



Chemical Communications

ELECTRONIC SUPPORTING INFORMATION

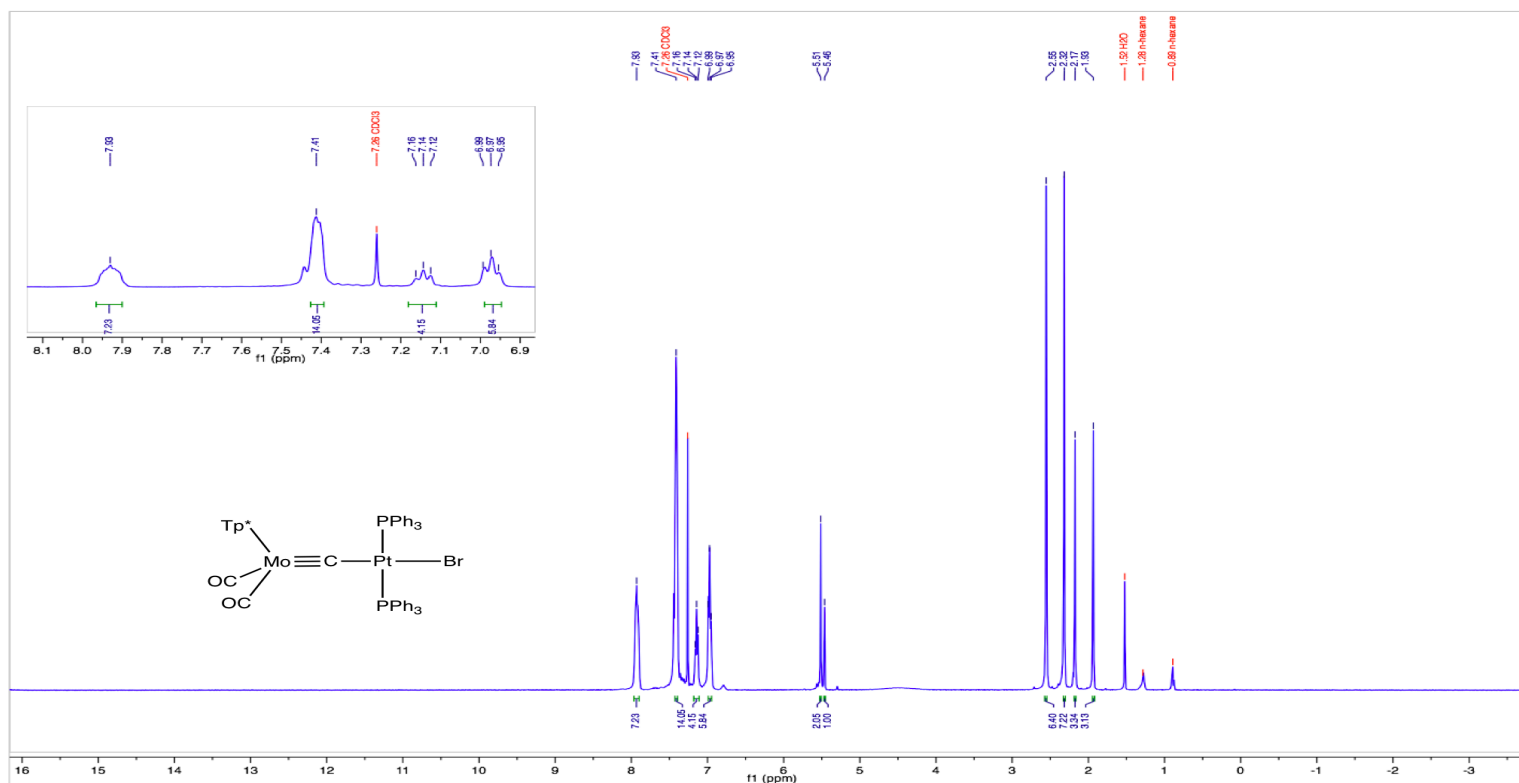


Figure S6. ^1H NMR Spectrum of $[\text{MoPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2a) in CDCl_3 , 25°C

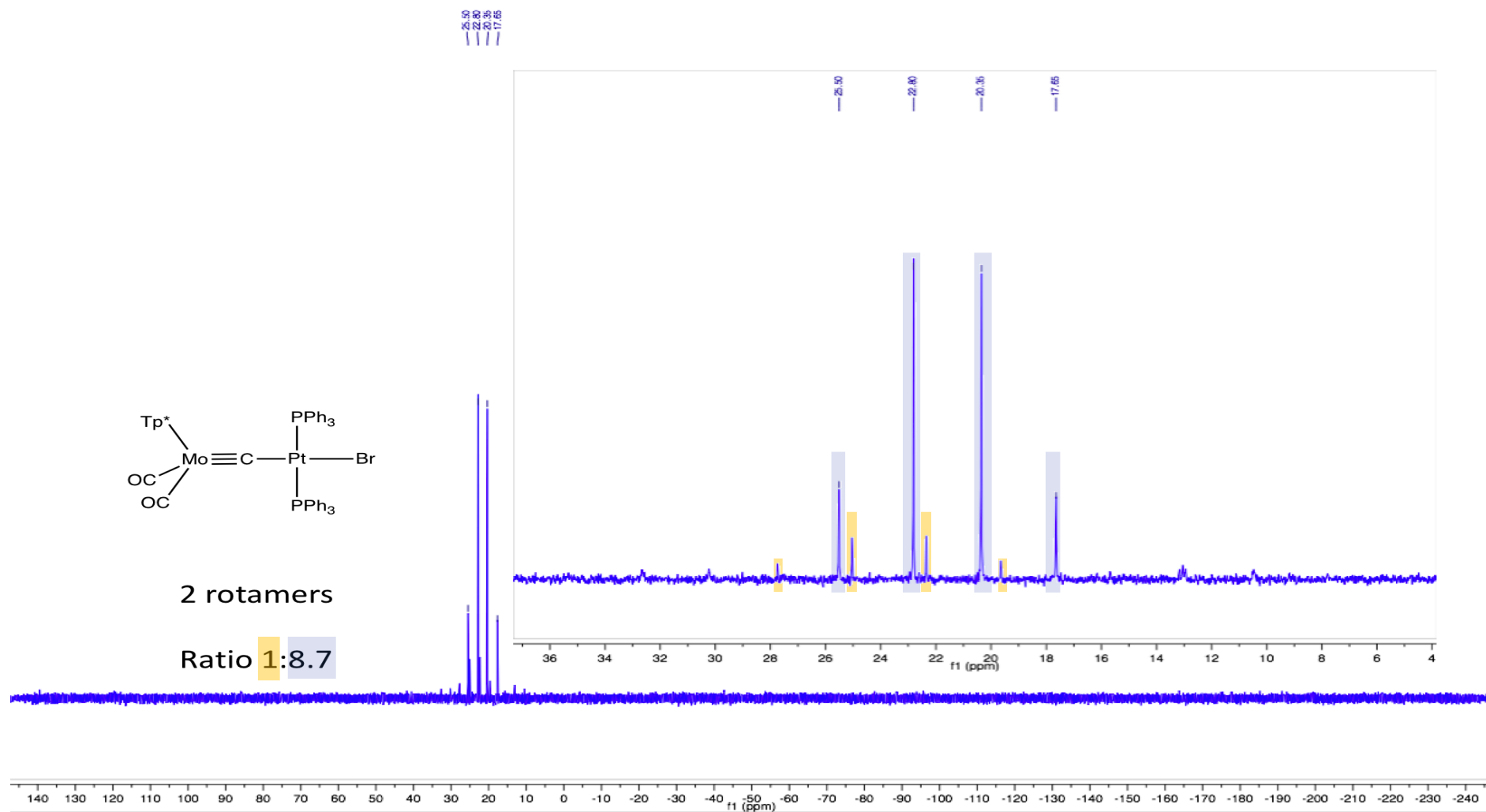


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2a) in CDCl_3 , 25 °C

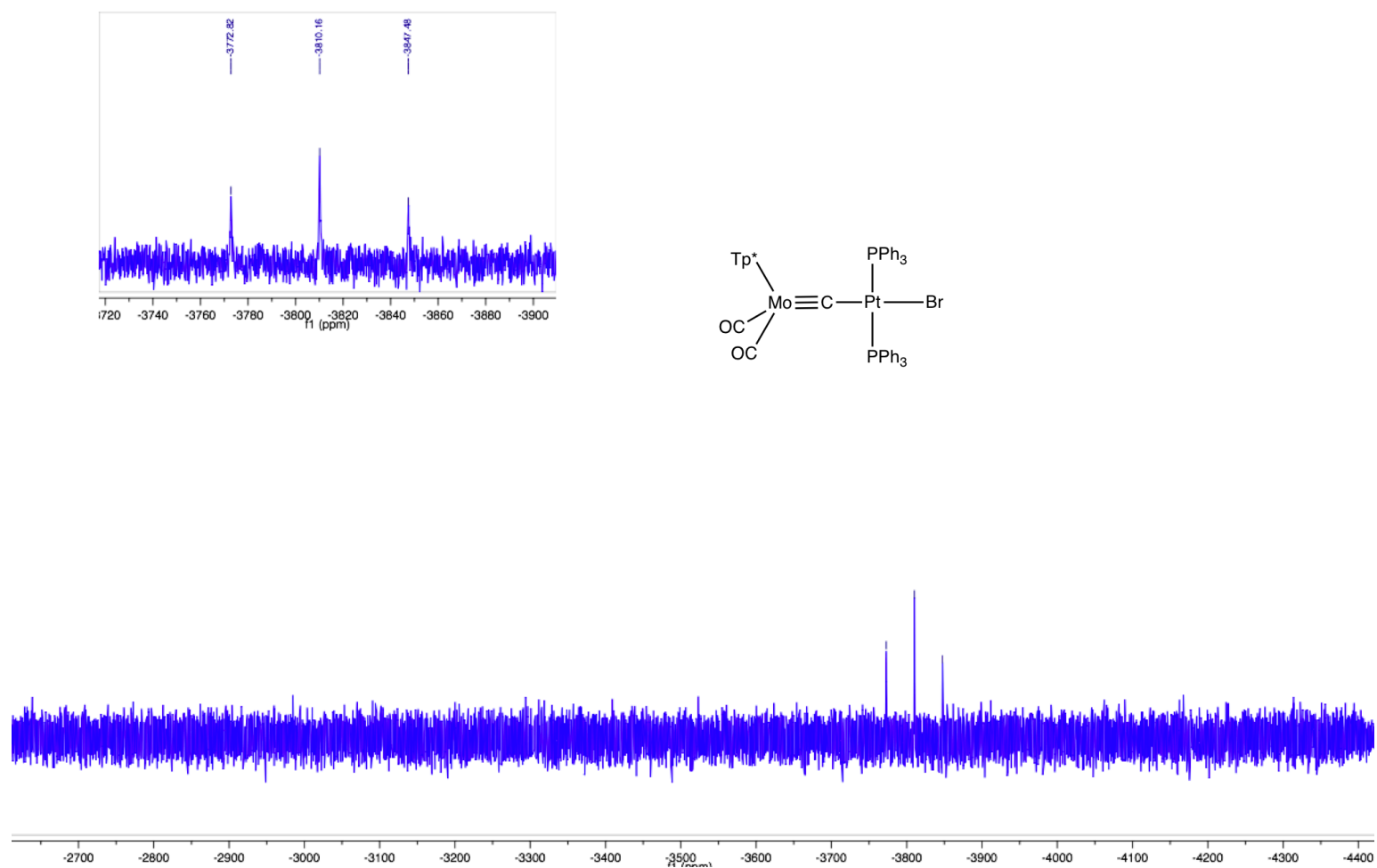


Figure S8. $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2a) in CDCl_3 , 25°C

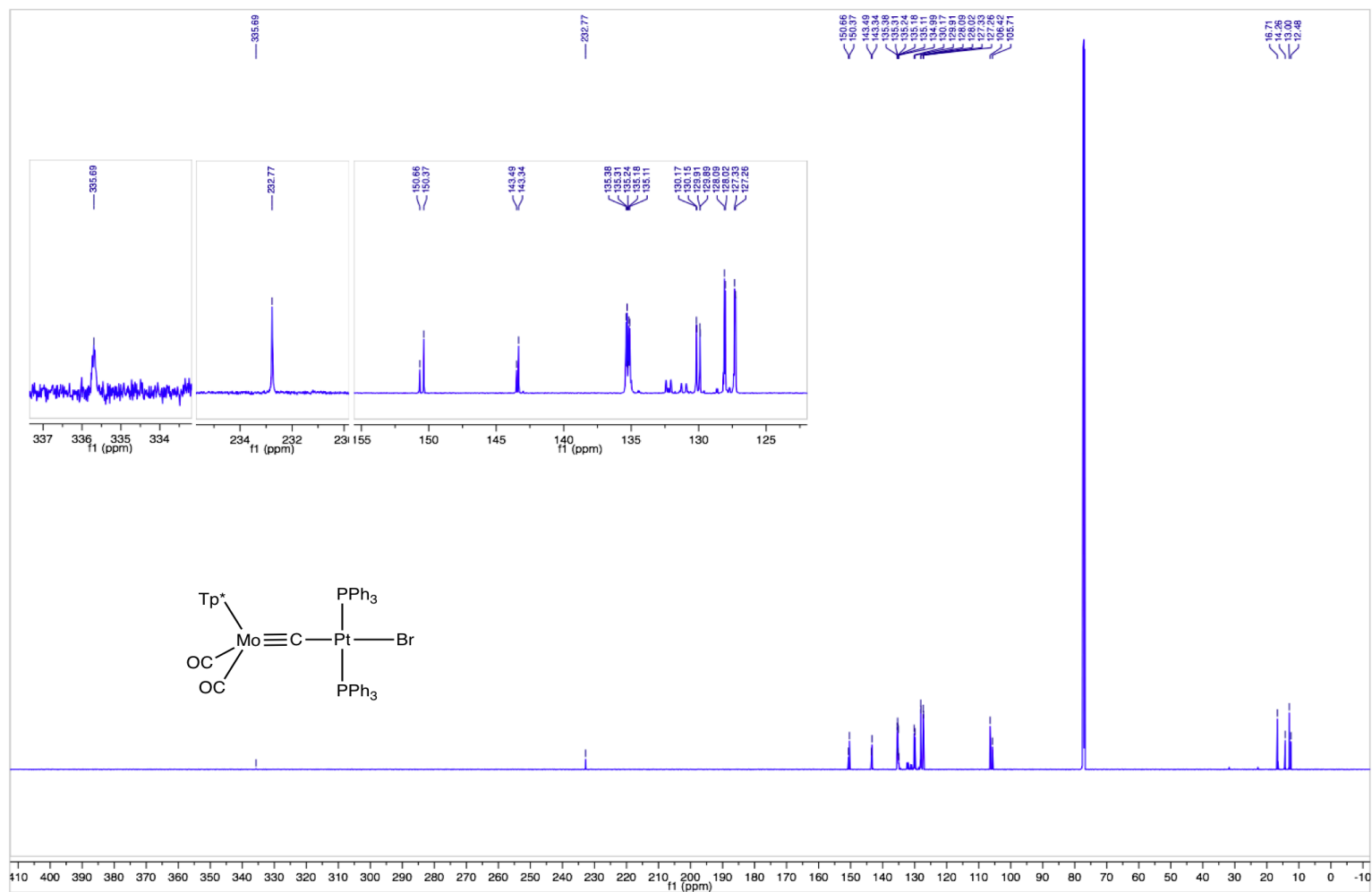


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2a) in CDCl_3 , 25 °C

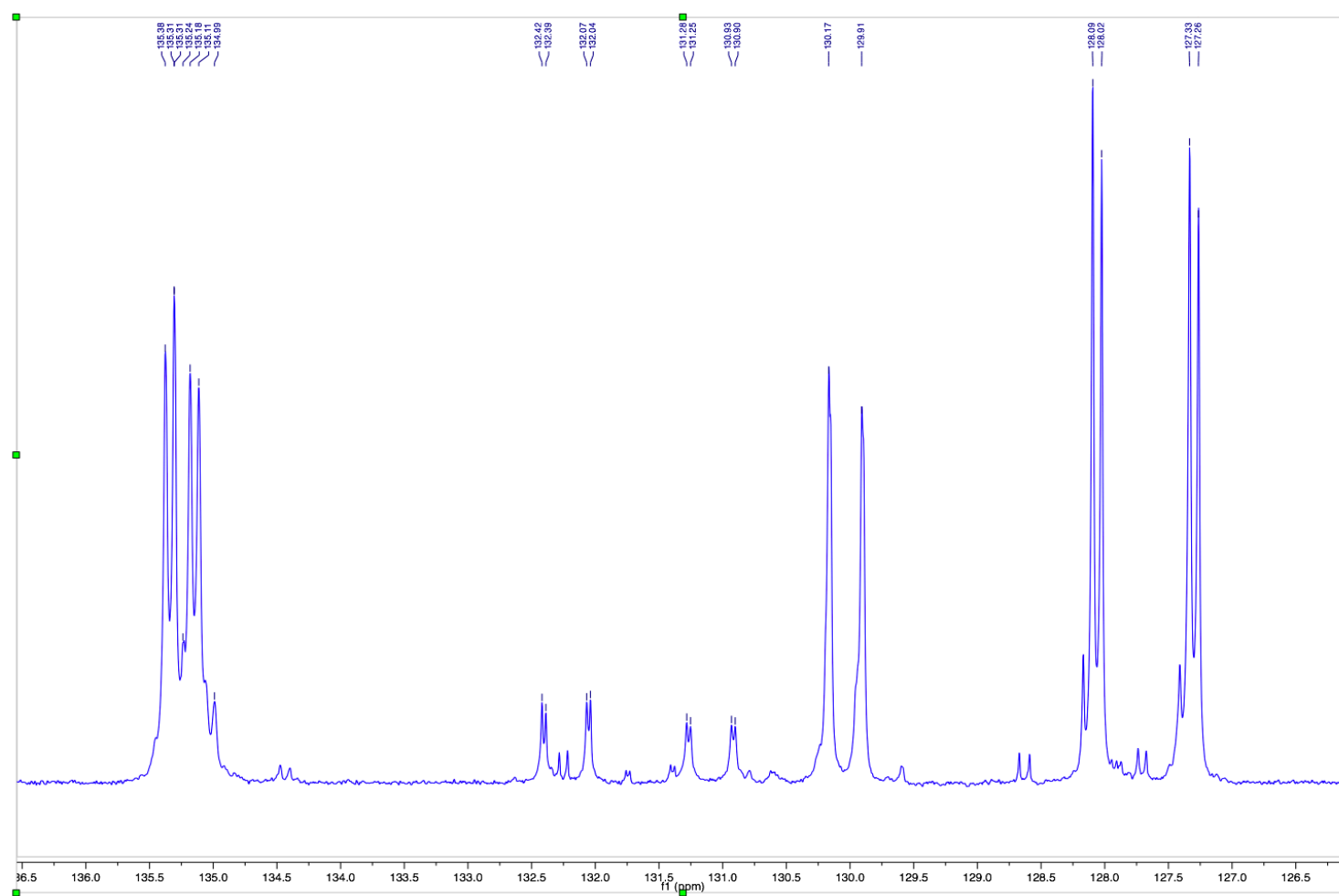


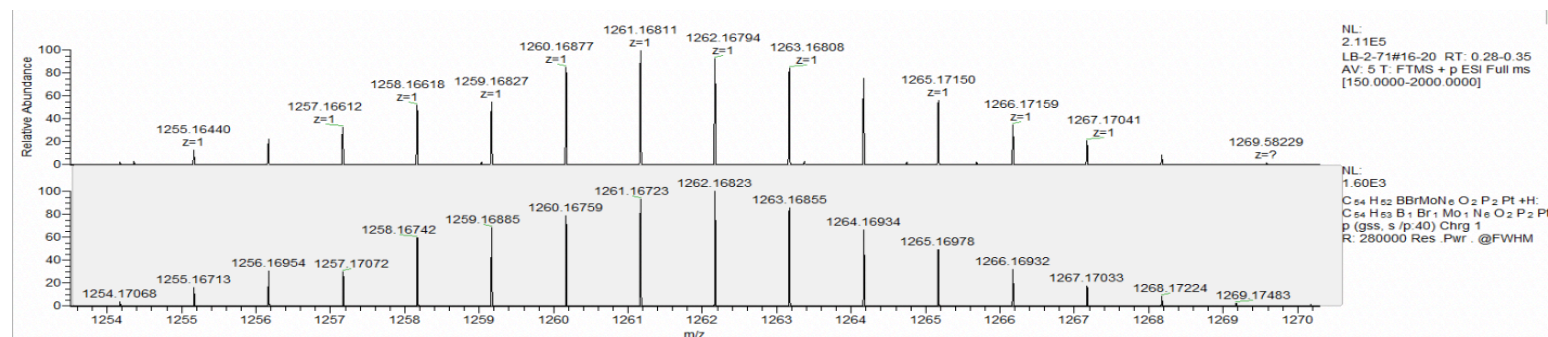
Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2a) in CDCl_3 , 25°C – Phenyl region

Figure S10. RSC/RSB Joint Mass Spectrometry Facility Analysis Report: [MoPt(μ -C)(CO)₂(PPh₃)₂(Tp*)] (2a)

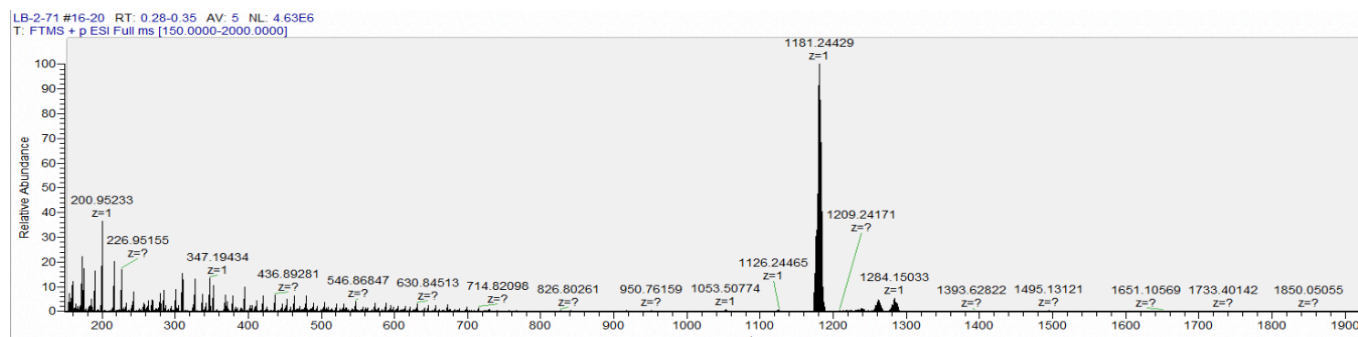
Instrument: Orbitrap QE, +ve mode ESI at 280k resolution **Analysis Date:** 2019-08-15

Theoretical m/z (most abundant isotopologue): [M+H]⁺ ion: 1262.16823 Observed m/z (most abundant isotopologue): [M+H]⁺ ion: 1262.16794 Mass error: 0.111 ppm

Observed versus simulated spectrum for detected target formulas [M+H]⁺ ion



Full Spectrum (m/z = 1181.24429 = [M-Br]⁺):



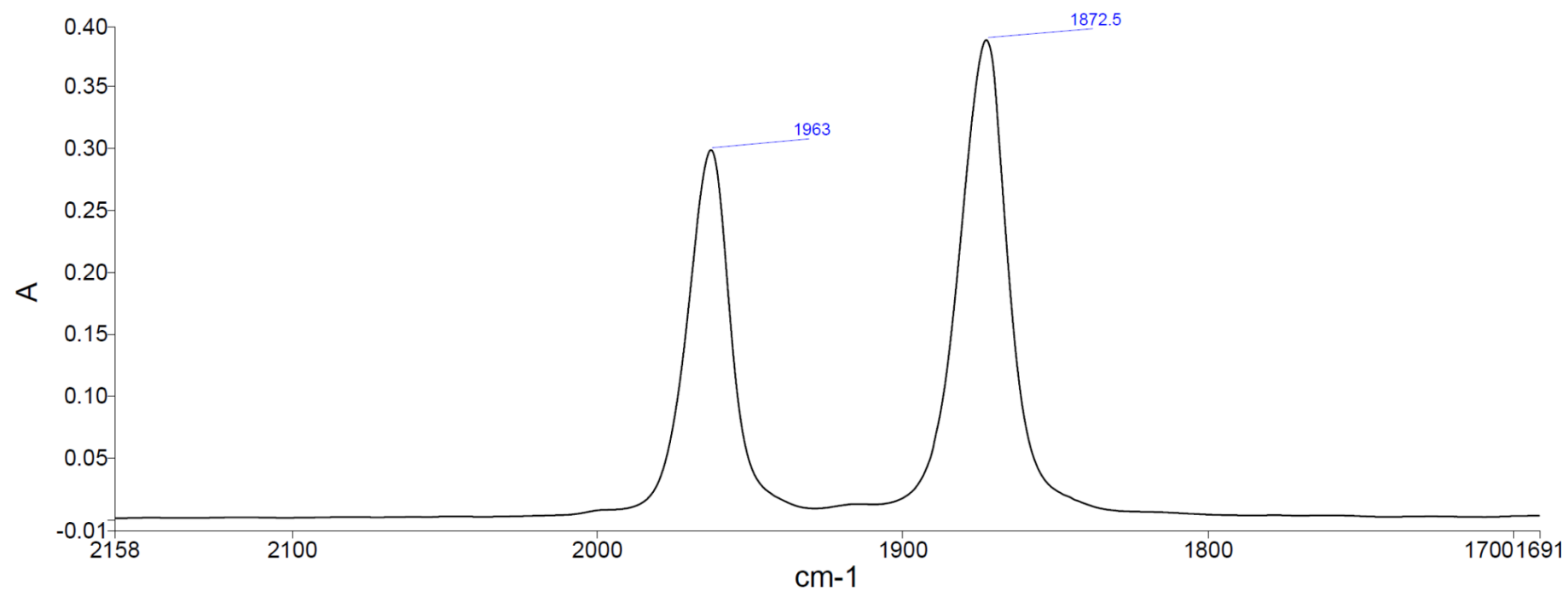


Figure S11. Infrared Spectrum of $[\text{MoPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2a) (CH_2Cl_2 , 25 °C).

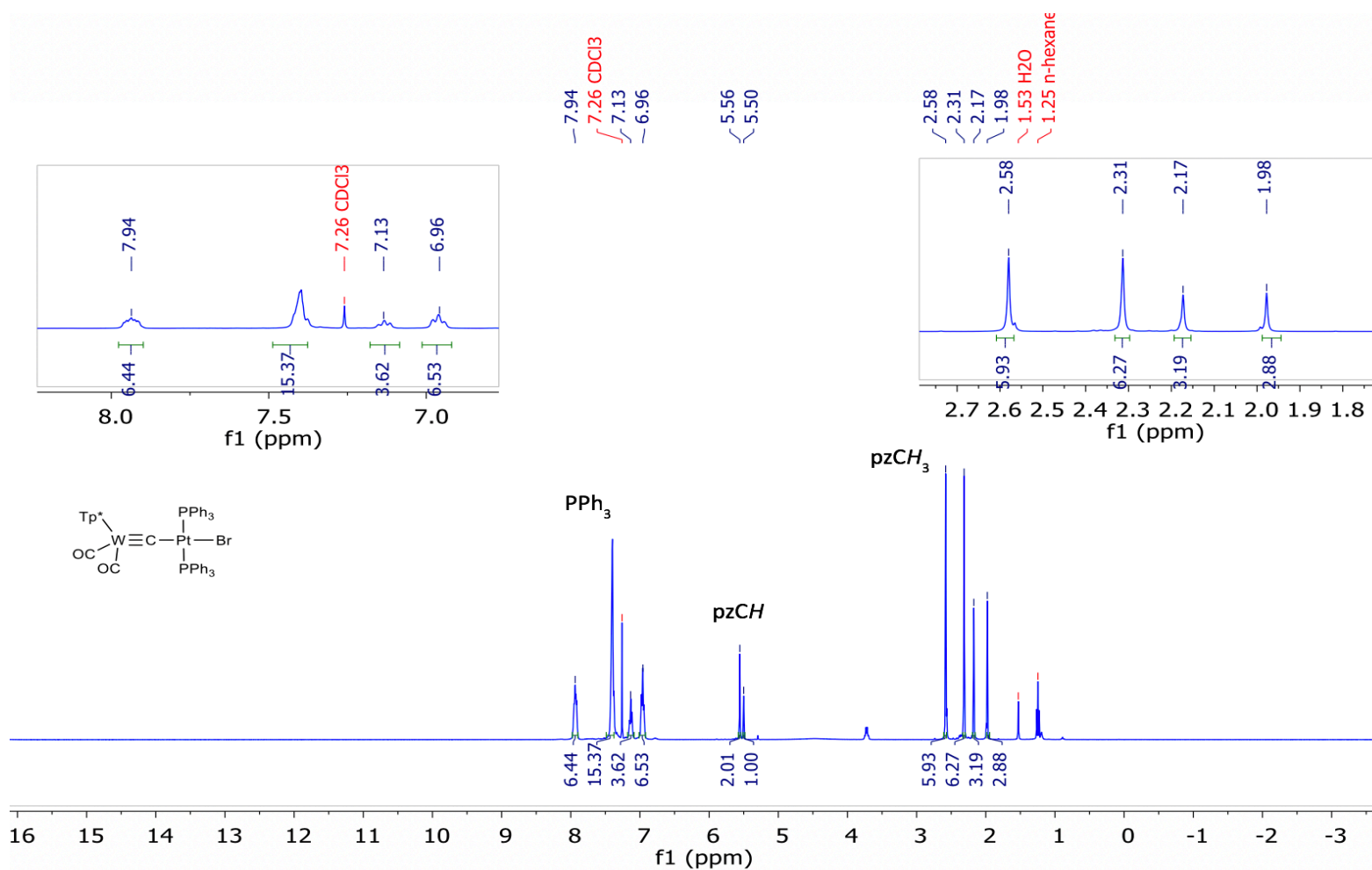


Figure S12. ^1H NMR Spectrum of $[\text{WPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2b) (400 MHz, CDCl_3 , 25 °C)

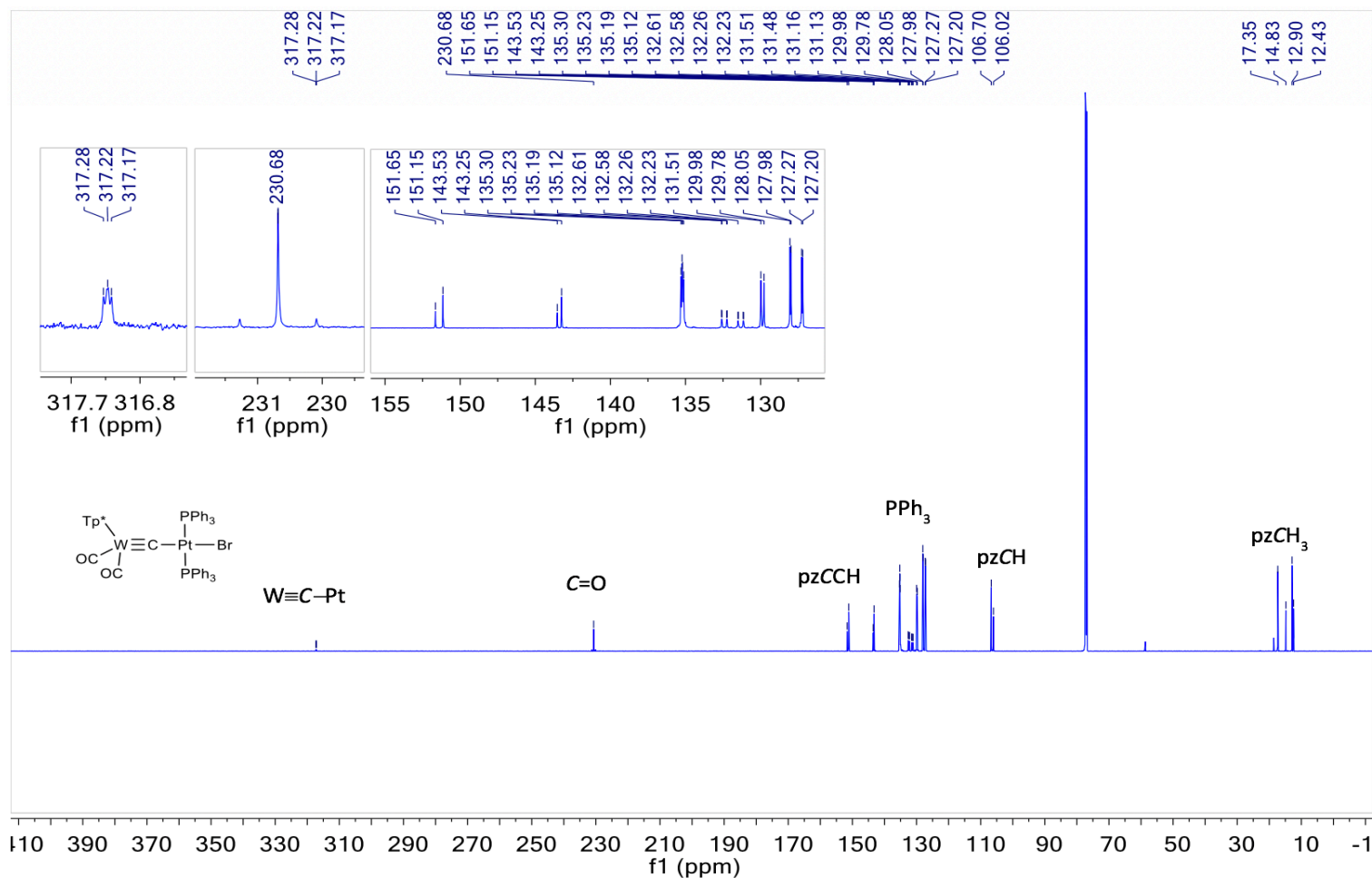


Figure S13. $^{13}C\{^1H\}$ NMR Spectrum of $[WPt(\mu-C)(CO)_2(PPh_3)_2(Tp^*)]$ (2b) (151 MHz, $CDCl_3$, 25 °C)

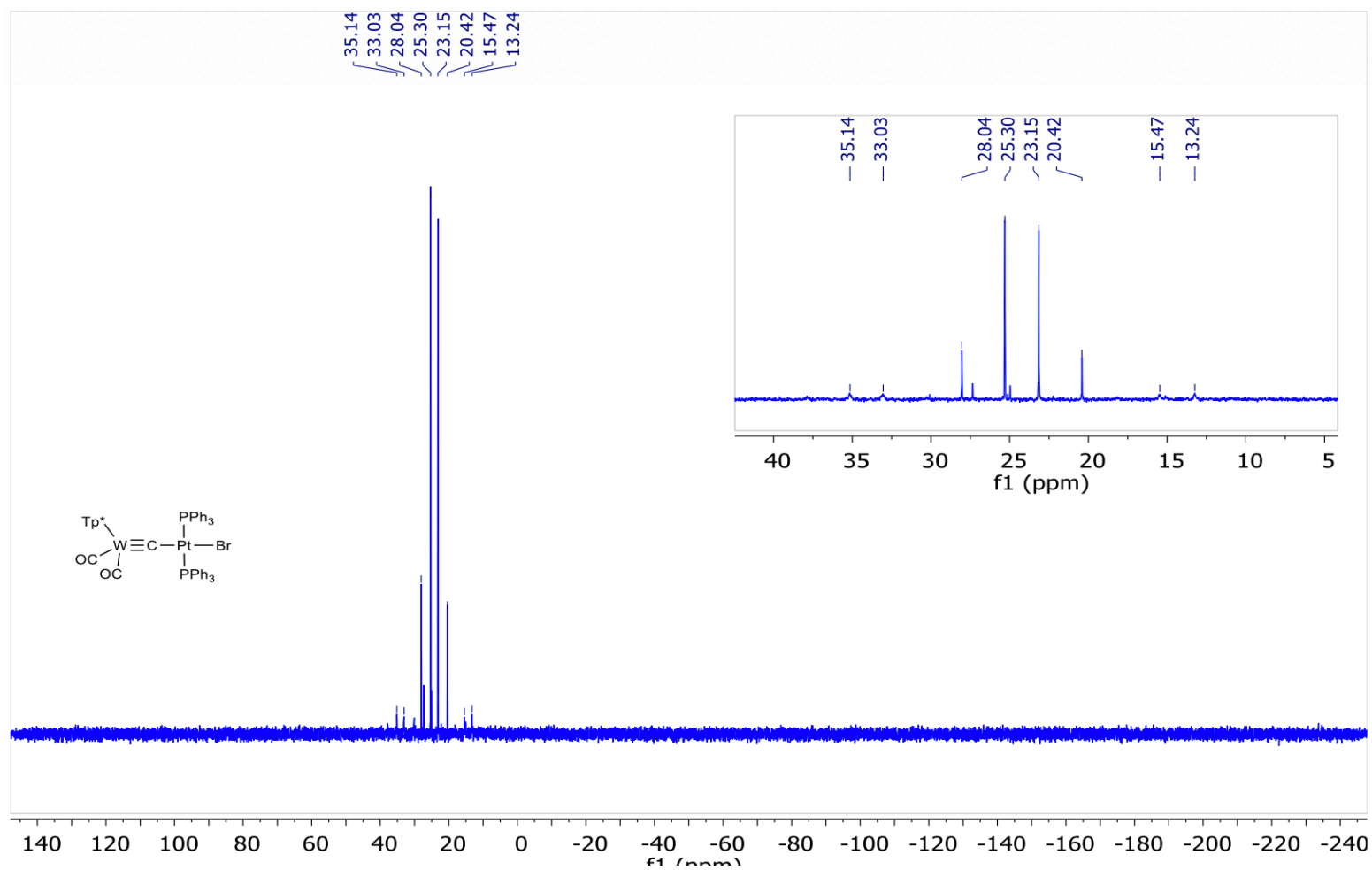


Figure S14. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2b) (162 MHz, CDCl_3 , 25 °C)

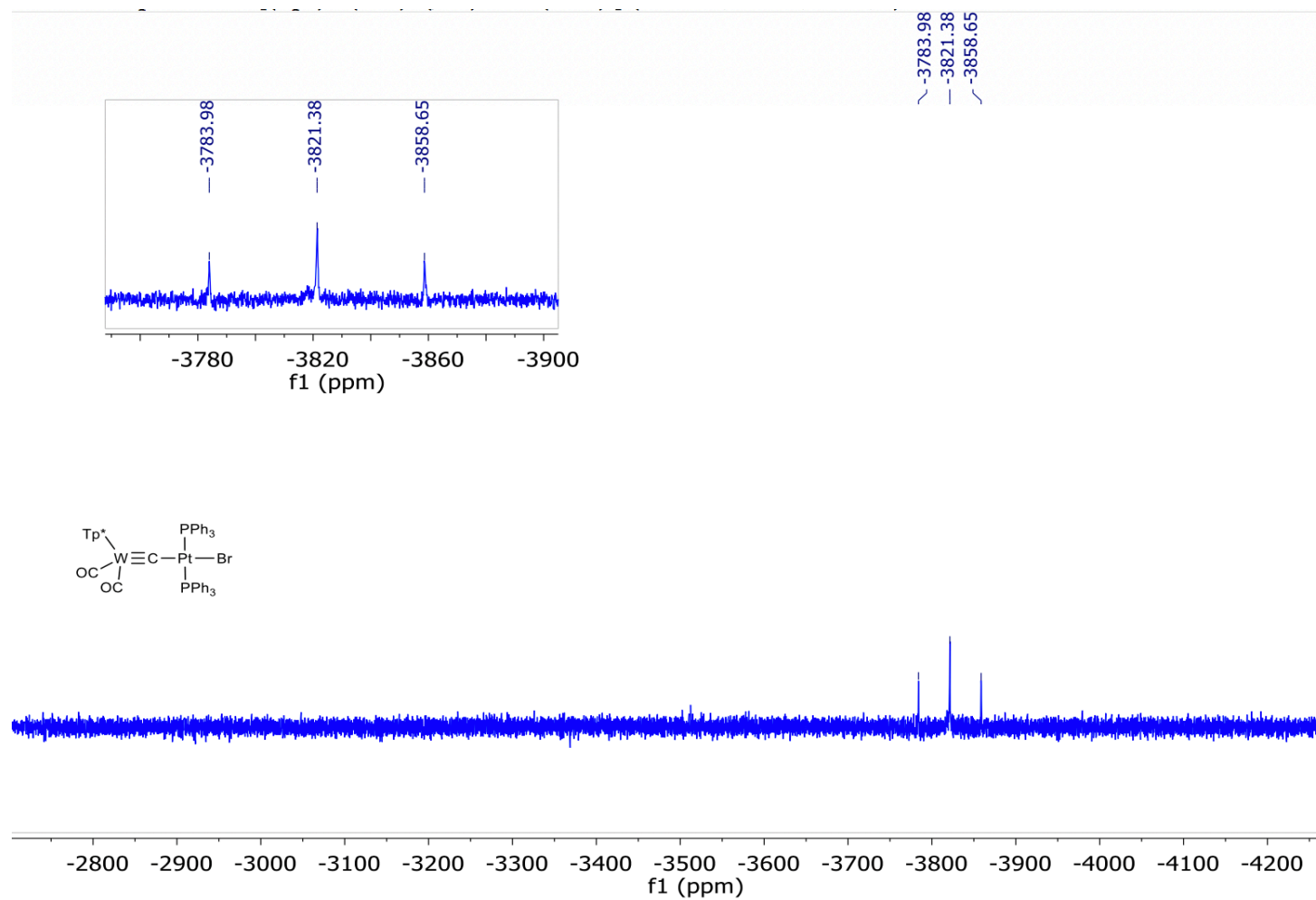


Figure S15. $^{195}\text{Pt}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPt}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2b) (86 MHz, CDCl_3 , 25 °C)

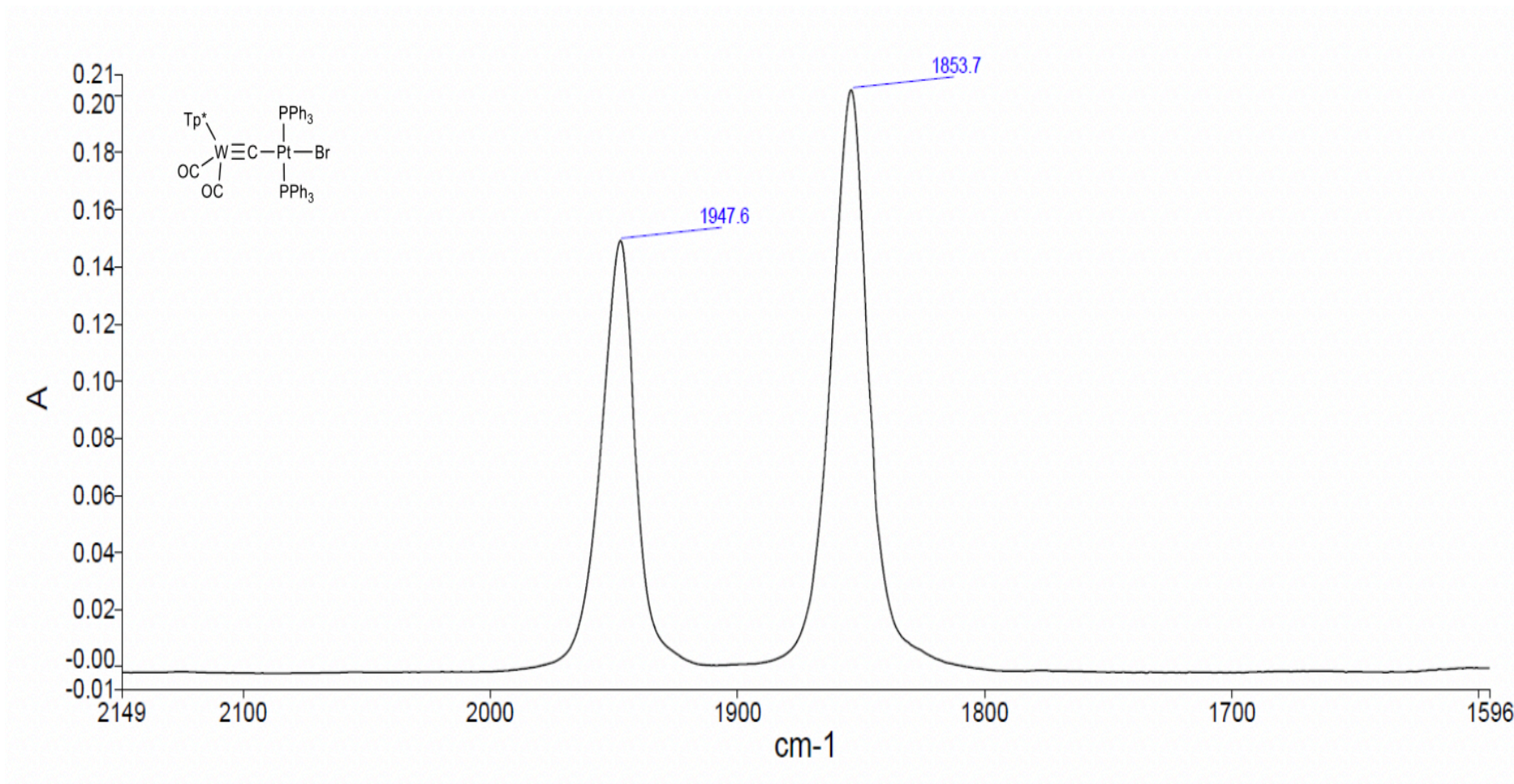
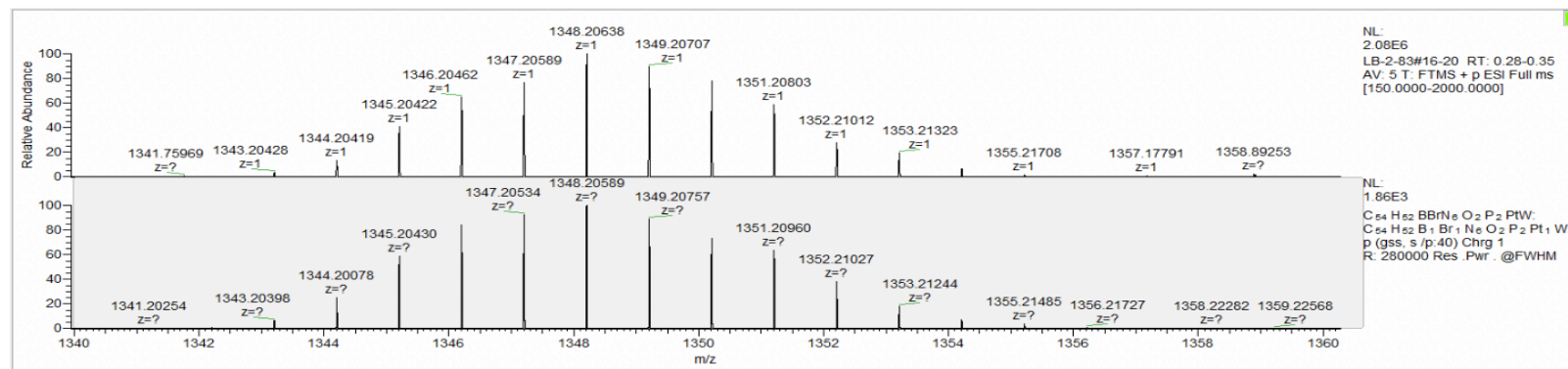


Figure S16. Infrared Spectrum of $[WPt(\mu-C)(CO)_2(PPh_3)_2(Tp^*)]$ (2b) (CH_2Cl_2 , 25 °C).

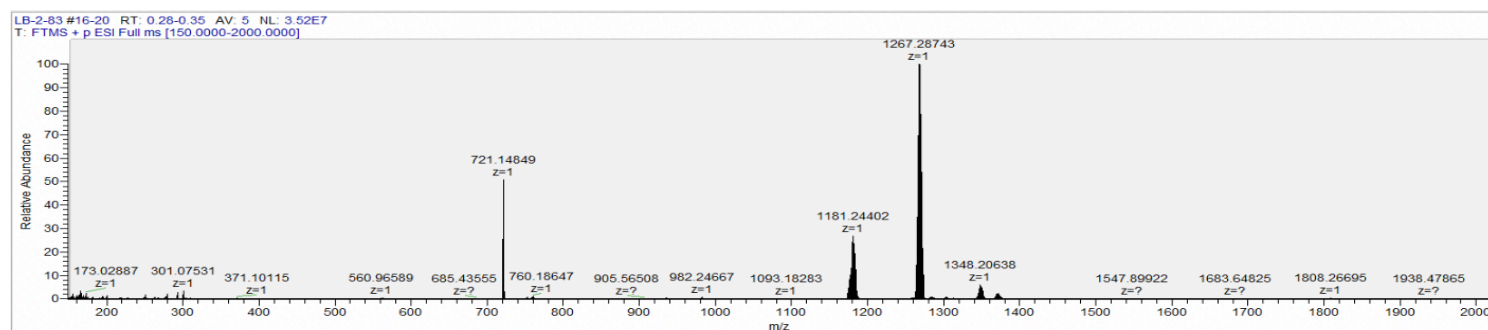
Figure S17. RSC/RSB Joint Mass Spectrometry Facility Analysis Report

Analyst: Anitha Jeyasingham **Instrument:** Orbitrap QE, +ve mode ESI at 280k resolution **Analysis Date:** 2019-08-15 **Sample code:** LB-2-83

Theoretical m/z (most abundant isotopologue): [M]⁺ ion: 1347.20534 **Observed m/z (most abundant isotopologue):** [M]⁺ ion: 1347.20589 **Mass error:** 0.290 ppm

Observed versus simulated spectrum for detected target formulas [M]⁺ ion

Full Spectrum



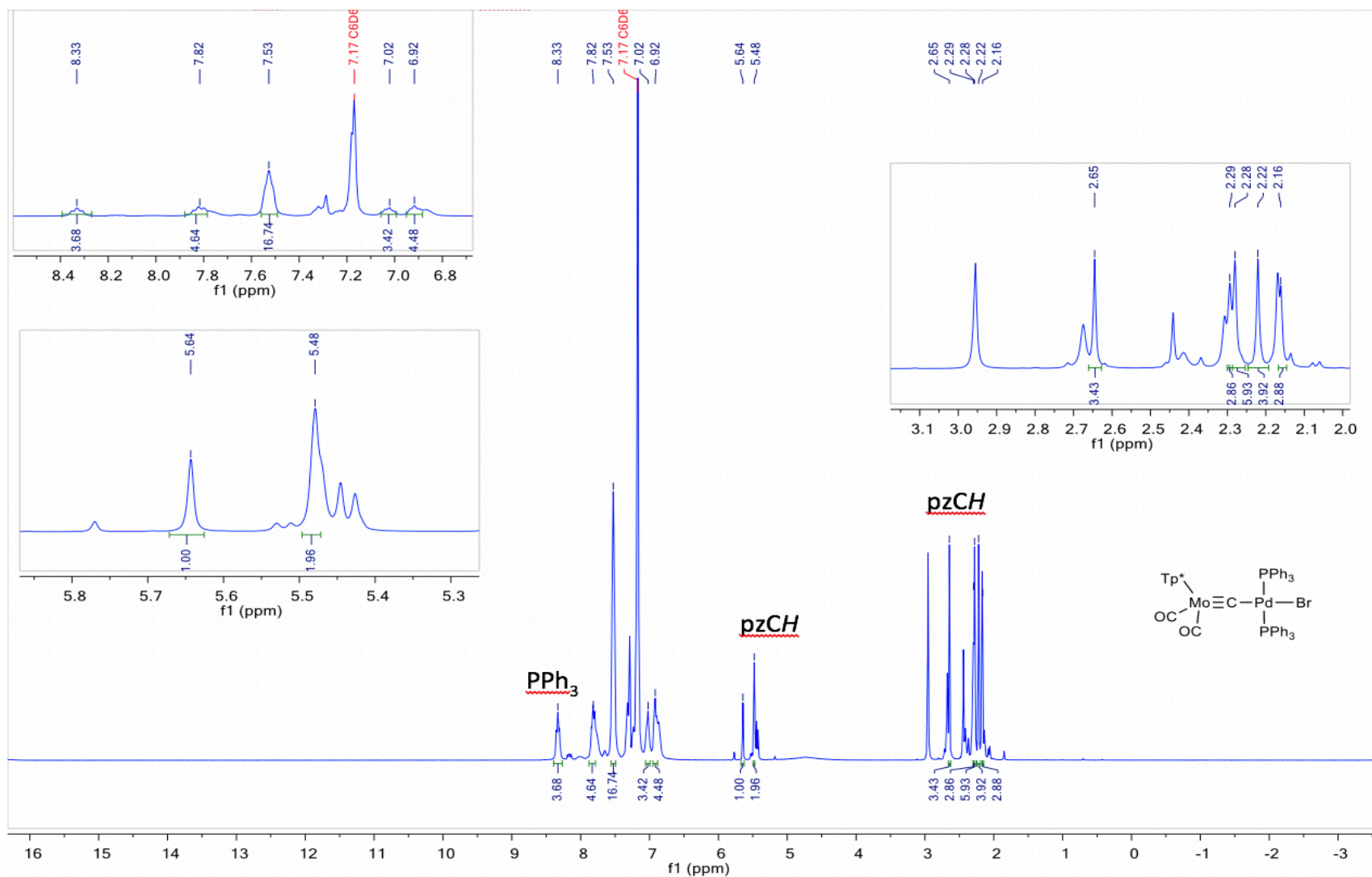


Figure S18. ^1H NMR Spectrum of $[\text{MoPd}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2c)– Observed *in situ* yet unable to be isolated (400 MHz, d_6 -benzene, 25°C , δ):

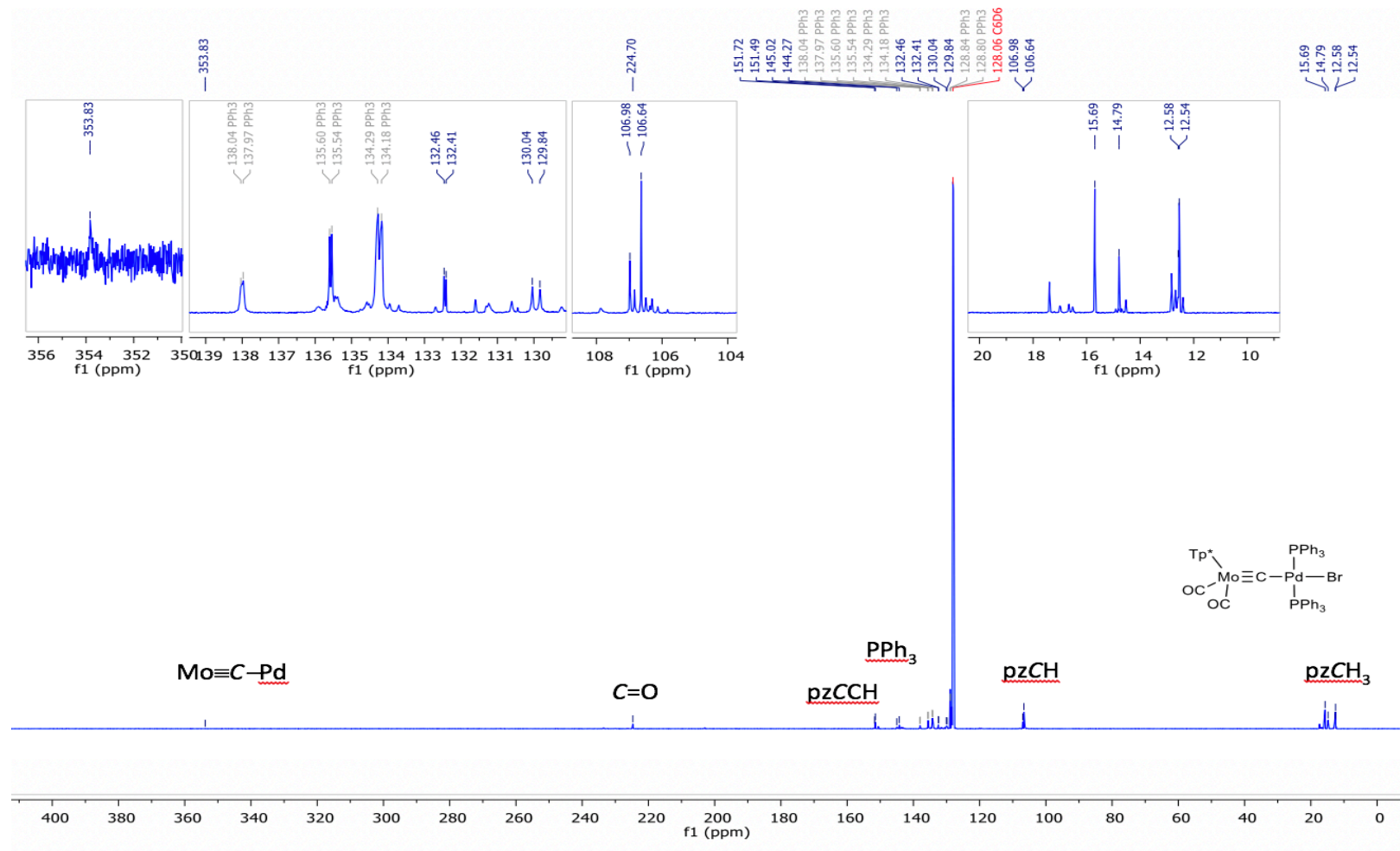


Figure S19. ^{13}C NMR Spectrum of $[\text{MoPd}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2c) – Observed *in situ* yet unable to be isolated (176 MHz, d_6 -benzene, 25 °C, δ):

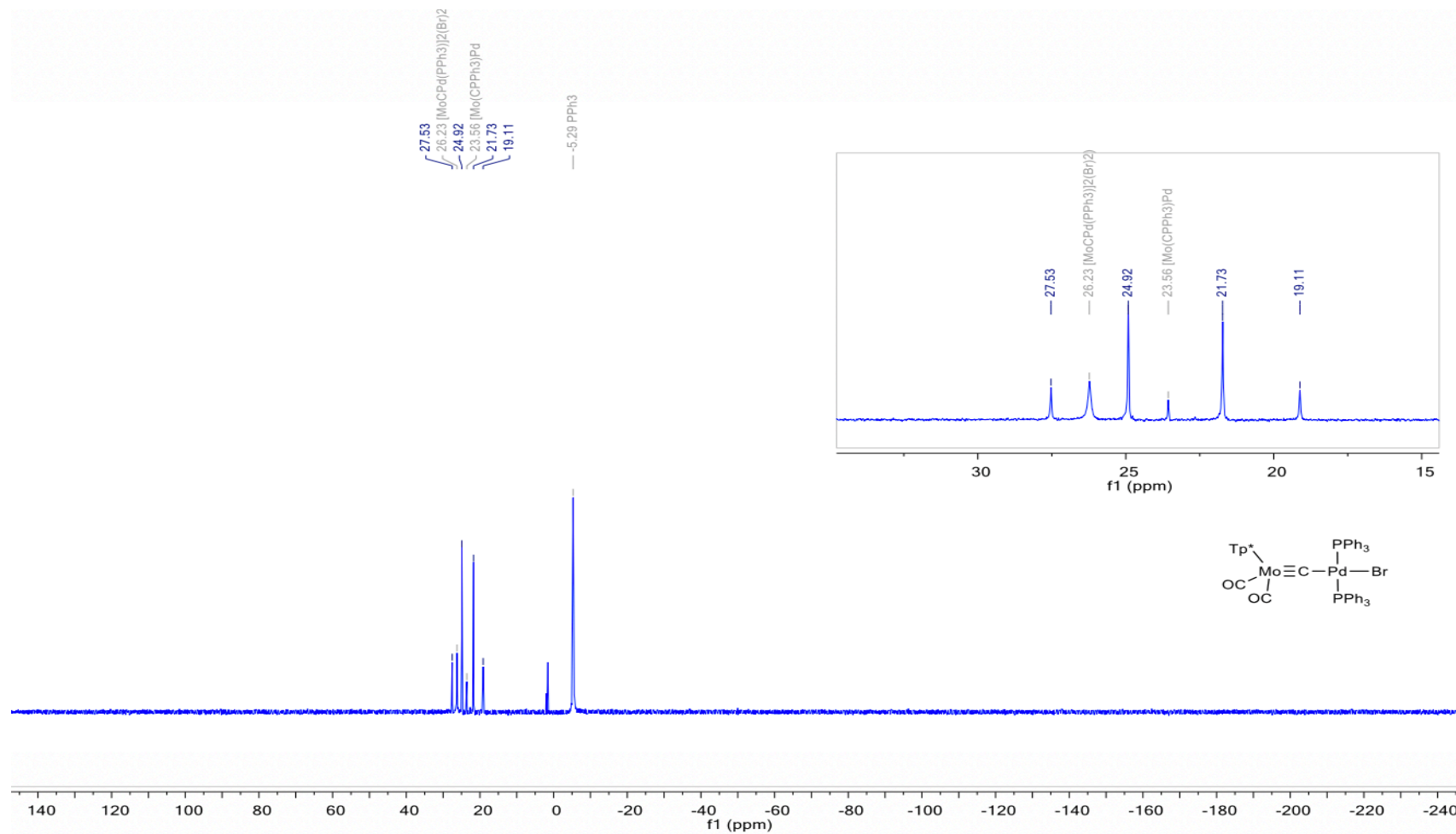


Figure S20. ^{31}P NMR Spectrum of $[\text{MoPd}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2c) – Observed *in situ* yet unable to be isolated (162 MHz, d_6 -benzene, 25 °C, δ):

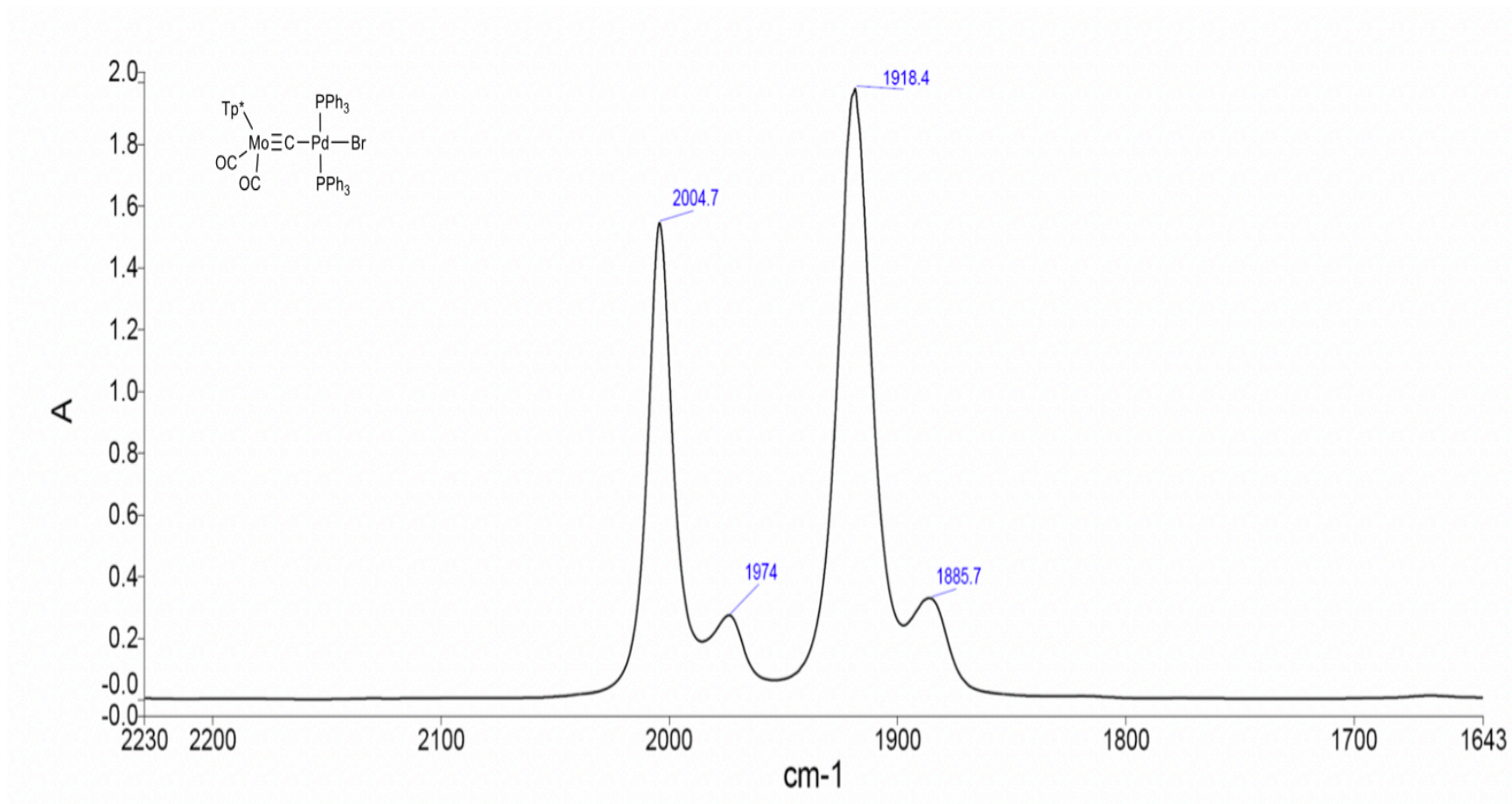


Figure S21. Infrared Spectrum of $[\text{MoPd}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2c) – Observed *in situ* yet unable to be isolated (CaF_2 , CH_2Cl_2 , 25 °C, ν):

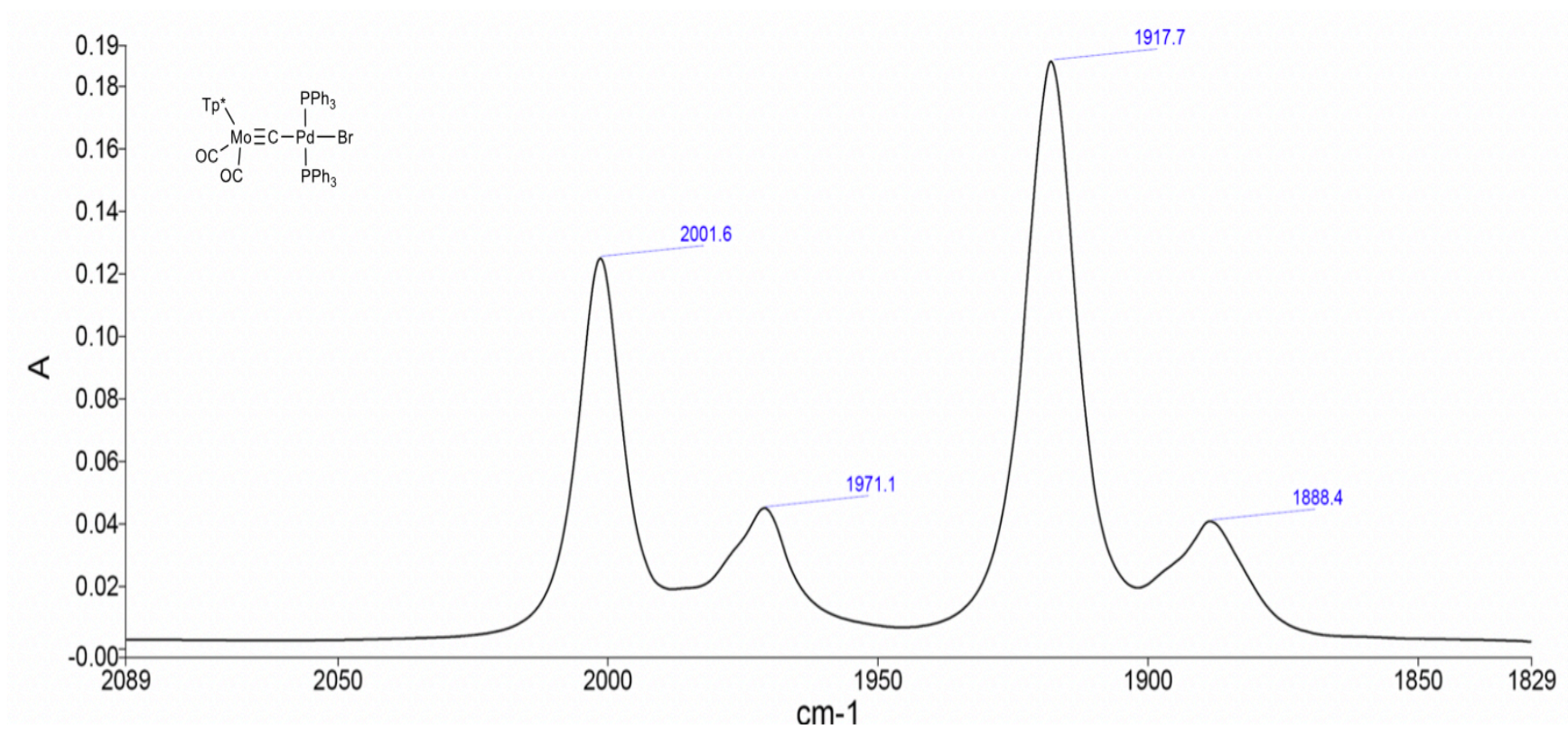


Figure S22. Infrared Spectrum of $[\text{MoPd}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2c) – Observed *in situ* yet unable to be isolated (CaF_2 , THF, 25 °C, v):

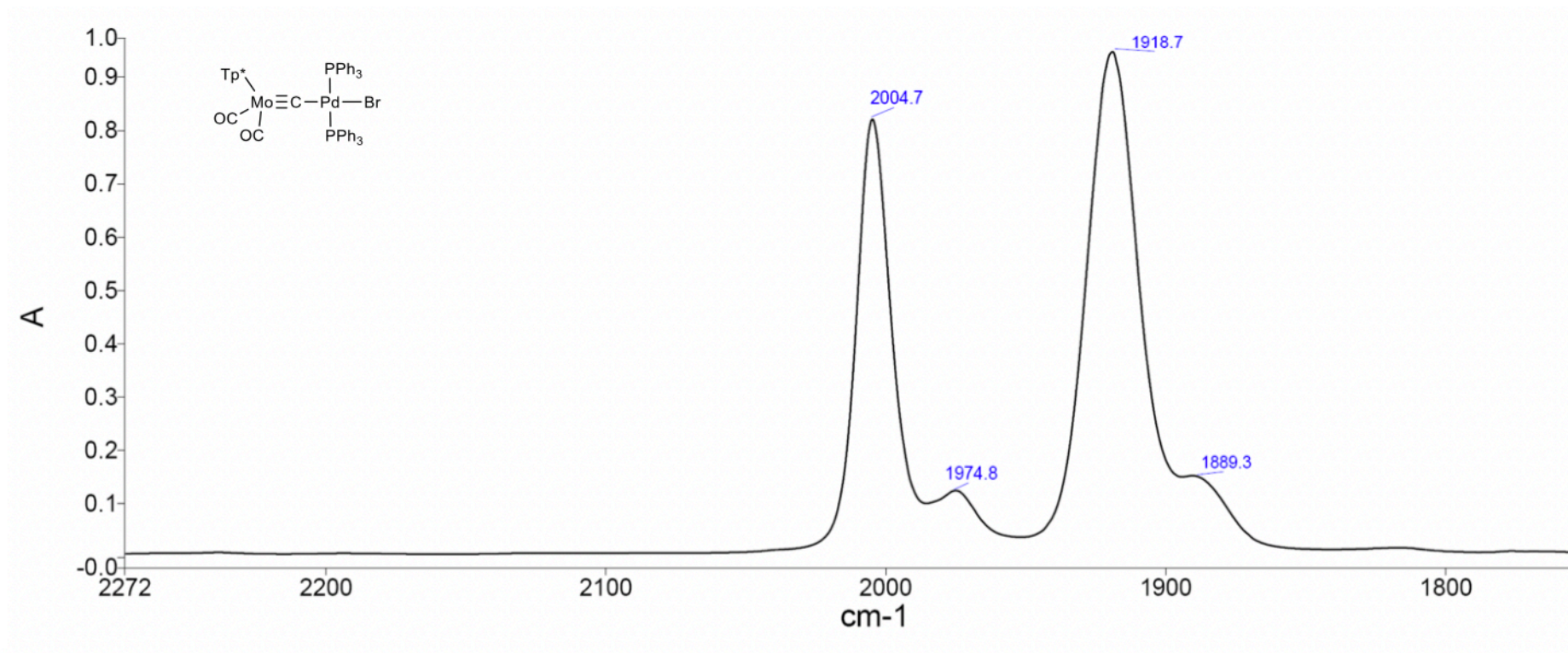


Figure S23. Infrared Spectrum of $[\text{MoPd}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2c) – Observed *in situ* yet unable to be isolated (CaF_2 , CHCl_3 , 25 °C, v):

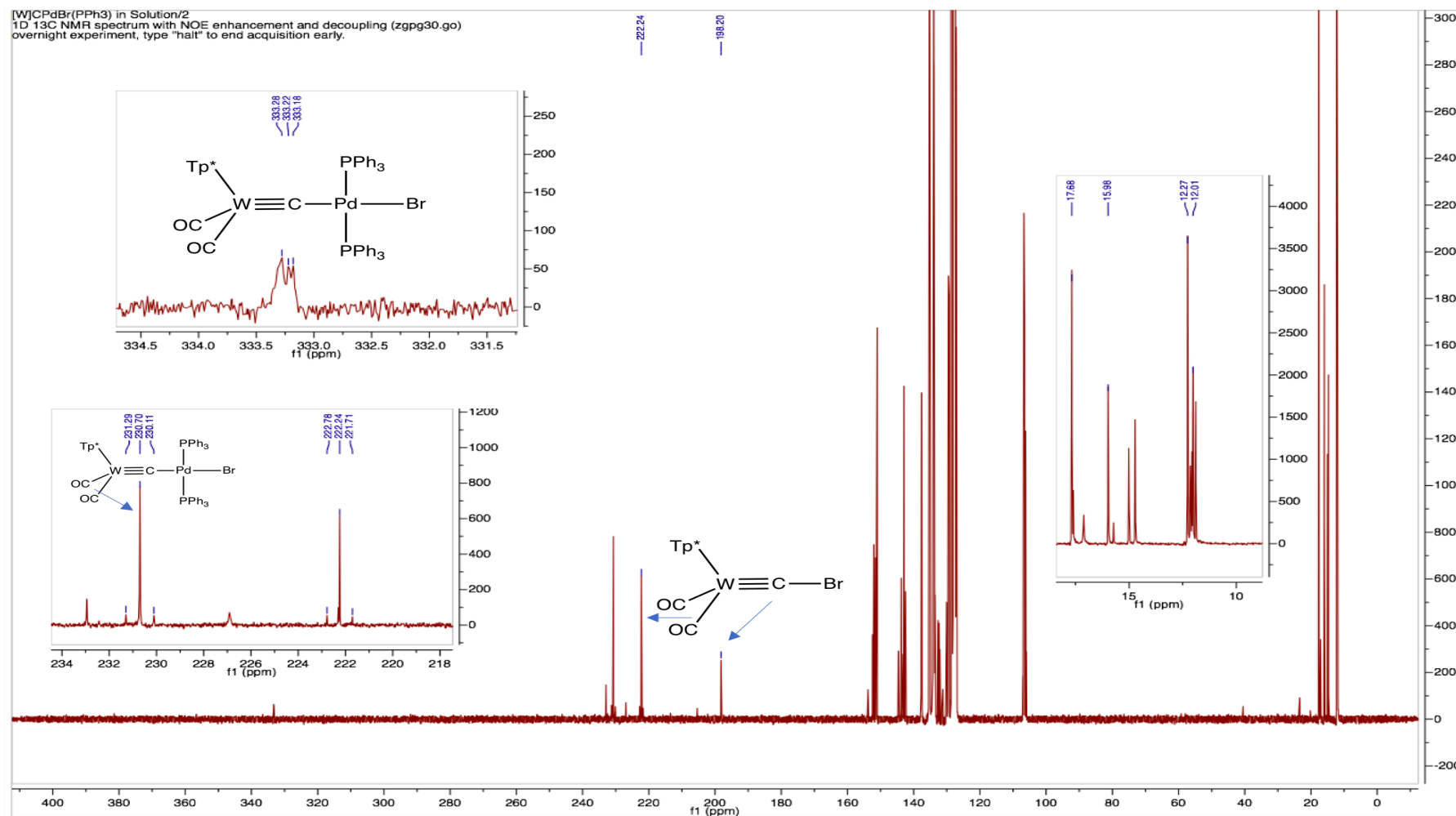


Figure S24. Observation of $[\text{WPd}(\mu\text{-C})\text{Br}(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2d) – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, C_6D_6 , 25 °C)

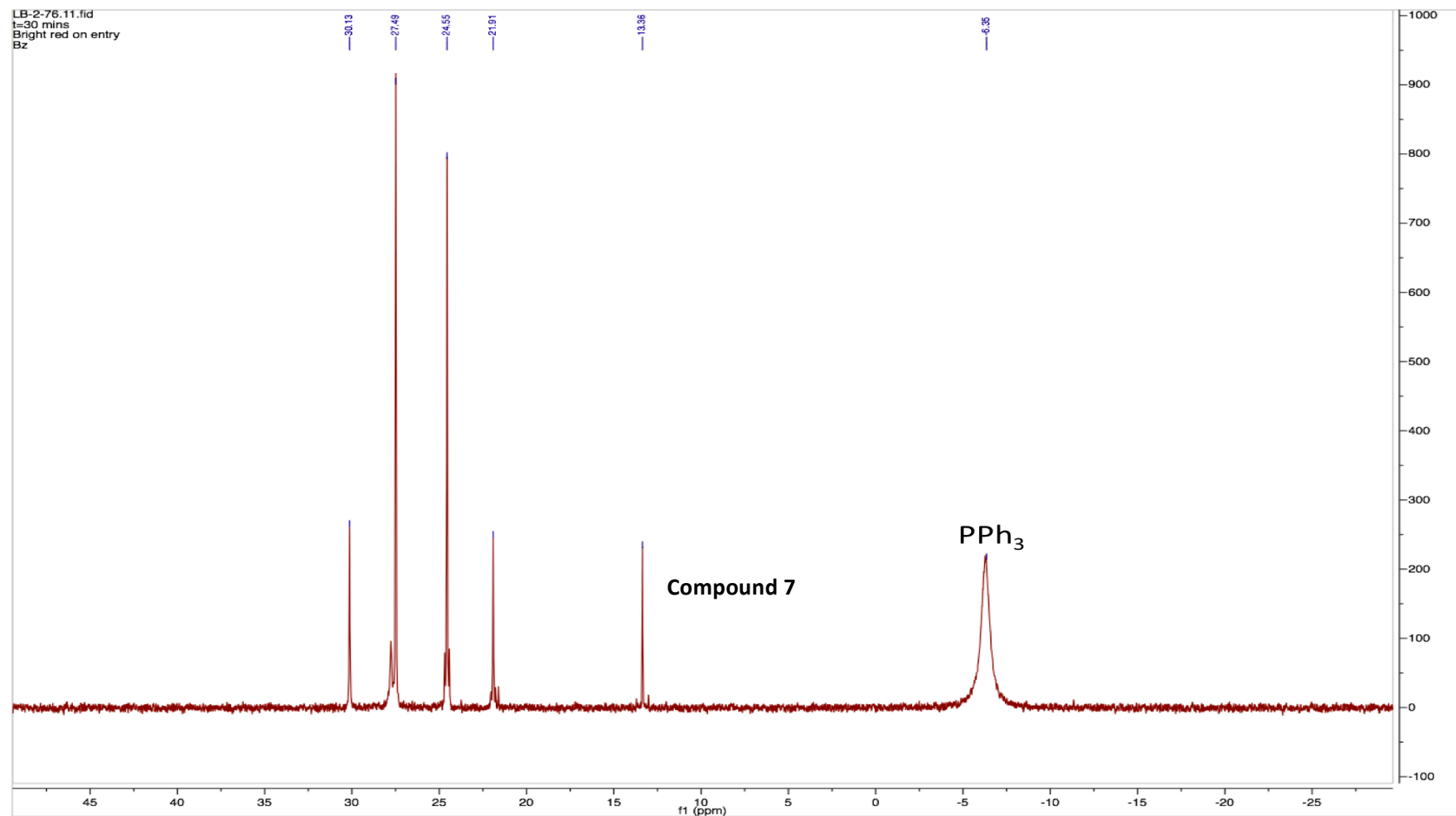


Figure S25. Observation of $[\text{WPd}(\mu\text{-C})\text{Br}(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2d) – $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz, C_6D_6 , 25 °C)

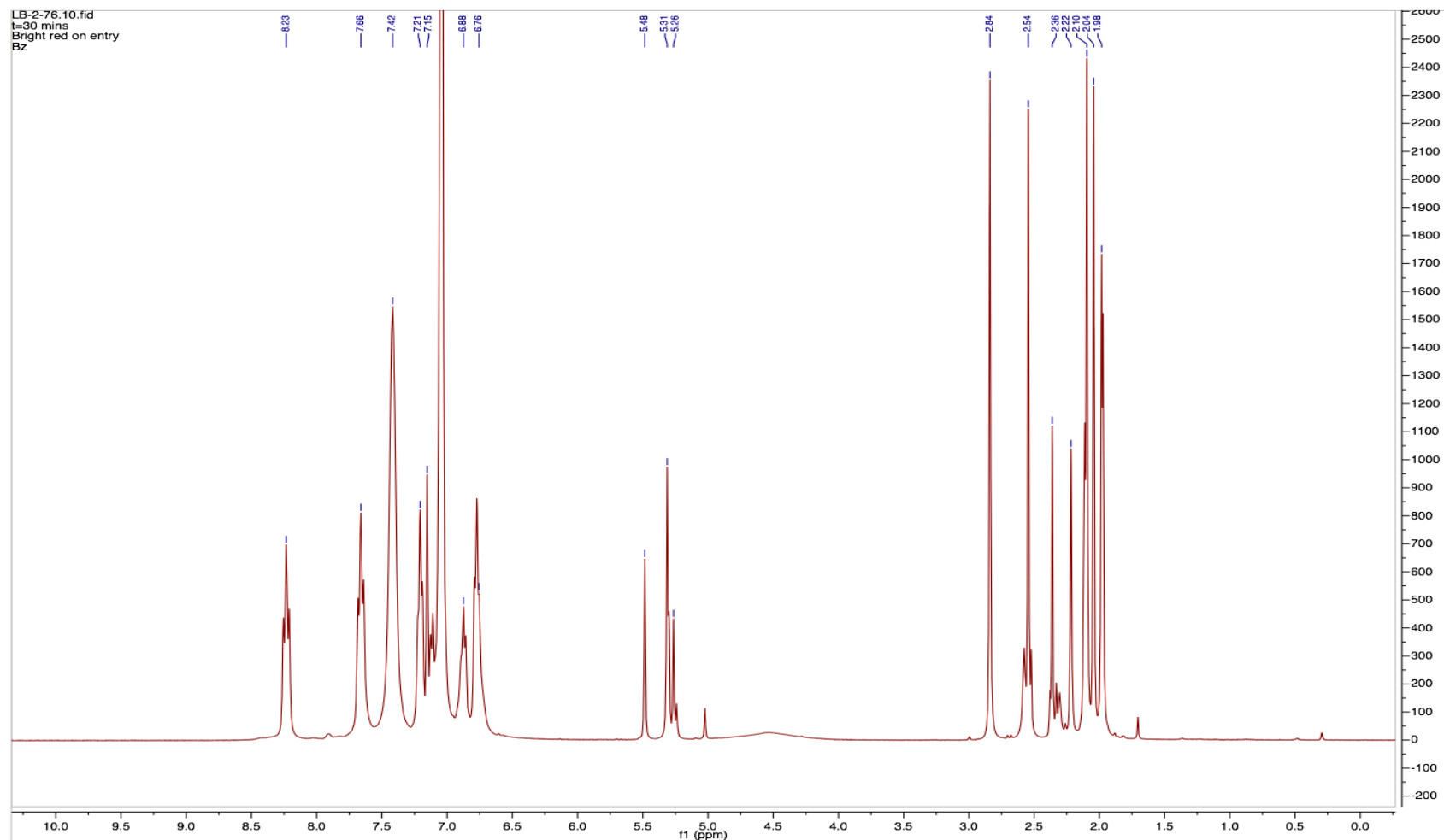


Figure S26. Observation of $[\text{WPd}(\mu\text{-C})\text{Br}(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2d) ^1H NMR spectrum (400 MHz, C_6D_6 , 25 °C)

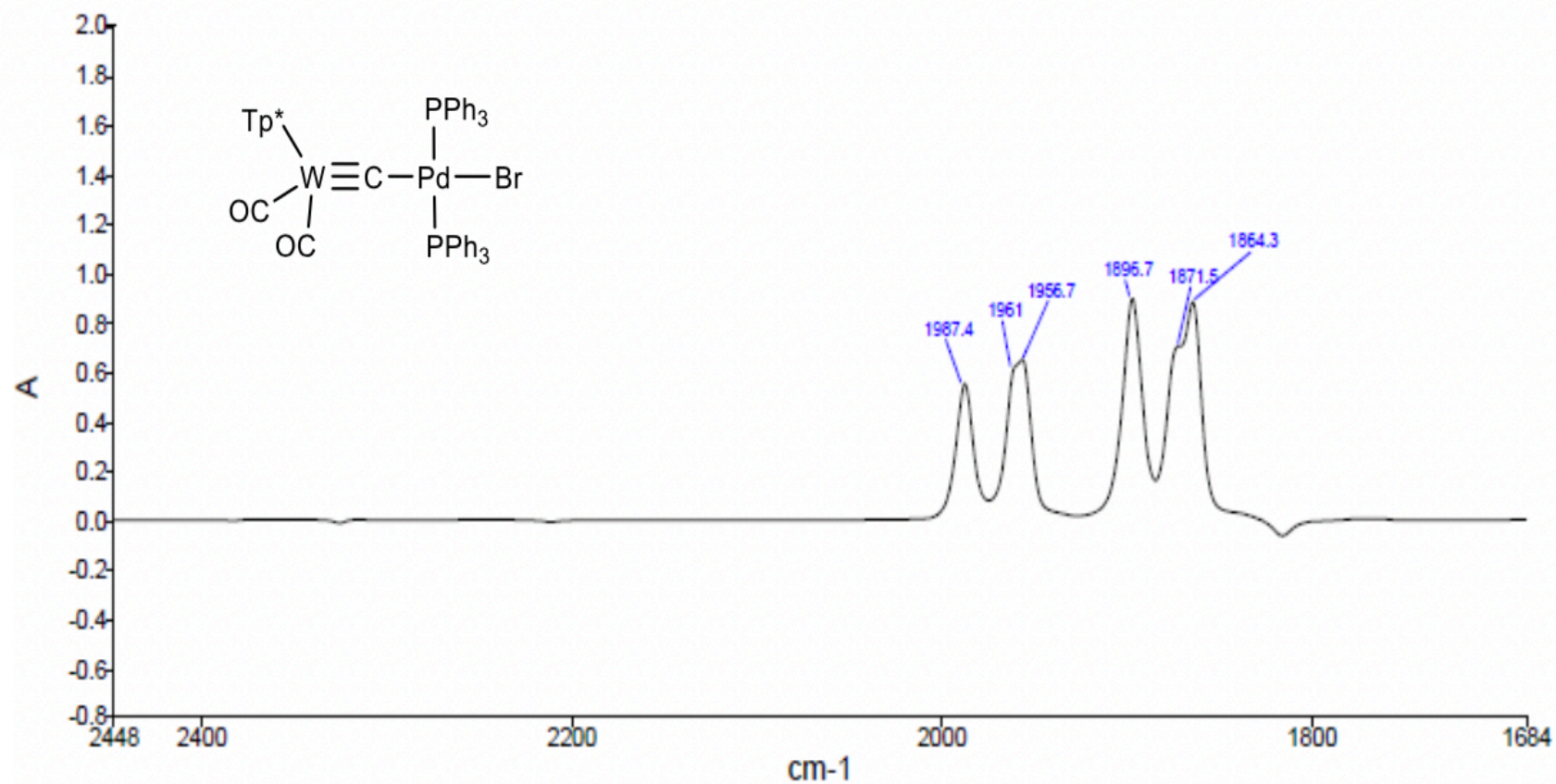


Figure S27. Infrared Spectrum of $[WPd(\mu-C)(CO)_2(PPh_3)_2(Tp^*)]$ (2d) – Observed *in situ* yet unable to be isolated (CaF_2 , CH_2Cl_2 , $25^\circ C$) Peaks at 1987 and 1895 cm^{-1} correspond to unreacted 1b.

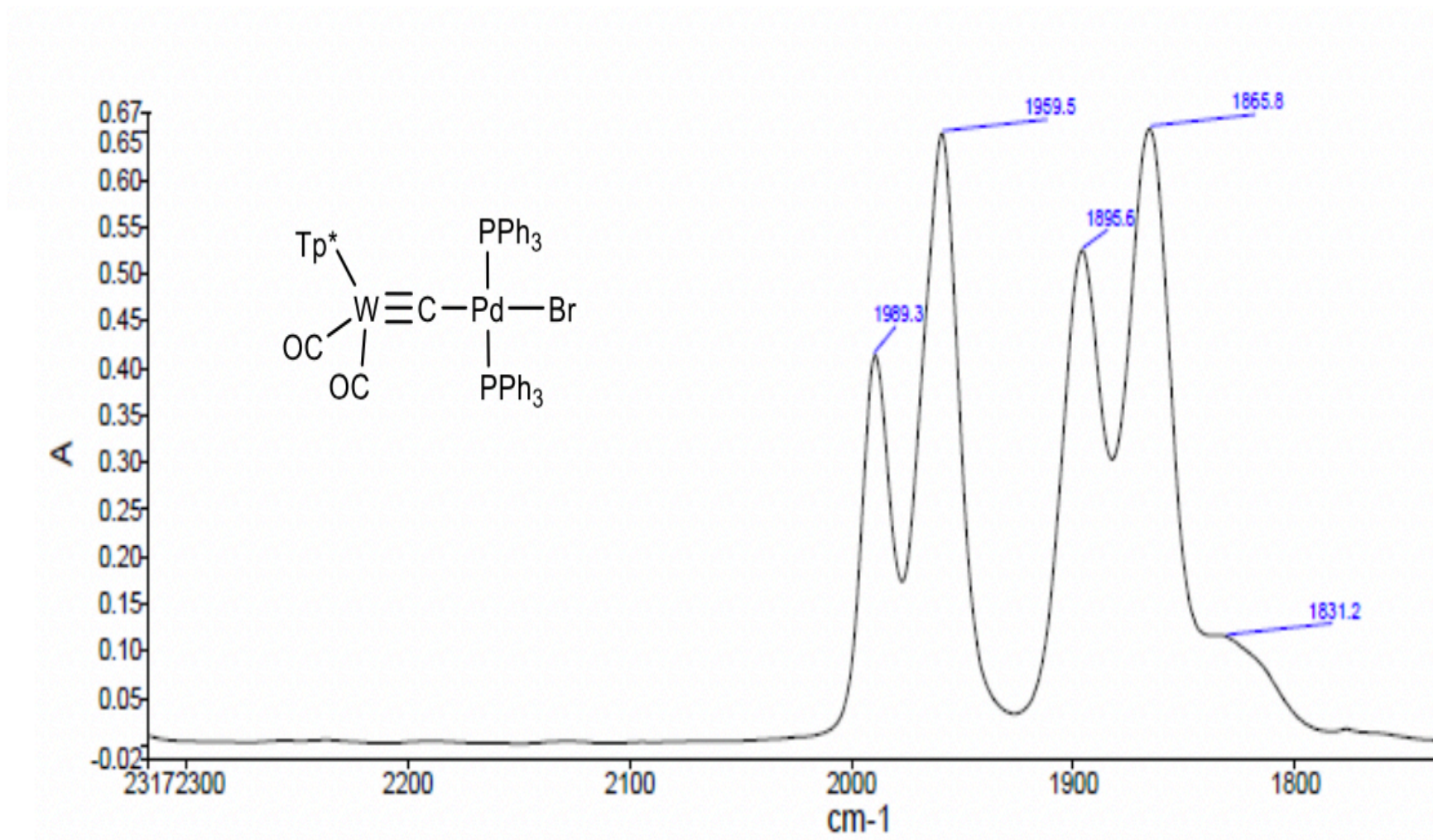


Figure S28. Infrared Spectrum of $[\text{WPd}(\mu\text{-C})(\text{CO})_2(\text{PPh}_3)_2(\text{Tp}^*)]$ (2d) – Observed *in situ* yet unable to be isolated (CaF_2 , CHCl_3 , 25°C) Peaks at 1989 and 1896 cm^{-1} correspond to unreacted 1b.

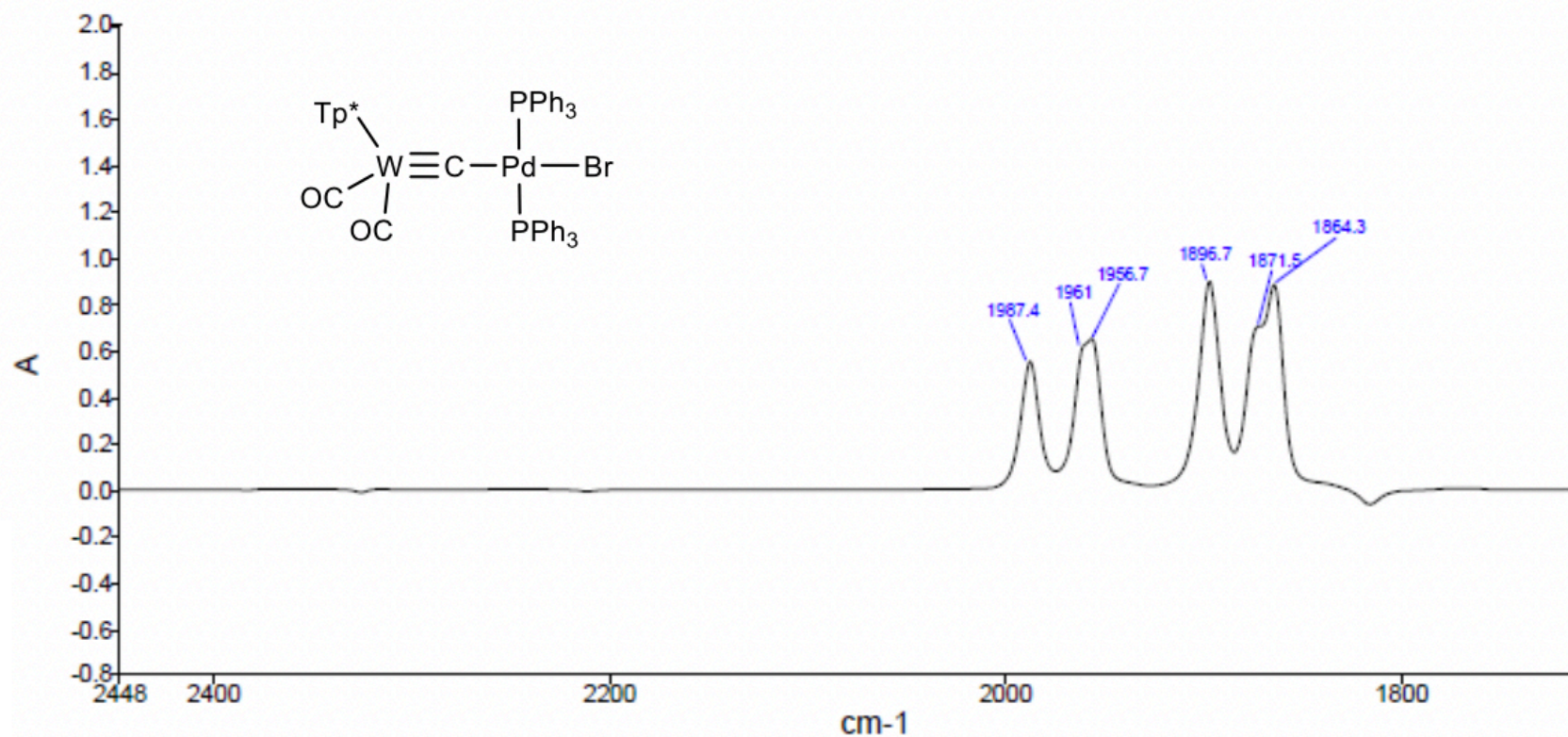


Figure S29. Infrared Spectrum of $[WPd(\mu-C)(CO)_2(PPh_3)_2(Tp^*)]$ (2d) – Observed *in situ* yet unable to be isolated (CaF_2 , benzene, 25 °C) Peaks at 1987 and 1897 cm^{-1} correspond to unreacted 1b.

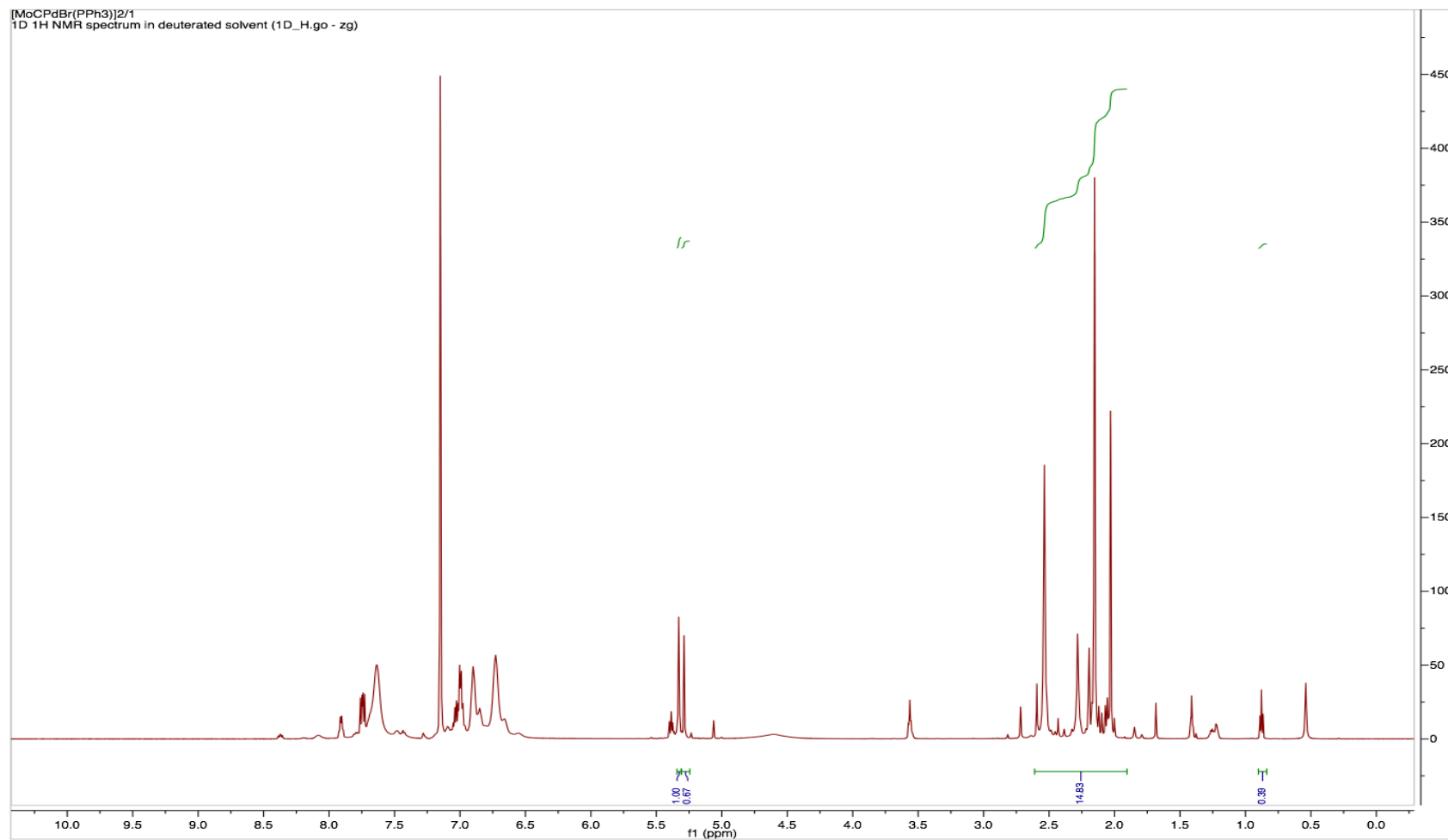


Figure S30. ¹H NMR Spectrum of [Mo₂Pd₂(μ-C)₂Br₂(CO)₄(PPh₃)₂(Tp*)₂] (5a) (400 MHz, CDCl₃, 25 °C)

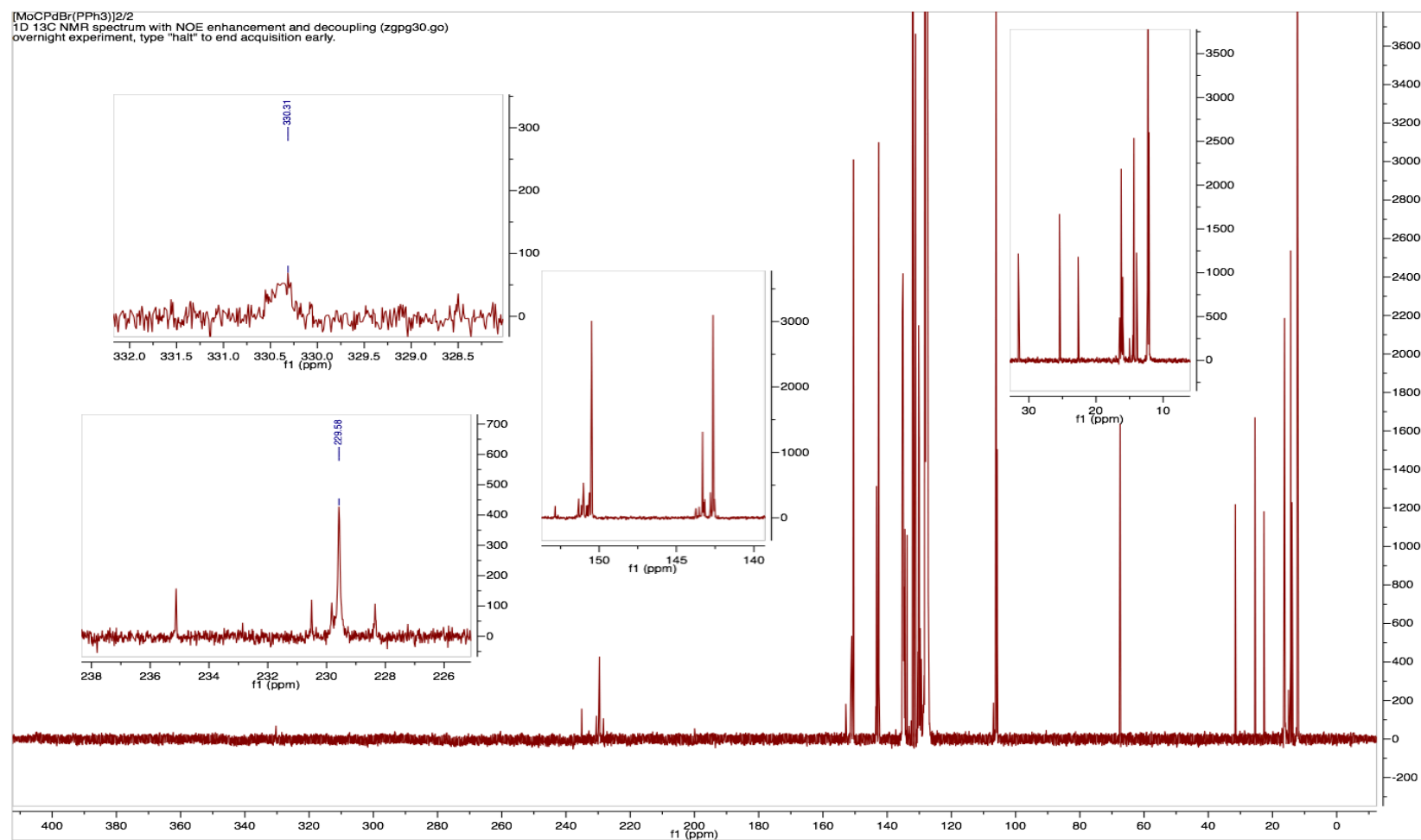


Figure S31. ¹³C{¹H} NMR Spectrum of [Mo₂Pd₂(μ-C)₂Br₂(CO)₄(PPh₃)₂(Tp*)₂] (5a) (151 MHz, C₆D₆, 25 °C)

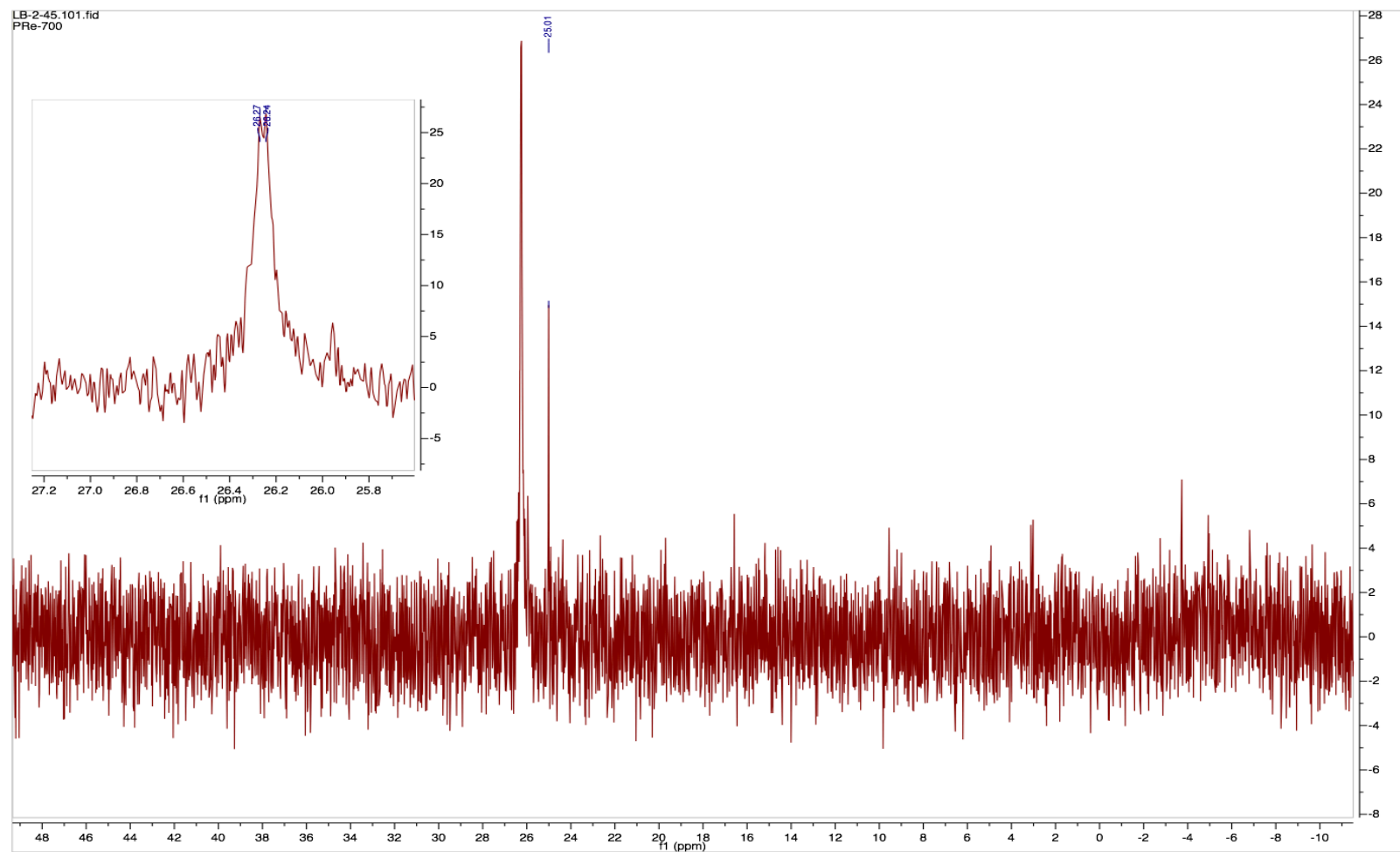


Figure S32. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{Mo}_2\text{Pd}_2(\mu\text{-C})_2\text{Br}_2(\text{CO})_4(\text{PPh}_3)_2(\text{Tp}^*)_2]$ (5a) (162 MHz, CDCl_3 , 25 °C) $\delta_{\text{P}} = 25.0$ (OPPh₃)

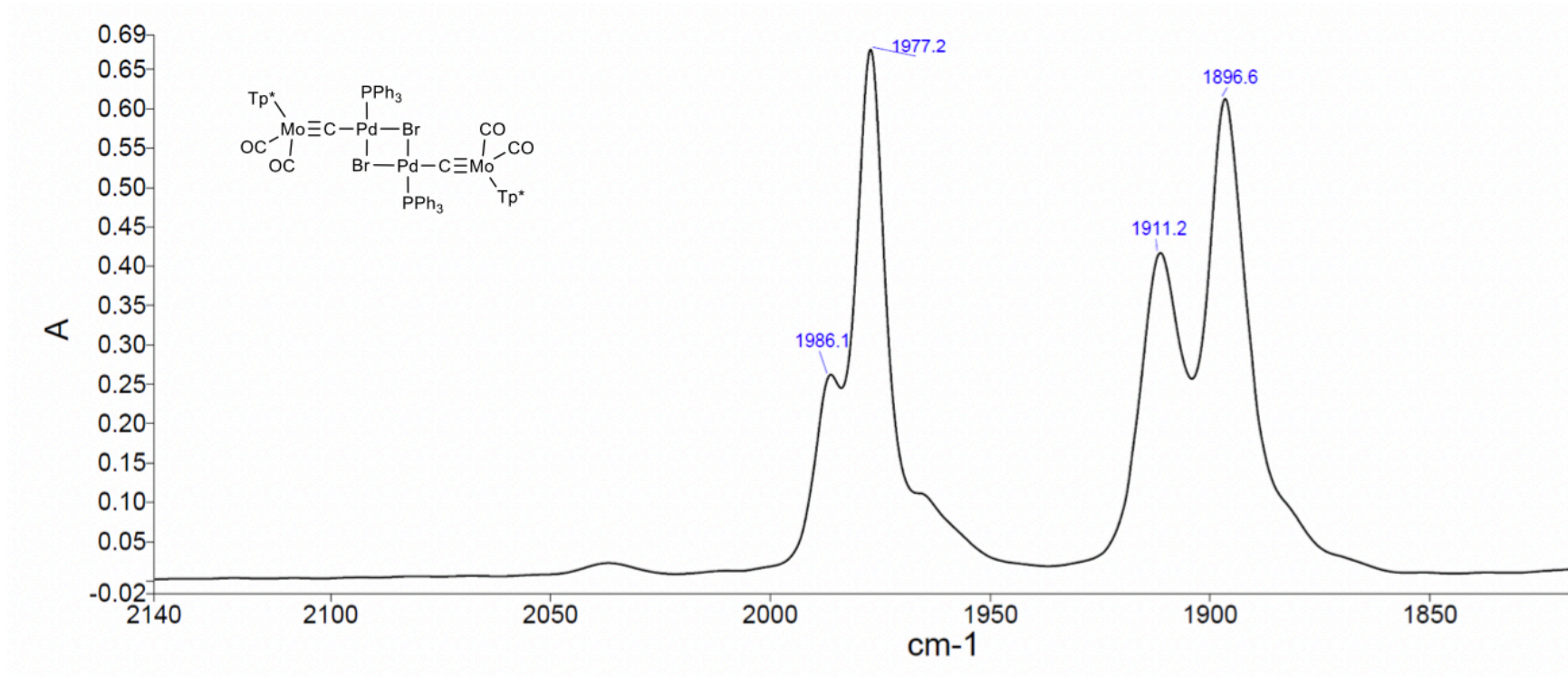


Figure S33. Infrared Spectrum of $[\text{Mo}_2\text{Pd}_2(\mu\text{-C})_2\text{Br}_2(\text{CO})_4(\text{PPh}_3)_2(\text{Tp}^*)_2]$ (5a) (THF, 25 °C)

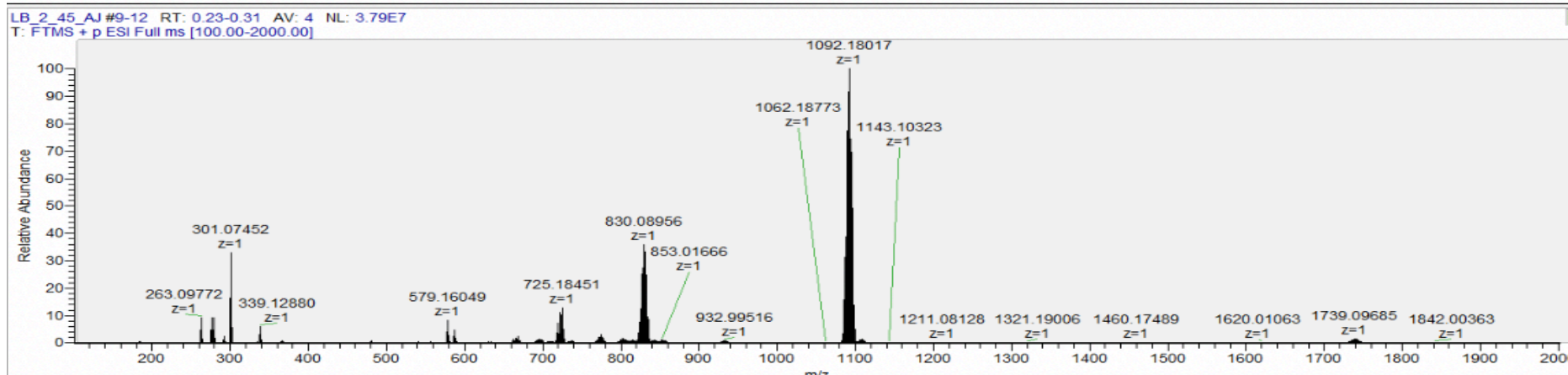
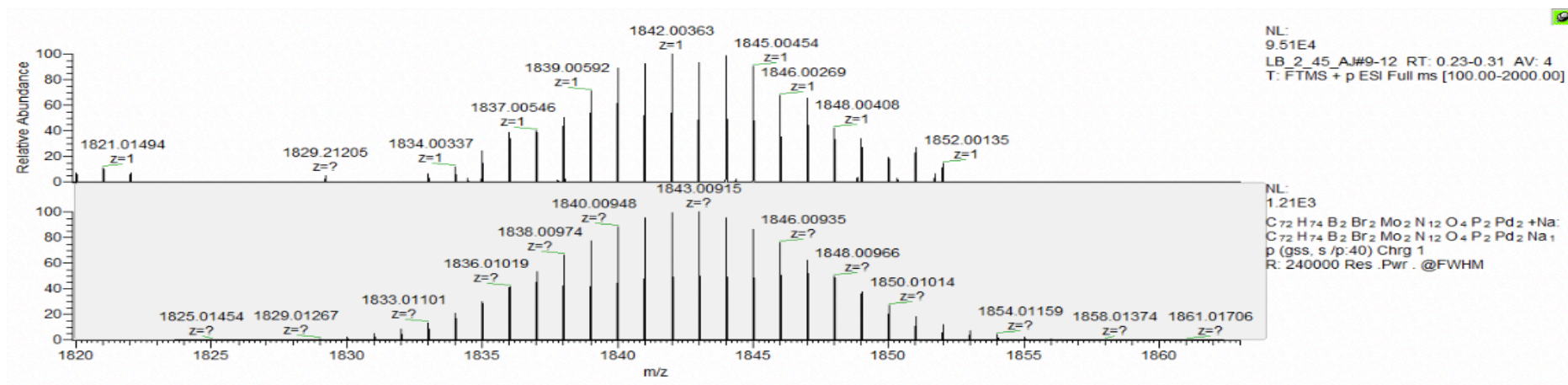


Figure S34. Mass Spectrum of $[(\text{Tp}^*)\text{Mo}(\text{CO})_2](\mu\text{-C})\text{-Pd}(\text{PPh}_3)_2(\mu\text{-Br})_2$ (5a) (ESI): $[\text{M}+\text{Na}]^+$

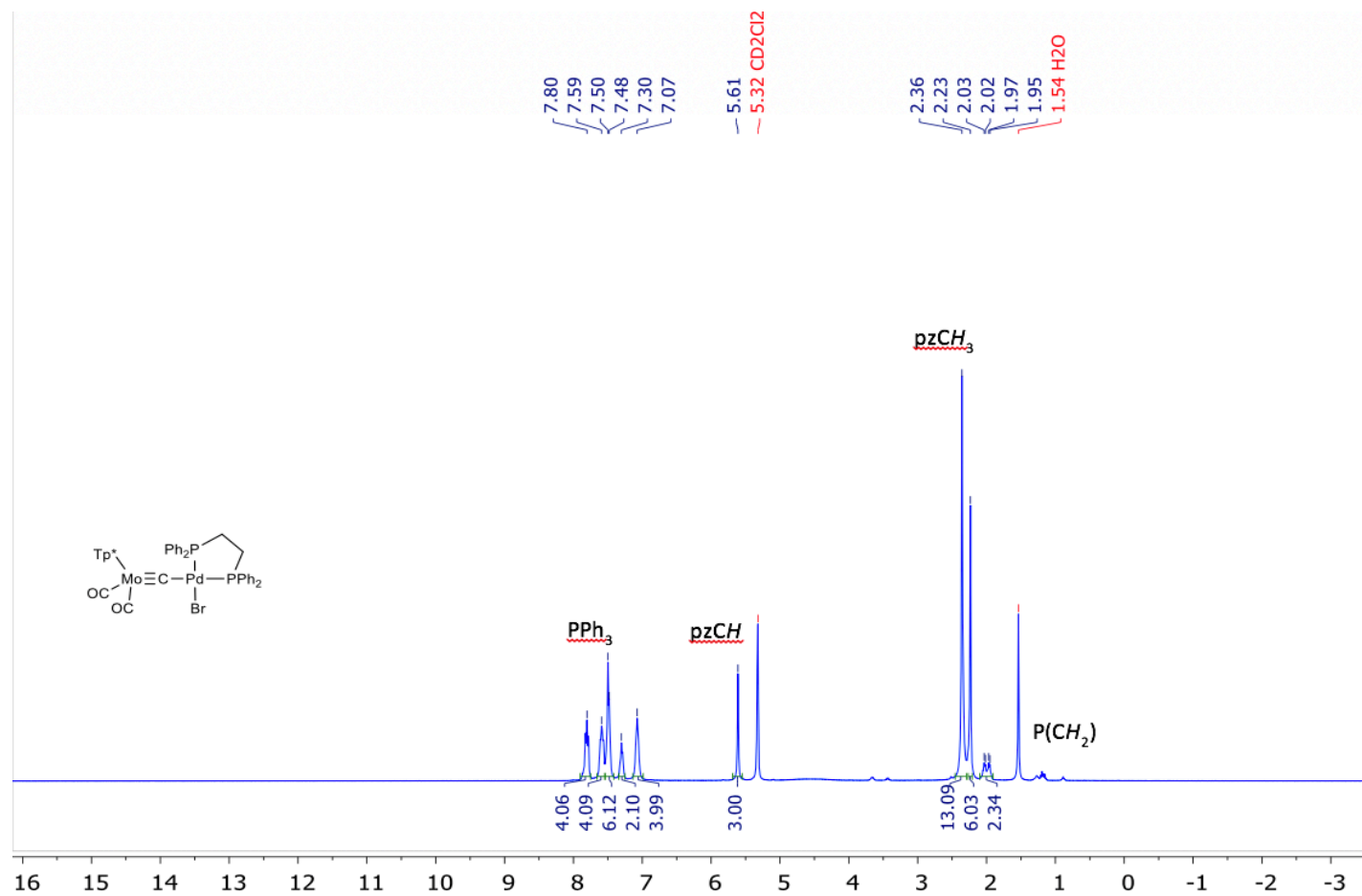


Figure S35. ^1H NMR Spectrum of $[\text{MoPd}(\mu\text{-C})\text{Br}(\text{CO})_2(\text{dppe})(\text{Tp}^*)]$ (6) (400 MHz, CD_2Cl_2 , 25 °C)

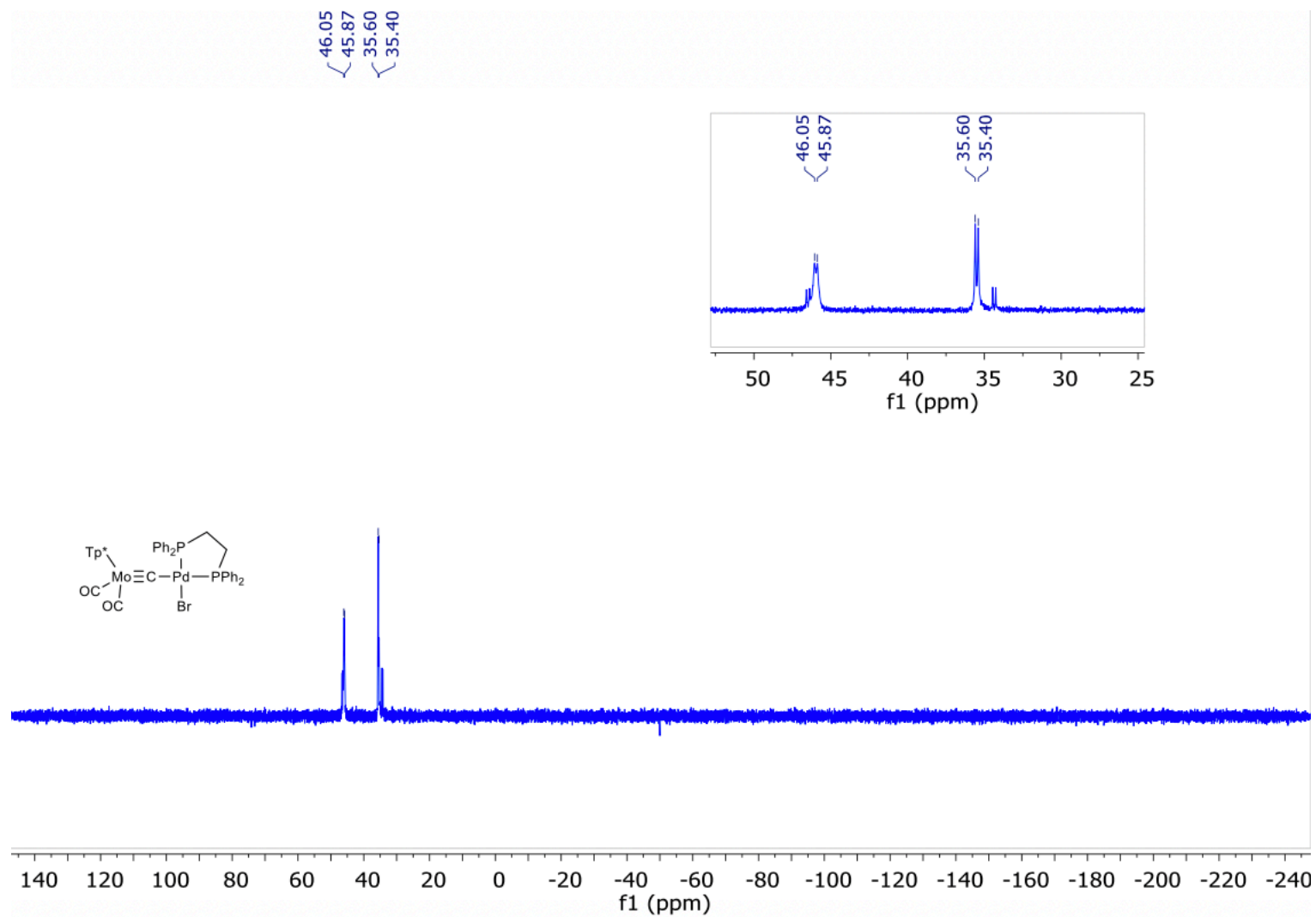


Figure S36. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPd}(\mu\text{-C})\text{Br}(\text{CO})_2(\text{dppe})(\text{Tp}^*)]$ (6) (162 MHz, CD_2Cl_2 , 25 °C)

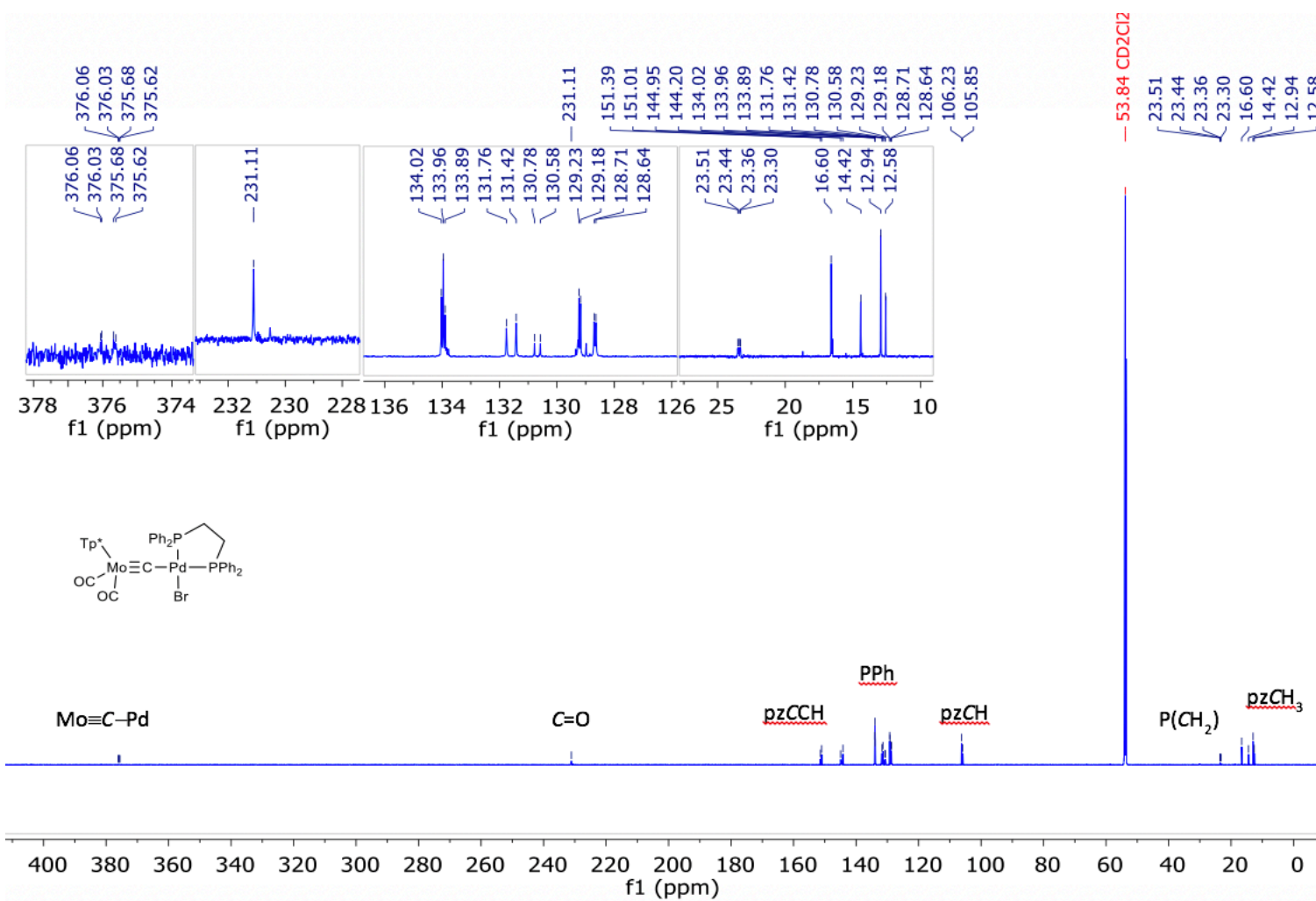


Figure S37. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{MoPd}(\mu\text{-C})\text{Br}(\text{CO})_2(\text{dppe})(\text{Tp}^*)]$ (6) (176 MHz, CD_2Cl_2 , 25 °C)

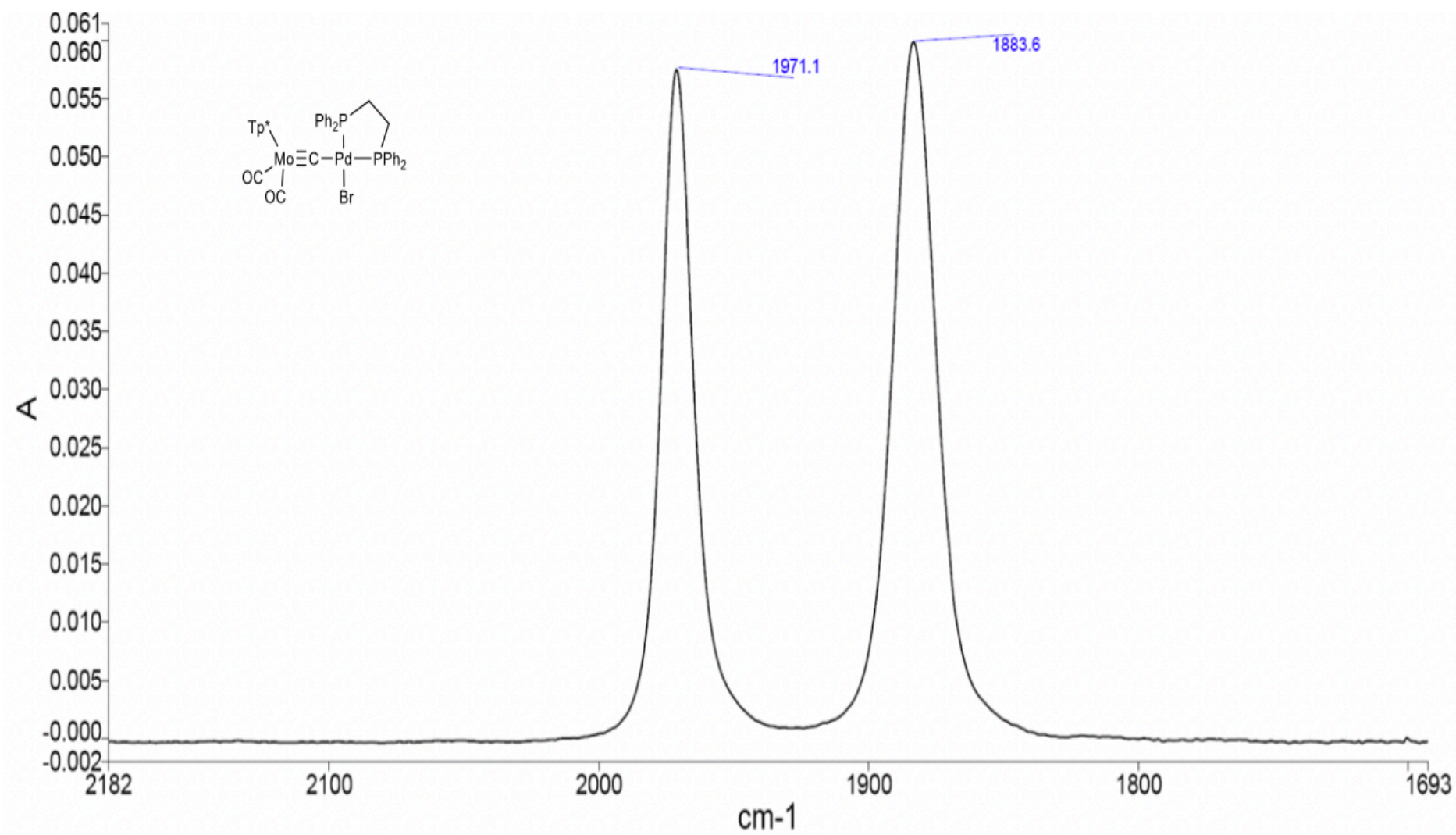
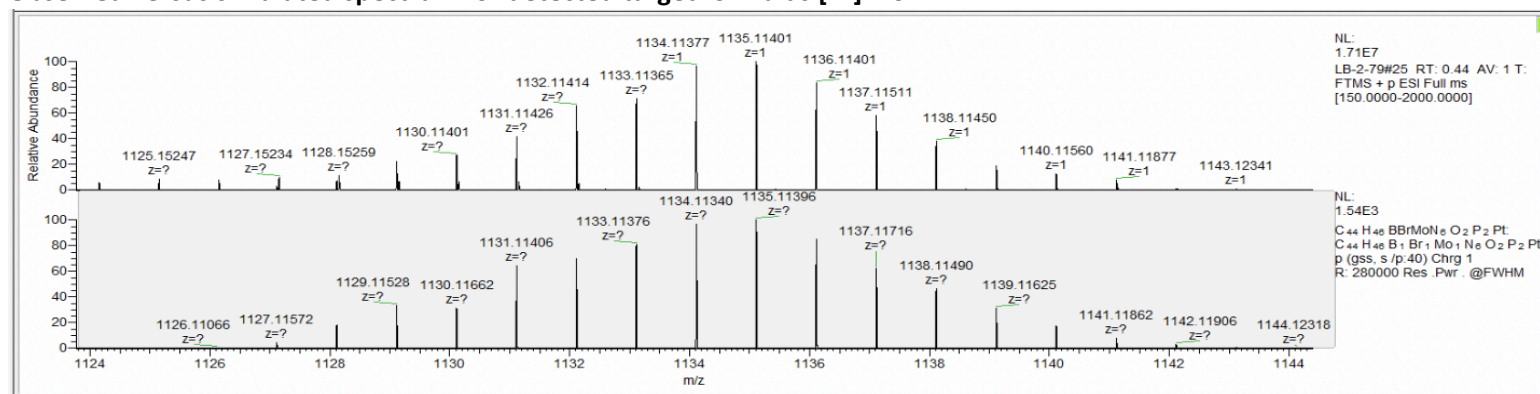
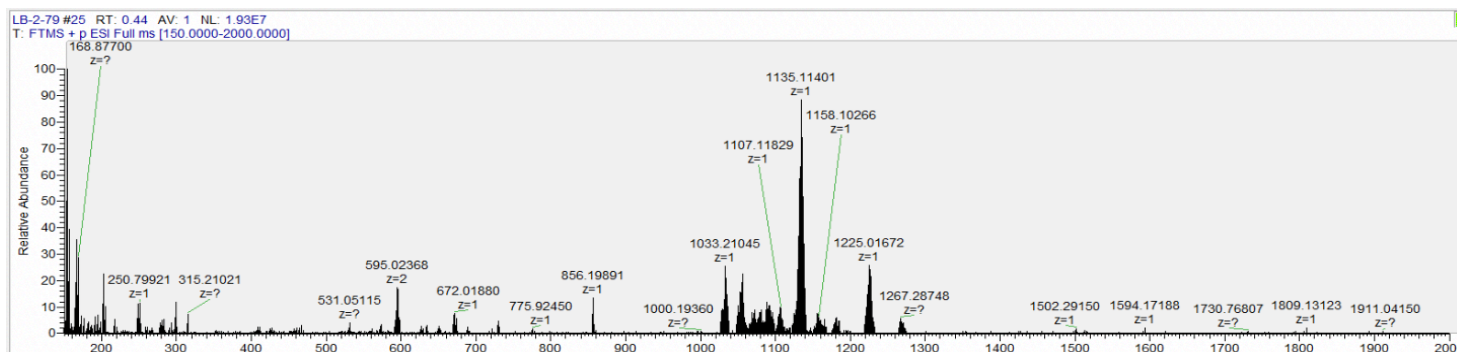


Figure S38. IR Spectrum of [MoPd(μ-C)Br(CO)₂(dppe)(Tp*)] (6) (CH₂Cl₂, 25 °C)

Figure S39. RSC/RSB Joint Mass Spectrometry Facility Analysis Report: IR Spectrum of [MoPd(μ -C)Br(CO)₂(dppe)(Tp*)] (6)
Instrument: Orbitrap QE, +ve mode ESI at 280k resolution **Analysis Date:** 2019-08-15

Theoretical m/z (most abundant isotopologue): [M]⁺ ion: 1135.11396 Observed m/z (most abundant isotopologue): [M]⁺ ion: 1135.11401 Mass error: 0.869 ppm
Observed versus simulated spectrum for detected target formulas [M]⁺ ion

Full Spectrum:


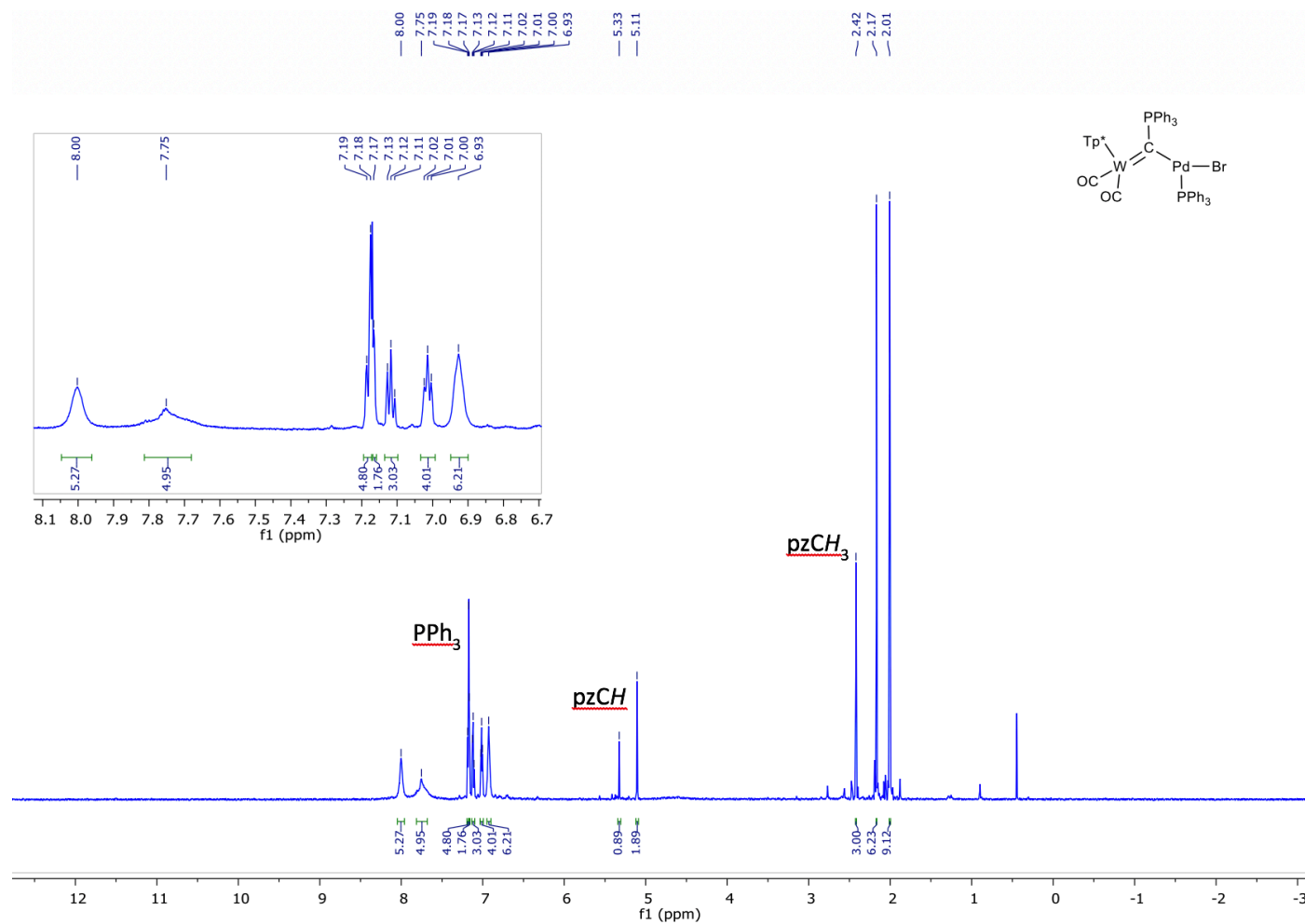


Figure S40. ^1H NMR Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (7) (400 MHz, CDCl_3 , 25°C)

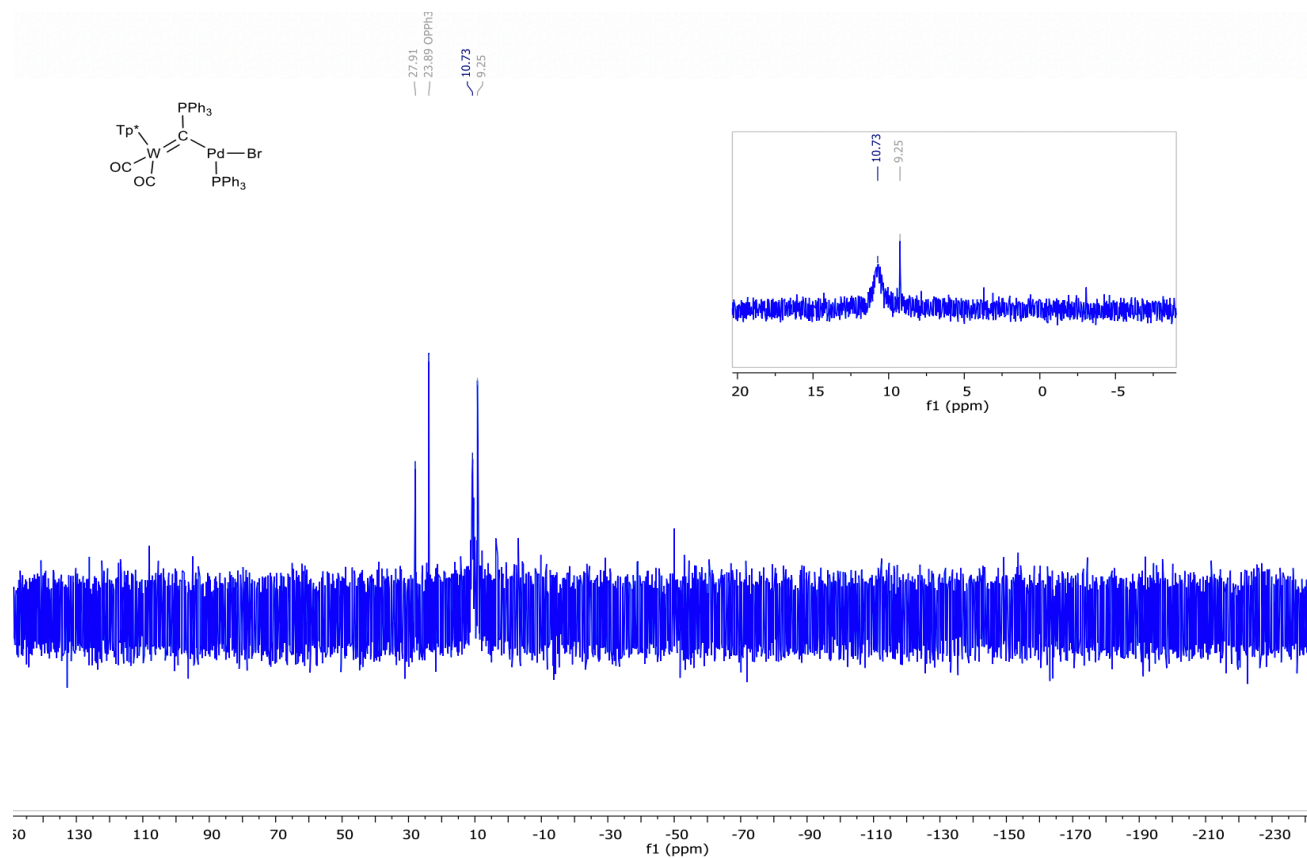


Figure S41. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (7) (162 MHz, CDCl_3 , 25 °C)

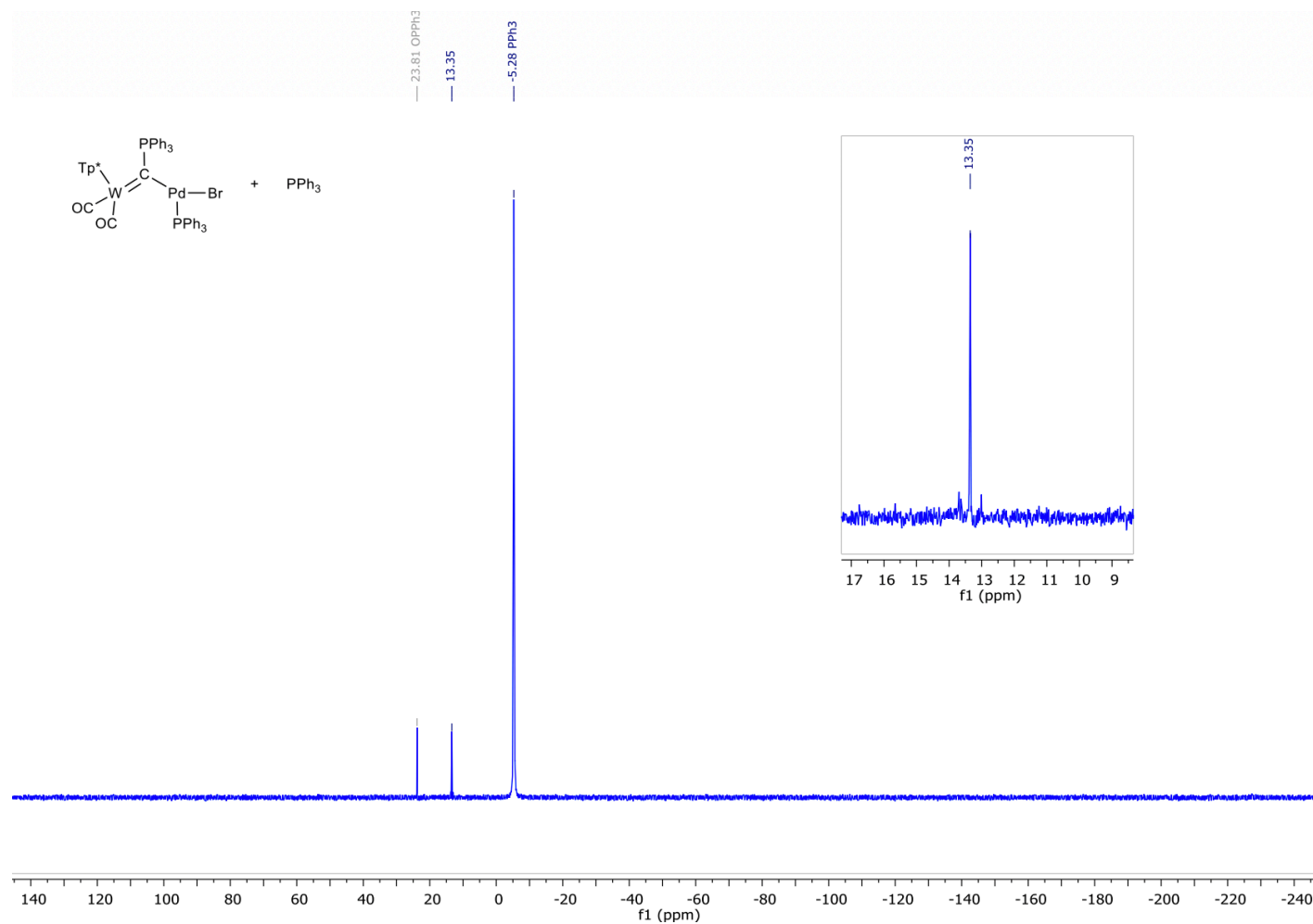


Figure S42. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (7) with excess PPh_3 (162 MHz, CDCl_3 , 25 °C)

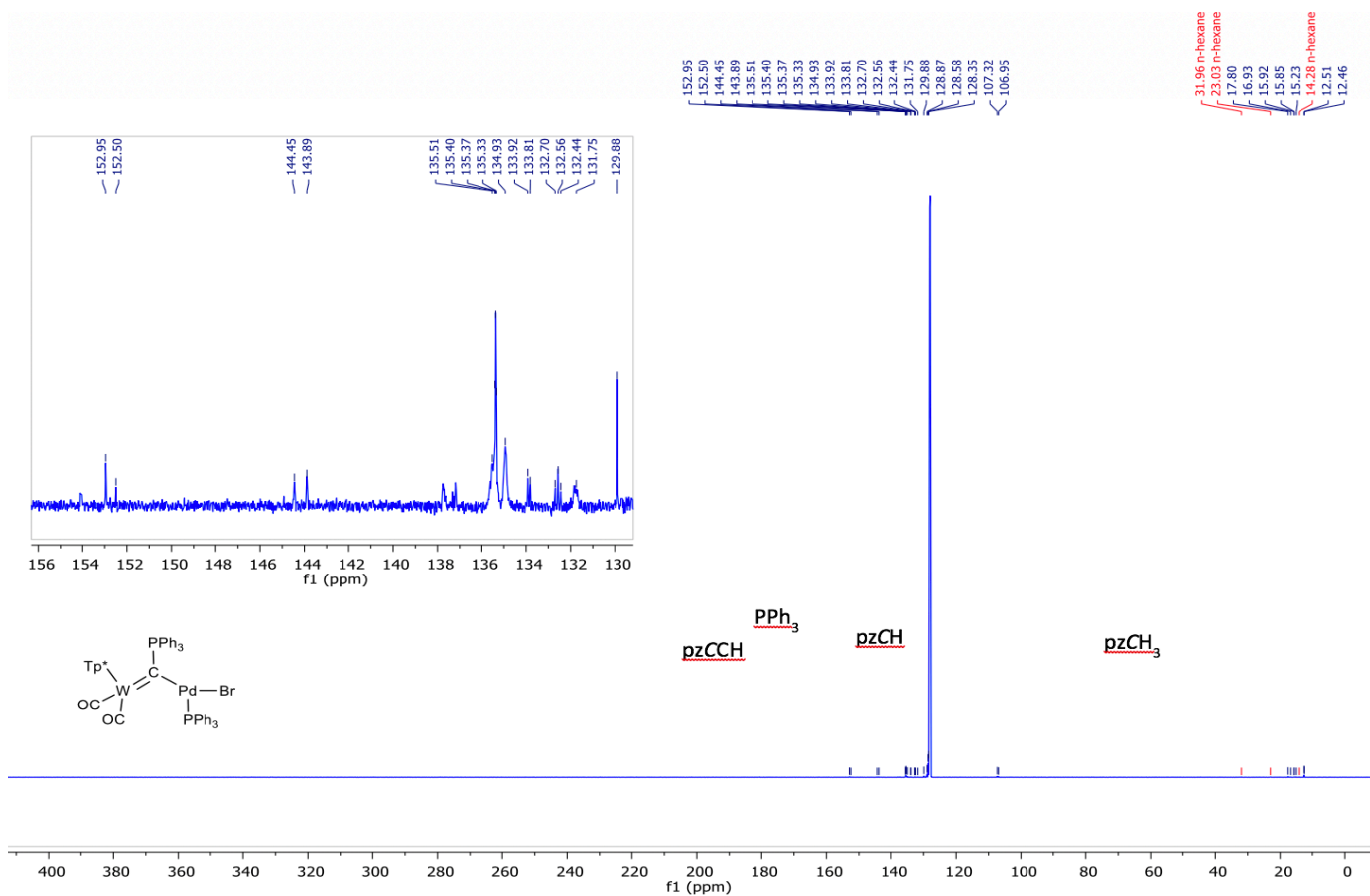


Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (7) (176 MHz , CDCl_3 , 50°C , sparingly soluble)

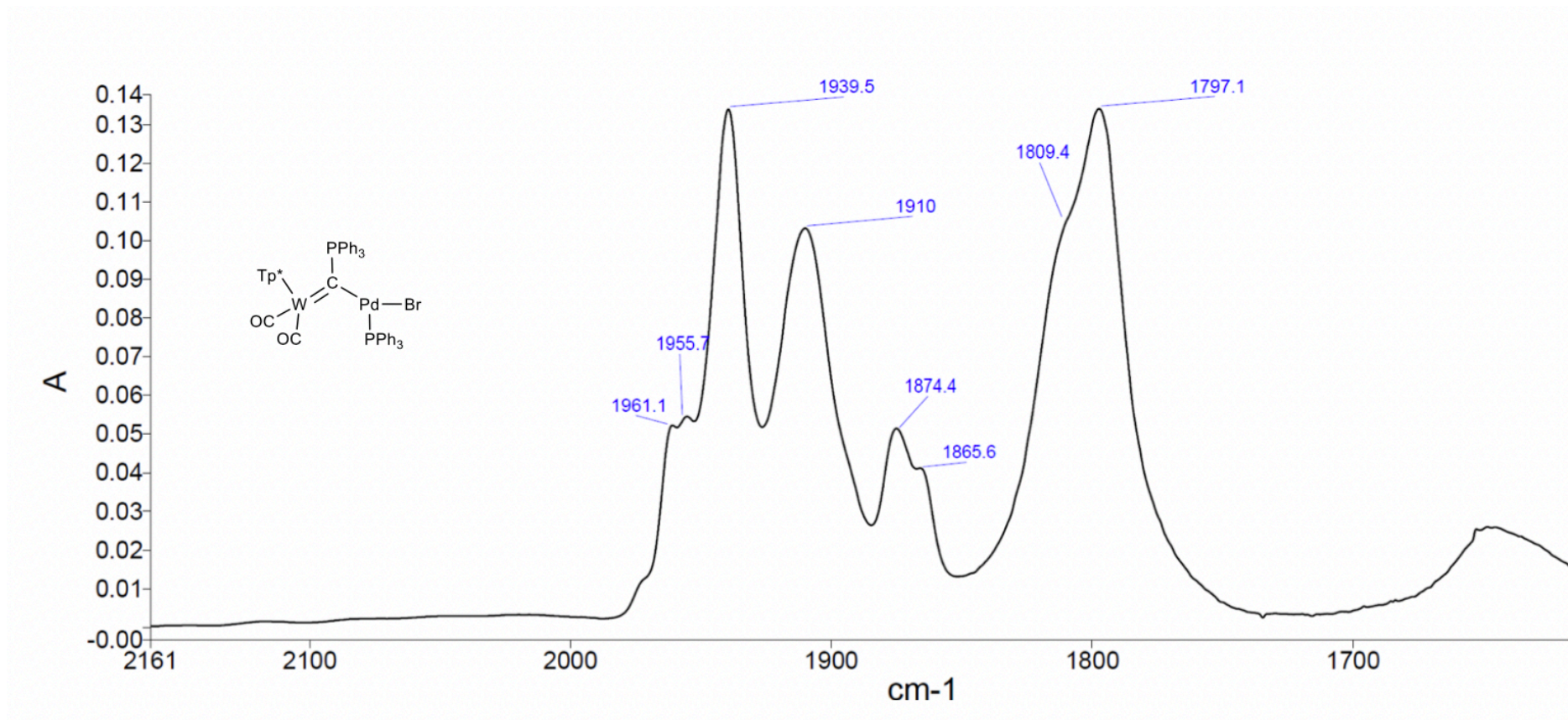


Figure S44. Infrared Spectrum of $[\text{WPd}(\mu\text{-CPPh}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (7) (THF, 25 °C)

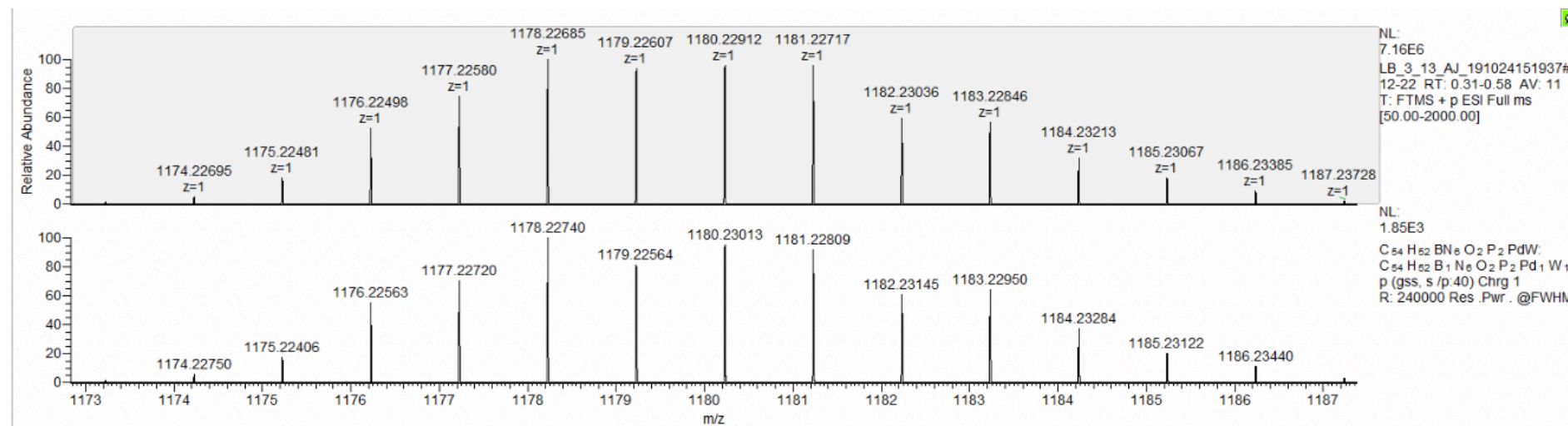


Figure S45. Mass Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (7) (ESI)

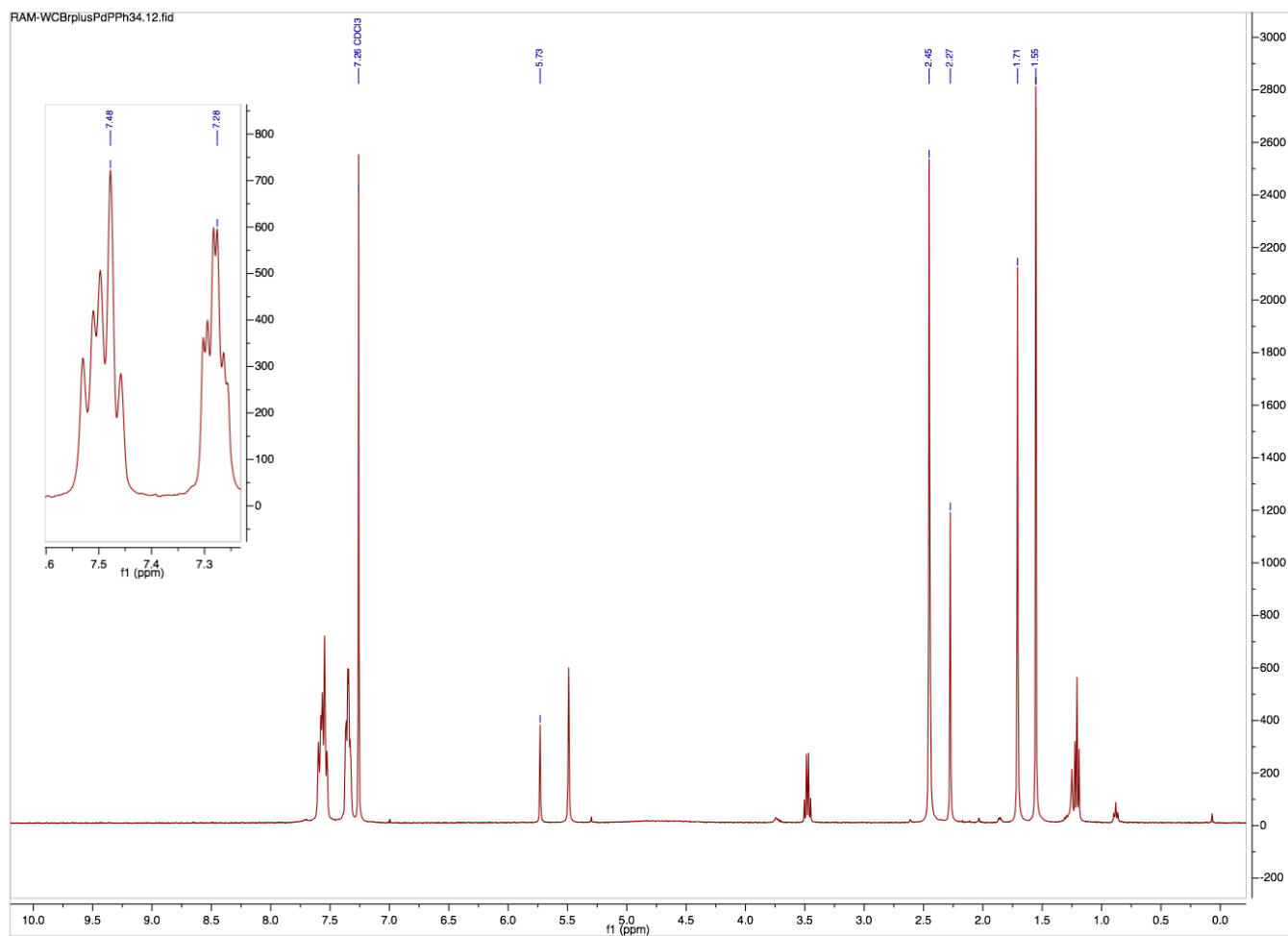


Figure S46. ^1H NMR Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (8) (400 MHz, CDCl_3 , 25 $^\circ\text{C}$)

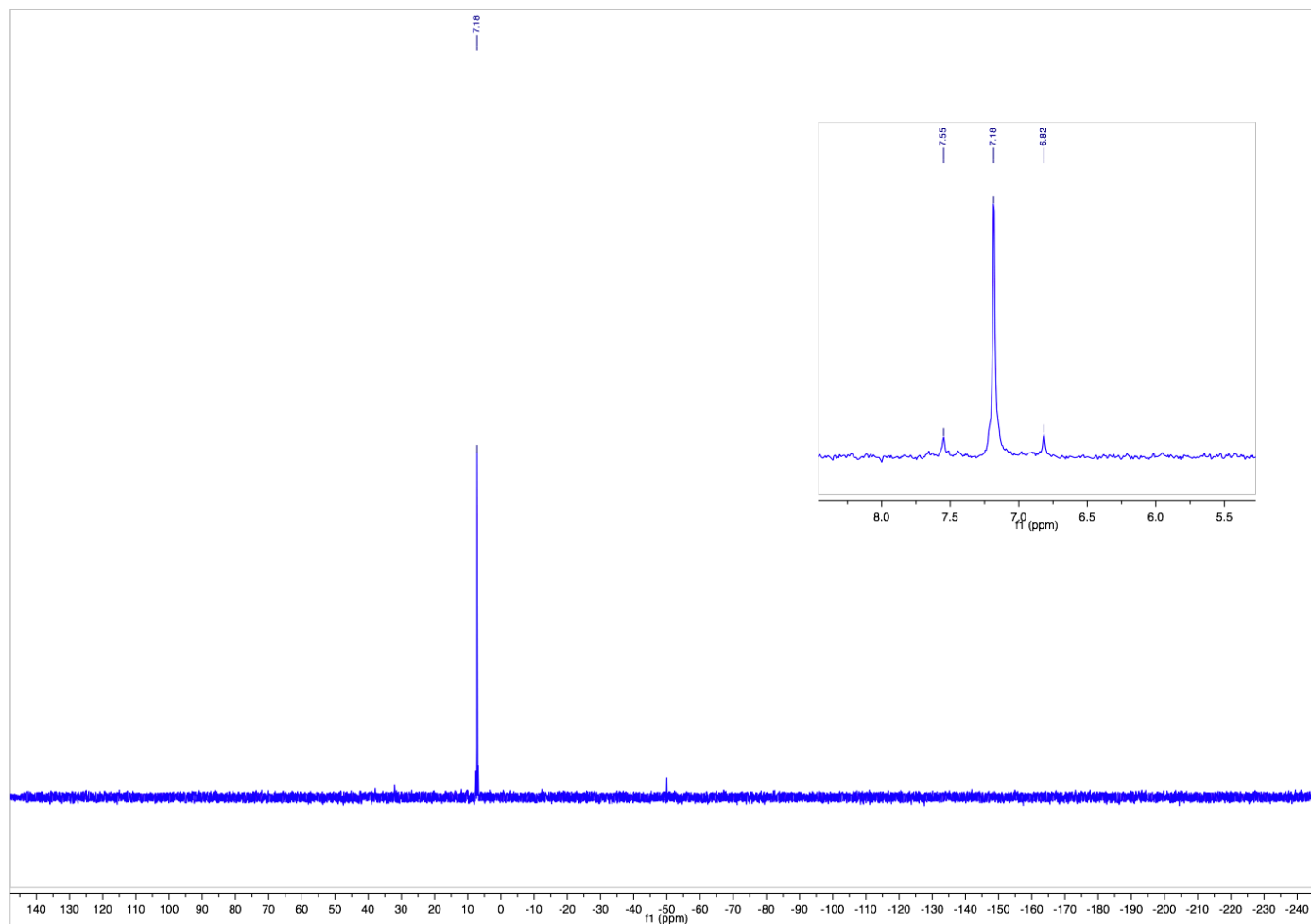


Figure S47. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{Tp}^*)]$ (8) (176 MHz, C_6D_6 , 25 °C)

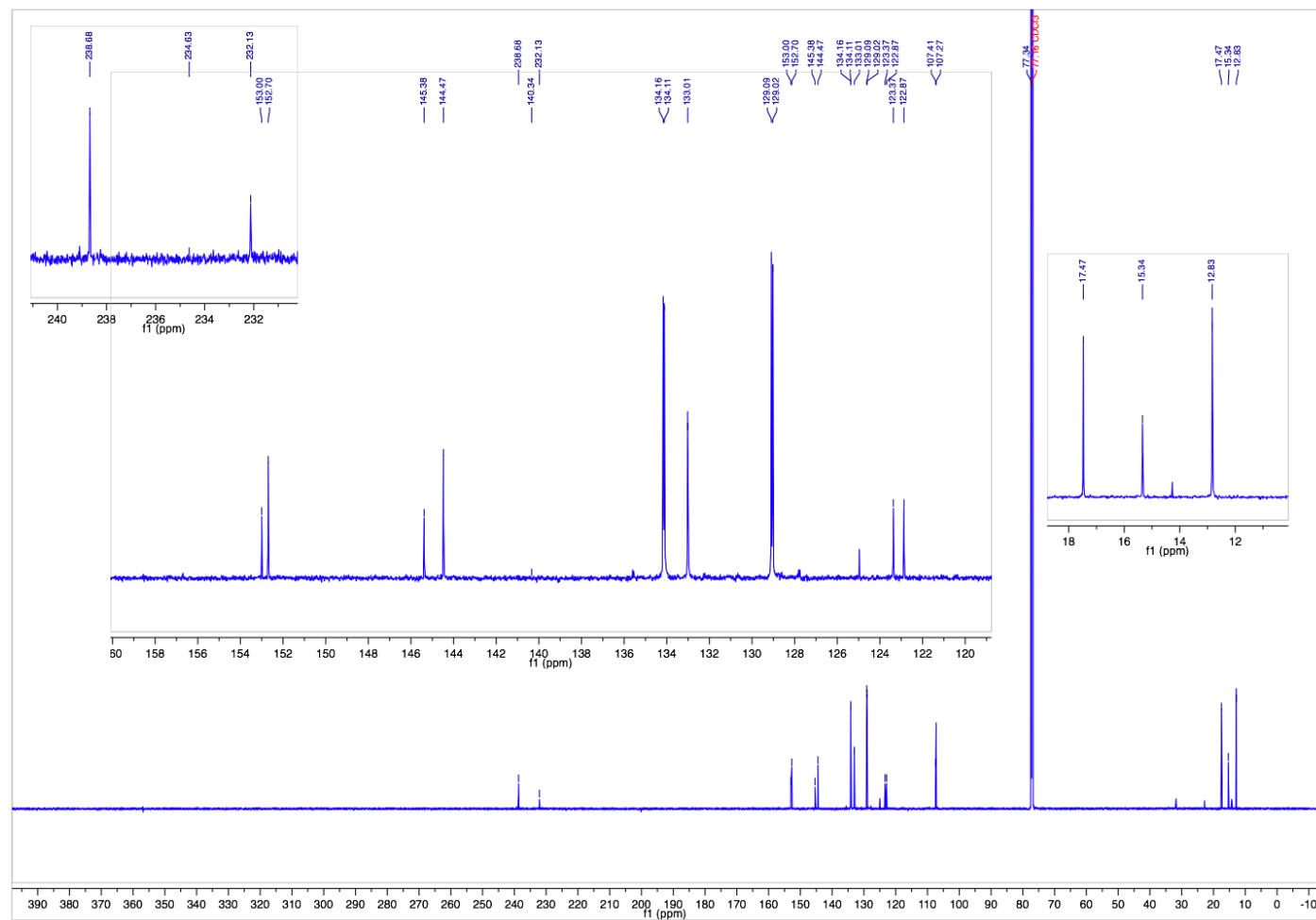


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{WPd}(\mu\text{-CPPH}_3)\text{Br}(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ (**8**) (141 MHz, CDCl_3 , 25 °C)

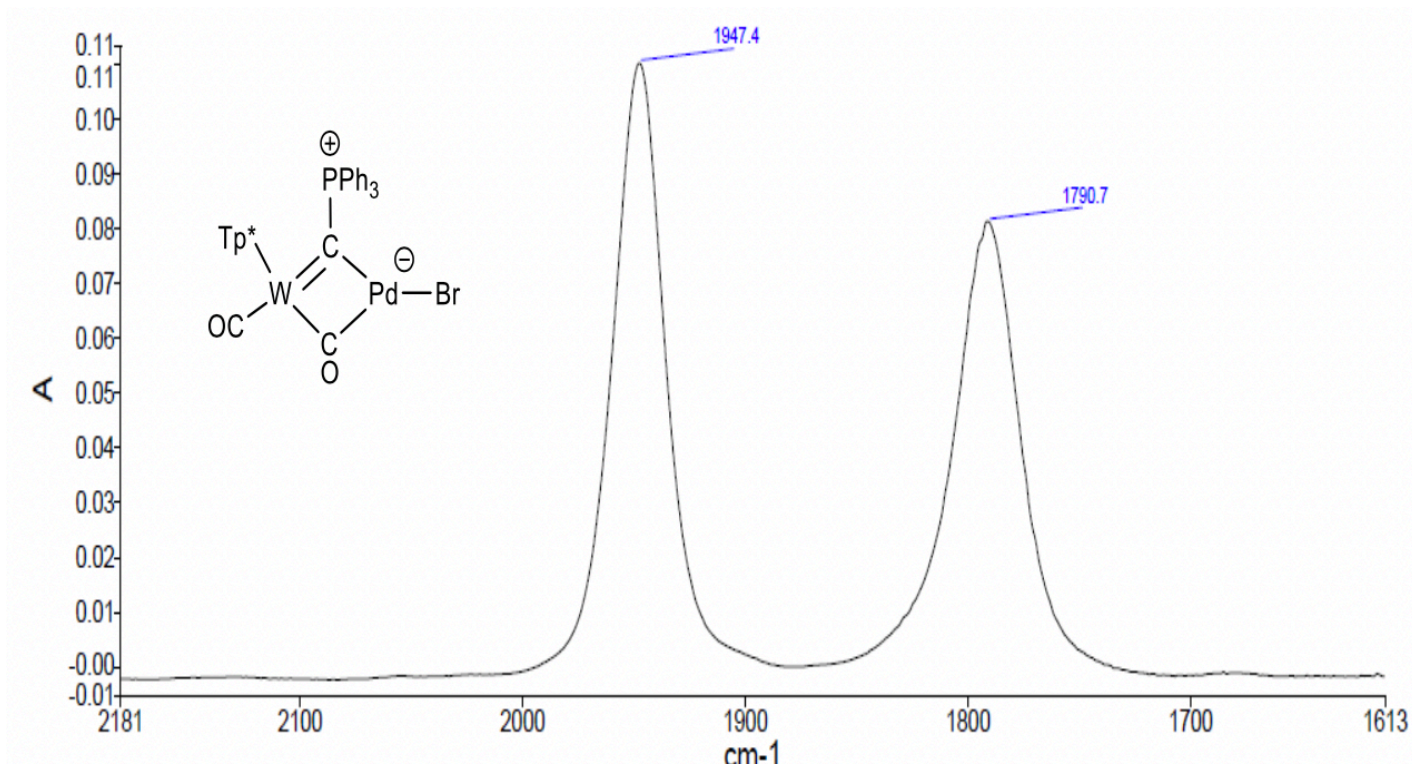


Figure S49. Infrared Spectrum of [WPd(μ-CPPh₃)Br(CO)₂(Tp*)] (8) (CH₂Cl₂, 25 °C)

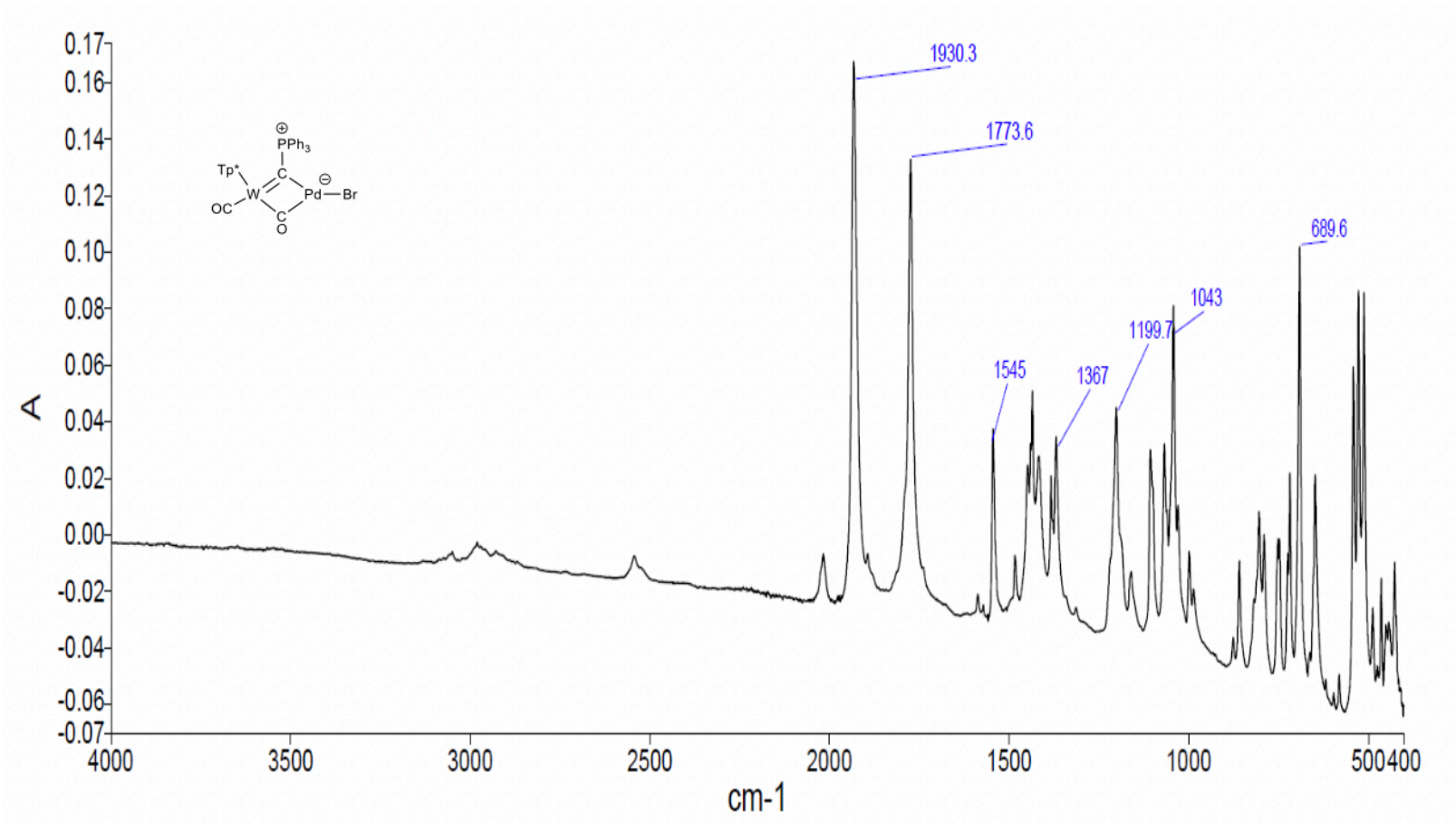
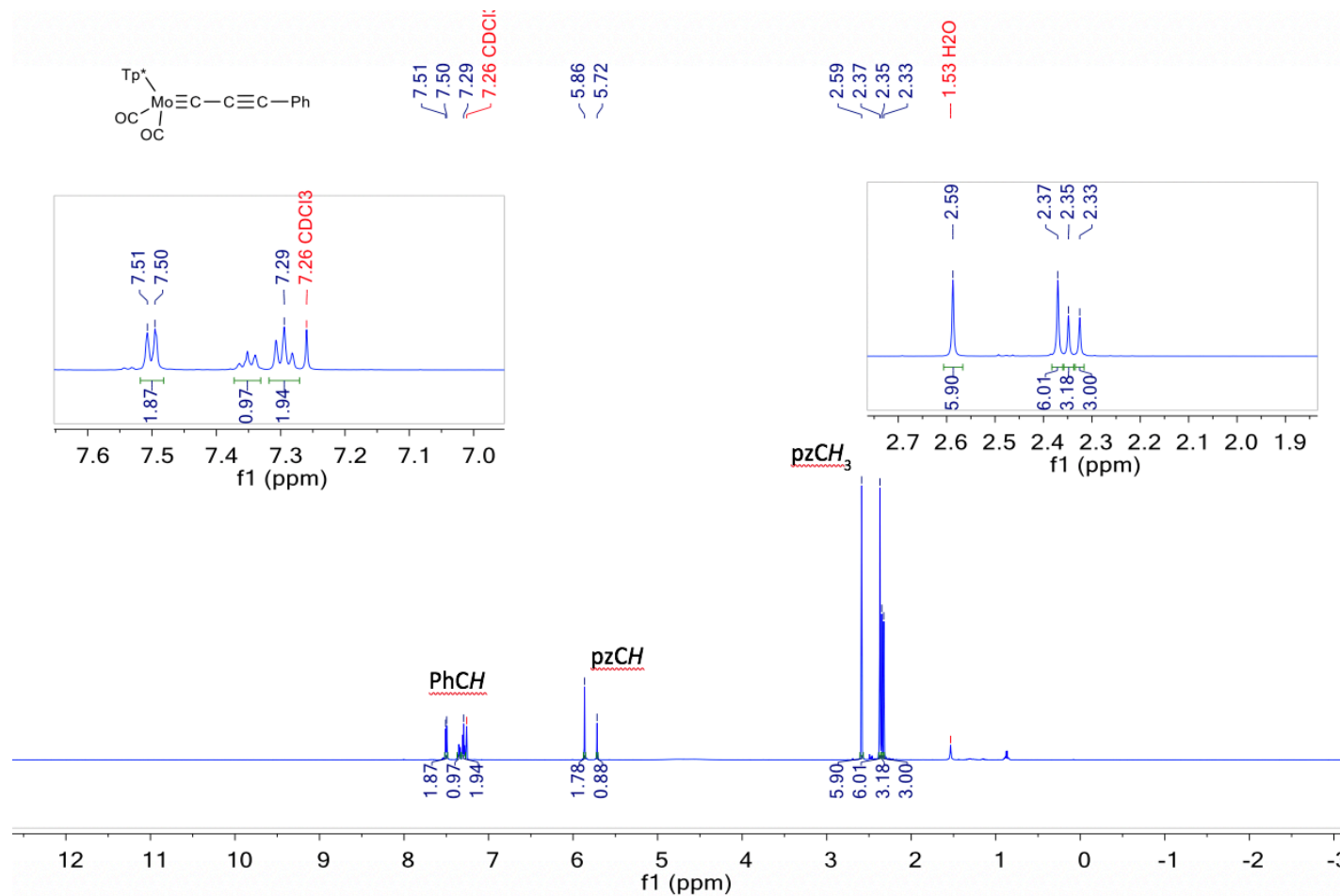


Figure S50. Infrared Spectrum of $[WPd(\mu-CPPH_3)Br(CO)_2(Tp^*)]$ (8) (ATR)

Selected Spectra for Propargylidynes – see also Reference 13

Figure S51. ¹H NMR Spectrum of [(Tp*)(CO)₂Mo(=C-C≡C-Ph)] (600 MHz, CDCl₃, 25 °C, δ):

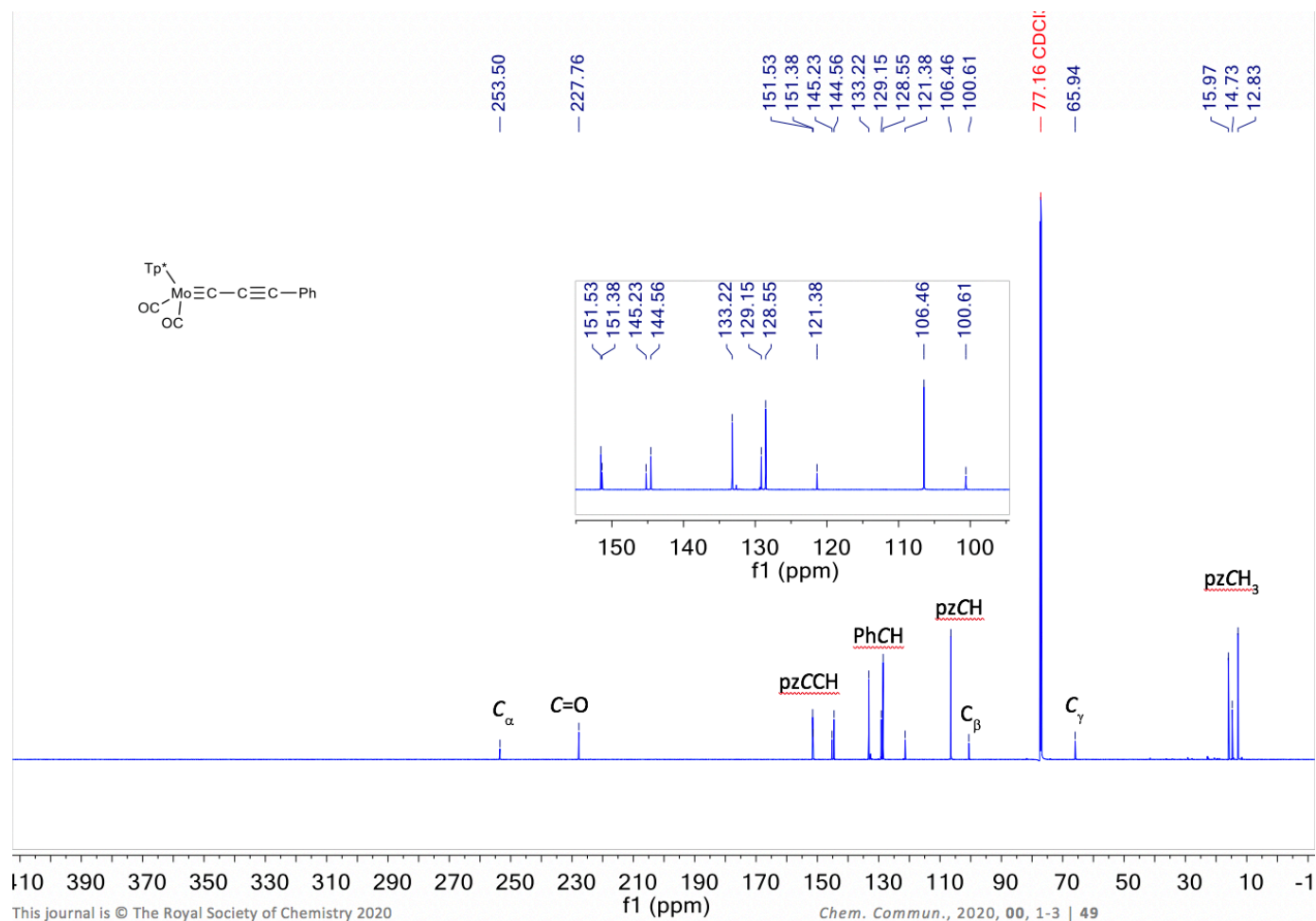


Figure S52. ^{13}C NMR Spectrum of $[(Tp^*)(CO)_2Mo(≡C-C≡C-Ph)]$ (151 MHz, $CDCl_3$, 25 °C, δ):

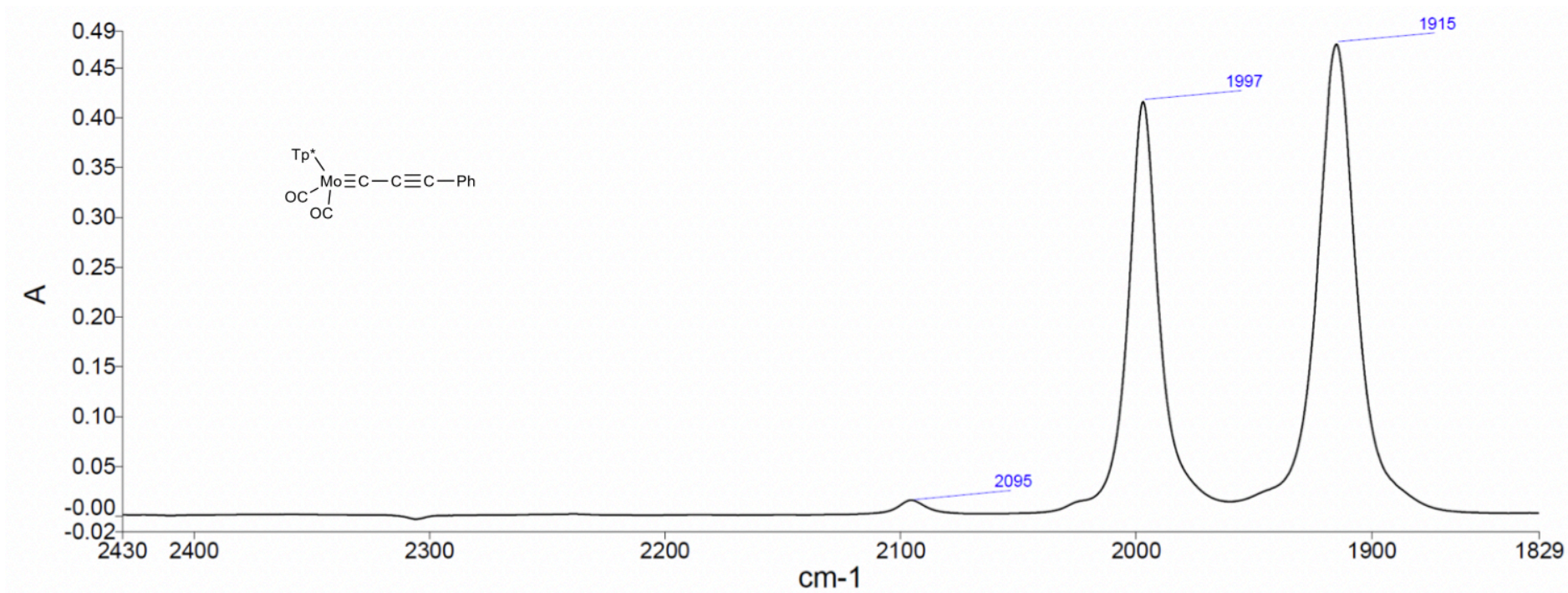


Figure S53. Infrared Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{Mo}(\equiv\text{C}-\text{C}\equiv\text{C}-\text{Ph})]$ (NaCl, CH_2Cl_2 , 25 °C)

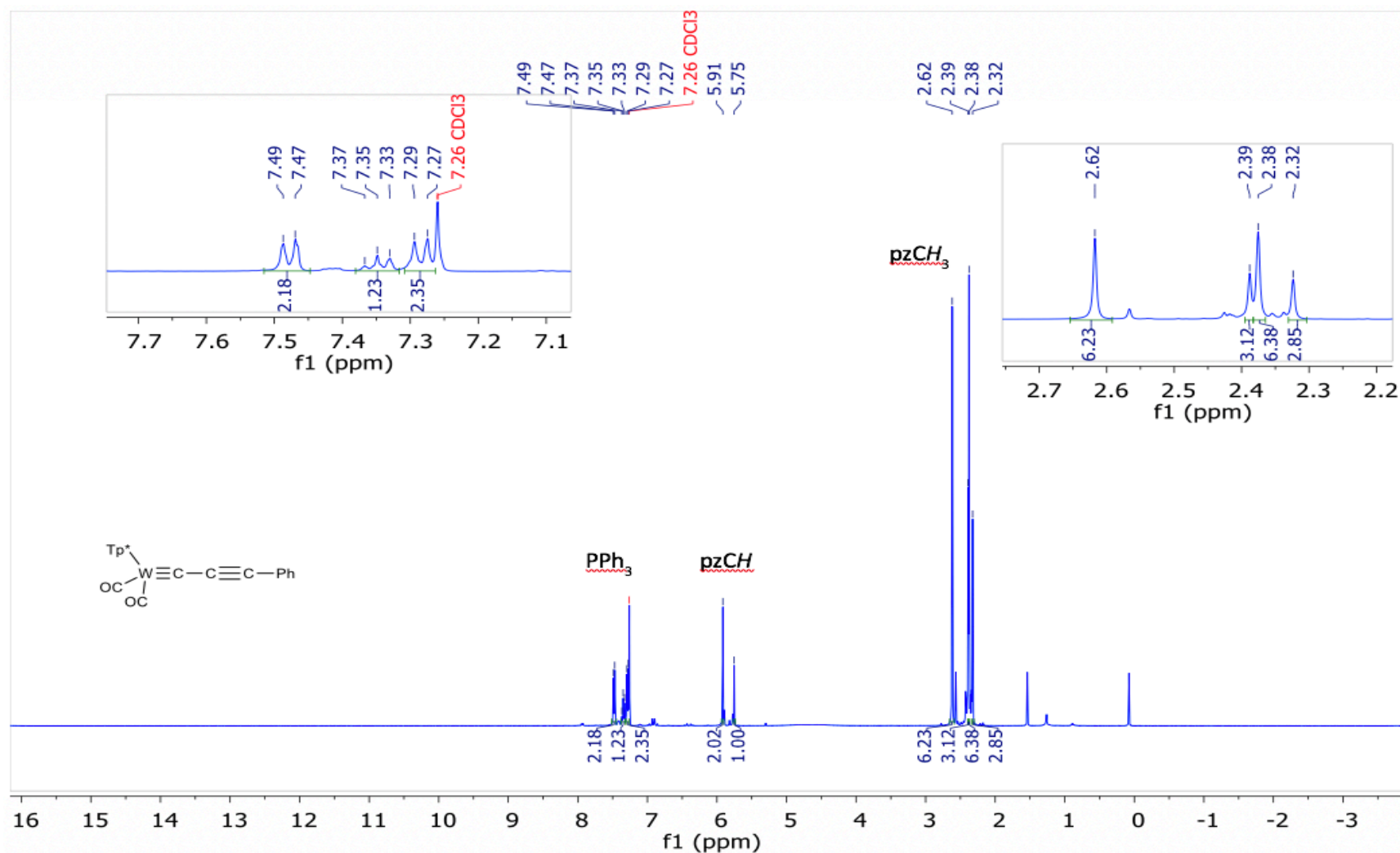


Figure S54. ^1H NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}(=\text{C}-\text{C} \equiv \text{C}-\text{Ph})]$ (400 MHz, CDCl_3 , 25 °C, δ):

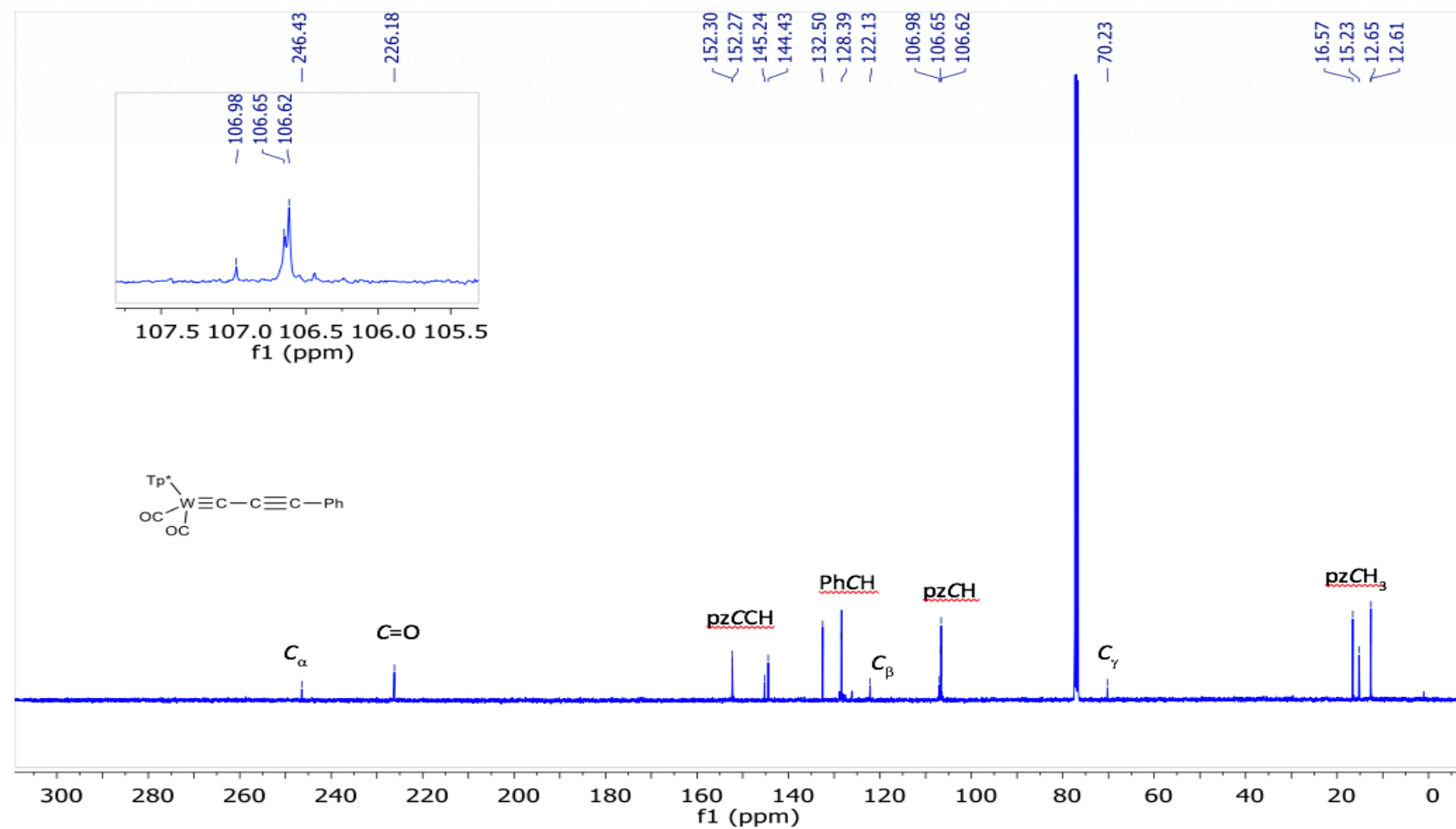


Figure S55. ^{13}C NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}(=\text{C}-\text{C}\equiv\text{C}-\text{Ph})]$ (101 MHz, CDCl_3 , 25 °C, δ):

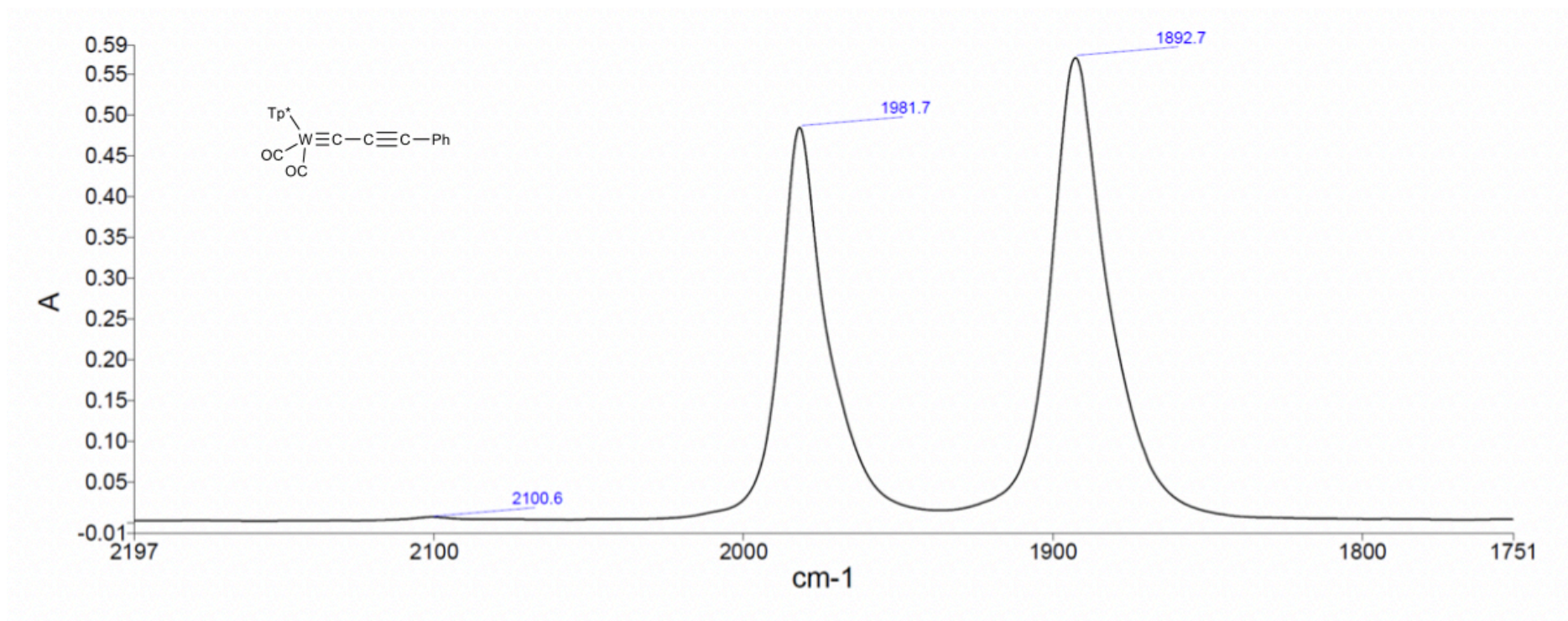


Figure S56. Infrared Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}(\equiv\text{C}-\text{C}\equiv\text{C}-\text{Ph})]$ (NaCl, CH_2Cl_2 , 25 °C)

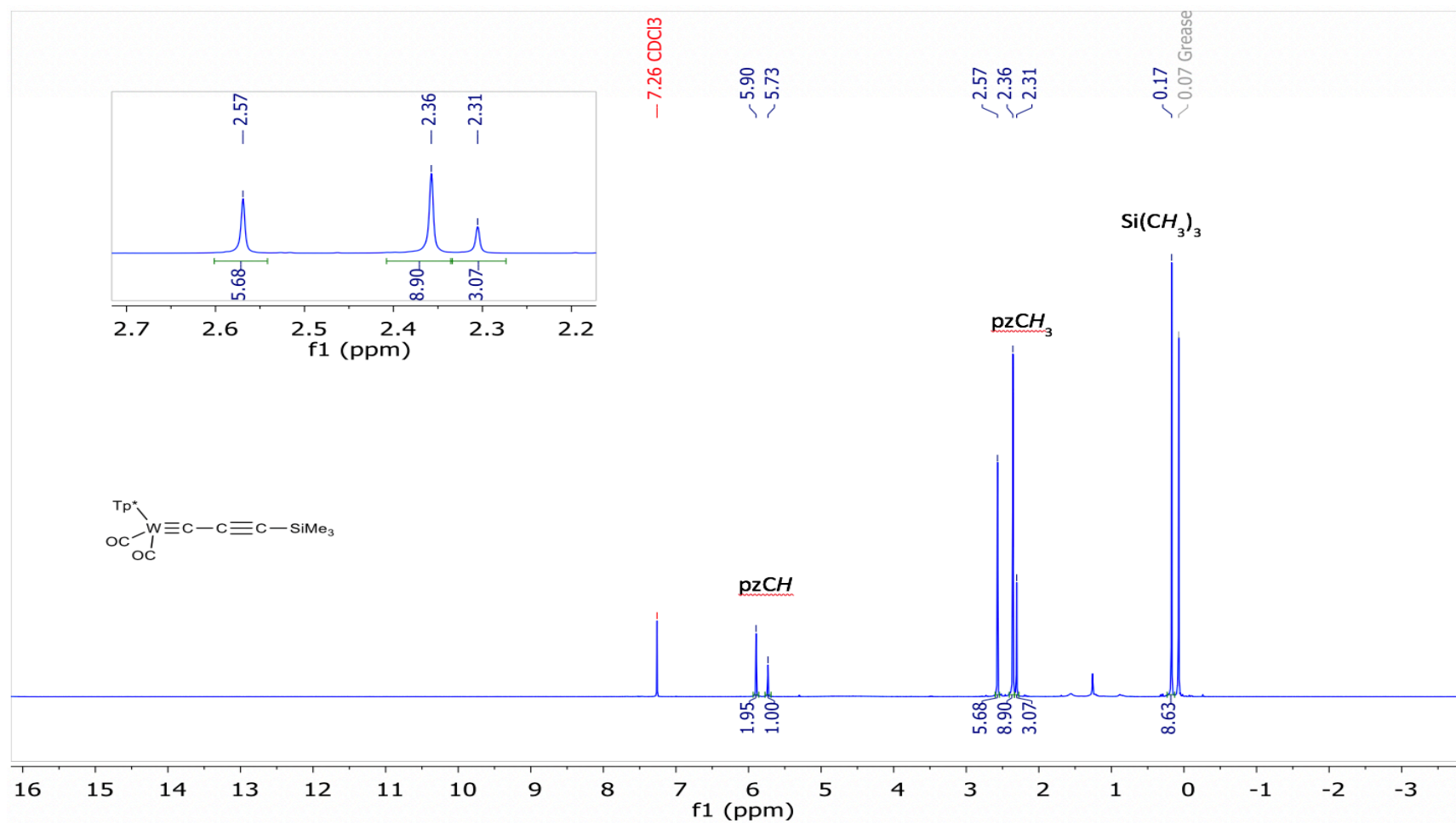


Figure S57. $^1\text{H NMR}$ Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}(\text{=C-C}\equiv\text{C-SiMe}_3)]$ (400 MHz, CDCl_3 , 25 °C, δ):

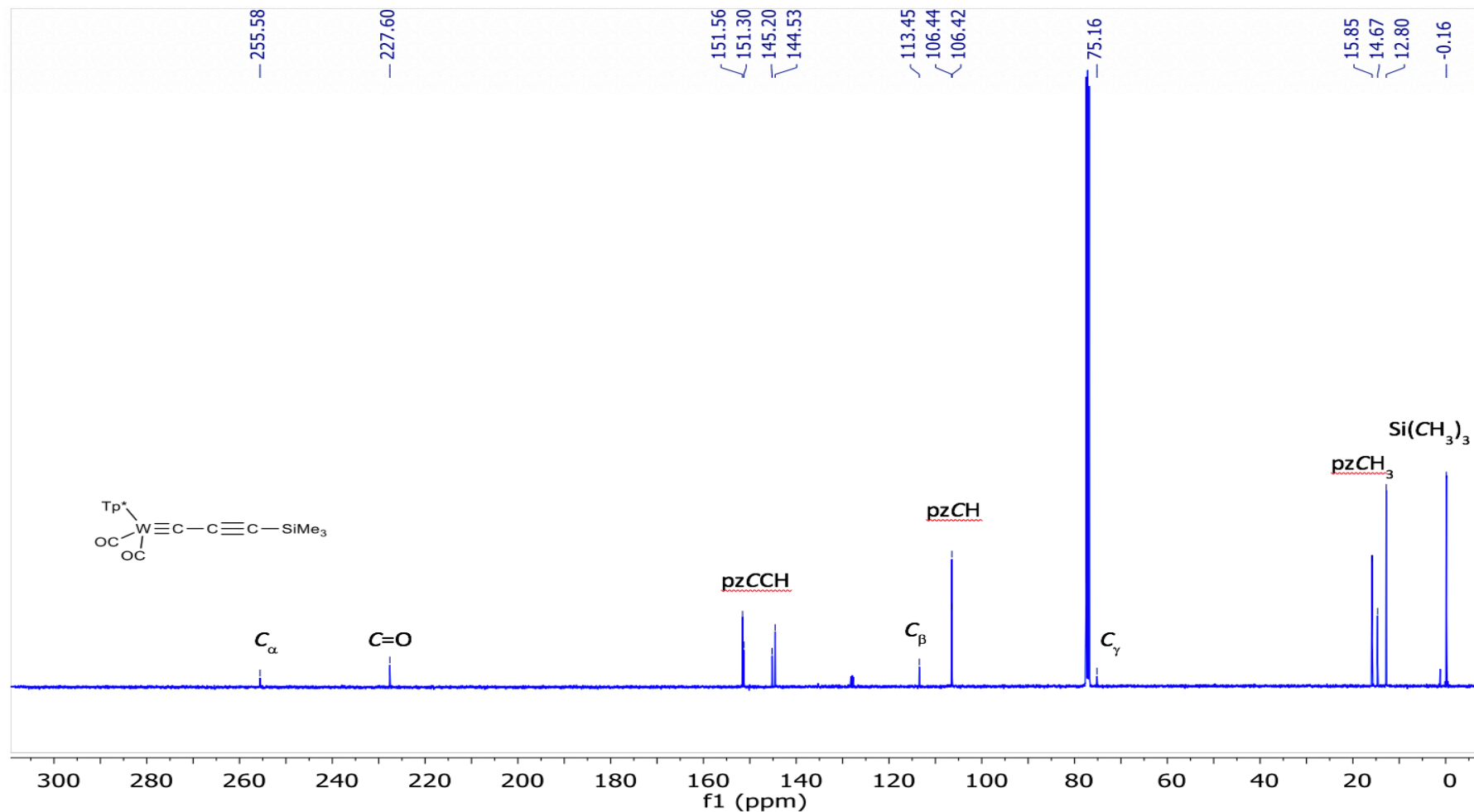


Figure S58. ^{13}C NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}(=\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3)]$ (101 MHz, CDCl_3 , 25 °C, δ):

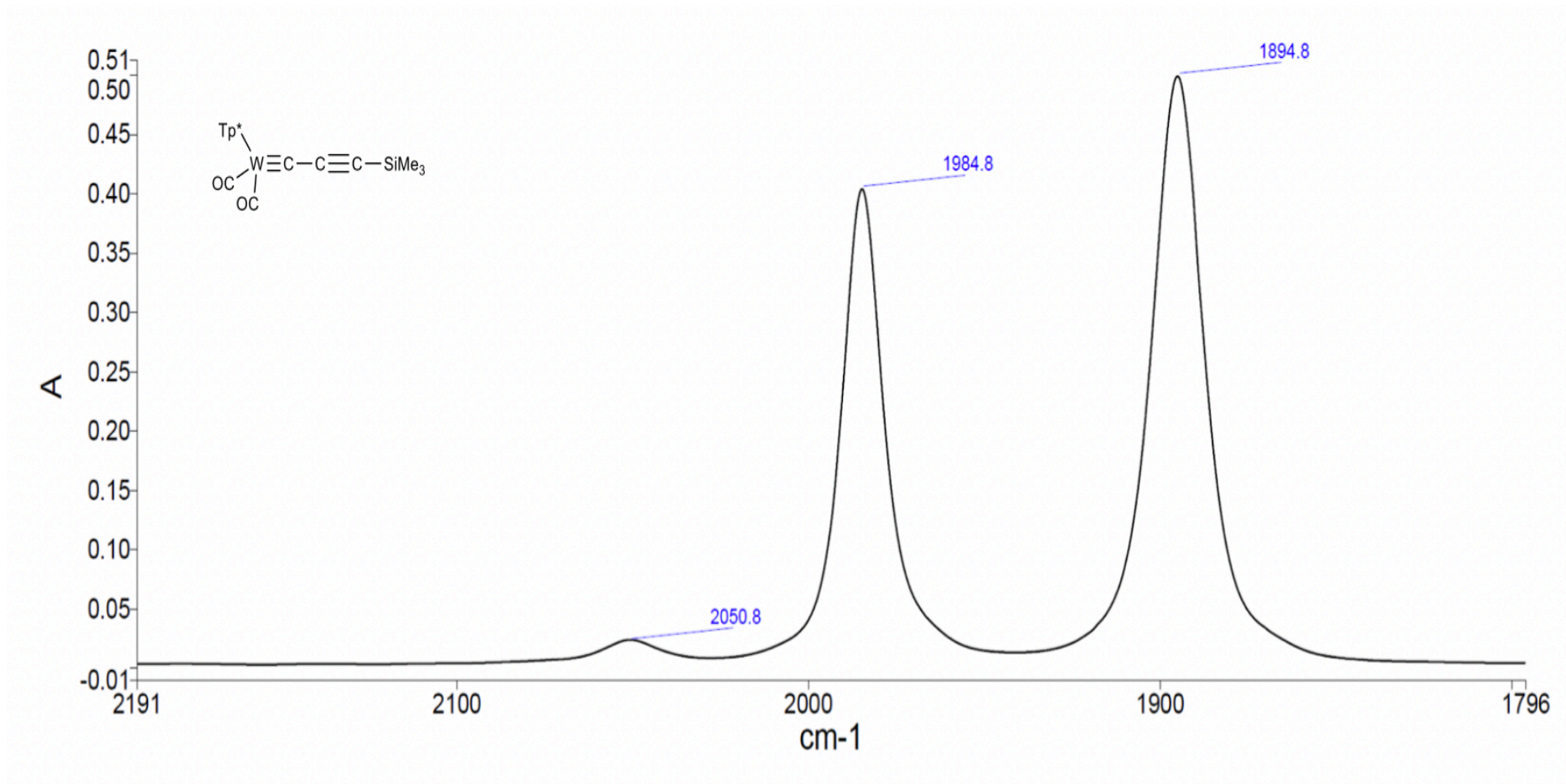


Figure S59. Infrared Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{W}(\equiv\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3)]$ (CH_2Cl_2 , 25 °C)

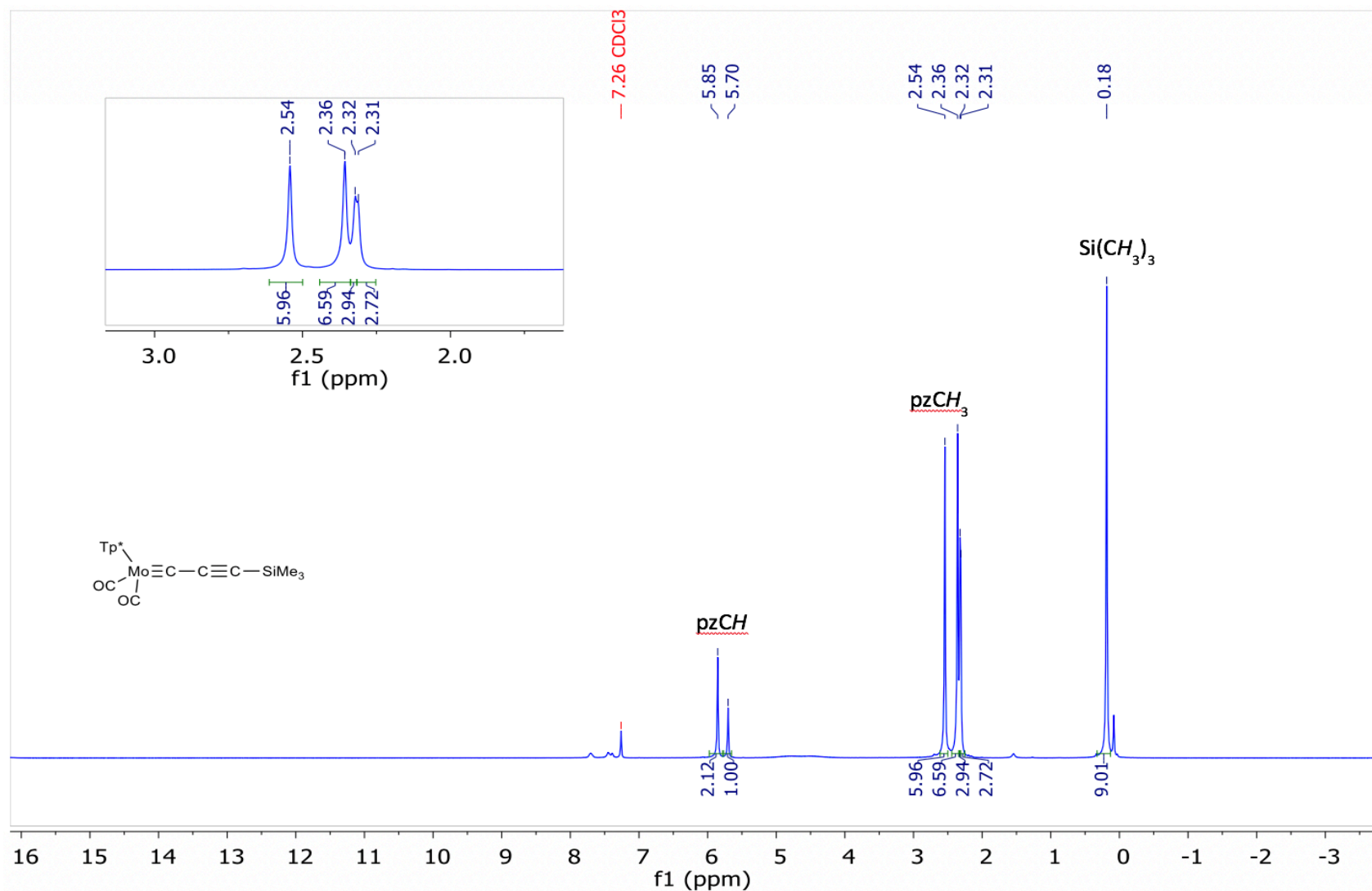


Figure S60. ^1H NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{Mo}(\text{=C-C}\equiv\text{C-SiMe}_3)]$ (600 MHz, CDCl_3 , 25 °C, δ):

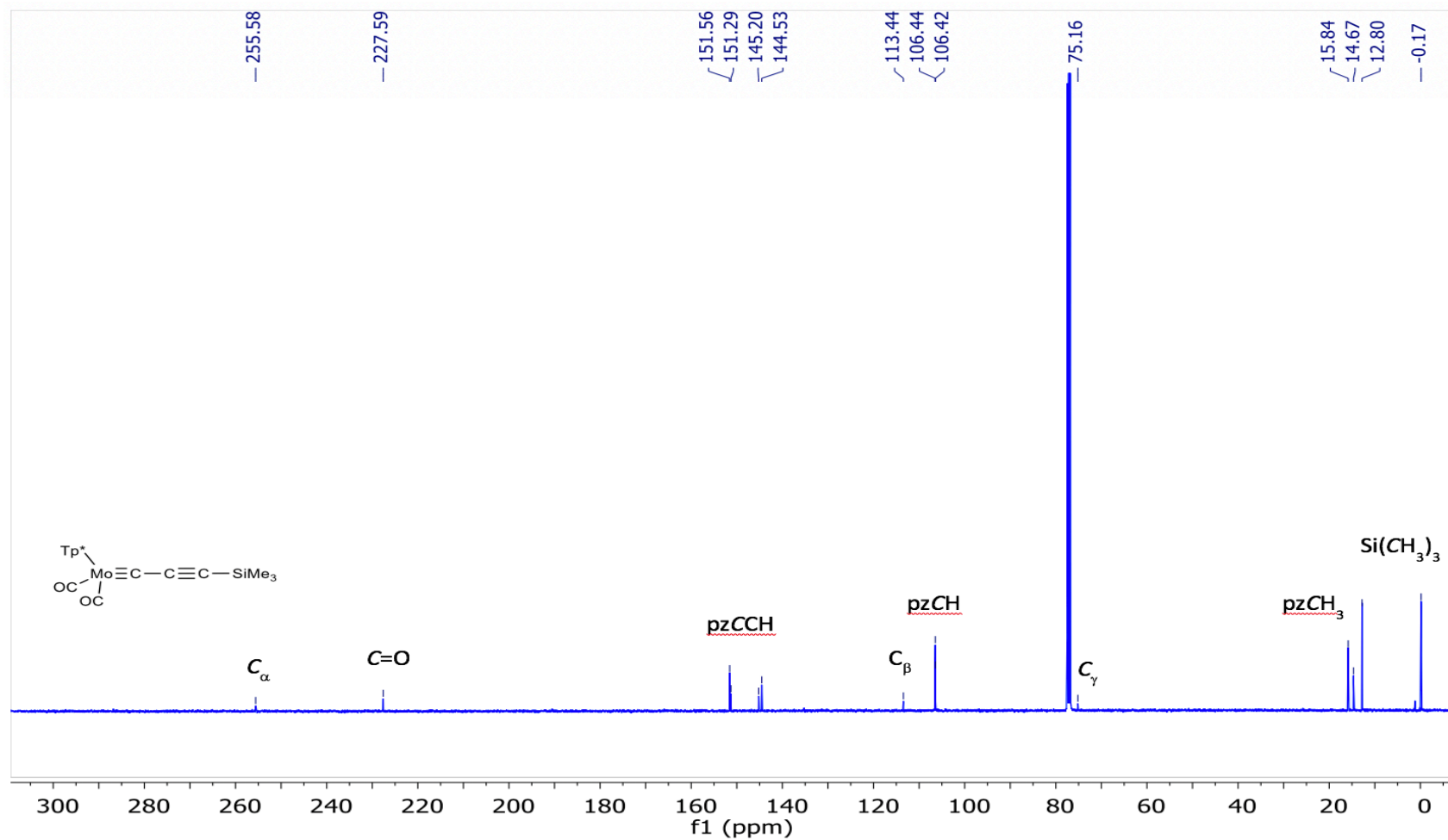


Figure S61. ^{13}C NMR Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{Mo}(\equiv\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3)]$ (151 MHz, CDCl_3 , 25 °C, δ):

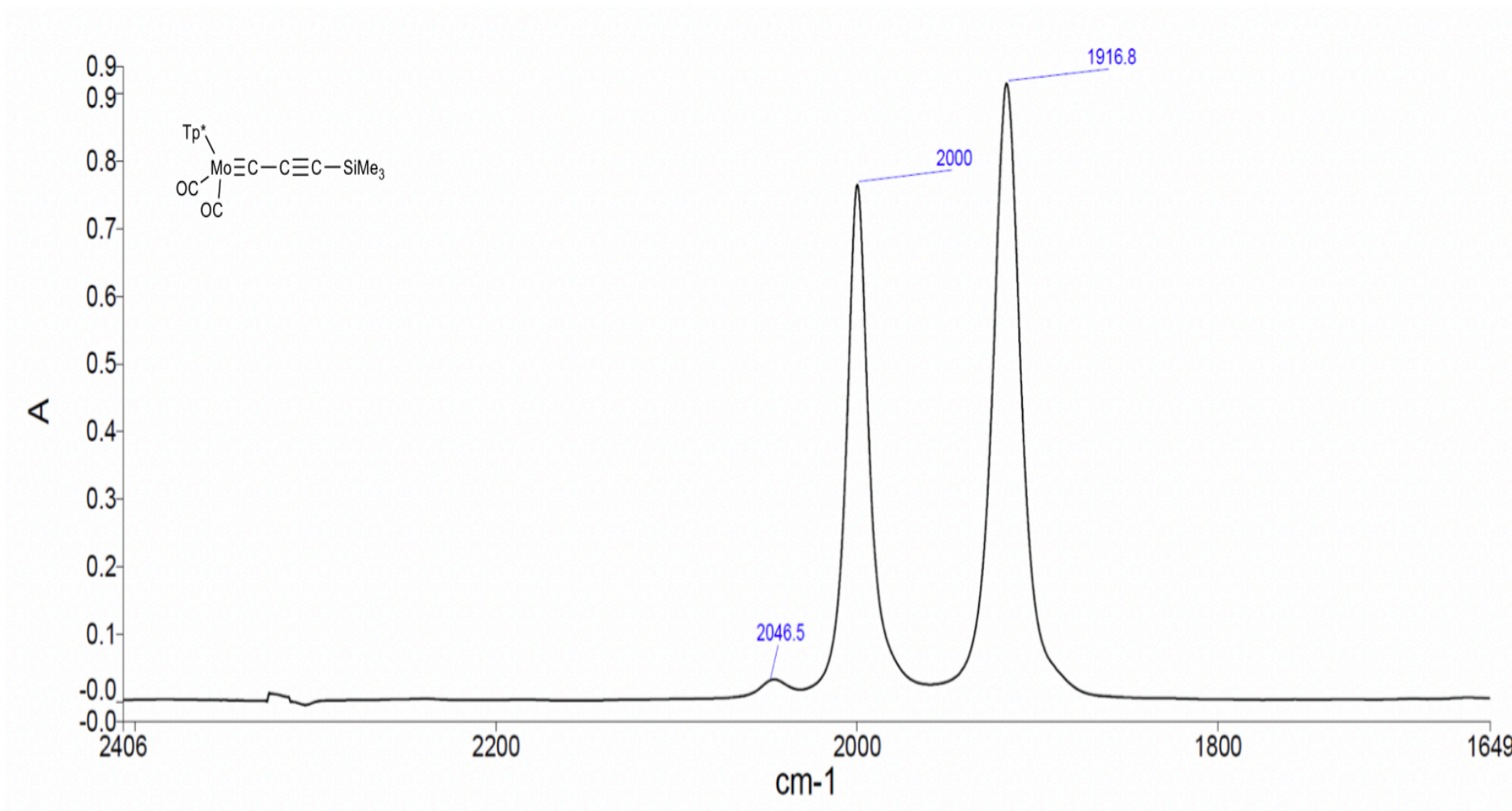


Figure S62. Infrared Spectrum of $[(\text{Tp}^*)(\text{CO})_2\text{Mo}(\equiv\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3)]$ (NaCl, CH_2Cl_2 , 25 °C)

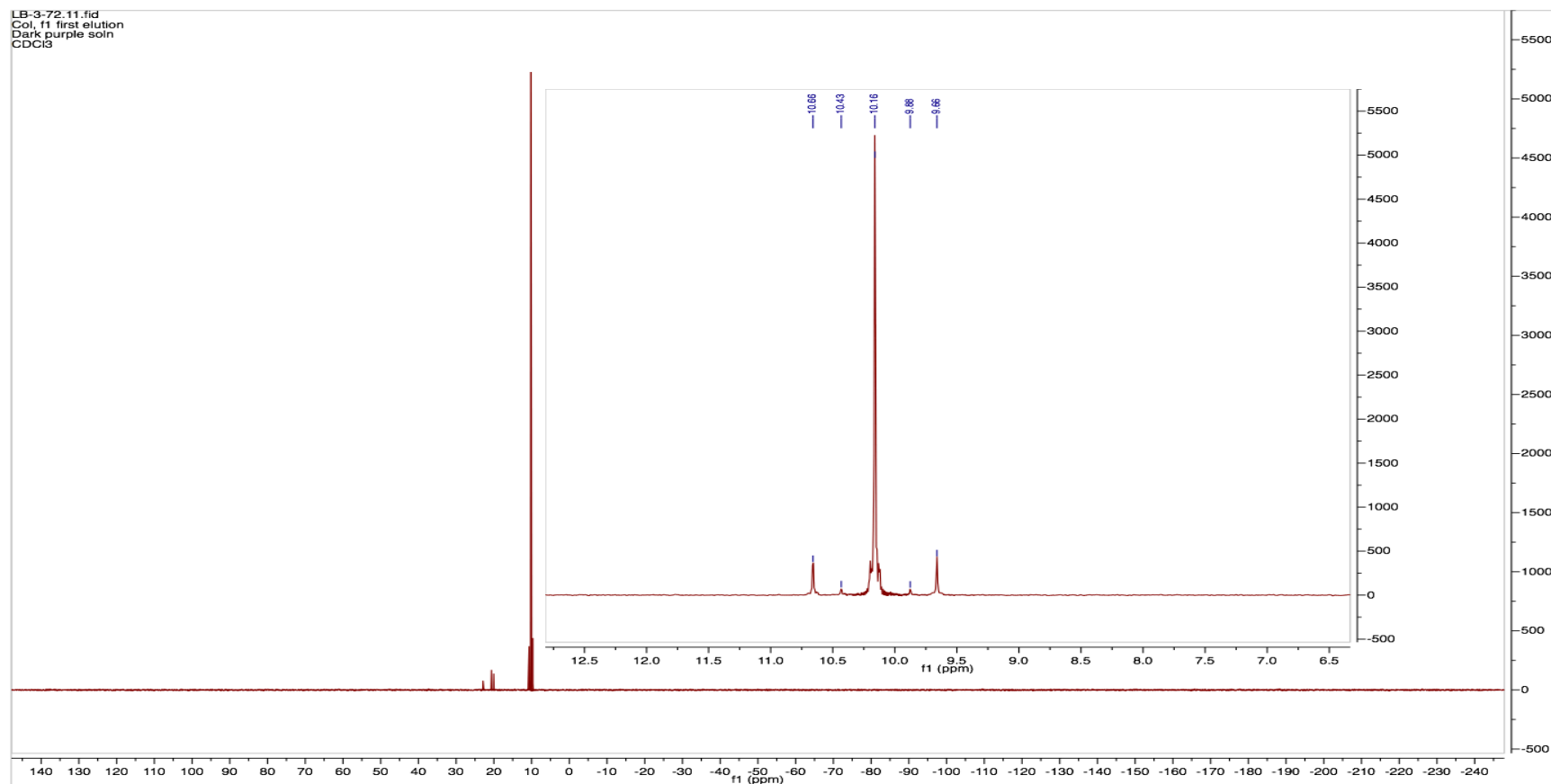


Figure S63. $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of $[\text{W}(\equiv\text{CPh}_3)(\text{CO})_2(\text{Tp}^*)]\text{Br}$ (**[9]Br**) (162 MHz, CDCl_3 , 25 °C). The salt $[\text{W}(\equiv\text{CPh}_3)(\text{CO})_2(\text{Tp}^*)]\text{PF}_6$ has been described previously however δ_{P} was not reported.

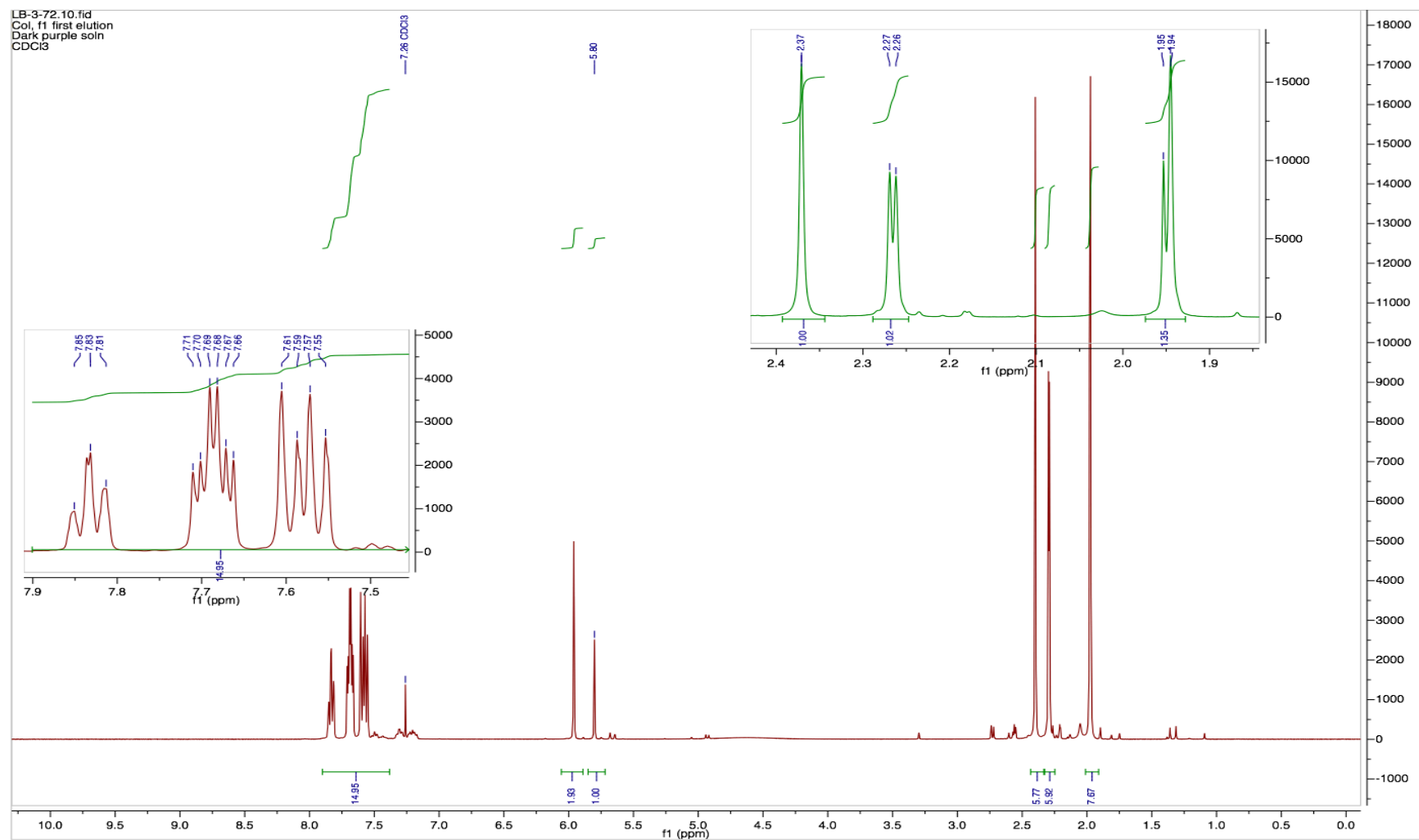


Figure S64. ^1H NMR Spectrum of $[\text{W}(\equiv\text{CPh}_3)(\text{CO})_2(\text{Tp}^*)]\text{Br}$ ($[\text{9}]\text{Br}$) (400 MHz, CDCl_3 , 25 °C). The salt $[\text{W}(\equiv\text{CPh}_3)(\text{CO})_2(\text{Tp}^*)]\text{PF}_6$ has been described previously with δ_{H} (CD_2Cl_2) = 7.79 (m, 15 H, C_6H_5), 6.00, 5.86 (pzH), 2.43, 2.34, 2.33, 2.02 (pzCH₃).

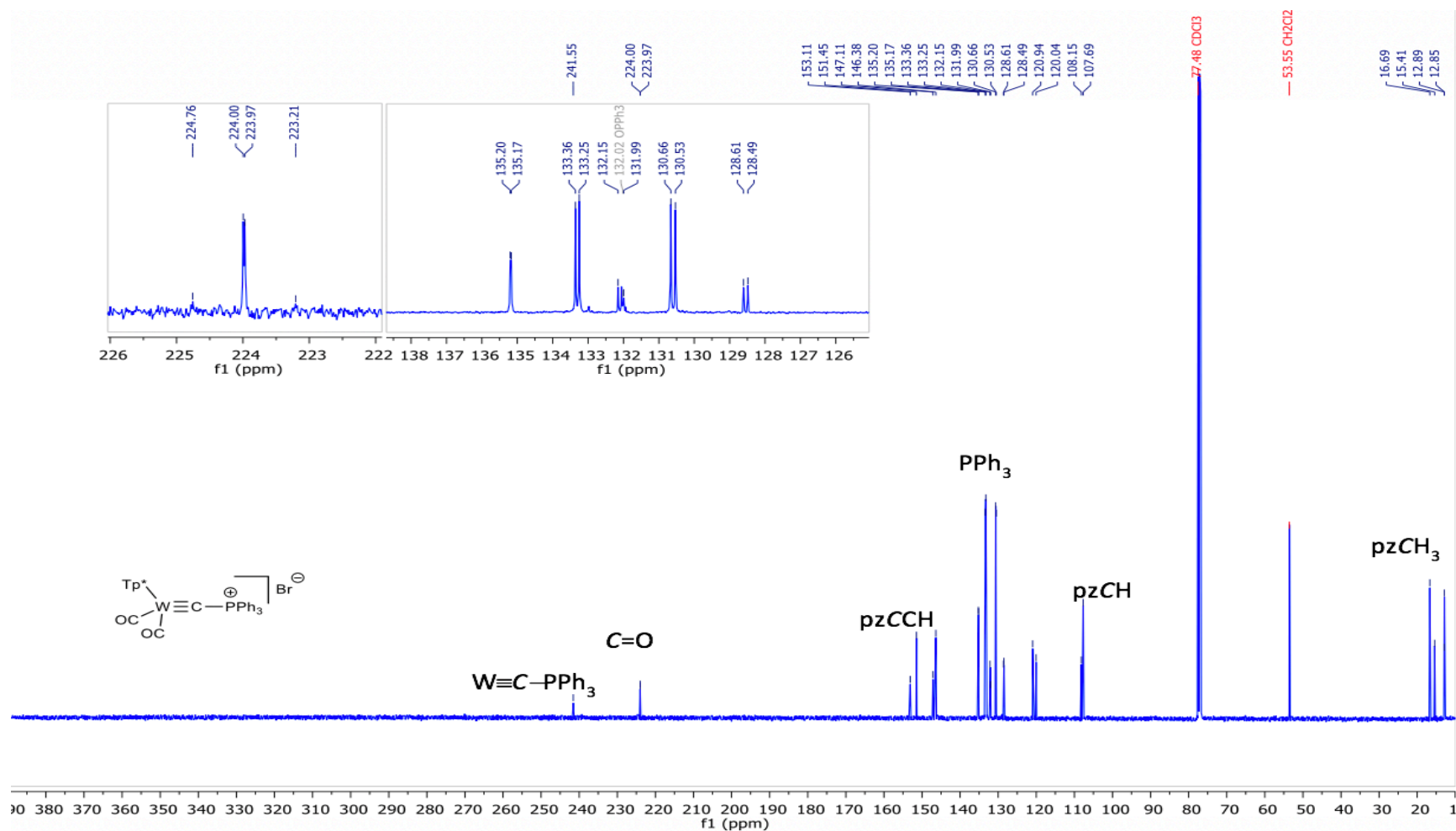


Figure S65. ^{13}C NMR Spectrum of $[(\text{Tp}^*)\text{W}(\text{CO})_2(\mu\text{-C})\text{PPh}_3][\text{Br}]$ (100 MHz, CDCl_3 , 25 °C, δ):

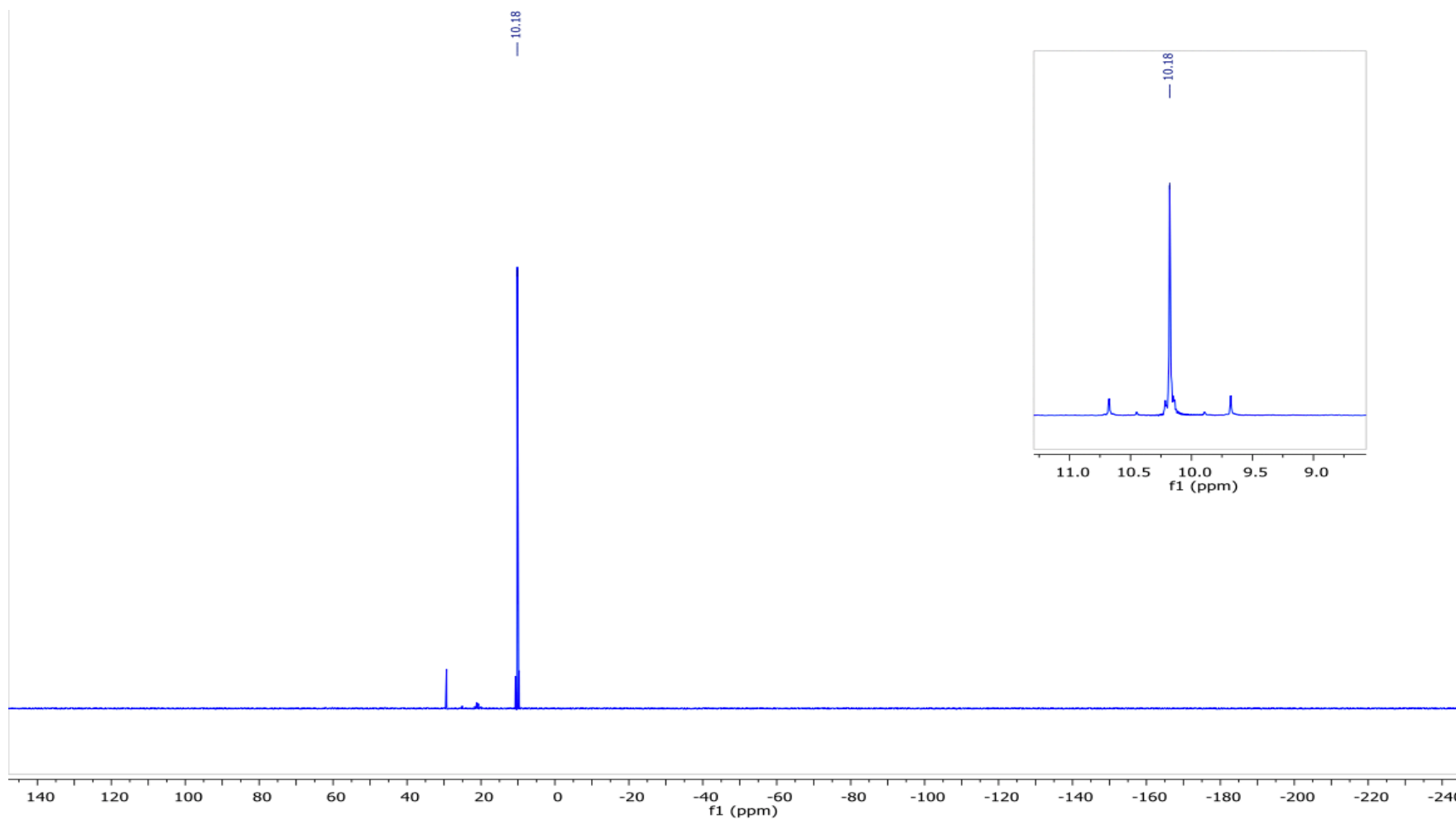


Figure S66. ^{31}P NMR Spectrum of $[(\text{Tp}^*)\text{W}(\text{CO})_2(\mu\text{-C})\text{-PPh}_3][\text{Br}]$ (162 MHz, CDCl_3 , 25 °C, δ):

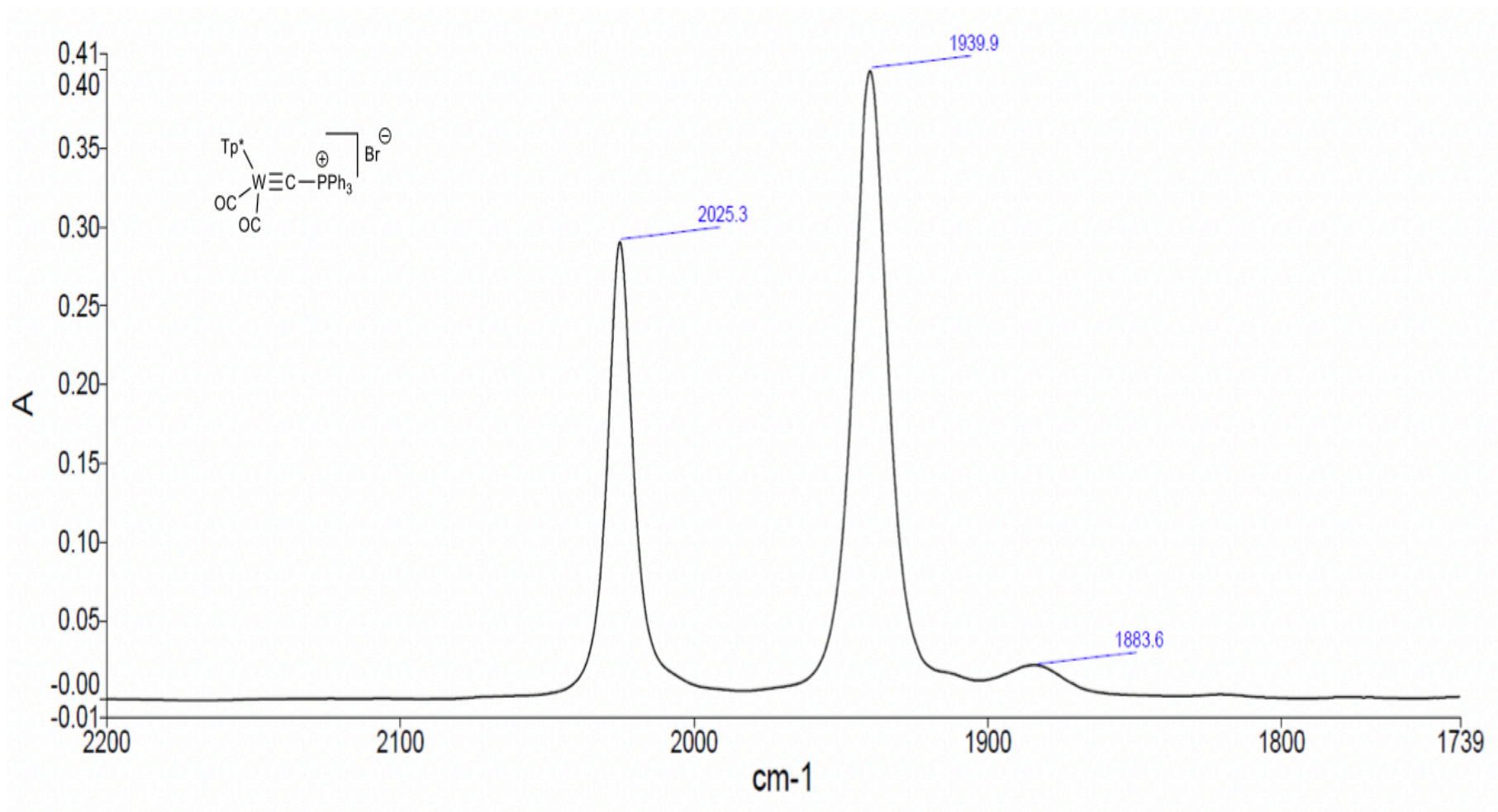


Figure S67. Infrared Spectrum of $[(\text{Tp}^*)\text{W}(\text{CO}_2)\equiv(\mu\text{-C})\text{-PtBr}(\text{PPh}_3)_2]$ (CaF_2 , CH_2Cl_2 , 25°C , ν):