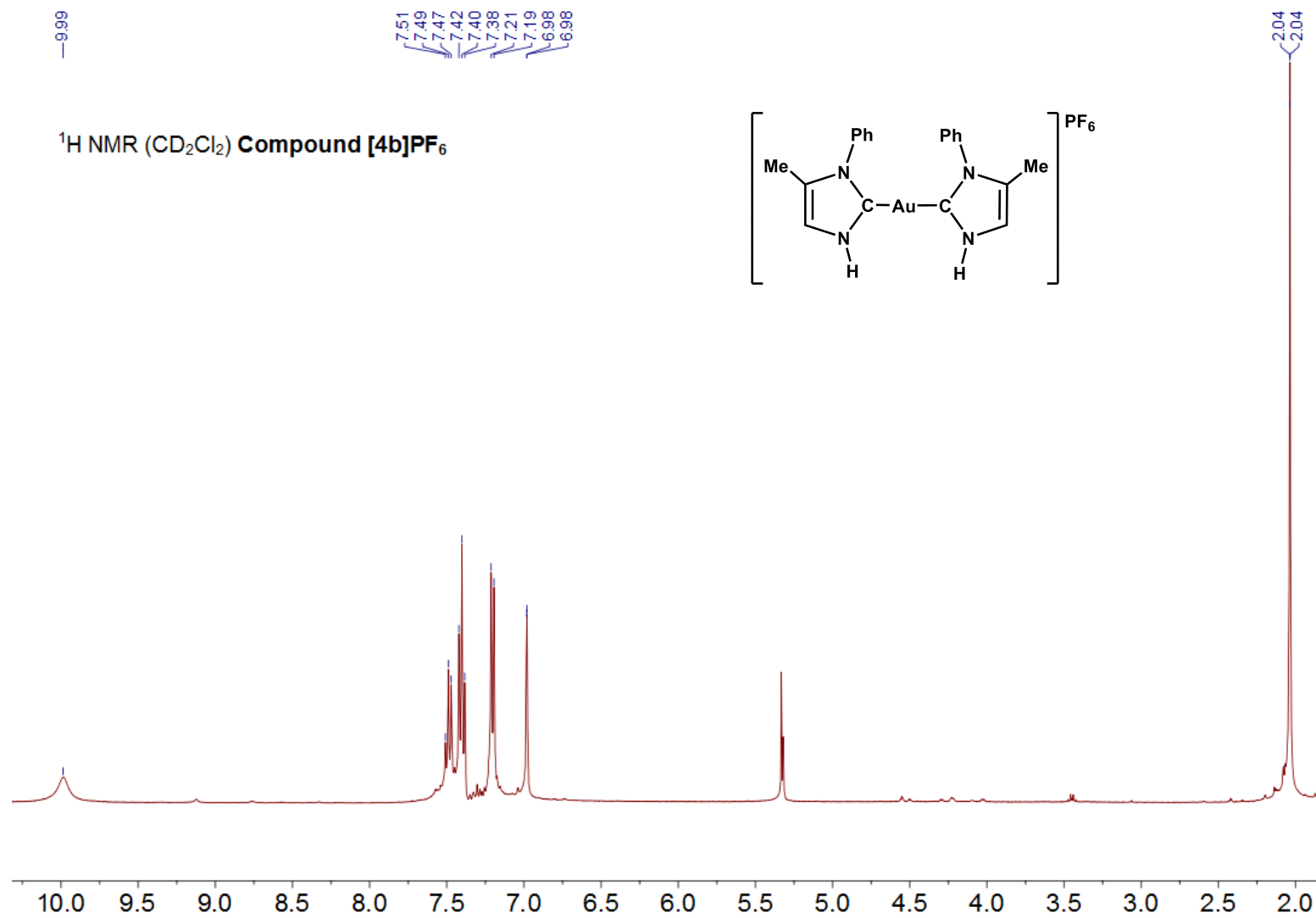


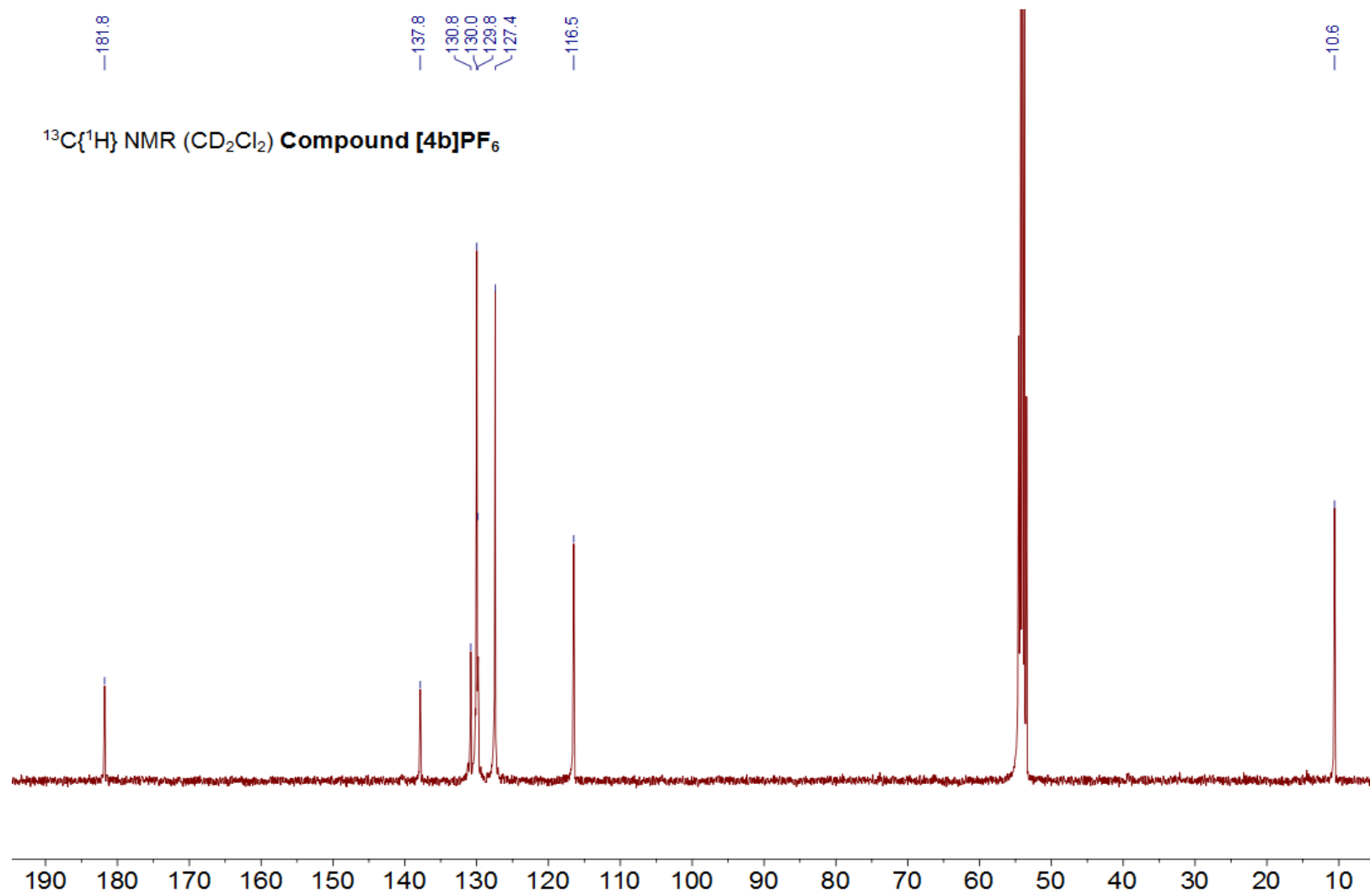


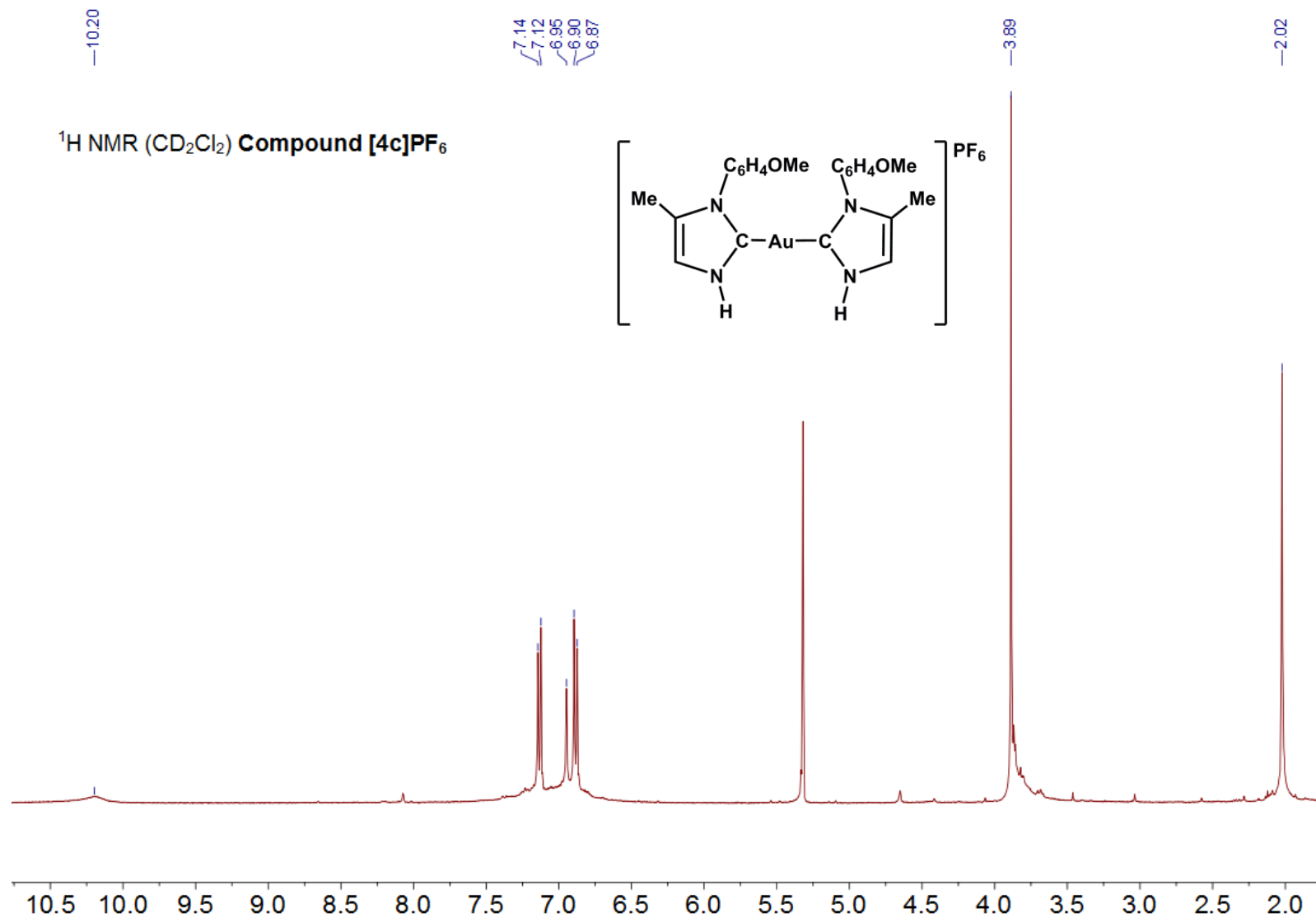
^1H NMR (CD_2Cl_2) Compound [4a] PF_6

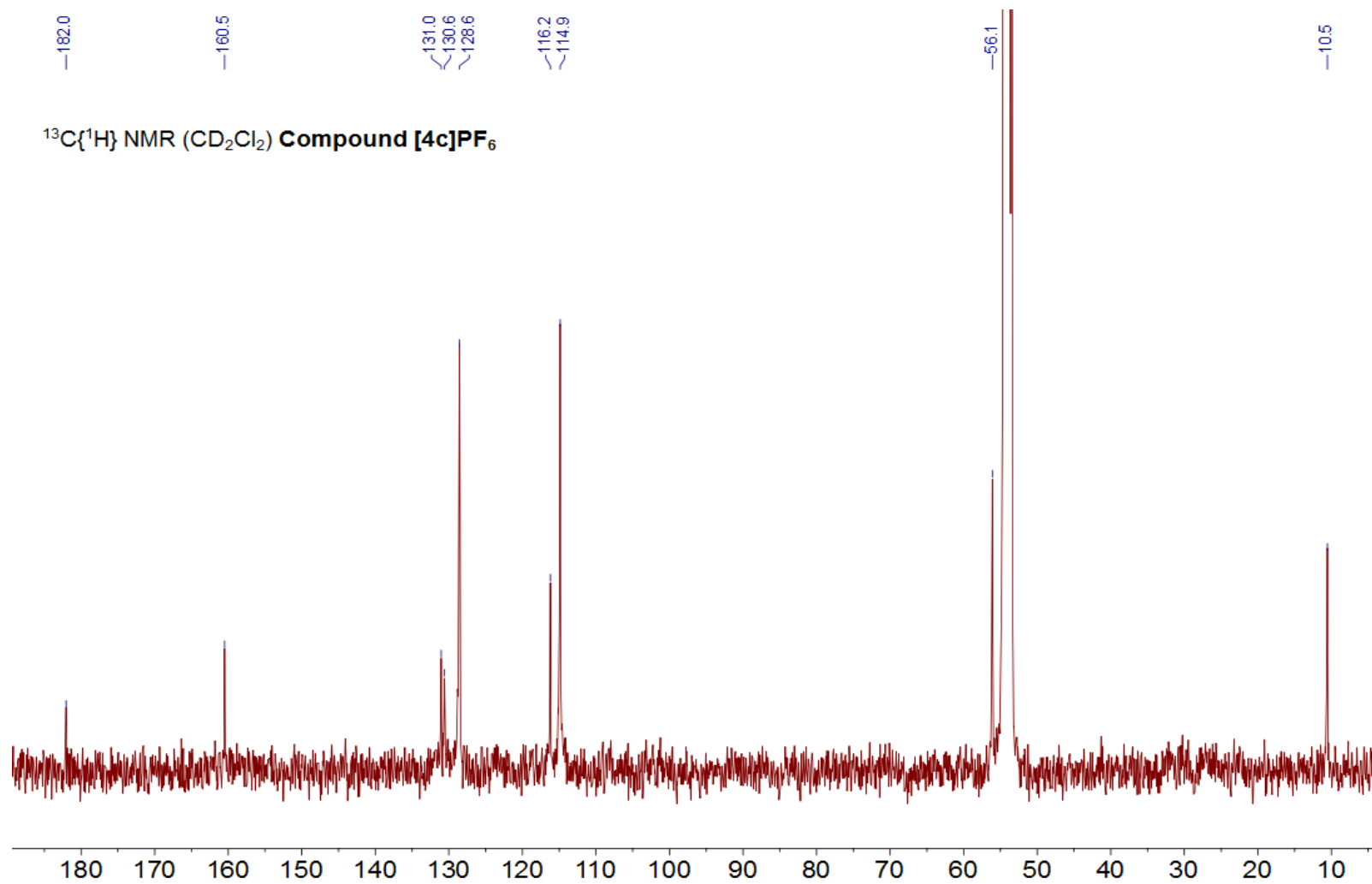


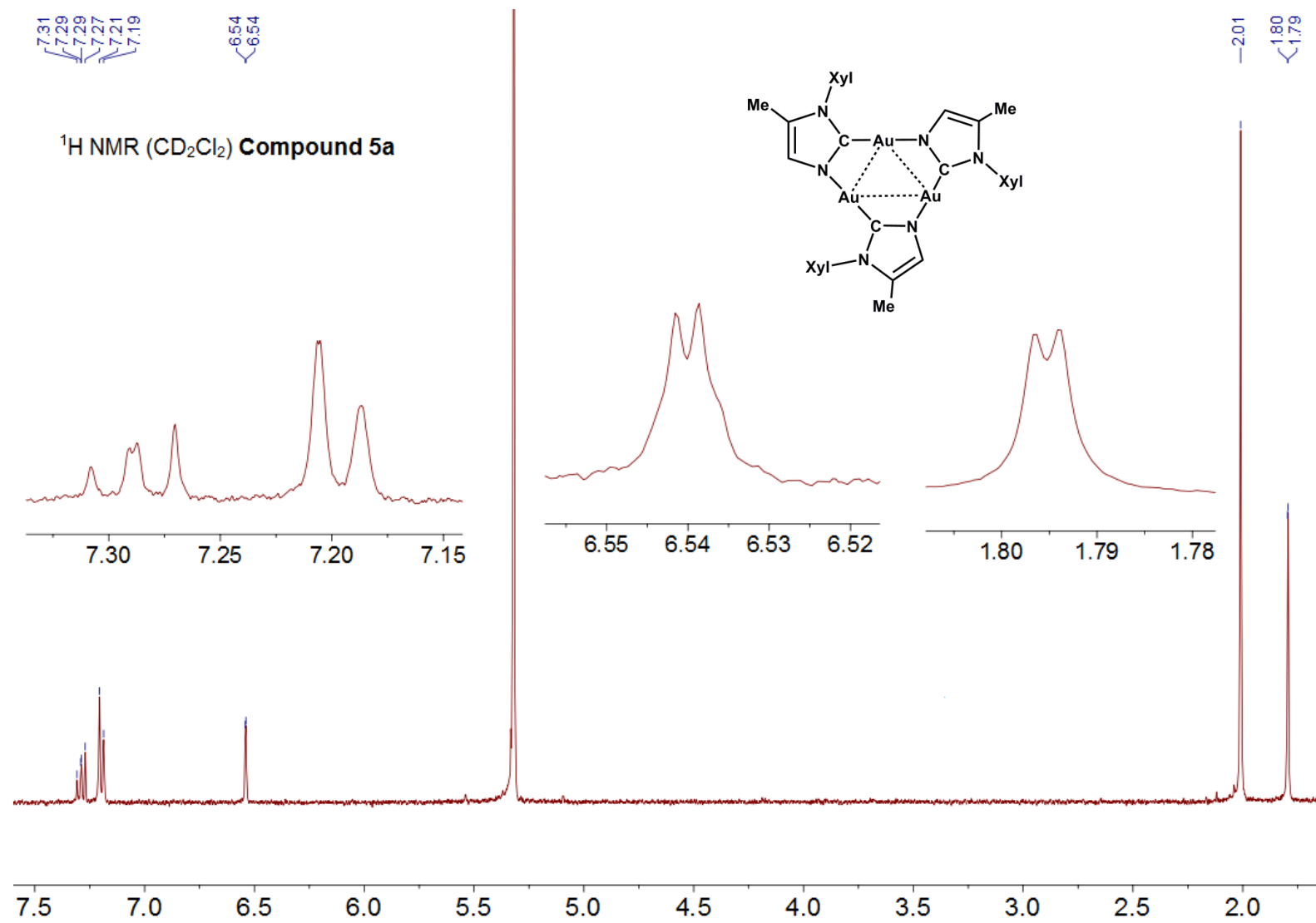


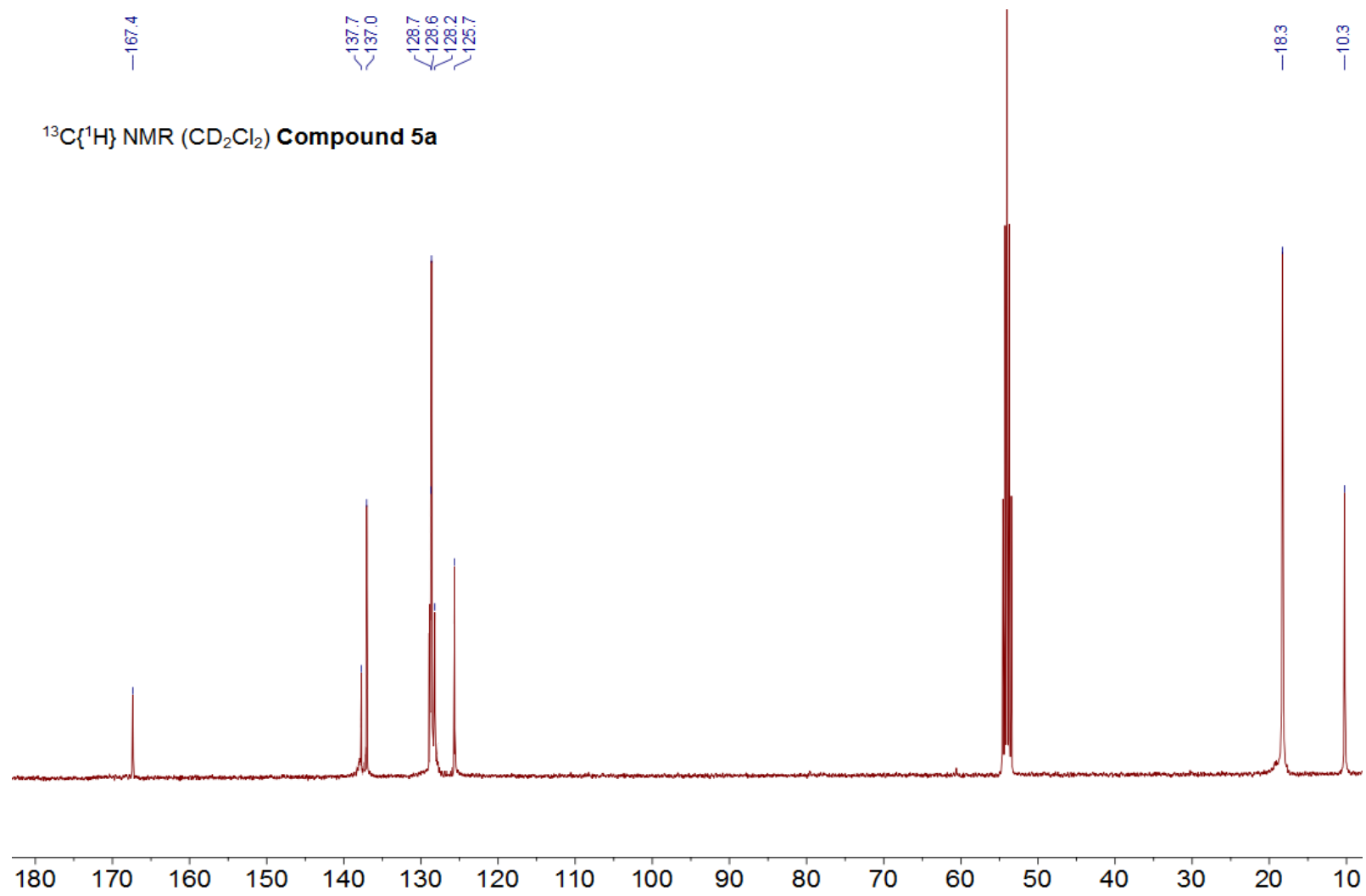


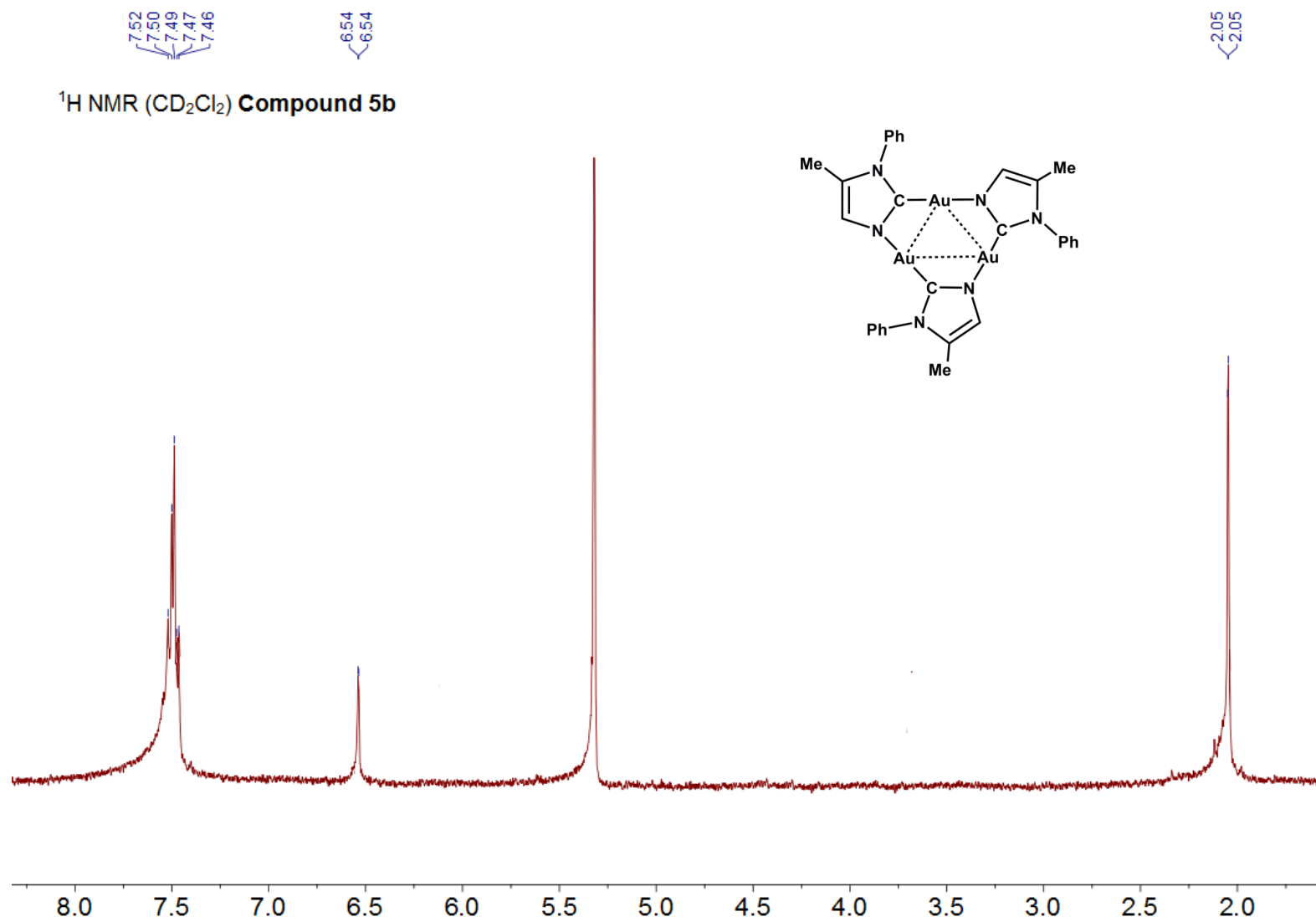


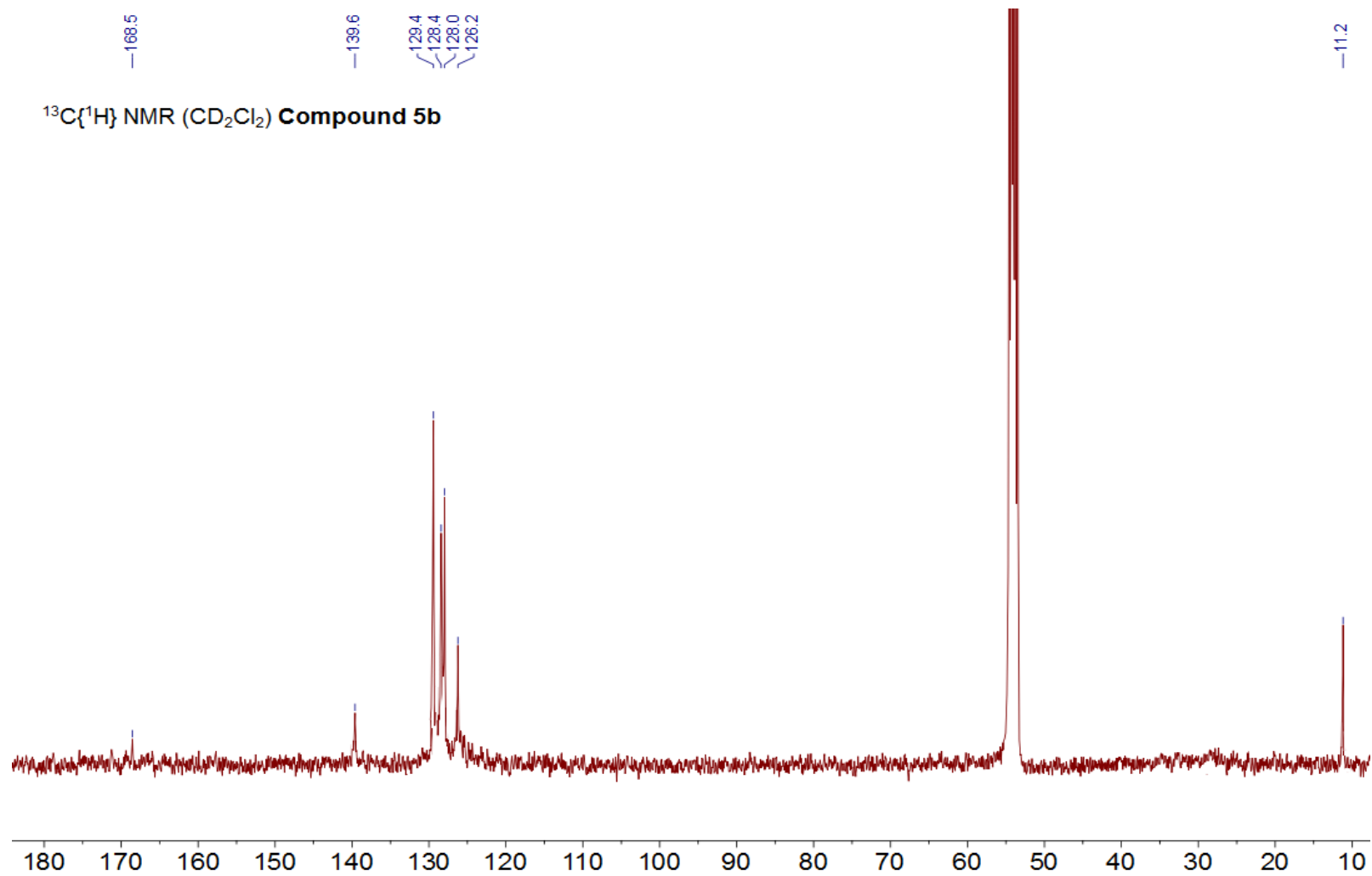


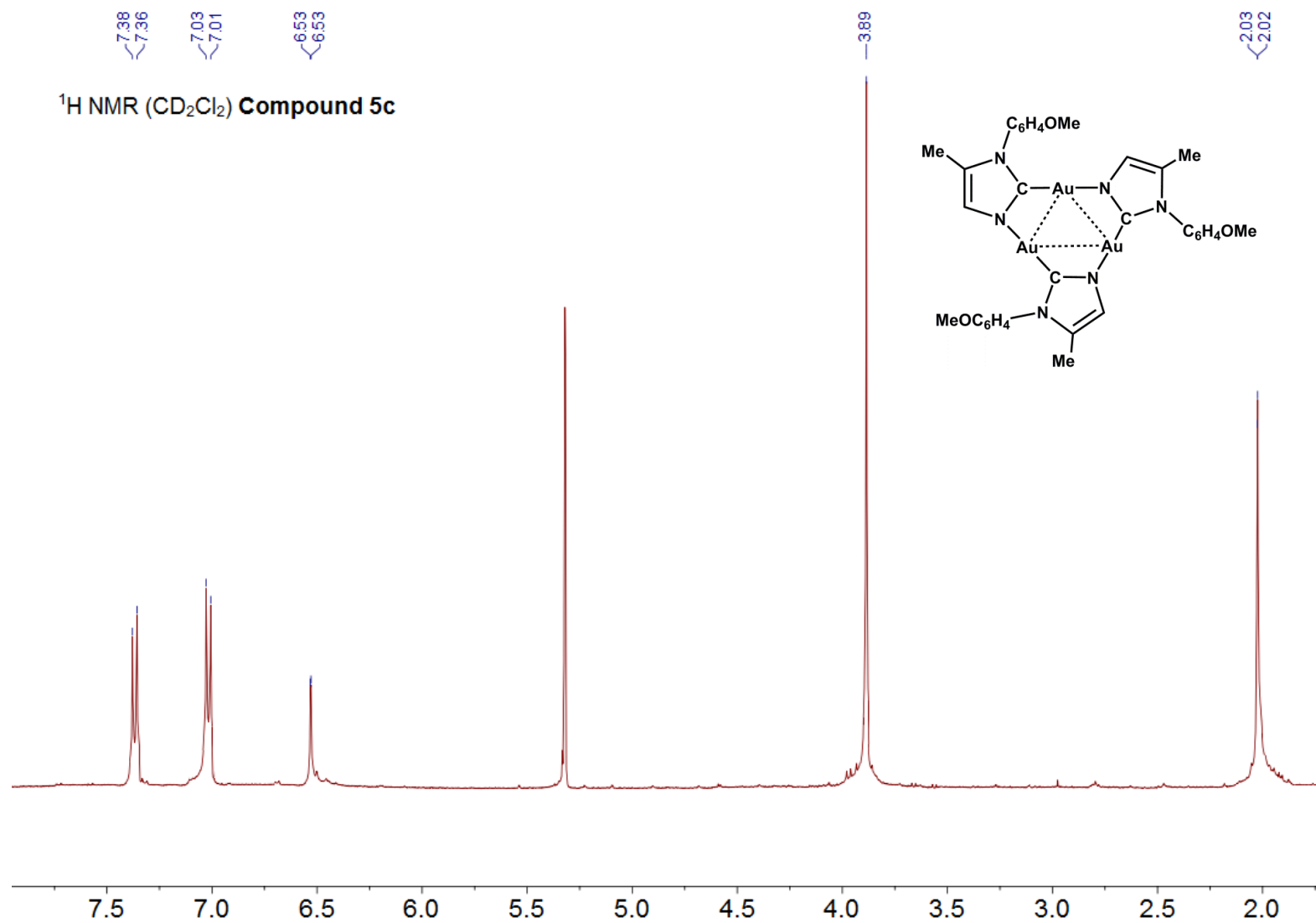


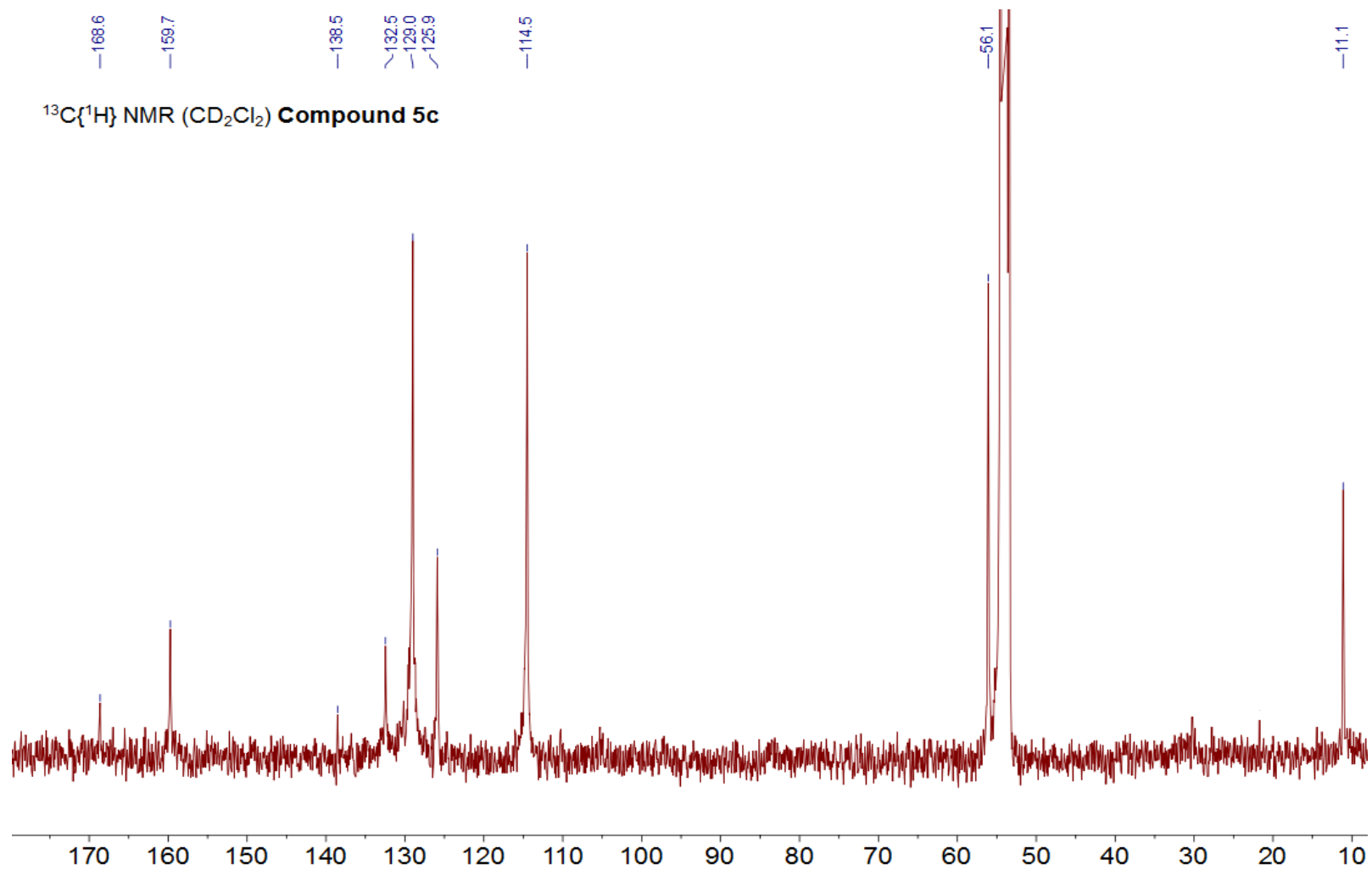


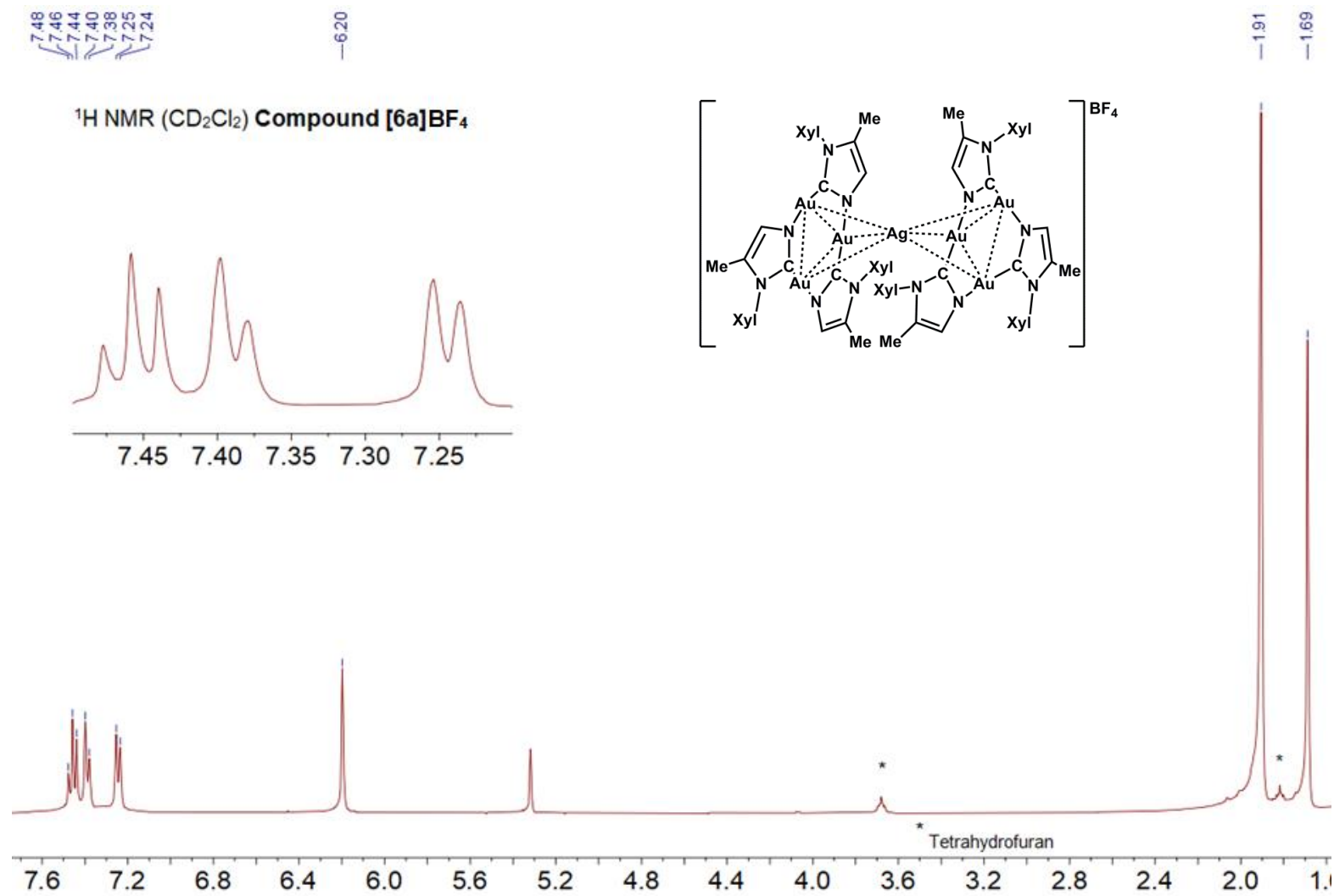


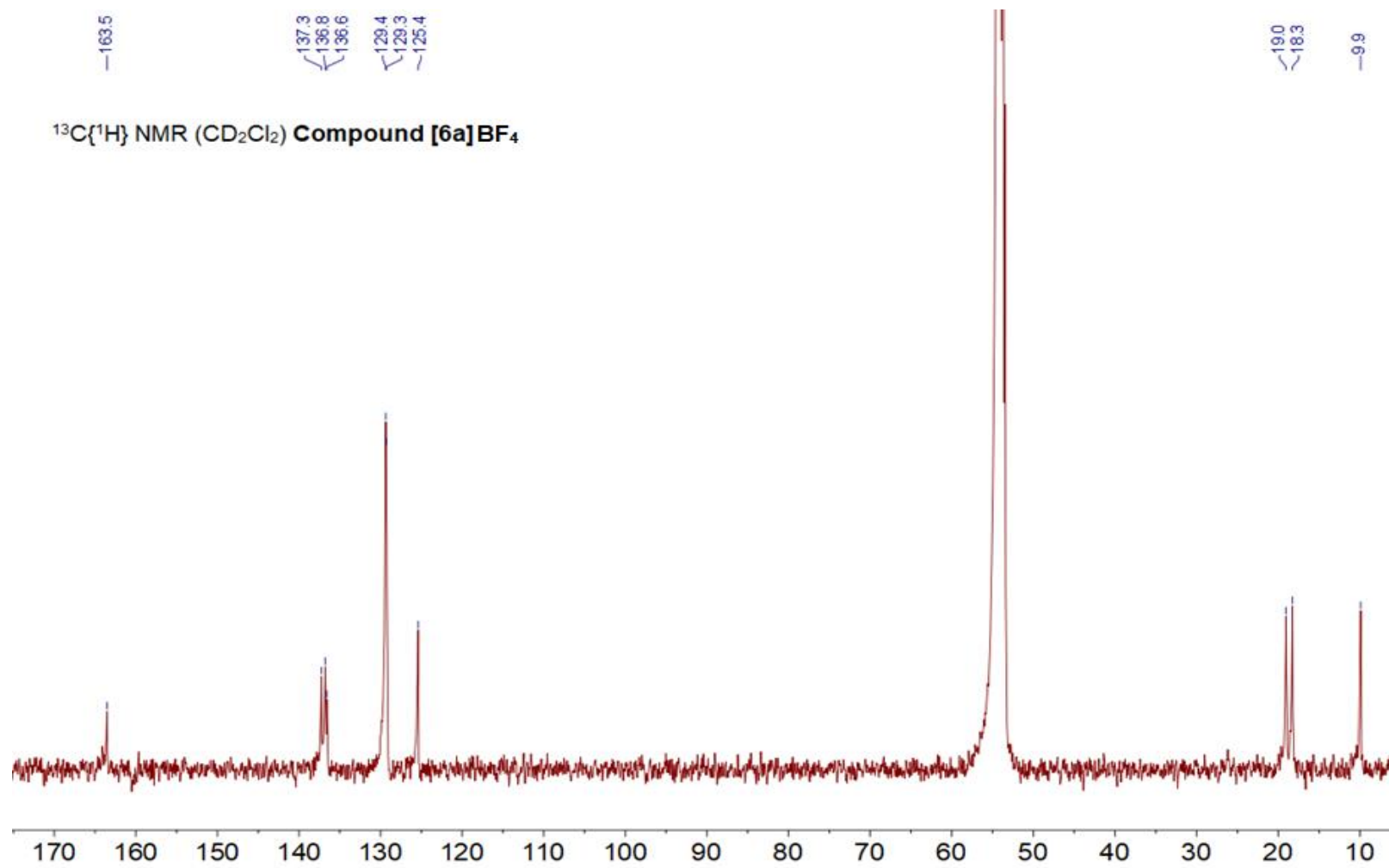




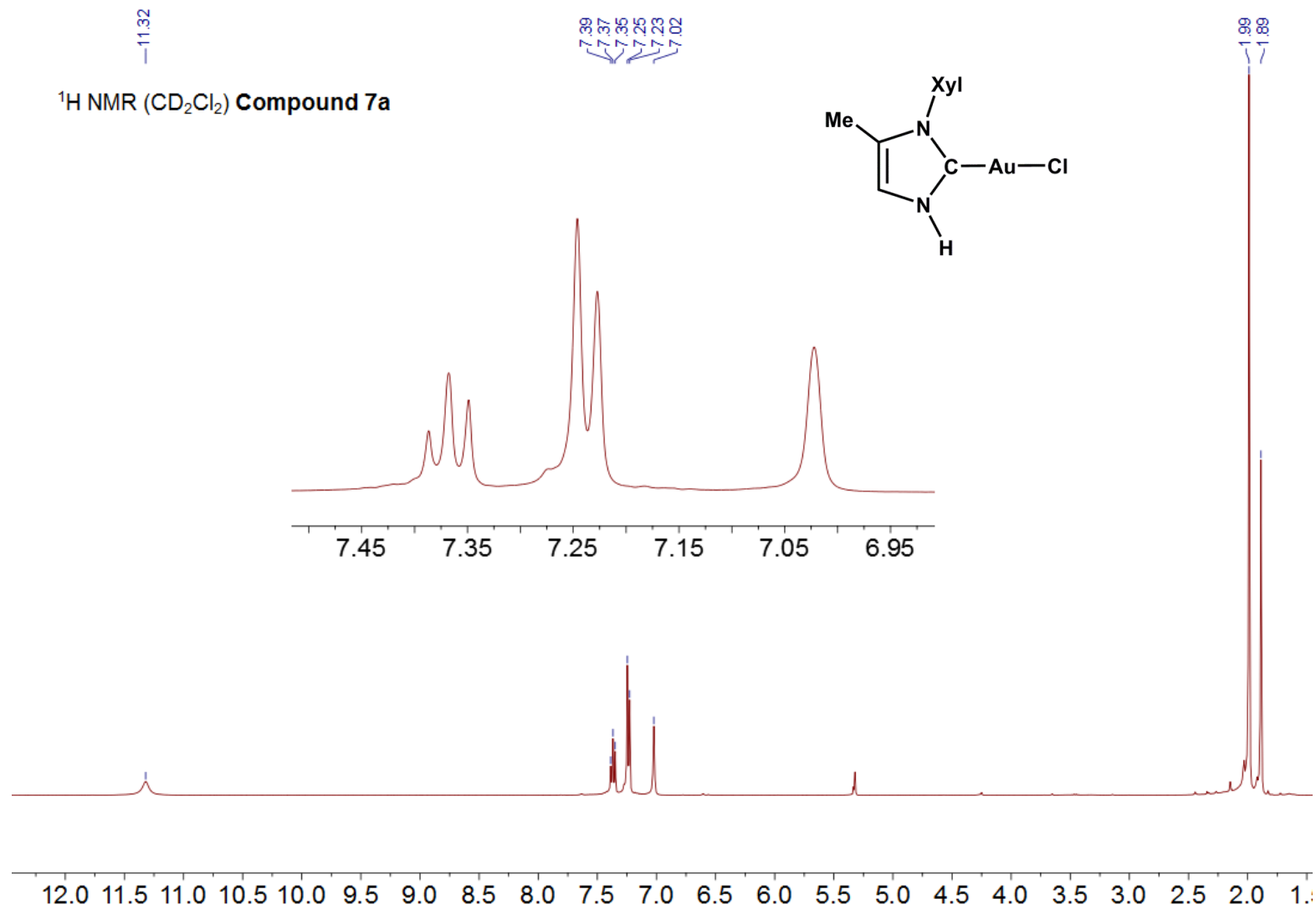


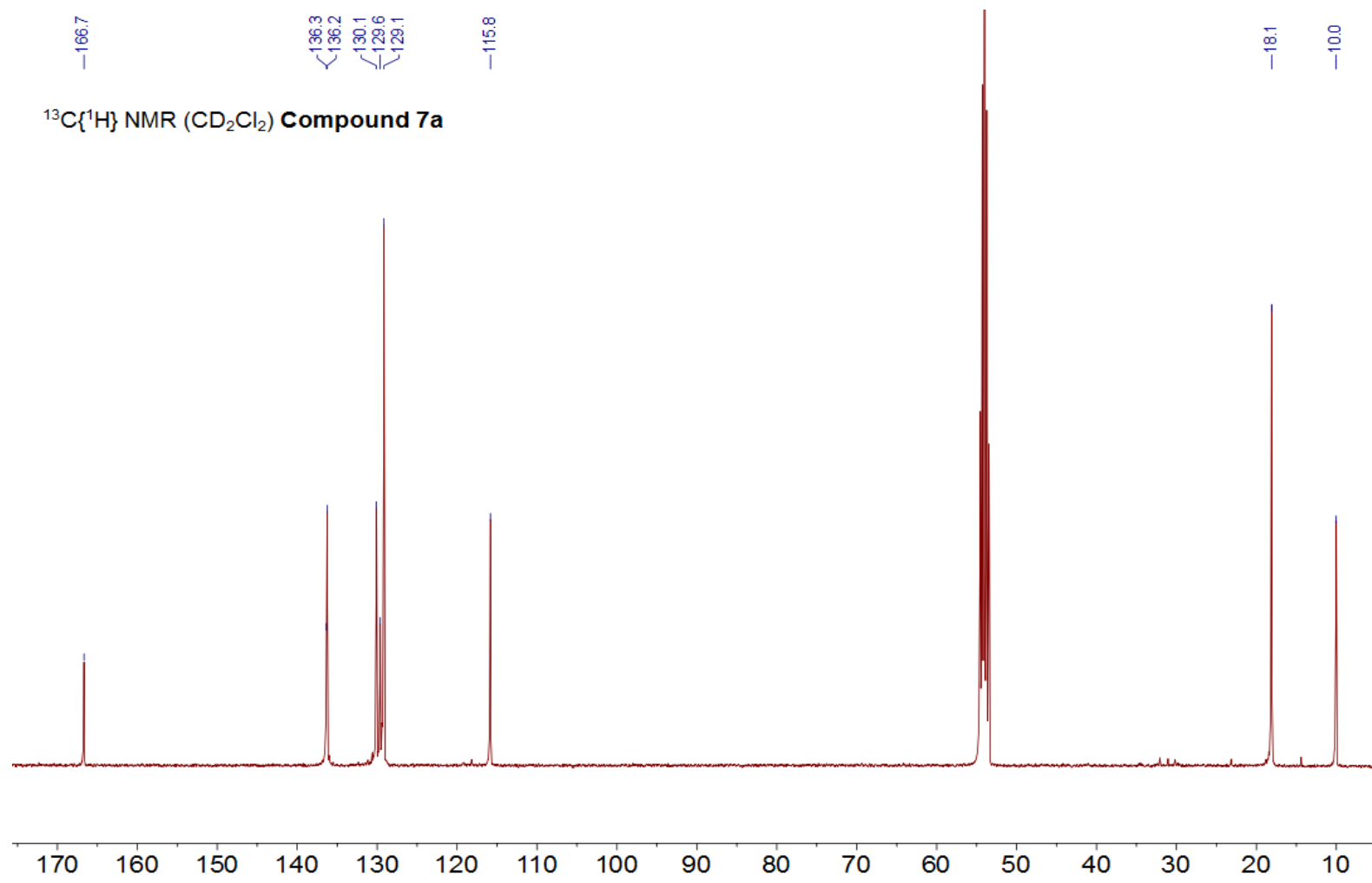






¹H NMR (CD₂Cl₂) **Compound 7a**





Variation of the N-H signal in the ^1H NMR spectrum of **7a** in CD_2Cl_2 at different concentrations.

