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The Mechanism of the Hydroalkoxycarbonylation of Ethene and Alkene-Co Copolymerization Catalyzed by Pd(II)-Diphosphine Cations

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Experimental details

All manipulations were carried out under dry oxygen-free nitrogen atmosphere using Schlenk techniques. All solvents were carefully purified by appropriate procedures. CD_2Cl_2 was subjected to three freeze-pump-thaw cycles and stored over 4 A molecular sieves. Air sensitive compounds were stored under nitrogen at 243 K. $^{31}P\{^1H\}$,$^{13}C\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker AMX2-200 WB spectrometer at 193 K unless otherwise specified. ^{13}CO (99%) was used in experiments in which ^{13}C NMR data was recorded; for simplicity, CO is used to designate both natural abundance and enriched carbon monoxide. ^{13}CO was purchased from ISOTEK, ethene from BOC. All other chemicals were purchased from Aldrich. 1,3-bis(di-isobutylphosphino)propane (dibpp) was prepared by reaction of di-isobutylphosphine with 1,3-dibromopropane to give the double HBr salt which was subsequently neutralized with sodium hydroxide and distilled to give the diphosphine product.[1] The palladium-dimethyl complex [Pd(dibpp)$(CH_3)_2$] was synthesized as described in the literature.[2, 3] [Pd(dibpp)$(CH_3CN)_2$]$(OTf)_2$ was prepared following the method of Drent.[4]

X-Ray Crystallography. Crystallographic data for [{Pd(dibpp)(μ-OH)}$_2$]$(OTf)_2$ were recorded on a Bruker Smart Apex diffractometer using $Mo_{K\alpha}$-radiation (λ = 0.71073 Å) at T = 100 K. The structure was solved by Direct Methods and refined by full-matrix least squares against F^2 using all data (SHELXTL). The crystal was of rather poor quality and weakly diffracting. Thus, the data were truncated at $2\theta = 45°$ and only Pd, P and S atoms were refined anisotropically. H-atoms were fixed in calculated positions at parent atoms, including those of the hydroxide units. Disordered atom positions, incl. one triflate ion, three methyl groups and the central C-atom of one propylene unit, were split on two positions and refined using similar distance and similar U restraints. Crystal data: $C_{40}H_{86}F_6O_8P_4Pd_2S_2$, M = 1209.89, T = 100 K, P-1, a = 9.872(3), b = 12.504(3), c= 21.947(6) Å,α = 88.350(4), β = 89.165(4), γ = 83.170(5)°, V = 2688.5(12) Å^3, Z = 2, $\mu(MoK_\alpha)$ = 0.930, 6898 independent reflections (R_{int} = 0.068), $R1$ ($I > 2\sigma(I)$) = 0.094, $wR2$ (all data) = 0.246.

1. Synthesis of palladium monomethyl complexes

[Pd(dibpp)(CH_3)(OTf)] (1-OTf). 64 mg (0.14 mmol) [Pd(dibpp)(CH_3)$_2$] was dissolved in 2 mL CH_2Cl_2 in a 10 mm NMR tube and then cooled to 195 K. 7 μL (0.14 mmol) CF_3SO_3H (1 equivalent) was then added and the solution warmed to room temperature briefly until the $^{31}P\{^1H\}$ NMR spectrum indicated that the reaction had gone to completion. $^{31}P\{^1H\}$ NMR: δ 11.0 (d, ^2J(PP) = 41 Hz); -15.6 (d, ^2J(PP) = 41 Hz). ^1H NMR(CD_2Cl_2): δ 0.36 (d, ^3J(HP) = 7 Hz, Pd-CH_3).

[Pd(dibpp)(CH_3)(OTs)] (1-OTs). 1-OTs was synthesized in an analogous manner to **1-OTf** using 20 mg (0.043 mmol) [Pd(dibpp)(CH_3)$_2$] and 8 mg $CH_3C_6H_4SO_3H$. $^{31}P\{^1H\}$ NMR: δ 17.2 (d, ^2J(PP) = 42 Hz); -12.2 (d, ^2J(PP) = 42 Hz).

[Pd(dibpp)(CH_3)(TFA)] (1-TFA). 1-TFA was synthesized in an analogous manner to **1-OTf** using 38 mg (0.08 mmol) [Pd(dibpp)(CH_3)$_2$] and 6.5 μl of CF_3CO_2H. $^{31}P\{^1H\}$ NMR: δ 12.7 (d, ^2J(PP) = 41 Hz); -11.4 (d, ^2J(PP) = 41 Hz). ^1H NMR(CD_2Cl_2): δ 0.27 (d, ^3J(HP) = 7 Hz, Pd-CH_3).

[Pd(dibpp)(CH_3)(Cl)] (1-Cl). 1-Cl was synthesized by adding [Bu_4N]Cl (9 mg, 0.04 mmol, 1 equivalent) to **1-TFA** generated in situ as described above from 19 mg (0.04 mmol) [Pd(dibpp)(CH_3)$_2$] and 3.2 μl of CF_3CO_2H. $^{31}P\{^1H\}$ NMR: δ 11.4 (d, ^2J(PP) = 41 Hz); -12.9 (d, ^2J(PP) = 41 Hz).

[Pd(dibpp)(CH_3)(PPh_3)](TFA) (1-PPh_3). 1-PPh_3 was synthesized by adding Ph_3P (20.9 mg, 0.08 mmol, 1 equivalent) to **1-TFA** generated in situ as described above from 38 mg (0.08 mmol) [Pd(dibpp)(CH_3)$_2$] and 6.4 μl of CF_3CO_2H. $^{31}P\{^1H\}$ NMR: δ 32.0 (PPh_3, dd, $^2J_{trans}$(PP) = 356 Hz, $^2J_{cis}$(PP) = 34 Hz); -3.7 (dd, $^2J_{trans}$(PP) = 356 Hz, $^2J_{cis}$(PP) = 49 Hz); -14.8 (dd, $^2J_{cis}$(PP) = 49 Hz, $^2J_{cis}$(PP) = 34 Hz).

[Pd(dibpp)(CH_3)(CH_3CN)](OTf) ([1-CH_3CN](OTf)). 23 mg (0.049 mmol) [Pd(dibpp)(CH_3)$_2$] was dissolved in a mixture of 1.8 mL CH_2Cl_2 and 0.2 mL CH_3CN in a 10 mm NMR tube and then cooled to 195 K; 3.5 μL CF_3SO_3H was then added and the solution warmed to room temperature briefly until the $^{31}P\{^1H\}$ NMR spectrum indicated that the reaction had gone to completion. $^{31}P\{^1H\}$ NMR: δ

11.0 (d, ^2J(PP) = 41 Hz); -15.6 (d, ^2J(PP) = 41 Hz). ^{1}H NMR(CD_2Cl_2/CD_3CN): δ 0.34 (d, ^3J(HP) = 7 Hz, Pd-CH_3).

[Pd(dibpp)(CH_3)(CH_3CN)](OTs)([1-CH_3CN](OTs)). Compound **[1-CH_3CN](OTs)** was synthesized in the same manner as **[1-CH_3CN](OTf)** using 23 mg (0.049 mmol) [Pd(dibpp)(CH_3)$_2$] and 9 mg $CH_3C_6H_4SO_3H$. $^{31}P\{^1H\}$ NMR: δ 11.1 (d, ^2J(PP) = 42 Hz); -15.7 (d, ^2J(PP) = 42 Hz).

[Pd(dibpp)(CH_3)(CH_3CN)](TFA)([1-CH_3CN](TFA)). Compound **[1-CH_3CN](TFA)** was synthesized in the same manner as **[1-CH_3CN](OTf)** using 22 mg (0.047 mmol) [Pd(dibpp)(CH_3)$_2$] and 3.5 μL of CF_3CO_2H. $^{31}P\{^1H\}$ NMR: δ 10.8 (d, ^2J(PP) = 41 Hz); -15.6 (d, ^2J(PP) = 41 Hz).

[Pd(dibpp)(CH_3)(CH_3OH)](OTf) ([1-CH_3OH](OTf)). 27 mg (0.058mmol) [Pd(dibpp)(CH_3)$_2$] was dissolved in a mixture of 1.8 mL CH_2Cl_2 and 0.2 mL CH_3OH in a 10 mm NMR tube and then cooled to 195 K; 3.5 μL (1 equivalent) CF_3SO_3H was then added and the solution warmed to room temperature briefly until the $^{31}P\{^1H\}$ NMR spectrum indicated that the reaction had gone to completion. $^{31}P\{^1H\}$ NMR: δ 18.8 (d, ^2J(PP) = 41 Hz); -14.2 (d, ^2J(PP) = 41 Hz).

[Pd(dibpp)(CH_3)(CH_3OH)](OTs)([1-CH_3OH](OTs)). Compound **[1-CH_3OH](OTs)** was synthesized in the same manner as **[1-CH_3OH](OTf)** using 18 mg (0.038 mmol) [Pd(dibpp)(CH_3)$_2$] and 7.7 mg $CH_3C_6H_4SO_3H$. $^{31}P\{^1H\}$ NMR: δ 18.9 (d, ^2J(PP) = 42 Hz); -14.3 (d, ^2J(PP) = 42 Hz).

2. Propagation reactions in the "hydride" cycle

Comments on the reactions with CO and ethene The palladium monomethyl complexes prepared above were used as precursors to demonstrate the alternating CO/ethylene insertion (propagation) reactions in single or mixed solvents under the desired conditions. All experiments were carried out in 10 mm NMR tubes and using *ca* 2 mL of the specified solvent; gaseous reactants were bubbled through the solutions and the progress of the reaction was monitored by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy at 193 K unless otherwise stated.

Synthesis of [Pd(dibpp)(CH_3)(CO)]X (1-CO, X = OTf, OTs TFA). Carbon monoxide was bubbled briefly (a few seconds) through solutions of **1-OTf** (84.5 mg, 0.14 mmol)**, 1-OTs** (26.9 mg,

0.04 mmol)**,** and **1-TFA** (45.4 mg, 0.08 mmol) in dichloromethane at 195 K; the $^{31}P\{^{1}H\}$ NMR spectra revealed the formation, *in situ*, of [**1-CO**](**OTf**), [**1-CO**](**OTs)**, [**1-CO**](**TFA**) respectively.

[Pd(dibpp)(CH_3)(CO)](OTf) ([1-CO](OTf)). $^{31}P\{^{1}H\}$ NMR: δ -0.5 (d, ^{2}J(PP) = 47 Hz); -12.3 (d, ^{2}J(PP) = 47 Hz); $^{13}C\{^{1}H\}$ NMR: δ 181.6 (dd, $^{2}J(P_{trans}\underline{C}O)$ = 114 Hz, $^{2}J(P_{cis}\underline{C}O)$ = 16 Hz).

[Pd(dibpp)(CH_3)(CO)](OTs) ([1-CO](OTs)). $^{31}P\{^{1}H\}$ NMR: δ -0.6 (d, ^{2}J(PP) = 47 Hz); -13.4 (d, ^{2}J(PP) = 47 Hz); $^{13}C\{^{1}H\}$ NMR: δ 181.7 (dd, $^{2}J(P_{trans}\underline{C}O)$ = 114 Hz, $^{2}J(P_{cis}\underline{C}O)$ = 16 Hz).

[Pd(dibpp)(CH_3)(CO)](TFA) ([1-CO](TFA)). $^{31}P\{^{1}H\}$ NMR: δ -0.8 (d, ^{2}J(PP) = 48 Hz); -13.5 (d, ^{2}J(PP) = 48 Hz); $^{13}C\{^{1}H\}$ NMR: δ 181.6 (dd, $^{2}J(P_{trans}\underline{C}O)$ = 114 Hz, $^{2}J(P_{cis}\underline{C}O)$ = 16 Hz).

Synthesis of [Pd(dibpp)($C(O)CH_3$)(CH_3OH)](OTf) ([2-CH_3OH](OTf)). CO was bubbled thoroughly (a few minutes) through a solution of [**1-CH_3OH**](**OTf**) (86.8 mg, 0.14 mmol) in a mixture of dichloromethane and methanol (9:1) at 195 K, the solution was then warmed to 243 K when the $^{31}P\{^{1}H\}$ NMR revealed the formation, *in situ*, of [**2-CO**](**OTf**) and [**2-CH_3OH**](**OTf**).

[Pd(dibpp)($C(O)CH_3$)(CO)](OTf) ([2-CO](OTf)). $^{31}P\{^{1}H\}$ NMR: δ -6.7 (d, ^{2}J(PP) = 73 Hz); -19.2 (d, ^{2}J(PP) = 73 Hz); $^{13}C\{^{1}H\}$ NMR: δ 235.2 (dd, $^{2}J(P_{trans}\underline{C}(O)CH_3)$ = 88 Hz, $^{2}J(P_{cis}\underline{C}(O)CH_3)$ = 5 Hz); 176.9 (dd, $^{2}J(P_{trans}\underline{C}O)$ = 80 Hz, $^{2}J(P_{cis}\underline{C}O)$ = 20 Hz).

[Pd(dibpp)($C(O)CH_3$)(CH_3OH)](OTf) ([2-CH_3OH](OTf)). $^{31}P\{^{1}H\}$ NMR: δ 13.4 (d, ^{2}J(PP) = 66 Hz); -19.1 (d, ^{2}J(PP) = 66 Hz); $^{13}C\{^{1}H\}$ NMR: δ 243.0 (dd, $^{2}J(P_{trans}\underline{C}(O)CH_3)$ = 116 Hz, $^{2}J(P_{cis}\underline{C}(O)CH_3)$ = 12 Hz).

Synthesis of [Pd(dibpp)($C(O)CH_3$)(TFA)] (2-TFA). CO was bubbled thoroughly (a few minutes) through a solution of **1-TFA** (45.4 mg, 0.08 mmol) in dichloromethane at 195 K. The solution was warmed to 243 K for 1 hour when the $^{31}P\{^{1}H\}$ NMR revealed the quantitative formation of **2-TFA**. $^{31}P\{^{1}H\}$ NMR: δ 10.0 (d, ^{2}J(PP) = 67 Hz); -15.8 (d, ^{2}J(PP) = 67 Hz); $^{13}C\{^{1}H\}$ NMR: δ 247.8 (dd, $^{2}J(P_{trans}\underline{C}(O)CH_3)$ = 125 Hz, $^{2}J(P_{cis}\underline{C}(O)CH_3)$ = 10 Hz). ^{1}H NMR(CD_2Cl_2): δ 2.25 (d, ^{2}J(CH) = 4 Hz, Pd-$^{13}C(O)CH_3$).

Synthesis of [Pd(dibpp)(C(O)CH$_3$)(OTs)] (2-OTs). CO was bubbled thoroughly (a few minutes) through a solution of **1-OTs** (26.9 mg, 0.04 mmol) in dichloromethane at 195 K. The solution was warmed to 243 K for 1 hour, then purged with nitrogen at 195 K for 10 minutes when the $^{31}P\{^1H\}$ NMR revealed the quantitative formation of **2-OTs**. $^{31}P\{^1H\}$ NMR: δ 12.5 (d, ^2J(PP) = 70 Hz); -16.6 (d, ^2J(PP) = 70 Hz); $^{13}C\{^1H\}$ NMR: δ 244.6 (dd, $^2J(P_{trans}\underline{C}(O)CH_3)$ = 122 Hz, $^2J(P_{cis}\underline{C}(O)CH_3)$ = 12 Hz).

Synthesis of [Pd(dibpp)(C(O)CH$_3$)(CH$_3$CN)]X (2-CH$_3$CN, X = OTf, OTs, TFA). Carbon monoxide was bubbled thoroughly (a few minutes) through a solution of **[1-CH$_3$CN](X)** (**[1-CH$_3$CN](OTf)** (31.6 mg, 0.049 mmol); **[1-CH$_3$CN](OTs)** (32.6 mg, 0.049 mmol); or **[1-CH$_3$CN](TFA)** (28.6 mg, 0.047 mmol) in a mixture of dichloromethane and acetonitrile (9:1) at 195 K, the solution was warmed to 243 K for 1 hour when the $^{31}P\{^1H\}$ NMR revealed the quantitative formation of **[2-CH$_3$CN](X)**.

[Pd(dibpp)(C(O)CH$_3$)(CH$_3$CN)](OTf) ([2-CH$_3$CN](OTf)). $^{31}P\{^1H\}$ NMR: δ 5.4 (d, ^2J(PP) = 70 Hz); -19.6 (d, ^2J(PP) = 70 Hz); $^{13}C\{^1H\}$ NMR: δ 242.6 (dd, $^2J(P_{trans}\underline{C}(O)CH_3)$ = 112 Hz, $^2J(P_{cis}\underline{C}(O)CH_3)$ = 10 Hz). ^1H NMR(CD_2Cl_2/CD_3CN): δ 2.42 (d, ^2J(CH) = 4 Hz, Pd-$^{13}C(O)CH_3$).

[Pd(dibpp)(C(O)CH$_3$)(CH$_3$CN)](TFA) ([2-CH$_3$CN](TFA)). $^{31}P\{^1H\}$ NMR: δ 4.9 (d, ^2J(PP) = 70 Hz); -19.7 (d, ^2J(PP) = 70 Hz); $^{13}C\{^1H\}$ NMR: δ 242.8(dd, $^2J(P_{trans}\underline{C}(O)CH_3)$ = 112 Hz, $^2J(P_{cis}\underline{C}(O)CH_3)$ = 16 Hz).

[Pd(dibpp)(C(O)CH$_3$)(CH$_3$CN)](OTs) ([2-CH$_3$CN](OTs)). $^{31}P\{^1H\}$ NMR: δ 4.9 (d, ^2J(PP) = 70 Hz); -19.7 (d, ^2J(PP) = 70 Hz); $^{13}C\{^1H\}$ NMR: δ 242.6 (dd, $^2J(P_{trans}\underline{C}(O)CH_3)$ = 113 Hz, $^2J(P_{cis}\underline{C}(O)CH_3)$ = 10 Hz).

Synthesis of [Pd(dibpp)(C(O)CH$_3$)(CO)]X (2-CO, X = OTf; OTs). Excess carbon monoxide was bubbled thoroughly (a few minutes) through a solution of **1-OTf** (84.5 mg, 0.14 mmol) or **1-OTs** (26.9 mg, 0.04 mmol) in dichloromethane at 195 K. The solution was then warmed to 243 K for 1 hour when the $^{31}P\{^1H\}$ NMR spectra revealed the quantitative formation, *in situ*, of [**2-CO**](**OTf**) and [**2-CO**](**OTs**) respectively.

[Pd(dibpp)(C(O)CH$_3$)(CO)](OTf) ([2-CO](OTf)). $^{31}P\{^1H\}$ NMR: δ -6.7 (d, ^2J(PP) = 73 Hz); -19.2 (d, ^2J(PP) = 73 Hz); $^{13}C\{^1H\}$ NMR: δ 235.2 (dd, $^2J(P_{trans}\underline{C}(O)CH_3)$ = 88 Hz, $^2J(P_{cis}\underline{C}(O)CH_3)$ = 5 Hz); 176.9 (dd, $^2J(P_{trans}\underline{C}O)$ = 80 Hz, $^2J(P_{cis}\underline{C}O)$ = 20 Hz).

[Pd(dibpp)(C(O)CH$_3$)(CO)](OTs) ([2-CO](OTs)). $^{31}P\{^1H\}$ NMR: δ -6.8 (d, ^2J(PP) = 73 Hz); -18.6 (d, ^2J(PP) = 73 Hz); $^{13}C\{^1H\}$ NMR: δ 235.5 (dd, $^2J(P_{trans}\underline{C}(O)CH_3)$ = 88 Hz, $^2J(P_{cis}\underline{C}(O)CH_3)$ = 5 Hz); 176.9 (dd, $^2J(P_{trans}\underline{C}O)$ = 80 Hz, $^2J(P_{cis}\underline{C}O)$ = 20 Hz).

Synthesis of [Pd(dibpp)(C(O)CH$_3$)(CO)][TFA] ([2-CO][TFA]). Excess carbon monoxide was bubbled thoroughly (a few minutes) through a solution of **1-TFA** (45.4 mg, 0.08 mmol) in a mixture of dichloromethane and methanol (9:1) at 195 K. The solution was then warmed to 243 K for 1 hour when the $^{31}P\{^1H\}$ NMR spectra revealed the formation, *in situ*, of [**2-CO**][**TFA**]. $^{31}P\{^1H\}$ NMR: δ -6.1 (d, ^2J(PP) = 73 Hz); -18.5 (d, ^2J(PP) = 73 Hz); $^{13}C\{^1H\}$ NMR: δ 234.7 (dd, $^2J(P_{trans}\underline{C}(O)CH_3)$ = 88 Hz, $^2J(P_{cis}\underline{C}(O)CH_3)$ = 6 Hz); 176.9 (dd, $^2J(P_{trans}\underline{C}O)$ = 79 Hz, $^2J(P_{cis}\underline{C}O)$ = 20 Hz).

[Pd(dibpp)(CH$_2$CH$_2$C(O)CH$_3$)](OTf) (3). Ethene was bubbled at 195 K through a solution of [**2-CH$_3$CN**](**OTf**) prepared as described above, and the progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR. **3** started to form after 15 minutes at 195 K, the reaction went to completion after 10 hrs at 243 K. $^{31}P\{^1H\}$ NMR: δ 12.7(d, ^2J(PP) = 46 Hz); -13.5 (d, ^2J(PP) = 46 Hz); $^{13}C\{^1H\}$NMR: δ 236.0 (d, $^2J(P,CH_2CH_2\underline{C}(O)CH_3)$ = 10 Hz).

[Pd(dibpp)(C(O)CH$_2$CH$_2$C(O)CH$_3$)(CH$_3$CN)](OTf) (4-CH$_3$CN). Exposure of a solution containing **3**, prepared as above, to CO at 243 K resulted in an equilibrium mixture of **3** and **4-CH$_3$CN**. $^{31}P\{^1H\}$ NMR: δ 3.9 (d, ^2J(PP) = 69 Hz); -19.1 (d, ^2J(PP) = 69 Hz); $^{13}C\{^1H\}$NMR: δ 240.3 (dd, $^2J(P_{trans},\underline{C}(O)CH_2CH_2C(O)CH_3)$ = 115 Hz, $^2J(P_{cis},\underline{C}(O)CH_2CH_2C(O)CH_3)$ = 10 Hz), 208.0 (s, $C(O)CH_2CH_2\underline{C}(O)CH_3$).

[Pd(dibpp)(C(O)CH$_2$CH$_2$C(O)CH$_3$)(CO)](OTf) (4-CO). On exposure of a solution containing **3** prepared as above to excess CO at 243 K, **3** is partially converted to a mixture of **4-CH$_3$CN** and **4-CO**. $^{31}P\{^1H\}$ NMR: δ -7.3 (d, ^2J(PP) = 72 Hz; -18.9 (d, ^2J(PP) = 72 Hz); $^{13}C\{^1H\}$NMR: δ 235.6 (dd,

$^2J(P_{trans},\underline{C}(O)CH_2CH_2C(O)CH_3)$ = 90 Hz, $^2J(P_{cis},\underline{C}(O)CH_2CH_2C(O)CH_3)$ = 4 Hz); 177.8 (dd, $^2J(P_{trans}\underline{C}O)$ = 80 Hz, $^2J(P_{cis}\underline{C}O)$ = 20 Hz); 207.7 (s, $C(O)CH_2CH_2\underline{C}(O)CH_3$).

[Pd(dibpp)CH$_2$CH$_2$(C(O)CH$_2$CH$_2$C(O)CH$_3$)](OTf) (5). 4 prepared above was converted to **5** on bubbling ethene for 5 minutes through the solution at 243 K. Some **3**, formed by deinsertion of CO from **4**, was also observed. $^{31}P\{^1H\}$ NMR: δ 14.7 (d, ^2J(PP) = 47 Hz); -13.6 (d, ^2J(PP) = 47 Hz); $^{13}C\{^1H\}$NMR: δ237.4 (d, $^2J(P,CH_2CH_2(\underline{C}(O)CH_2CH_2C(O)CH_3)$ = 10 Hz), 206.4 (s).

3. Preparation of palladium carbomethoxy complexes

[Pd(dibpp)(OCH$_3$)(CH$_3$CN)](OTf) (6). [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ (42 mg, 0.05 mmol) was dissolved in a CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN (9:1:(5 equivalent)) mixture and cooled to 193 K, 1 equivalent Et$_3$N (6.5 μL) was added to give a pale yellow solution, **6** and **7** were detected as major products by $^{31}P\{^1H\}$ NMR at 193 K. $^{31}P\{^1H\}$ NMR: δ 3.7 (d, ^2J(PP) = 28 Hz); 15.0 (d, ^2J(PP) = 28 Hz).

[Pd(dibpp)(Et$_3$N)(CH$_3$CN)](OTf) (7). [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ (42 mg, 0.05 mmol) was dissolved in a CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN (9:1:5) mixture cooled to 193 K, 1 equivalent Et$_3$N (6.5 μL) was then added to give a pale yellow solution, **6** and **7** were detected as major products by $^{31}P\{^1H\}$ NMR at 193 K. $^{31}P\{^1H\}$ NMR: δ 8.0 (d, ^2J(PP) = 35 Hz); 11.7 (d, ^2J(PP) = 35 Hz).

[Pd(dibpp)(C(O)OCH$_3$)(CH$_3$CN)](OTf) (8-CH$_3$CN). [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ (42 mg, 0.05 mmol) was dissolved in a CH$_2$Cl$_2$/CH$_3$OH/CH$_3$CN (9:1:trace) mixture saturated with CO at 193 K, 1 equivalent Et$_3$N (6.5 μL) was then added to give a clear yellow solution. Further CO was then bubbled through the solution to drive the reaction to completion in *ca.* 10 minutes. The solvents were evaporated quickly and the red oily residue was extracted into 2 mL CH$_2$Cl$_2$ to give a yellow solution. $^{31}P\{^1H\}$ NMR: δ 8.3 (d, ^2J(PP) = 47 Hz); -15.5 (d, ^2J(PP) = 47 Hz); $^{13}C\{^1H\}$NMR: δ 191.7 (dd, $^2J(P_{trans}\underline{C}(O)OCH_3)$ = 167 Hz, $^2J(P_{cis}\underline{C}(O)OCH_3)$ = 9 Hz).

[Pd(dibpp)(C(O)OCH$_3$)(CO)](OTf) (8-CO). 8-CO was synthesized by an analogous procedure to **8-CH$_3$CN** using a 1:1 mixture of CH$_2$Cl$_2$ and CH$_3$OH as solvent. When excess CO was passed through

the solution, **8-CO** was the only product obtained. $^{31}P\{^{1}H\}$ NMR: δ -1.4 (d, ^{2}J(PP) = 49 Hz); -14.1 (d, ^{2}J(PP) = 49 Hz); $^{13}C\{^{1}H\}$NMR: δ 185.5 (dd, $^{2}J(P_{trans}\text{-}\underline{C}(O)OCH_3)$ = 141 Hz, $^{2}J(P_{cis}\text{-}\underline{C}(O)OCH_3)$ = 9 Hz); δ 177.3 (dd, $^{2}J(P_{trans}\underline{C}O)$ = 98 Hz, $^{2}J(P_{cis}\underline{C}O)$ = 12 Hz).

[Pd(dppp)(C(O)OCH$_3$)(CH$_3$CN)](OTf) (9). 9 was synthesized in an analogous manner to **8-CH$_3$CN** using 63 mg (0.07mmol) $[Pd(dppp)(CH_3CN)_2](OTf)_2$ and 10 μL Et_3N using methanol as solvent. $^{31}P\{^{1}H\}$ NMR: δ 11.8 (d, ^{2}J(PP) = 57 Hz); -3.8 (d, ^{2}J(PP) = 57 Hz); $^{13}C\{^{1}H\}$NMR: δ 190.3 (dd, $^{2}J(P_{trans}\underline{C}(O)OCH_3)$ = 174 Hz, $^{2}J(P_{cis}\underline{C}(O)OCH_3)$ = 18 Hz).

[Pd(dibpp)(^{13}C(O)OCH$_3$)$_2$] (10). 10 was synthesized in a similar manner to **8** but using 2 equivalents Et_3N. $^{31}P\{^{1}H\}$ and ^{13}C NMR spectroscopy shows a AA′XX′ pattern. The chemical shifts and coupling constants were obtained from simulation of the experimental spectrum using gNMR 4.1. $^{31}P\{^{1}H\}$ NMR: δ -8.2; $^{13}C\{^{1}H\}$NMR: δ 203.0; (^{2}J(PP) = 45.2 Hz, $^{2}J(P_{trans}C)$ = 151.7 Hz, $^{2}J(P_{cis}C)$ = 12.3 Hz, ^{2}J(CC) = 6.2 Hz).

4. Investigation of the mechanism of the formation of 8

[Pd(dibpp)(C(O)O^{13}CH$_3$)(CH$_3$CN)](OTf)(8-CH$_3$CN). $[Pd(dibpp)(CH_3CN)_2](OTf)_2$ (62 mg, 0.076 mmol) was dissolved in a mixture of 1.8 mL CH_2Cl_2 and 20 μL CH_3CN (5 equivalents), the mixture was saturated with ^{13}CO at 193 K, 0.1 mL $^{13}CH_3OH$ and 10.5 μL Et_3N (1 equivalent) were then added. The solution was kept at 243 K for 3 hours to give a clear yellow solution. $^{31}P\{^{1}H\}$ NMR: δ 8.3 (d, ^{2}J(PP) = 47 Hz); -15.5 (d, ^{2}J(PP) = 47 Hz); $^{13}C\{^{1}H\}$NMR: δ 191.7 (dd, $^{2}J(P_{trans}\underline{C}(O)OCH_3)$ = 167 Hz, $^{2}J(P_{cis}\underline{C}(O)OCH_3)$ = 9 Hz, $^{2}J(P_{cis}\underline{C}(O)O\underline{C}H_3)$ = 4 Hz) (Figure S9).

[Pd(dibpp)(C(O)O^{13}CH$_3$)(PPh$_3$)](OTf)(8-PPh$_3$). $[Pd(dibpp)(CH_3CN)_2](OTf)_2$ (48 mg, 0.059 mmol) was dissolved in a mixture of 1.5 mL CH_2Cl_2, 0.1 mL $^{13}CH_3OH$ and 15 μL CH_3CN (5 equivalents), the mixture was saturated with ^{13}CO at 193 K, 8 μL Et_3N (1 equivalent) was then added and the solution was kept at 243 K for 4 hours. Then the solution was purged with nitrogen for 5 minutes and 15 mg Ph_3P (1 equivalent to Pd) was added as a solid, A clear yellow solution **8-PPh$_3$** was

formed immediately as indicated by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies. $^{31}P\{^1H\}$ NMR: δ 13.3 (PPh_3, dd, $^2J_{trans}(\underline{P}Ph_3P)$ = 298 Hz, $^2J_{cis}(\underline{P}Ph_3P)$ = 36 Hz); -4.3 (dibpp, dd, $^2J_{trans}(\underline{P}Ph_3P)$ = 298 Hz, $^2J_{cis}(PP)$ = 50 Hz); -17.8 (dibpp, dd, $^2J_{cis}(PP)$ = 50 Hz, $^2J_{cis}(\underline{P}Ph_3P)$ = 36 Hz); $^{13}C\{^1H\}$NMR: δ 192.8 (ddd, $^2J(P_{trans}\underline{C}(O)OCH_3)$ = 153 Hz, $^2J(P_{cis}\underline{C}(O)OCH_3)$ = 5 Hz, $^2J(\underline{P}Ph_{3cis}\underline{C}(O)OCH_3)$ = 3 Hz).

Scrambling of ^{12}CO with ^{13}C-enriched 8-CH_3CN $[Pd(dibpp)(CH_3CN)_2](OTf)_2$ (25 mg, 0.03 mmol) was dissolved in a mixture of 1.5 mL CH_2Cl_2, 0.2 mL CH_3OH and 70 μL CH_3CN (50 equivalents), and the mixture saturated with ^{13}CO at 193 K, 4.1 μL Et_3N (1 equivalent) was then added and the solution kept at 243 K for 4 hours until NMR spectroscopy confirmed the formation of **8-CH_3CN**. The solution was then purged thoroughly with nitrogen to remove residual ^{13}CO, ^{12}CO was bubbled through the solution for 5 minutes at 193 K, the tube capped, and the reaction monitored by $^{31}P\{^1H\}$ NMR at time intervals of 1, 2.5 and 60 hours at 243 K.

Scrambling of ^{12}CO with 8-PPh_3 $[Pd(dibpp)(CH_3CN)_2](OTf)_2$ (20 mg, 0.024 mmol) was dissolved in a mixture of 1.5 mL CH_2Cl_2, 0.2 mL CH_3OH and 7 μL CH_3CN (5 equivalents), and the mixture saturated with ^{13}CO at 193 K, 3.8 μL Et_3N (1 equivalent) was then added and the solution was kept at 243 K for 4 hours until NMR spectroscopy revealed that the formation of **8-CH_3CN** had occurred. 7 mg PPh_3 was then added to convert **8-CH_3CN** to **8-PPh_3.** The solution was then purged with nitrogen thoroughly to remove residual ^{13}CO, ^{12}CO was bubbled through the solution for 5 minutes at 193 K, the tube was capped and the reaction monitored by $^{31}P\{^1H\}$ NMR at time intervals of 1, 2.5 and 60 hours at 243 K.

5. Propagation reactions in the "carbomethoxy" cycle

$[\overline{Pd(dibpp)(CH_2CH_2C(O)OCH_3)}](OTf)$ (11). Ethene was passed through a solution of **3** prepared as above, at 195 K for 2 minutes, and the solution then slowly warmed to 243 K. The $^{31}P\{^1H\}$ NMR spectroscopy revealed that **11** was formed quantitatively after 1.5 hrs at 243 K. $^{31}P\{^1H\}$ NMR: δ

13.3(d, ^2J(PP) = 46 Hz); -12.0 (d, ^2J(PP) = 46 Hz); $^{13}C\{^1H\}$NMR: δ 193.3 (d, ^2J(P,$CH_2CH_2\underline{C}$(O)OCH_3) = 10 Hz).

[Pd(dppp)($CH_2CH_2C(O)OCH_3$)](OTf) (12). **12** was synthesized from **9** in an analogous manner to **11** but using pure methanol as solvent. $^{31}P\{^1H\}$ NMR: δ 29.4 (d, ^2J(PP) = 57 Hz); -3.9 (d, ^2J(PP) = 57 Hz); $^{13}C\{^1H\}$NMR: δ 192.4 (d, ^2J(P,$CH_2CH_2\underline{C}$(O)OCH_3) = 12 Hz).

[Pd(dibpp)($CH_2CH_2C(O)OCH_3$)(CH_3CN)](OTf) (13). 0.05 mL CH_3CN was added to the solution of **11** prepared above to give **13**. $^{31}P\{^1H\}$ NMR: δ 12.7 (d, ^2J (PP) = 46 Hz); -12.6 (d, ^2J(PP) = 46 Hz); $^{13}C\{^1H\}$NMR: δ 179.0 (dd, ^4J($P_{trans}CH_2CH_2\underline{C}(O)OCH_3$) = 4 Hz, ^4J($P_{cis}CH_2CH_2\underline{C}(O)OCH_3$) = 2 Hz).

[Pd(dibpp)(C(O)$CH_2CH_2C(O)OCH_3$)(CH_3CN)](OTf) (14-CH_3CN) and [Pd(dibpp)(C(O)$CH_2CH_2C(O)OCH_3$)(CH_3CN)](OTf) (14-CO). On bubbling CO through a CH_2Cl_2 solution of **11** prepared as described above, a mixture of **14-CH_3CN** and **14-CO** was formed as revealed by NMR spectroscopy. **14-CH_3CN**: $^{31}P\{^1H\}$ NMR: δ 4.1 (d, ^2J(PP) = 68 Hz) -18.6 (d, ^2J(PP) = 68 Hz); $^{13}C\{^1H\}$ NMR: δ 241.5 (dd, ^2J($P_{trans}\underline{C}(O)(C_2H_4)C(O)OCH_3$) = 116 Hz, ^2J($P_{cis}\underline{C}(O)(C_2H_4)C(O)OCH_3$) = 9 Hz); 173.0 (s, C(O)(C_2H_4)$\underline{C}$(O)OCH_3); **14-CO**: $^{31}P\{^1H\}$ NMR: δ -7.1 (d, ^2J(PP) = 71 Hz), -18.6 (d, ^2J(PP) = 71 Hz); $^{13}C\{^1H\}$NMR: δ 234.9 (dd, ^2J($P_{trans}\underline{C}(O)(C_2H_4)C(O)OCH_3$) = 91 Hz, ^2J($P_{cis}\underline{C}(O)(C_2H_4)C(O)OCH_3$) = 5 Hz); δ 176.7 (dd, ^2J($P_{trans}CO$) = 81 Hz, ^2J($P_{cis}CO$) = 20 Hz), 172.7 (s, C(O)(C_2H_4)$\underline{C}$(O)OCH_3).

[Pd(dibpp)CH_2CH_2(C(O)$CH_2CH_2C(O)OCH_3$)](OTf) (15). Ethene was bubbled through a solution of **14-CH_3CN**, prepared as above, for a few minutes. After 1 hr at 243 K, **15** was detected as the major species. $^{31}P\{^1H\}$ NMR: δ 13.2 (d, ^2J(PP) = 46 Hz), –13.7 (d, ^2J(PP) = 46 Hz); $^{13}C\{^1H\}$ NMR: δ 237.5 (d, ^2J(P, $CH_2CH_2\underline{C}$(O) $CH_2CH_2C(O)OCH_3$) = 10 Hz); 174.0 (s, $CH_2CH_2C(O)(C_2H_4)\underline{C}(O)OCH_3$).

6. Termination of the "hydride" cycle by methanolysis of palladium-acyls

Methanolysis of [Pd(dibpp)(C(O)CH_3)(CH_3CN)]X (2-CH_3CN, X = OTf, TFA, OTs). 0.2 mL CH_3OH was added to a solution of **2-CH_3CN** in a mixture of CH_2Cl_2 and CH_3CN (9:1) at 195 K, the

solution was then warmed to 243 K and the reactions followed by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR. No methyl acetate or any other organic product was observed by $^{13}C\{^1H\}$ NMR after 20 hours at 243 K. On warming the solutions to room temperature, **1-CH_3CN** was detected as the only new species by $^{31}P\{^1H\}$ NMR indicating that decarbonylation reactions dominate.

Methanolysis of [Pd(dibpp)(C(O)CH_3)(TFA)] (2-TFA). 0.2 mL CH_3OH was added to a CH_2Cl_2 solution of **2-TFA**, prepared as above, at 195 K, and the mixture allowed to warm up to 243 K. Progress of the reaction was followed by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR and progressive formation of methyl acetate was observed by $^{13}C\{^1H\}$ NMR over a period of tens of minutes.

Methanolysis of [Pd(dibpp)(C(O)CH_3)(OTs)] (2-OTs). 0.2 mL CH_3OH was added to a CH_2Cl_2 solution of **2-OTs**, prepared as above, at 195 K, and the reaction mixture warmed to 243 K. The reactions were followed by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR, [**2-CH_3OH**](**OTs**) was detected as an intermediate and progressive formation of methyl acetate was observed by $^{13}C\{^1H\}$ NMR over a period of tens of minutes.

Methanolysis of [Pd(dibpp)(C(O)CH_3)(CO)]X (2-CO, X = TFA, OTs). 0.2 mL CH_3OH was added to a CH_2Cl_2 solution of [**2-CO**](**OTs**) or [**2-CO**][**TFA**] , prepared as above, at 195 K, and the solutions were warmed to 243 K. The reactions were followed by $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR and progressive formation of methyl acetate was observed by $^{13}C\{^1H\}$ NMR over a period of tens of minutes.

Methanolysis of [Pd(dibpp)(C(O)CH_3)(CO)](OTf) ([2-CO](OTf)). 0.2 mL CH_3OH was added to a CH_2Cl_2 solution of [**2-CO**](**OTf**) , prepared as above, at 195 K, and the solution warmed to 243 K. [Pd(dibpp)C(O)CH_3(CH_3OH)](**OTf**) ([**2-CH_3OH**](**OTf**)) was detected as an intermediate and its decay was followed by $^{31}P\{^1H\}$ NMR. (Figure S13) Progressive formation of methyl acetate was observed by $^{13}C\{^1H\}$ NMR over a period of tens of minutes. The organometallic product of the methanolysis is presumably the Pd-hydride $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)(dibpp)_2]^{2+}$ by analogy with Bianchini's reports.[5] However, the major organometallic species isolated after the methanolysis reaction is $[\{Pd(dibpp)(\mu\text{-}OH)\}_2]OTf_2$. An X-ray crystal structure determination showed that the crystals contain the dicationic complex $[\{Pd(dibpp)(\mu\text{-}OH)\}_2]^{2+}$ in which the two Pd(II) centres are bridged by two hydroxide ions.

Coordination to the bidentate diphosphine ligands completes the square planar environment of the Pd centres. The Pd-O distances within the planar four-membered Pd_2O_2 ring are on average 2.10 Å and thus similar to those of related complexes $[\{Pd(L\text{-}L)(\mu\text{-}OH)\}_2]^{2+}$ containing diphosphine ligands.[6-8] There are two triflate ions for every dicationic complex in the crystal structure. Both interact *via* hydrogen bonds with the hydroxide ions of the Pd complex (Figure S15). $[\{Pd(dibpp)(\mu\text{-}OH)\}_2]OTf_2$ is presumably formed *via* a decomposition pathway involving adventitious water. Other bond lengths and interbond angles mirror those reported by Bianchini for similar μ-OH species.

7. Termination of the "hydride" cycle by methanolysis of chelating palladium-alkyls Chain crossover to the "carboalkoxy" cycle

Methanolysis of 3 and 5. 0.2 mL CH_3OH was added to the mixture of palladium complexes, **3** and **5** prepared above at 243 K. Methanolysis occurred on the timescale of hours at room temperature, and was monitored by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR. After several hours, an additional resonance at 209.0 ppm was observed in the $^{13}C\{^1H\}$ NMR spectrum (Figure S17c), together with an increase in intensity of the resonance at 211.8 ppm. These resonances can be attributed to heptan-2,5-dione, the diketone product of methanolysis of the 3rd generation β-chelate **5**. The remaining resonances in the $^{13}C\{^1H\}$ NMR spectrum may be due to CO/ethene multiple insertion products which are unavoidable even though the solution was purged thoroughly with nitrogen at low temperatures in an effort to remove residual CO and/or ethene. No deposition of metallic palladium was observed after 3 days at room temperature. Butan-2-one and heptan-2, 5-dione were detected as the principal organic products of the methanolysis. (Figure S16, S17)

After bubbling CO through this solution, **8** and some unidentified species were detected by $^{31}P\{^1H\}$ NMR (Figure S18). NMR data: for palladium enolate: $^{31}P\{^1H\}$ NMR: δ 12.5 (d, ^2J(PP) = 52 Hz); -16.5 (d, ^2J(PP) = 52 Hz); $^{13}C\{^1H\}$NMR: δ 206.3 (s); for **8**: $^{31}P\{^1H\}$ NMR: δ 8.3 (d, ^2J(PP) = 47 Hz); -15.5 (d, ^2J(PP) = 47 Hz); $^{13}C\{^1H\}$NMR: δ 191.7 (dd, $^2J(P_{trans},\underline{C}(O)OCH_3)$ = 167 Hz, $^2J(P_{cis},\underline{C}(O)OCH_3)$ = 9

Hz); for the organic products: $^{13}C\{^{1}H\}$ NMR: δ 209.0, (s, $CH_3\underline{C}(O)CH_2CH_2$-); 211.8 (s, $CH_3CH_2\underline{C}(O)CH_2CH_2$-).

8. Termination of the "carboalkoxy" cycle

Methanolysis of 11. 0.2 mL CH_3OH was added to a solution of **11**, prepared as above, and the progress of the reaction monitored by $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy. No deposition of metallic palladium was observed after 3 days at room temperature; **8** was regenerated on bubbling CO through this solution. (Figure S19) Methyl propanoate was detected as the only organic product by $^{13}C\{^{1}H\}$ NMR, singlet at 173.0 (s) ppm.

List of Supplementary Figures

Figure S1. $^{13}C\{^{1}H\}$ NMR spectra recorded at 193 K of key stages in the "hydride" cycle: (a) [Pd(dibpp)(CH_3)(CH_3CN)](OTf) **(1-CH_3CN)** after ^{13}CO bubble at 213 K, 1 minute; (b) bubble ^{13}CO at 213 K, 5 minutes then purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K, 5 minutes then purge with N_2 at 213 K.

Figure S2. Plot of ln(K) versus 1/T for the equilibrium of Equation 1, K=([1-TFA][CH_3CN])/([1-CH_3CN][TFA]) over the temperature ranging from 193 K to 243 K.

Figure S3. $^{13}P\{^{1}H\}$ NMR spectra of the reaction of [Pd(dibpp)(CH_3)(OTs)] **(1-OTs)** with ^{13}CO (a) bubble excess ^{13}CO through the solution of **1-OTs**; (b) purge the solution with N_2 for 1 minute; (c) purge the solution with N_2 for 5 minutes.

Figure S4. $^{13}C\{^{1}H\}$ NMR spectra of the reaction of [Pd(dibpp)(CH_3)(OTs)] **(1-OTs)** with CO (a) bubble excess ^{13}CO through the solution of 1-OTs; (b) purge the solution with N_2 for 1 minute; (c) purge the solution with N_2 for 5 minutes.

Figure S5. $^{31}P\{^{1}H\}$ NMR spectra of key stages in the second pass "hydride" cycle: (a) [Pd(dibpp)($CH_2CH_2C(O)CH_3$)](OTf) (**3**); (b) bubble ^{13}CO at 213 K, then purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K.

Figure S6. $^{13}C\{^{1}H\}$ NMR spectra of key stages in the second pass "hydride" cycle: (a) [Pd(dibpp)($CH_2CH_2C(O)CH_3$)][CF_3SO_3]; (b) bubble ^{13}CO at 213 K, then purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K.

Figure S7. Experimental(up) and simulated(down) $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra for **10**.

Figure S8. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of [Pd(dibpp)($MeCN)_4$][$OTf]_2$ with : (a) 1 equivalent $NaOCH_3$**;** (b) ^{13}CO 5 min at 213 K; (c) ^{13}CO overnight at 243K.

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of [Pd(dibpp)($^{13}C(O)O^{13}CH_3$)(MeCN)] [OTf] prepared in a similar manner to **8** but using $^{13}CH_3OH$ as reactant.

Figure S10. Experimental(up) and simulated(down) $^{31}P\{^{1}H\}$ NMR spectra for **8-PPh_3**

Figure S11. $^{31}P\{^{1}H\}$ NMR spectra recorded in dichloromethane: CH_3CN (9:1) at 193 K of key stages in the "carboalkoxy" cycle: (a) [Pd(dibpp)($^{13}C(O)OCH_3$)(MeCN)](OTf) **(8-CH_3CN)** and [Pd(dibpp)($^{13}C(O)OCH_3$)(^{13}CO)](OTf) **(8-CO);** (b) purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K, 5 minutes then purge with N_2 at 213 K.

Figure S12. $^{31}P\{^{1}H\}$ NMR spectra recorded in dichloromethane at 193 K of chain propagation stages in the "carbomethoxy" cycle: (a) **11** was synthesized by successive addition of ^{13}CO and ethene into **8** formed in situ**;** (b) ^{13}CO bubbled through the solution then at 243 K for 2 hours; (c) purged with nitrogen and then bubbled with ethene at 213 K, warmed up to 243 K for 2 hours.

Figure S13. $^{31}P\{^{1}H\}$ NMR spectra of the methanolysis of **2-CO** showing **2-CH_3OH** as an intermediate: (a) [**2-CO**](**OTf**) in 1.8 ml CH_2Cl_2 at 193 K plus 0.2 ml CH_3OH; (b) after 45 minutes at 243 K.

Figure S14. $^{13}C\{^{1}H\}$ NMR spectra of the methanolysis of **2-CO** showing **2-CH_3OH** as an intermediate: (a) **[2-CO]OTf** in 1.8 mL CH_2Cl_2 at 193 K with 0.2 mL CH_3OH added; (b) warmed to 243 K and then after 45 minutes at that temperature.

Figure S15. Crystal structure of $[\{(L\text{-}L)Pd\ (\mu\text{-}OH)\}_2](CF_3SO_3)_2$.

Figure S16. $^{31}P\{^{1}H\}$ NMR spectra of the methanolysis of **3** and **5**, showing the difference in reactivity of the *β*-chelates: CD_3OD was added to the mixture of **3** and **5** at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d). (spectra (a) and (b) are recorded at 253 K, spectra (c) and (d) recorded at room temperature).

Figure S17. $^{13}C\{^{1}H\}$ NMR spectra of the methanolysis of **3** and **5**, showing the difference in reactivity of the *β*-chelates: CD_3OD was added to the mixture of **3** and **5** at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d).(spectra (a) and (b) are recorded at 253 K, spectra (c) and (d) recorded at room temperature).

Figure S18. $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of the methanolysis of **3** in the presence of CO (crossover reaction to carboalkoxy cycle).

Figure S19. $^{31}P\{^{1}H\}$ NMR spectra of methanolysis of chelate in carbomethoxy cycle showing methanolysis of the *β*-chelate giving reinitiation: (a) a mixture of **11** and **12** generated in the presence of 4 equivalents CH_3CN following the procedure described above otherwise; (b) after 1 day at room temperature, ^{13}CO was bubbled through the solution at 213 K and then kept at 243 K for 1.5 hrs (both spectra taken at 193K).

Figure S1. $^{13}C\{^{1}H\}$ NMR spectra recorded at 193 K of key stages in the "hydride" cycle: (a) [Pd(dibpp)(CH_3)(CH_3CN)](OTf) **(1-CH_3CN)** after ^{13}CO bubble at 213 K, 1 minute; (b) bubble ^{13}CO at 213 K, 5 minutes then purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K, 5 minutes then purge with N_2 at 213 K.

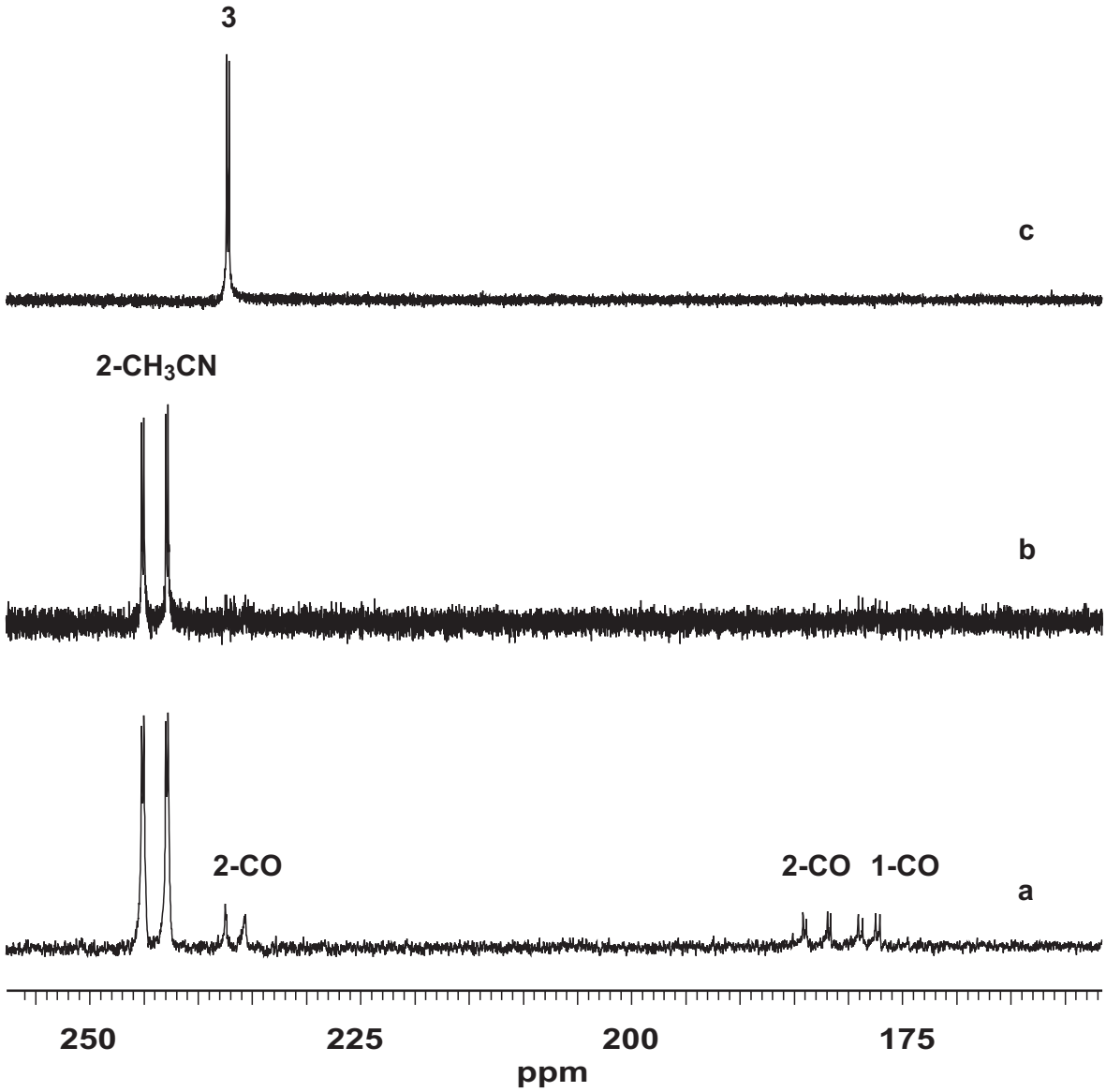


Figure S2. Plot of ln(K) versus 1/T for the equilibrium of Equation 1, K=([1-TFA][CH_3CN])/([1-CH_3CN][TFA]) at the temperature ranging from 193 K to 243 K.

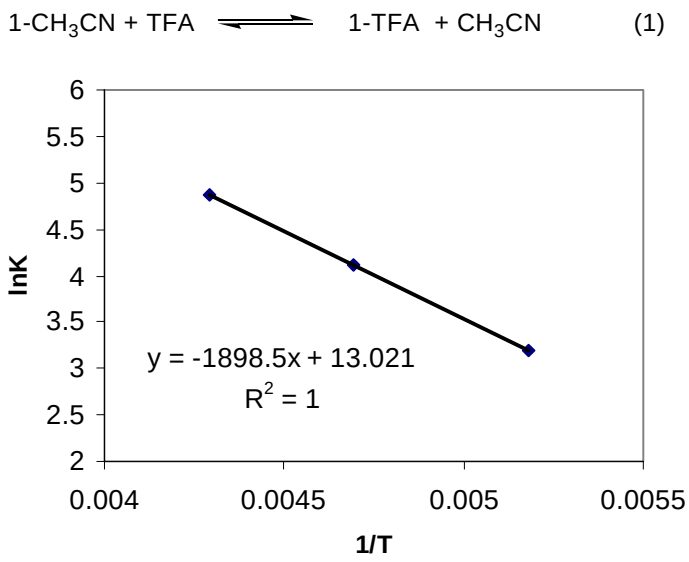


Figure S3. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of [Pd(dibpp)(CH_3)(OTs)] **(1-OTs)** with CO (a) bubble excess ^{13}CO through the solution of **1-OTs**; (b) purge the solution with N_2 for 1 minute; (c) purge the solution with N_2 for 5 minutes.

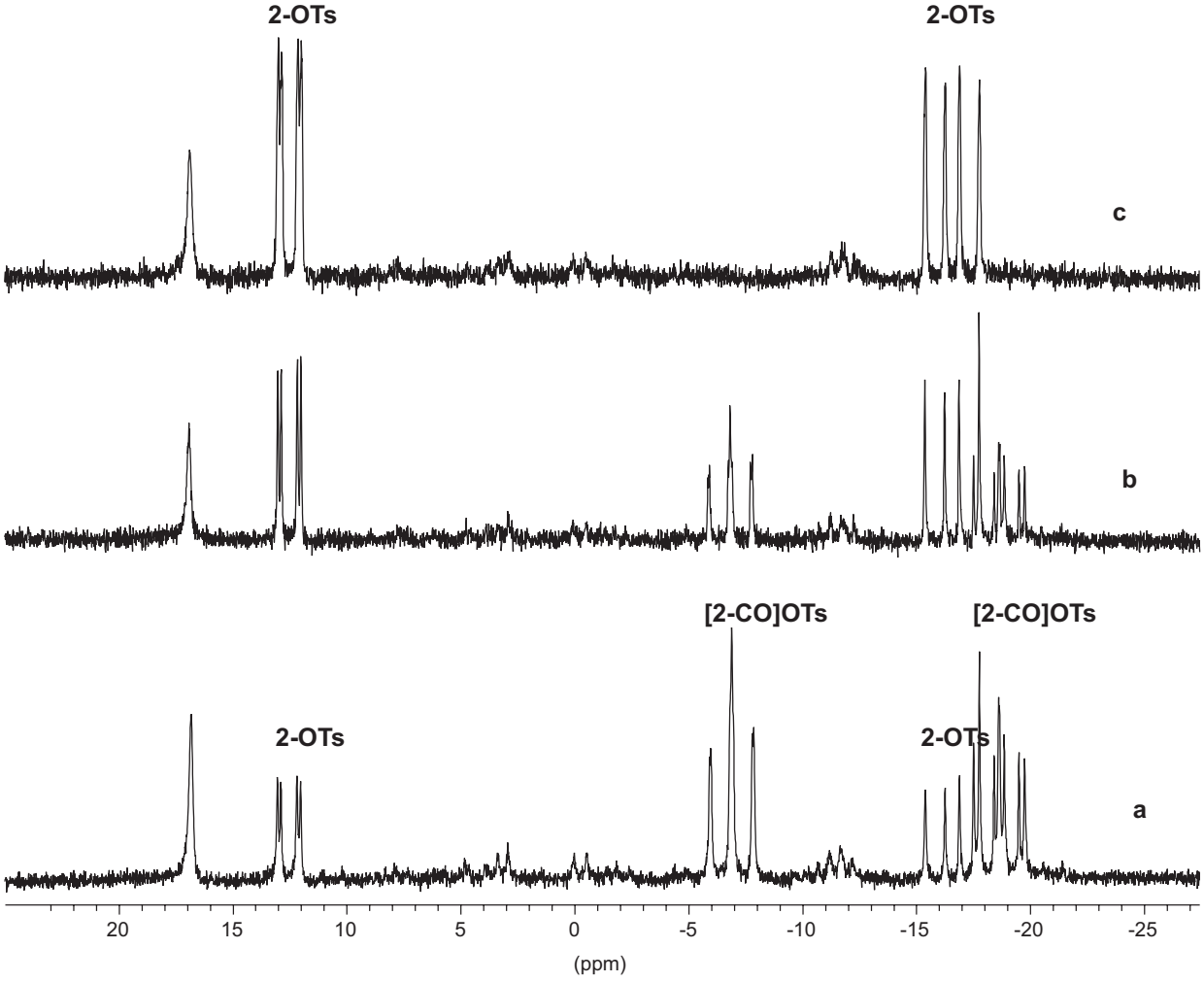


Figure S4. $^{13}C\{^{1}H\}$ NMR spectra of the reaction of [Pd(dibpp)(CH_3)(OTs)] **(1-OTs)** with CO (a) bubble excess ^{13}CO through the solution of 1-OTs; (b) purge the solution with N_2 for 1 minute; (c) purge the solution with N_2 for 5 minutes.

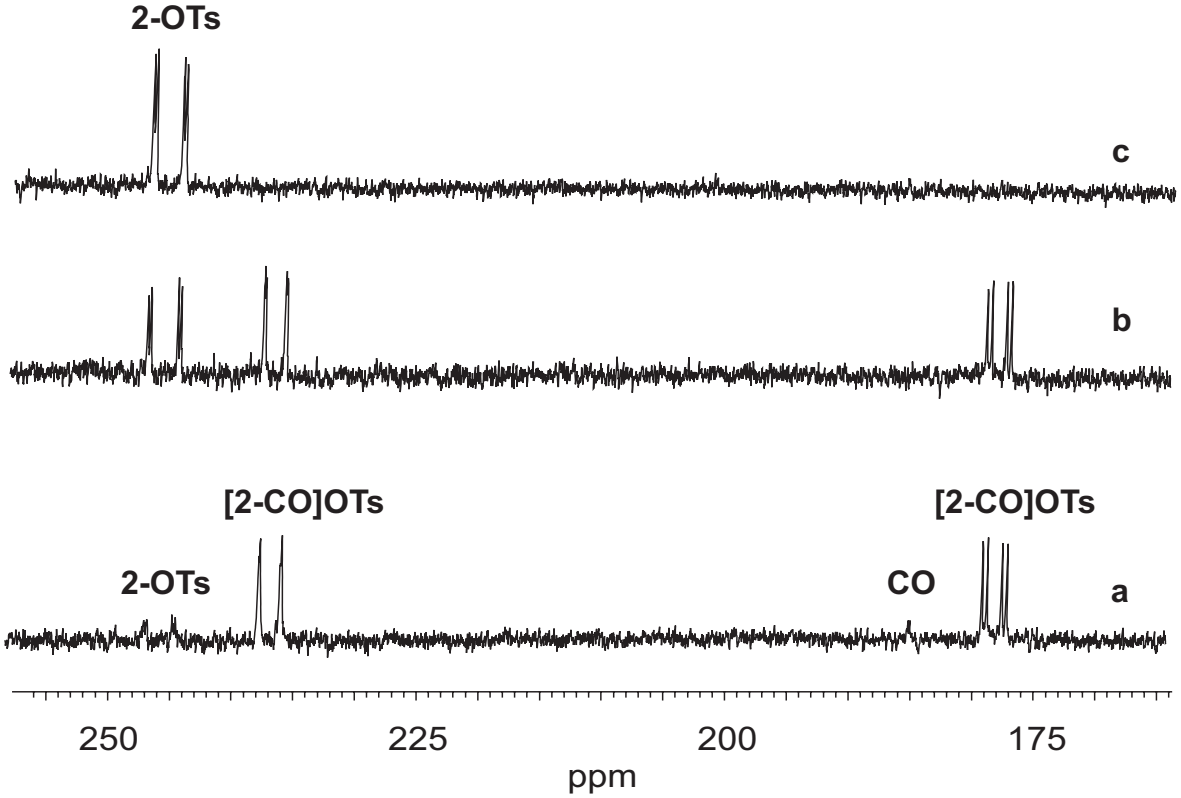


Figure S5. $^{31}P\{^{1}H\}$ NMR spectra of key stages in the second pass "hydride" cycle: (a) [Pd(dibpp)($CH_2CH_2C(O)CH_3$)](OTf) (**3**); (b) bubble ^{13}CO at 213 K, then purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K.

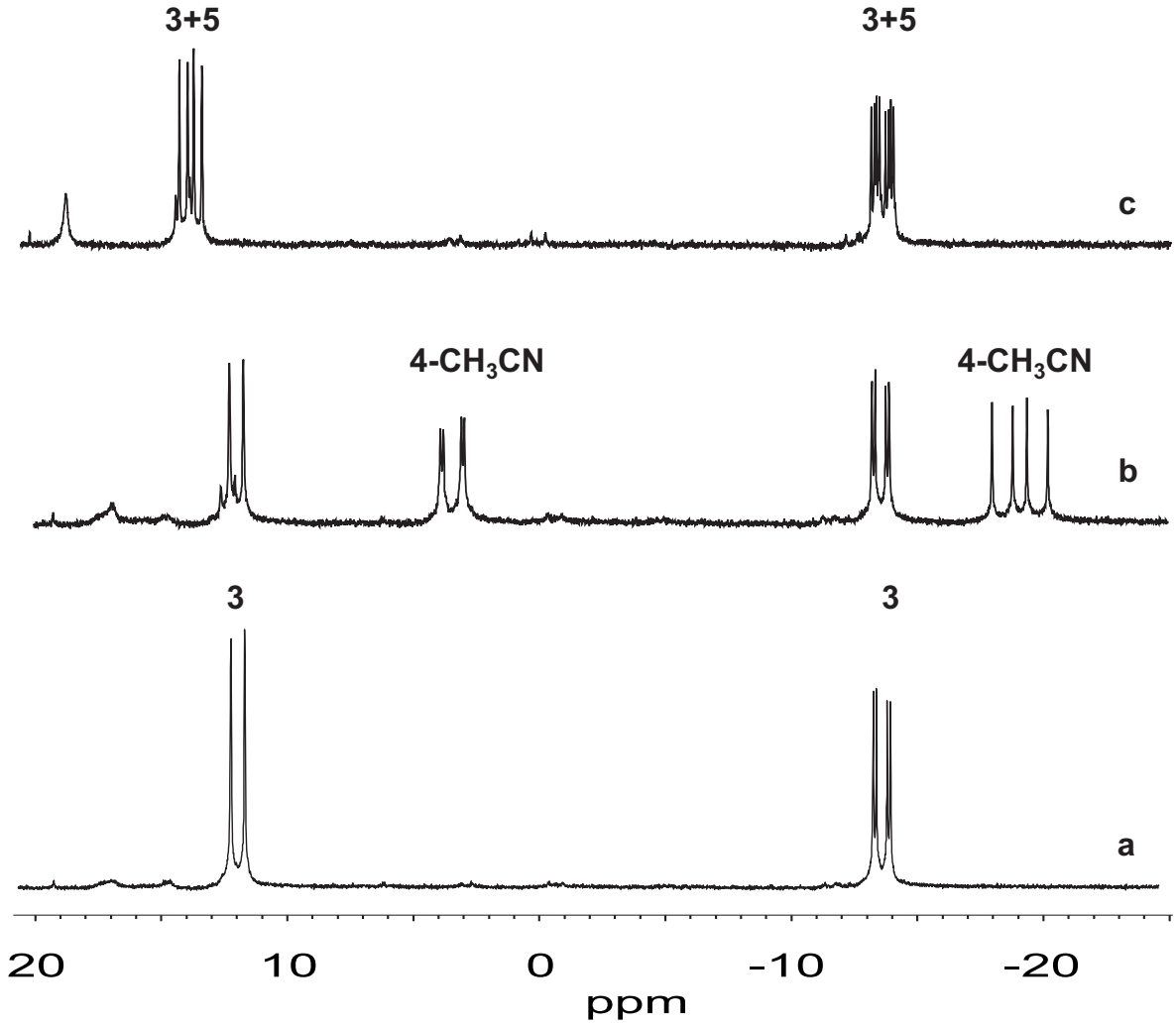


Figure S6. $^{13}C\{^{1}H\}$ NMR spectra of key stages in the second pass "hydride" cycle: (a) [Pd(dibpp)($CH_2CH_2C(O)CH_3$)][CF_3SO_3]; (b) bubble ^{13}CO at 213 K, then purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K.

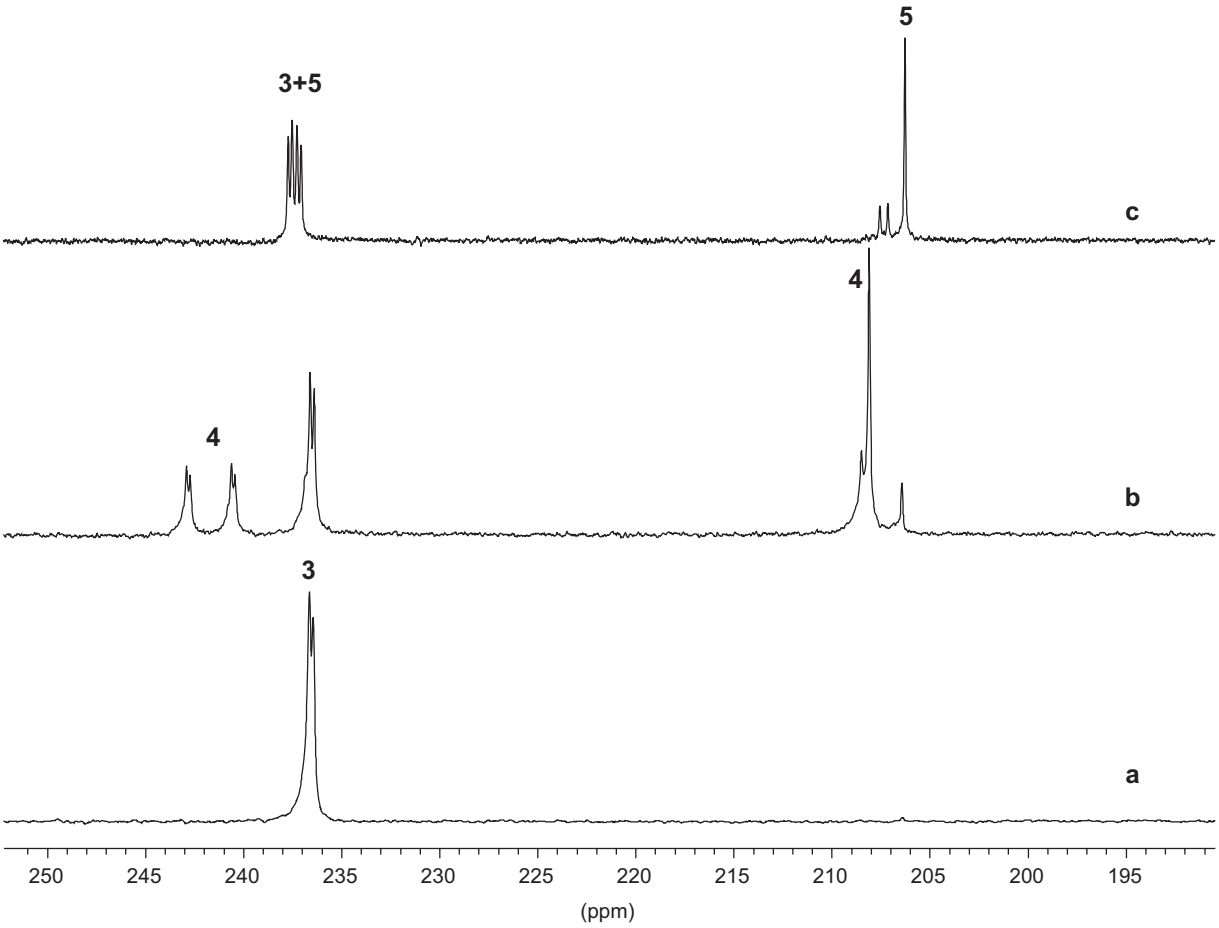


Figure S7. Experimental(up) and simulated(down) $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of the **10**.

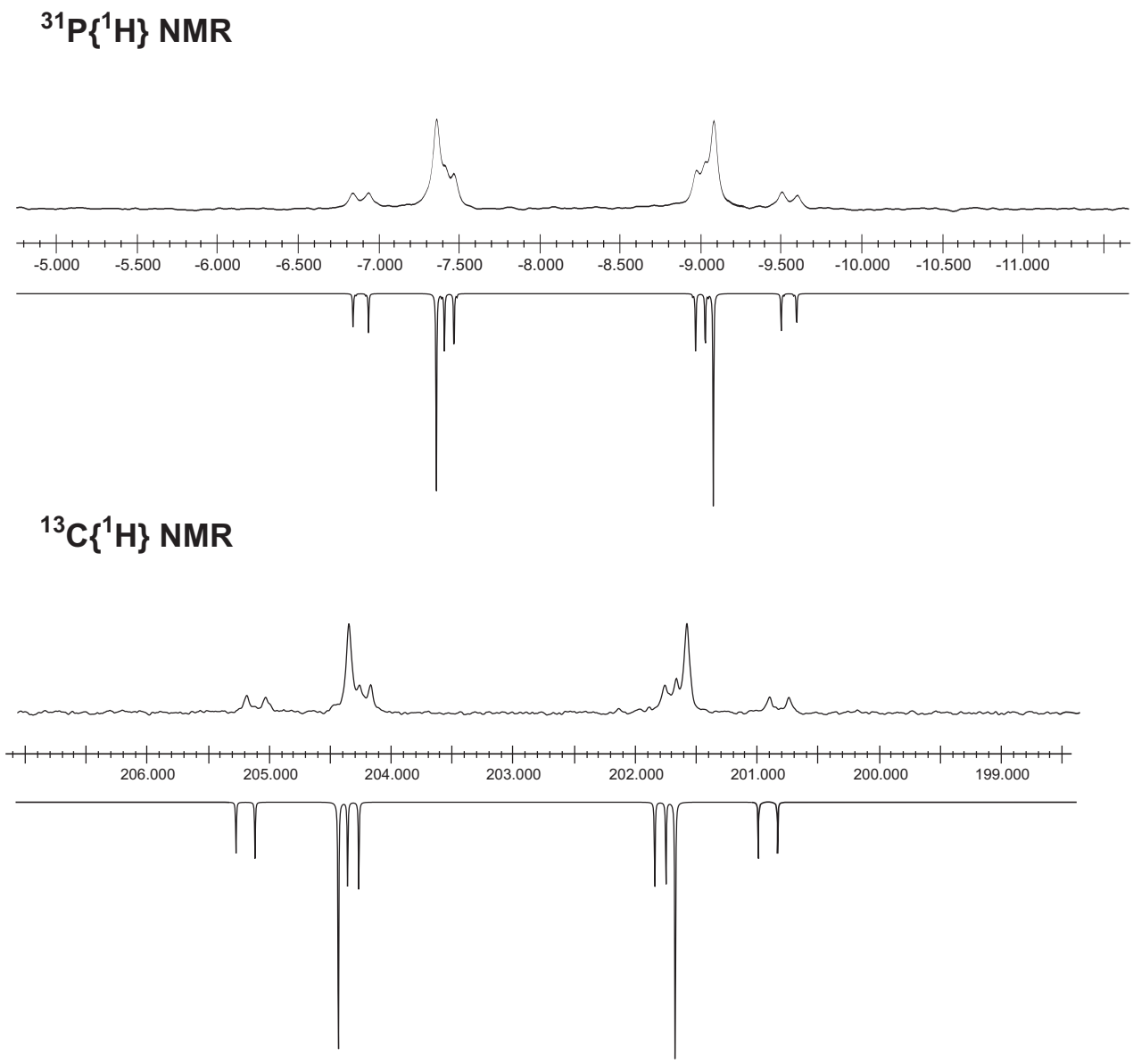


Figure S8. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of[Pd(dibpp)(MeCN)$_4$][OTf]$_2$ with : (a) 1 equivalent $NaOCH_3$**;** (b) ^{13}CO 5 min at 213 K; (c) ^{13}CO overnight at 243 K.

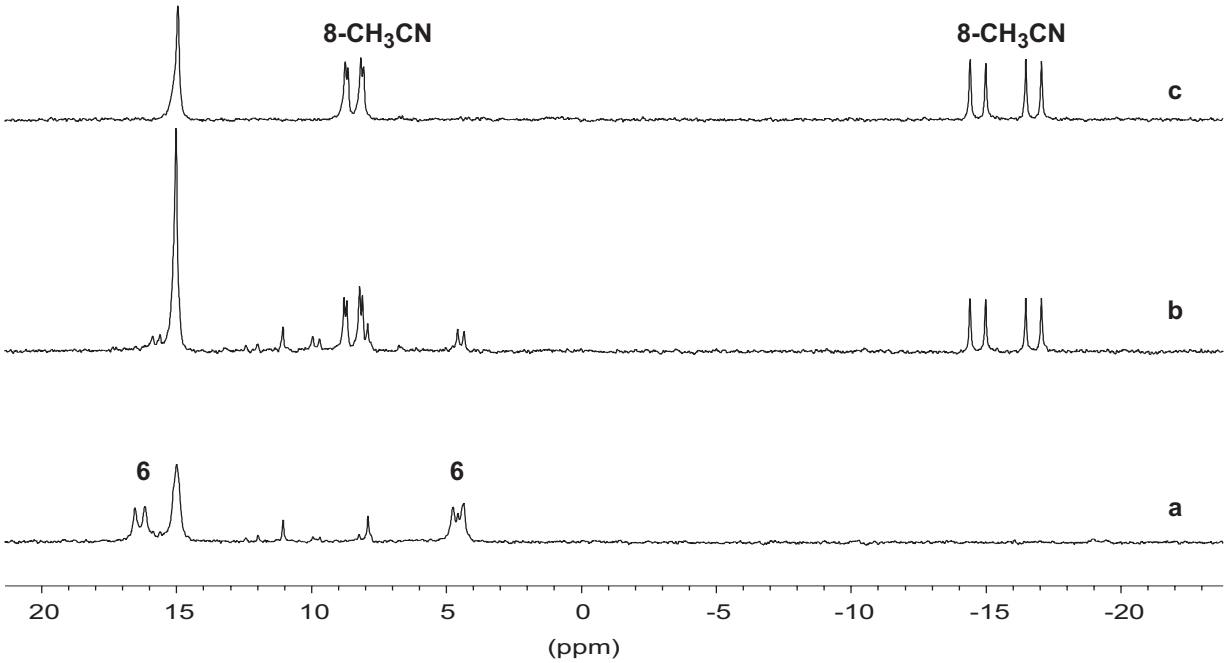


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of [Pd(dibpp)($^{13}C(O)O^{13}CH_3$)(MeCN)] [OTf] prepared in a similar manner to **8** but using $^{13}CH_3OH$ as reactant

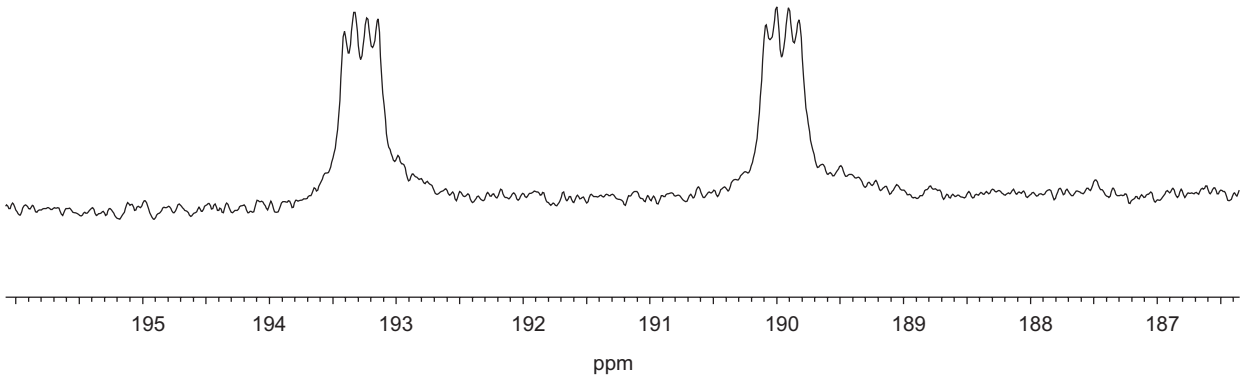


Figure S10. Experimental(up) and simulated(down) $^{31}P\{^{1}H\}$ NMR spectra for **8-PPh$_3$**

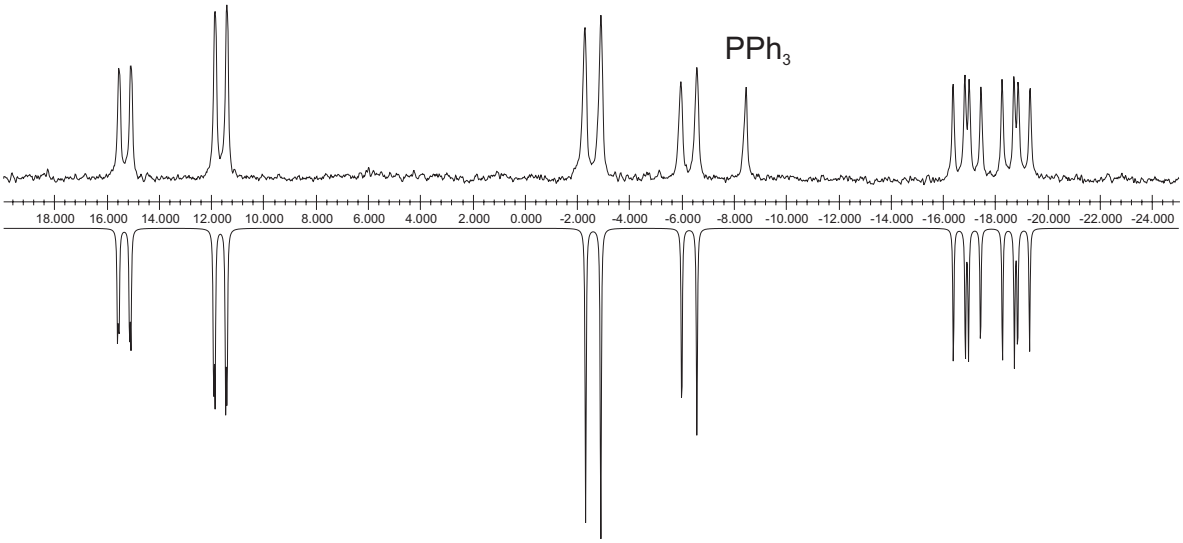


Figure S11. $^{31}P\{^{1}H\}$ NMR spectra recorded in dichloromethane: CH_3CN (9:1) at 193 K of key stages in the "carboalkoxy" cycle: (a) [Pd(dibpp)($^{13}C(O)OCH_3$)(MeCN)](OTf) **(8-CH_3CN)** and [Pd(dibpp)($^{13}C(O)OCH_3$)(^{13}CO)](OTf) **(8-CO);** (b) purge with N_2 at 213 K; (c) bubble C_2H_4 at 213 K, 5 minutes then purge with N_2 at 213 K.

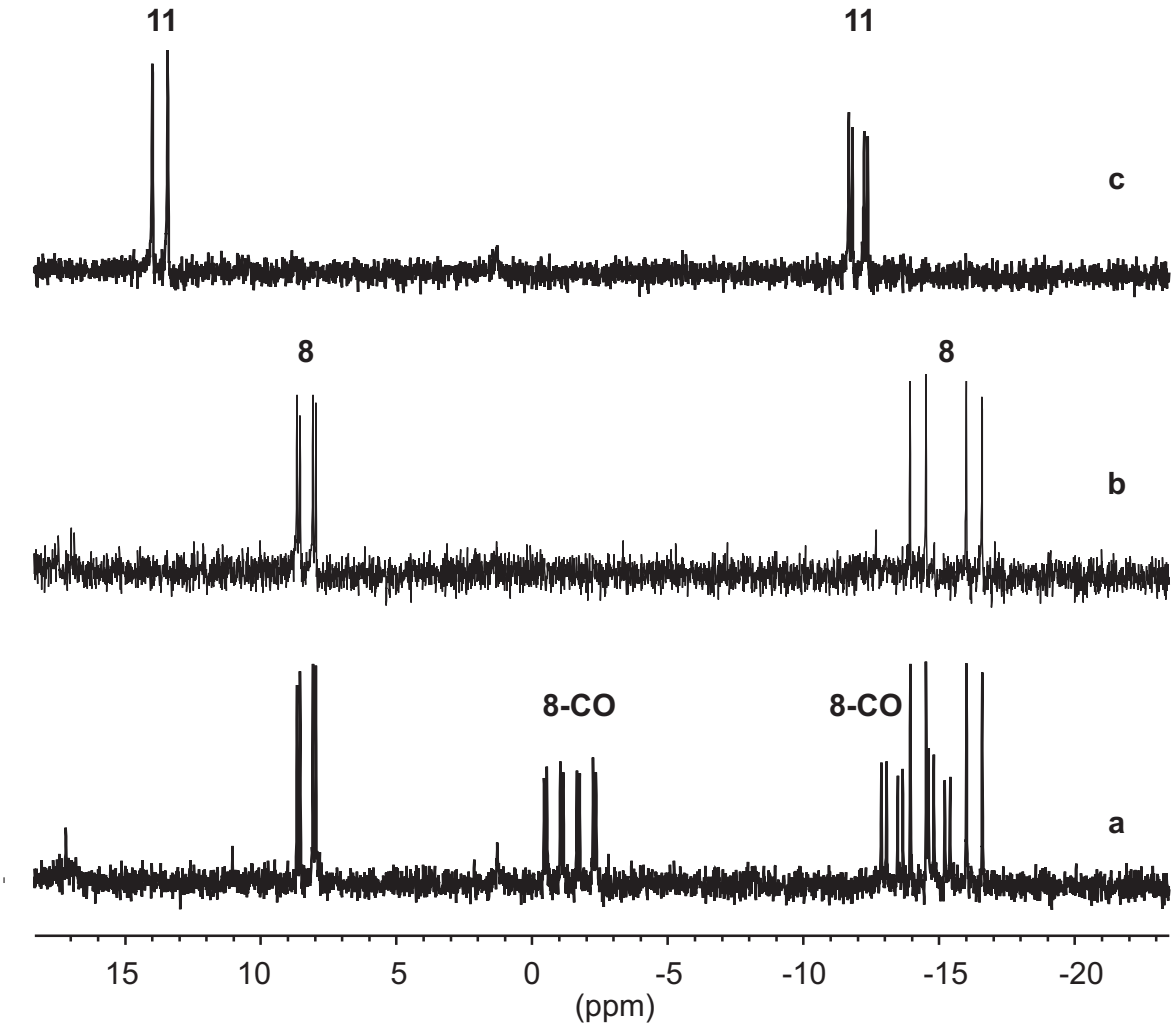


Figure S12. $^{31}P\{^{1}H\}$ NMR spectra recorded in dichloromethane at 193 K of chain propagation stages in the "carbomethoxy" cycle: (a) **11** was synthesized by successive addition of ^{13}CO and ethene into **8** formed in situ**;** (b) ^{13}CO bubbled through the solution then at 243 K for 2 hours; (c) purged with nitrogen and then bubbled with ethene at 213 K, warmed to 243 K for 2 hours.

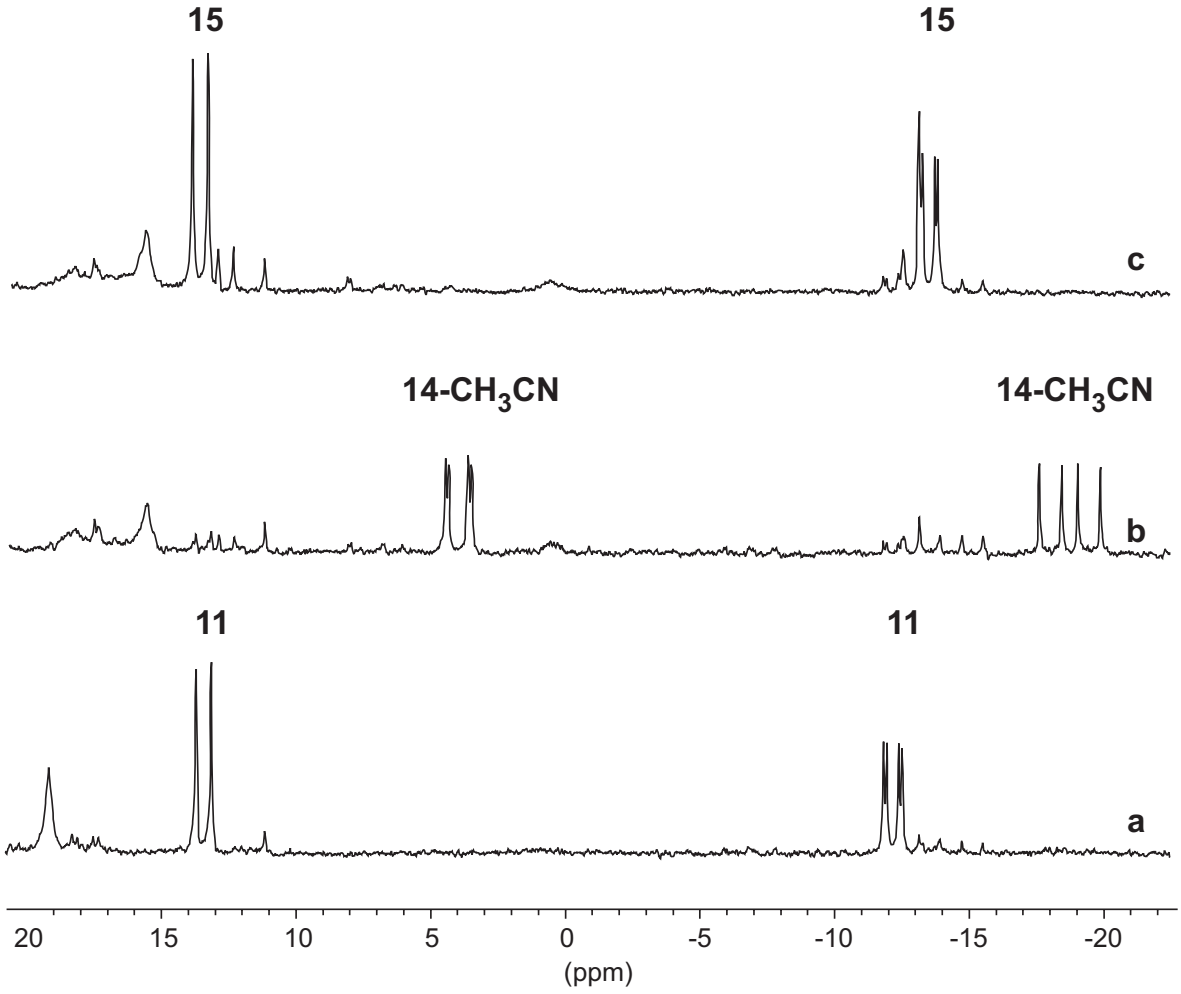


Figure S13. $^{31}P\{^{1}H\}$ NMR spectra of the methanolysis of **2-CO** showing **2-CH_3OH** as an intermediate: (a) [**2-CO**](**OTf**) in 1.8 ml CH_2Cl_2 at 193 K plus 0.2 ml CH_3OH; (b) after 45 minutes at 243 K.

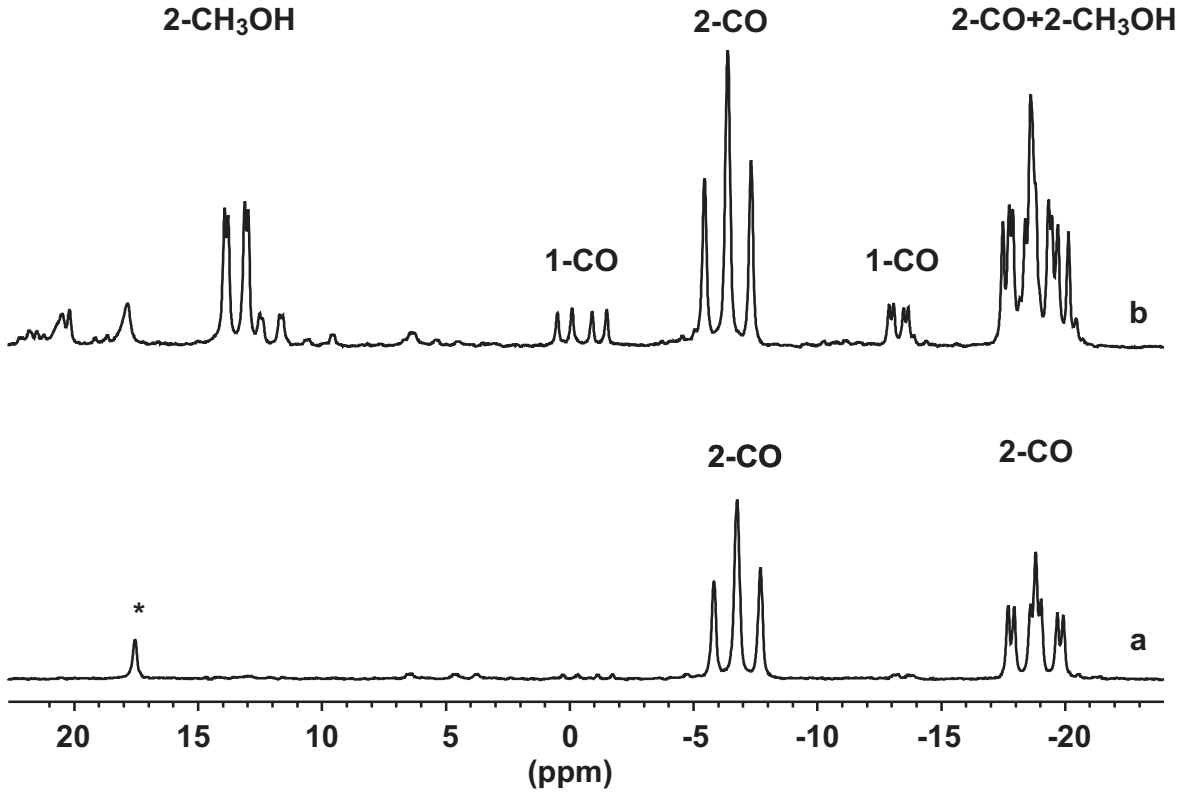


Figure S14. $^{13}C\{^{1}H\}$ NMR spectra of the methanolysis of **2-CO** showing **2-CH_3OH** as an intermediate: (a) **[2-CO]OTf** in 1.8 mL CH_2Cl_2 at 193 K with 0.2 mL CH_3OH added; (b) warmed to 243 K and then after 45 minutes at that temperature.

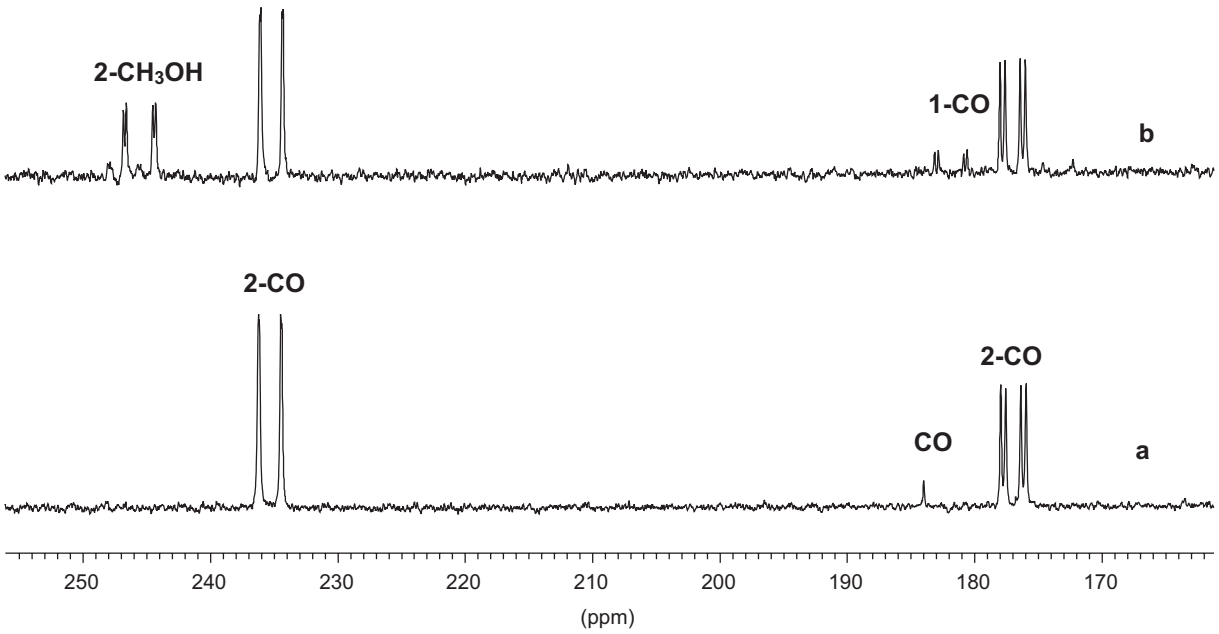


Figure S15. Crystal structure of [{(L-L)Pd (μ-OH)}$_2$](CF$_3$SO$_3$)$_2$.

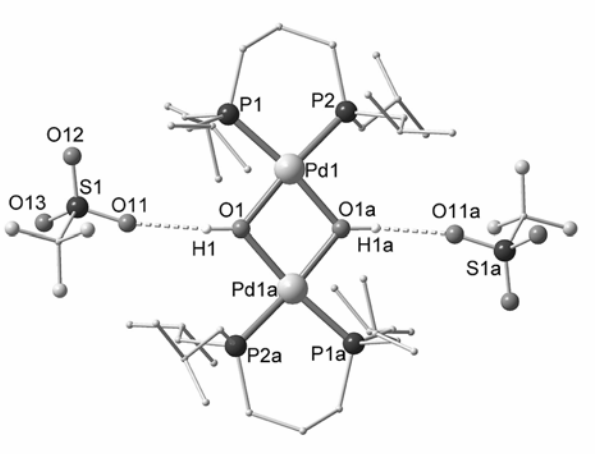


Figure S16. $^{31}P\{^{1}H\}$ NMR spectra of the methanolysis of **3** and **5**, showing the difference in reactivity of the *β*-chelates: CD_3OD was added to the mixture of **3** and **5** at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d). (spectra (a) and (b) recorded at 253 K, spectra (c) and (d) recorded at room temperature).

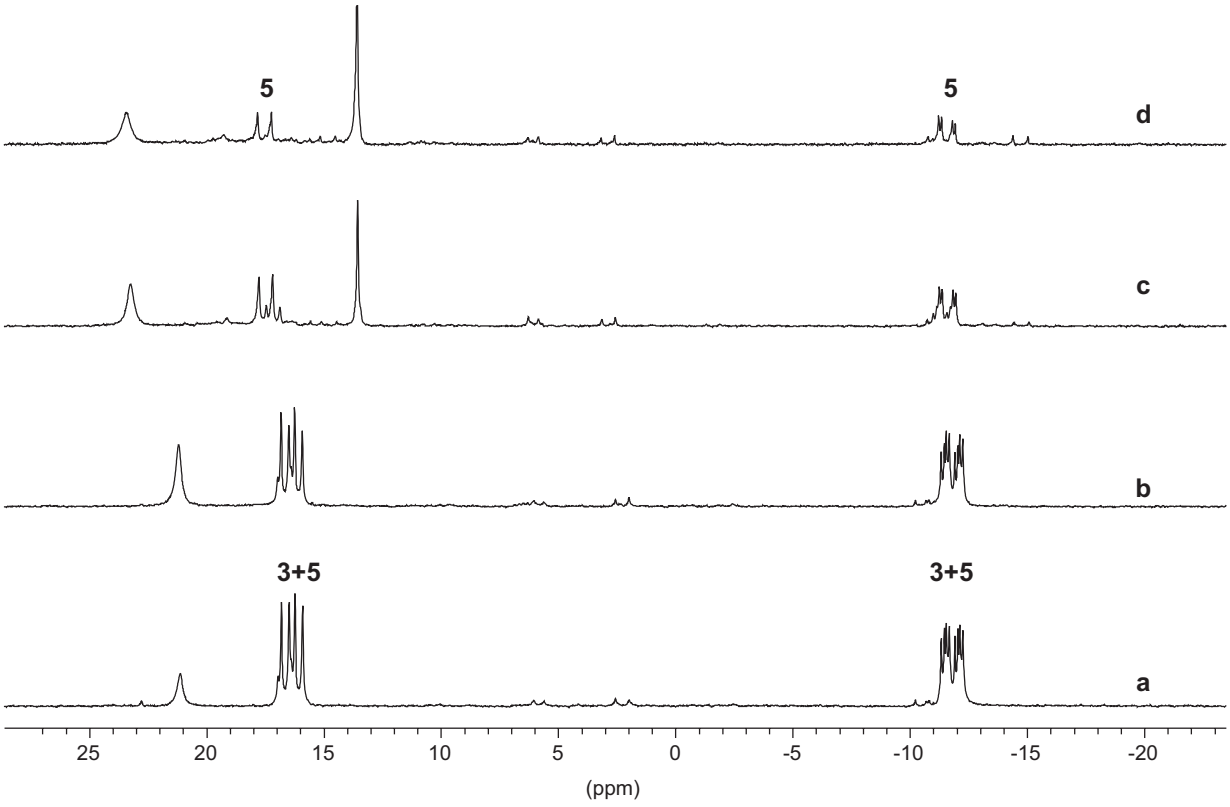


Figure S17. $^{13}C\{^{1}H\}$ NMR spectra of the methanolysis of **3** and **5**, showing the difference in reactivity of the *β*-chelates: CD_3OD was added to the mixture of **3** and **5** at 213 K (a) and then warmed to room temperature for 1 hour (b), 3 hours (c) and 10 hours (d). (spectra (a) and (b) recorded at 253 K, spectra (c) and (d) recorded at room temperature).

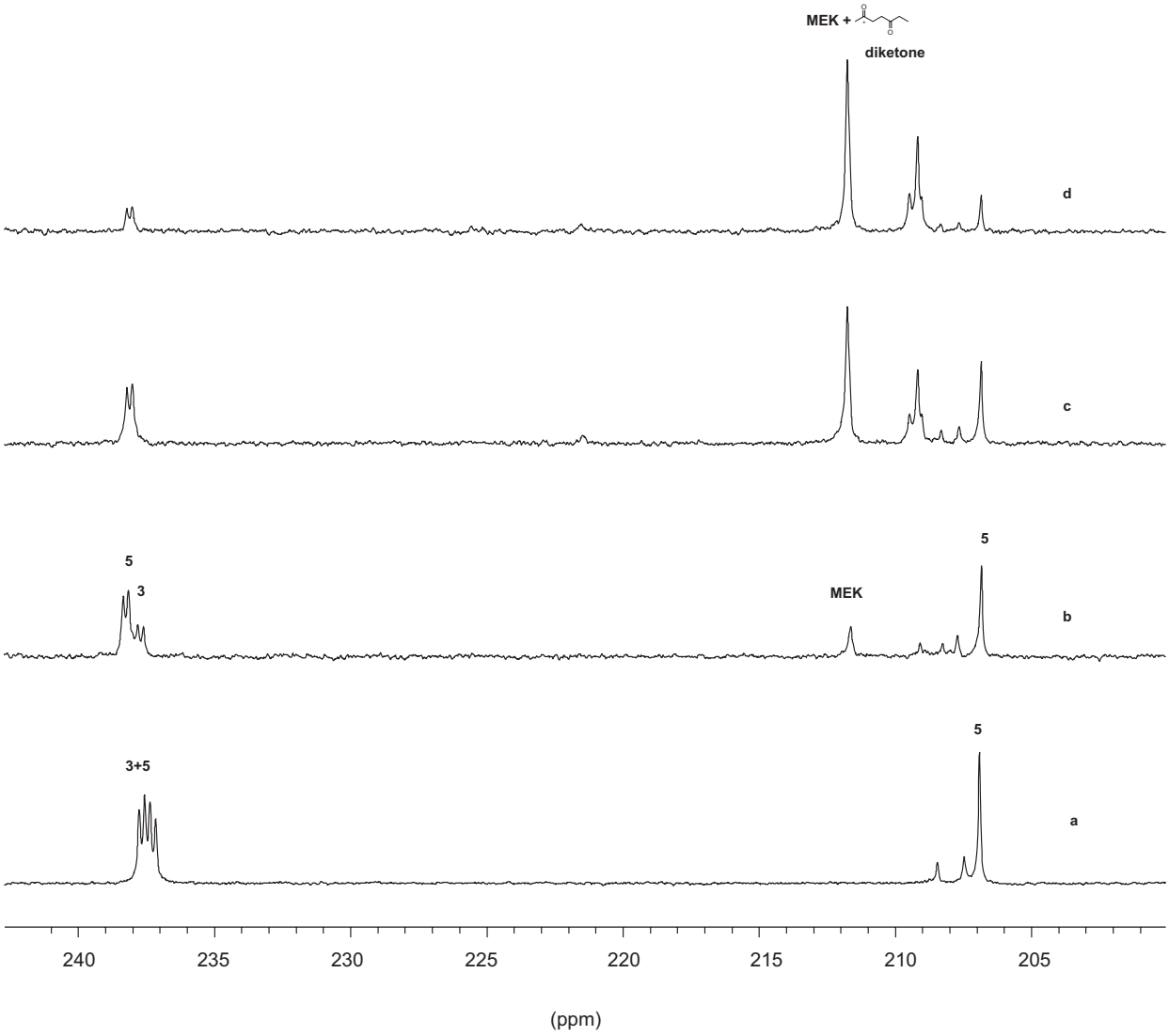


Figure S18. $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of the methanolysis of **3** in the presence of CO (crossover reaction to carboalkoxy cycle).

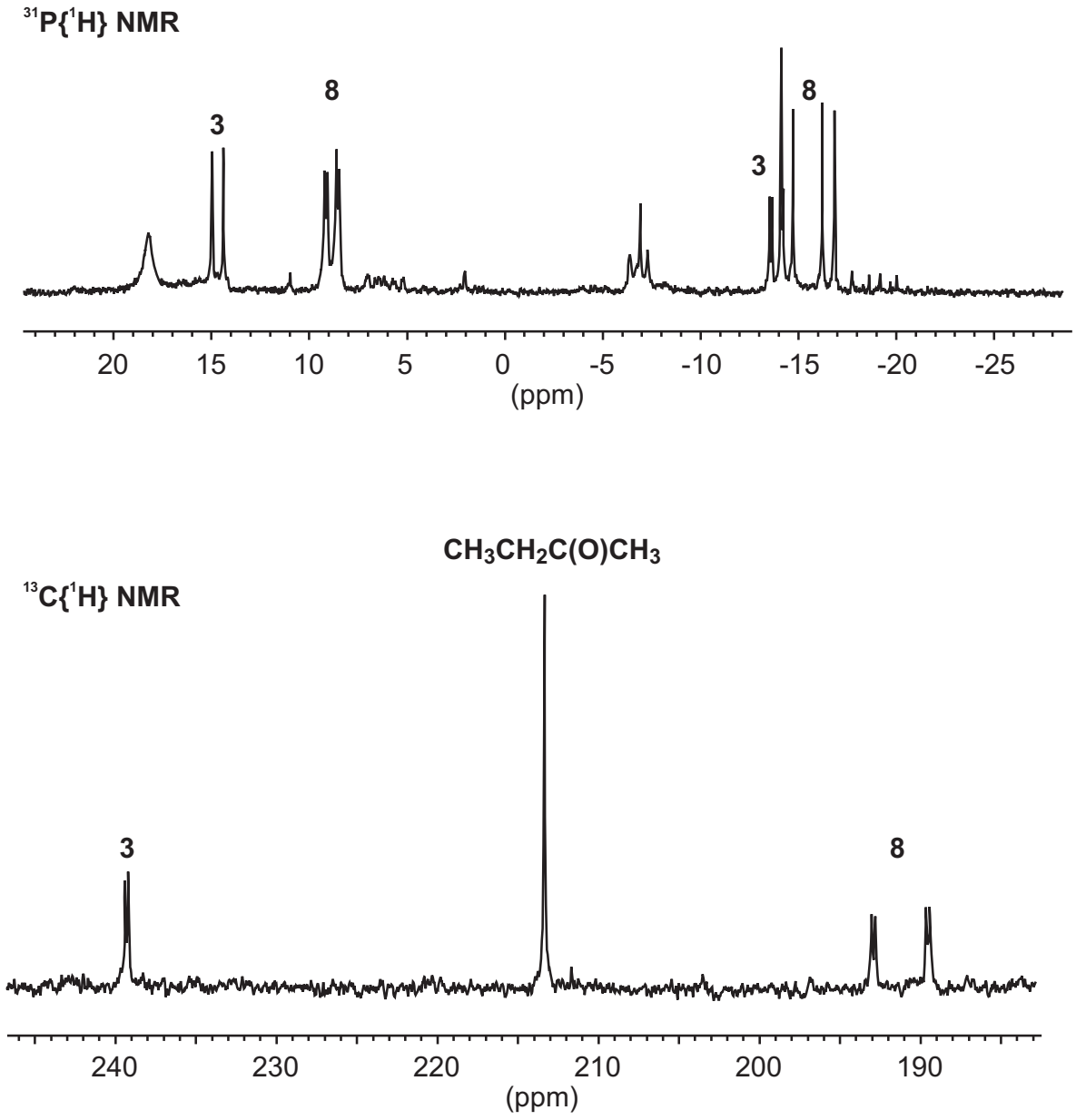
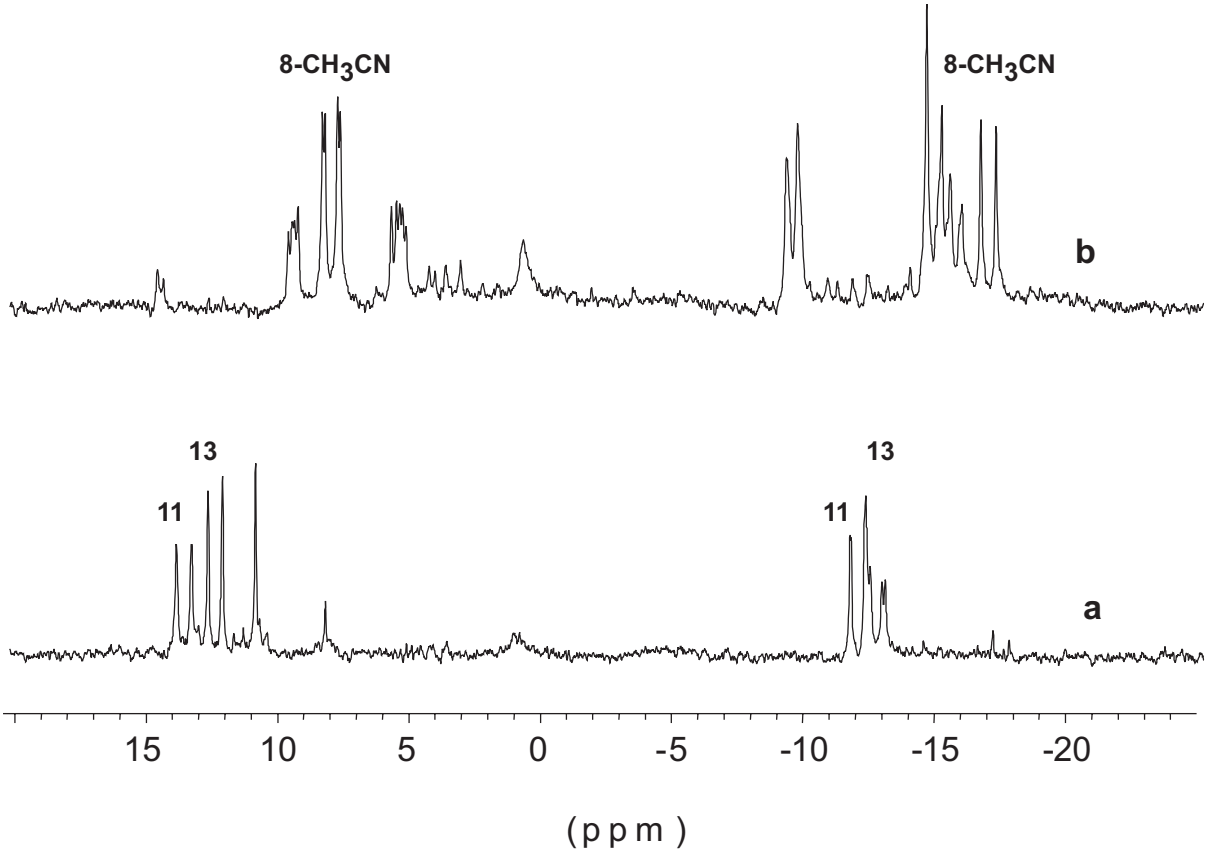


Figure S19. $^{31}P\{^{1}H\}$ NMR spectra of methanolysis of chelate in carbomethoxy cycle showing methanolysis of the β-chelate giving reinitiation: (a) a mixture of **11** and **12** generated in the presence of 4 equivalents CH_3CN following the procedure described above otherwise; (b) after 1 day at room temperature, ^{13}CO was bubbled through the solution at 213 K and then kept at 243 K for 1.5 hrs (both spectra taken at 193K).



References

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(2) W, D. G.; J, B.; W. J. J. Smeets; A. L. Spek; Koten, G. V. *Organometallics* **1989,** 8, (12), 2907-2917.
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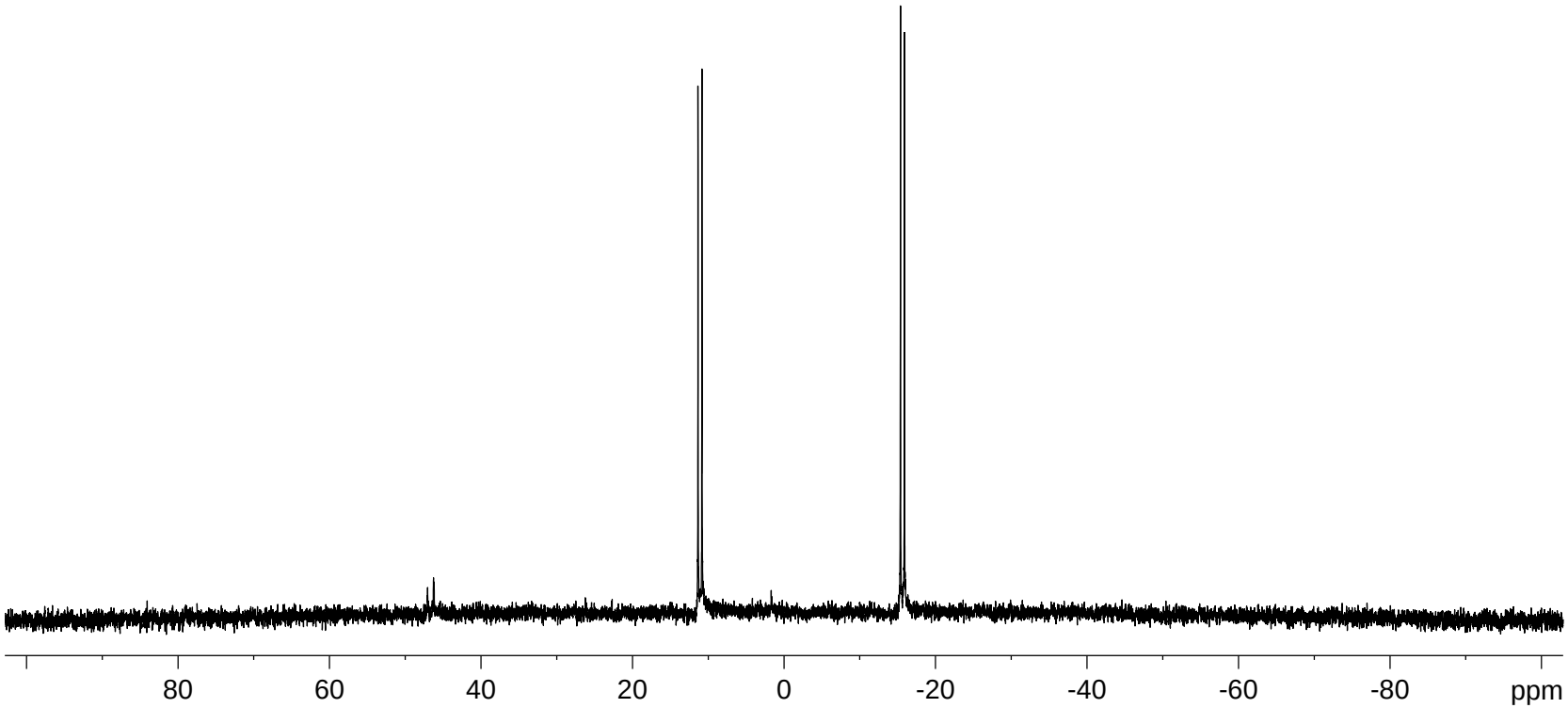
Collection of $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra

Representative $^{31}P\{^{1}H\}$ and/or $^{13}C\{^{1}H\}$ NMR spectra of following compounds are listed here:

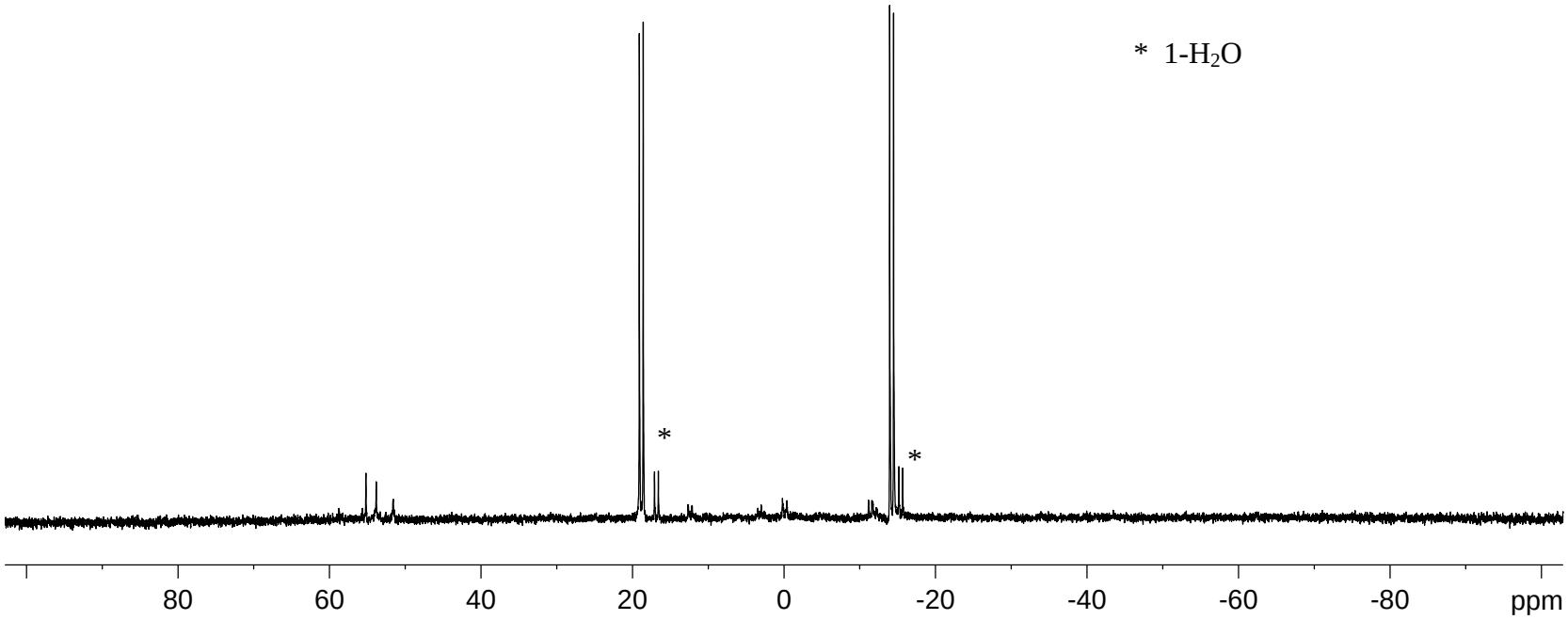
[1-CH_3CN](OTf), 1-OTf, 1-TFA, 1-PPh_3, 1-Cl, 1-H_2O,
2-TFA,2-OTs,[2-CH_3CN](OTf), [2-CO](OTf),3, [4-CH_3CN](OTf),5
[8-CH_3CN](OTf), [8-CO](OTf), [8-PPh_3](OTf),9,11,12,13, [14-CO](OTf),
[14-CH_3CN](OTf), 15

The spectra of all other compounds, transient intermediates and sequential reactions are given **Figure 1,2,3** in main text and **Figure S1-S19** above, which are not reproduced here.

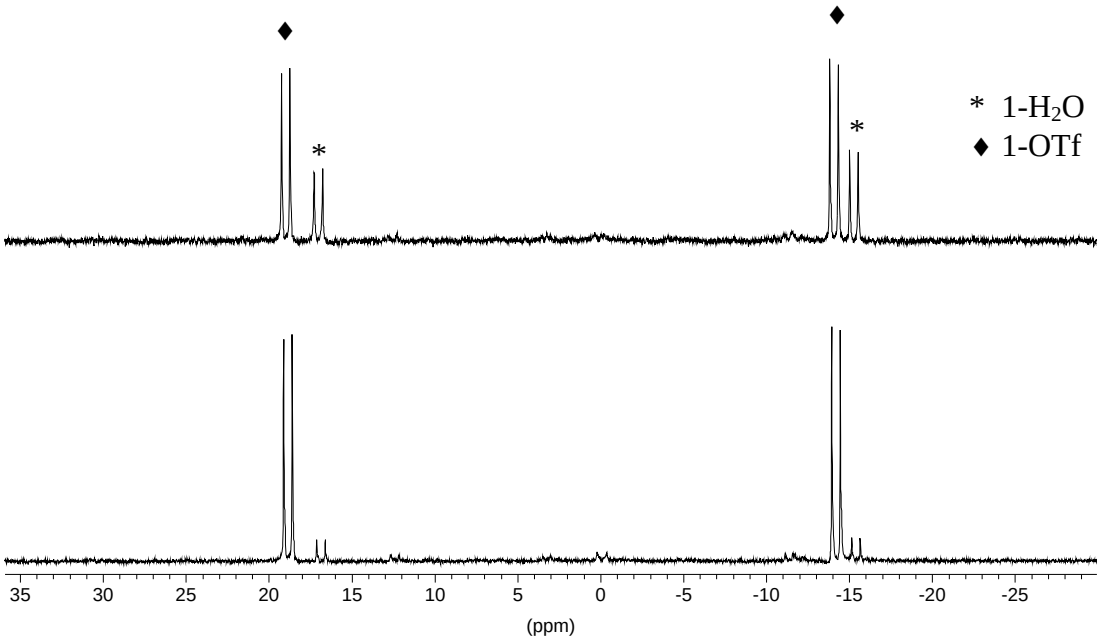
$^{31}P\{^{1}H\}$ NMR spectrum of [**1-CH_3CN**](OTf) recorded at 193 K in dichloromethane



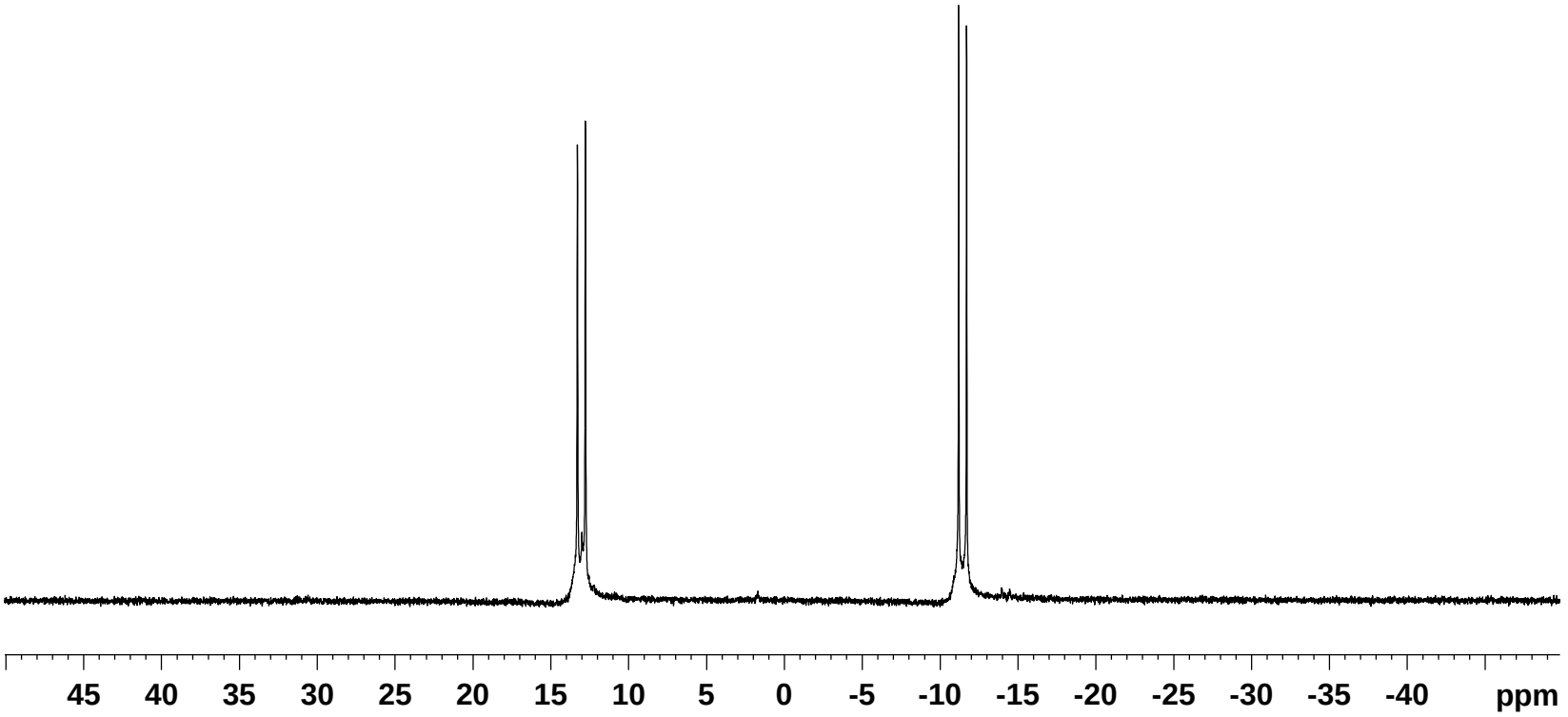
$^{31}P\{^{1}H\}$ NMR spectrum of **1-OTf** recorded at 193 K in dichloromethane



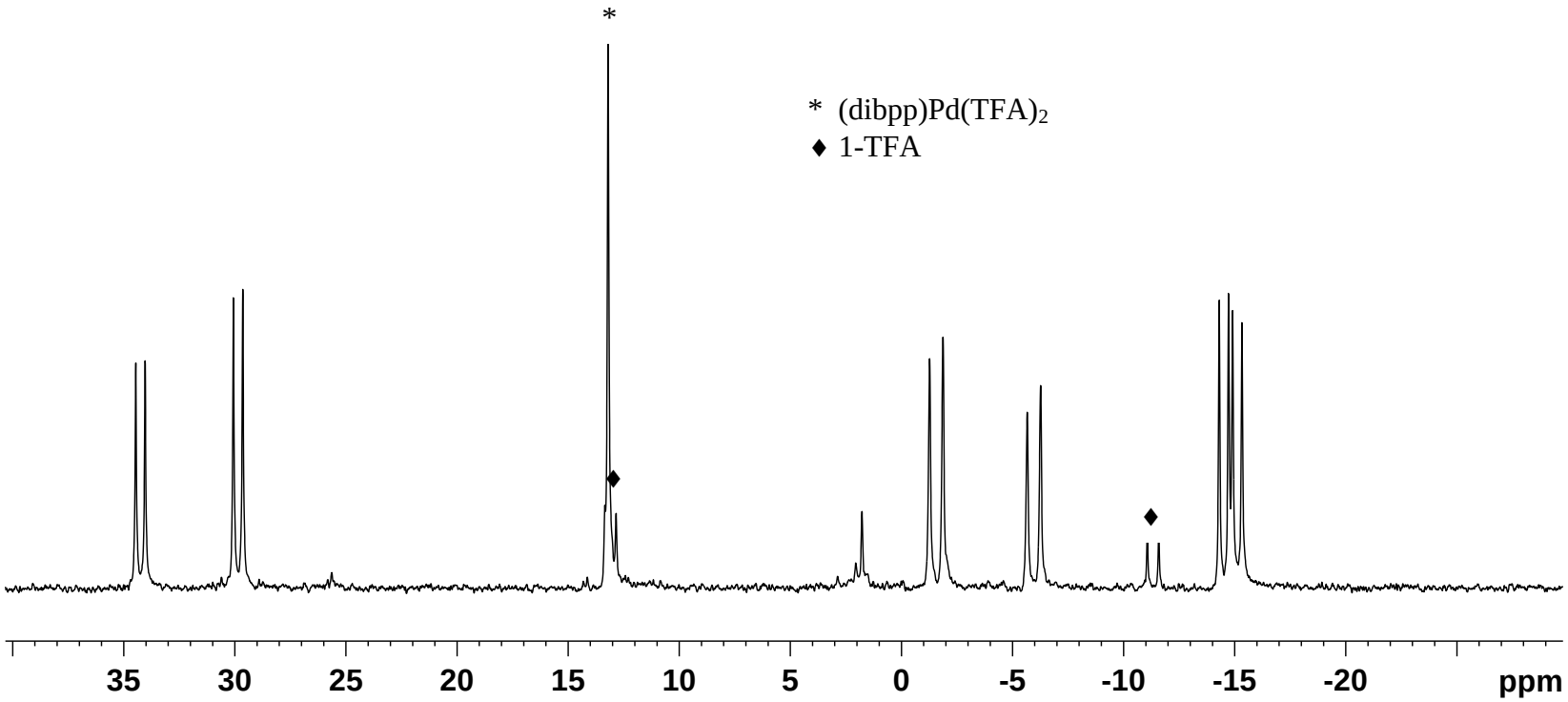
$^{31}P\{^{1}H\}$ NMR spectrum of a mixture of **1-H_2O** and **1-OTf** recorded at 193 K in dichloromethane
(1-H_2O formed due to trace of water in triflic acid is identified by the significant growth of those resonances(top spectrum) by addition of 1 eq H_2O to a "dry" solution of 1-OTf(bottom spectrum))



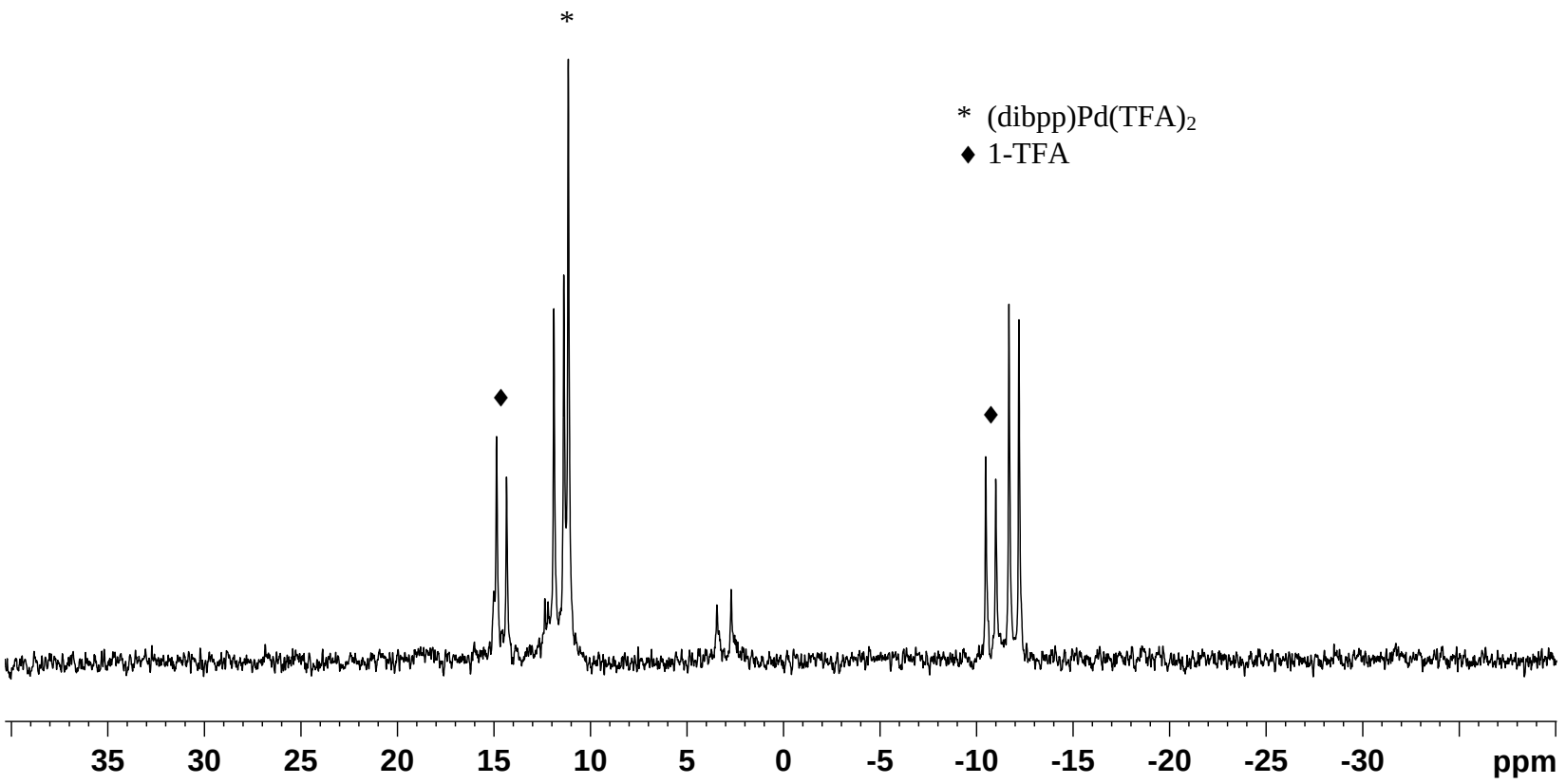
$^{31}P\{^{1}H\}$ NMR spectrum of **1-TFA** recorded at 193 K in dichloromethane



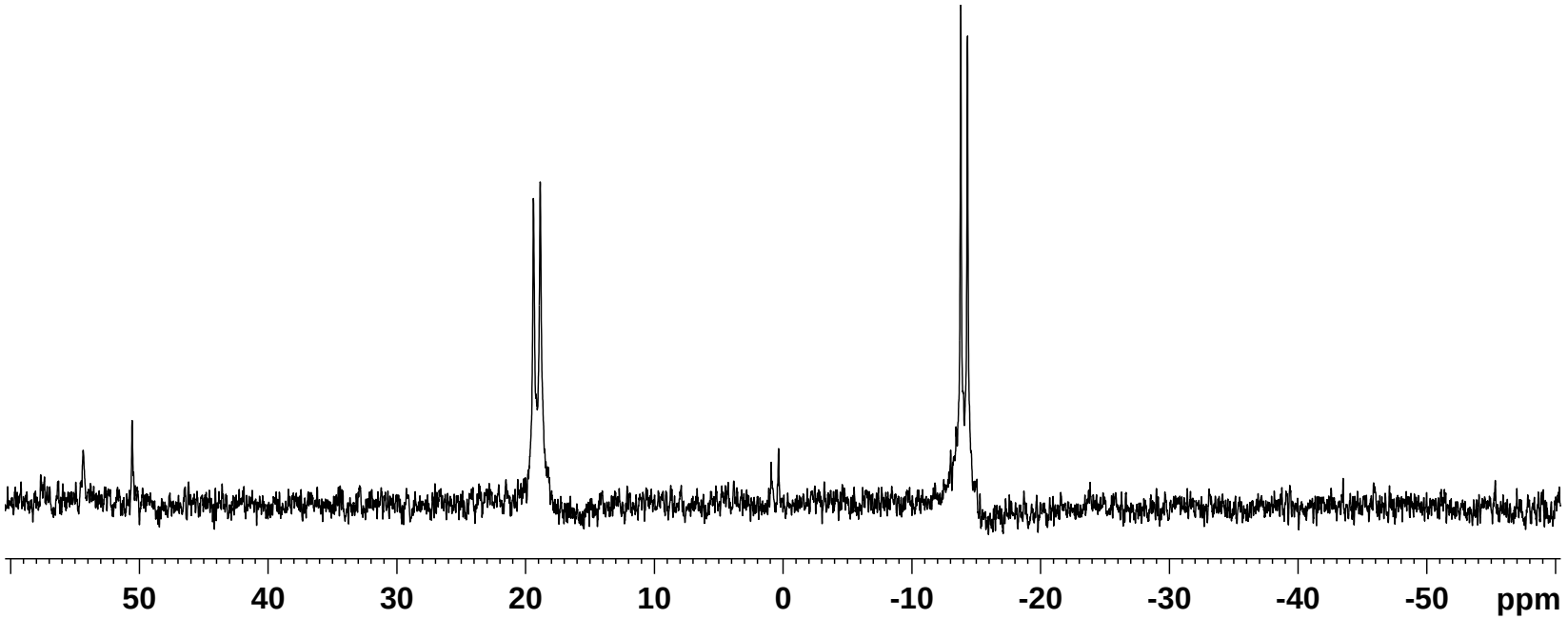
$^{31}P\{^{1}H\}$ NMR spectrum of **1-PPh$_3$** recorded at 193 K in dichloromethane
(**1-PPh$_3$** prepared by addition of 1 eq. PPh_3 to **1-TFA**, [1-PPh_3]/[1-TFA]=12.3 by integration of corresponding resonances)



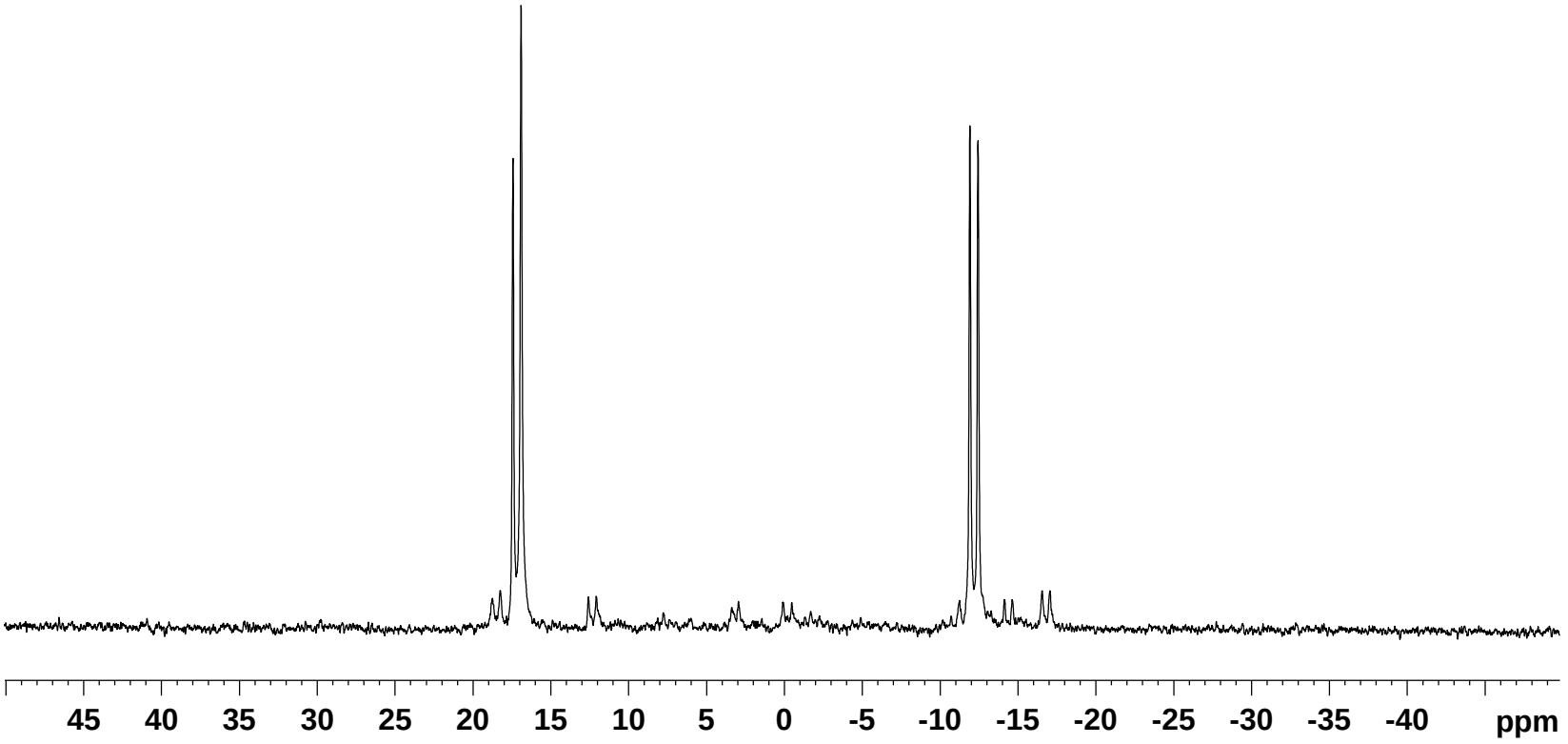
$^{31}P\{^{1}H\}$ NMR spectrum of **1-Cl** recorded at 193 K in dichloromethane
(**1-Cl** prepared by addition of 1 eq. Bu_4NCl to **1-TFA**, [1-Cl]/[1-TFA]=1.7 by integration of corresponding resonances)



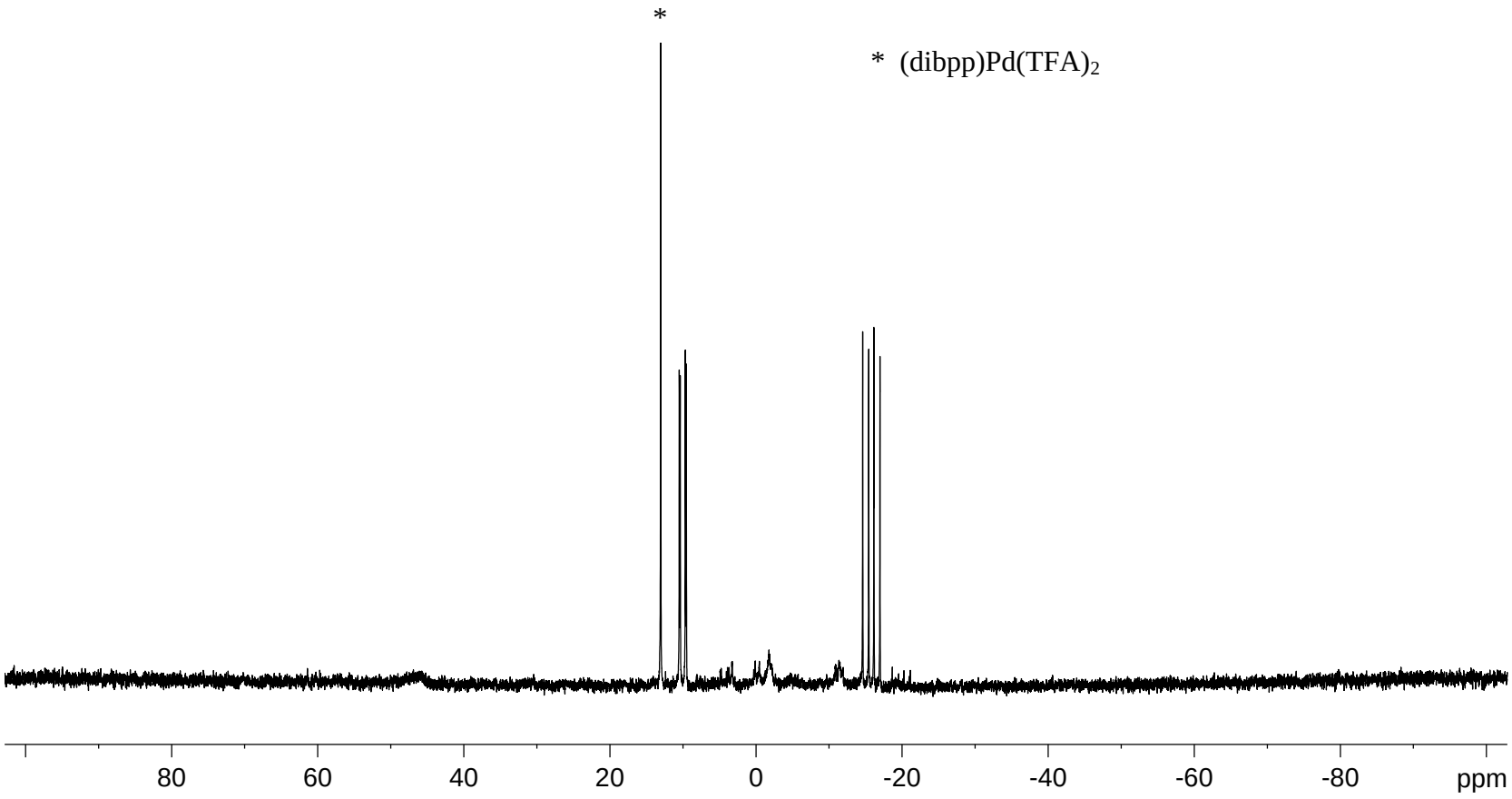
$^{31}P\{^{1}H\}$ NMR spectrum of **1-CH_3OH** recorded at 193 K in dichloromethane



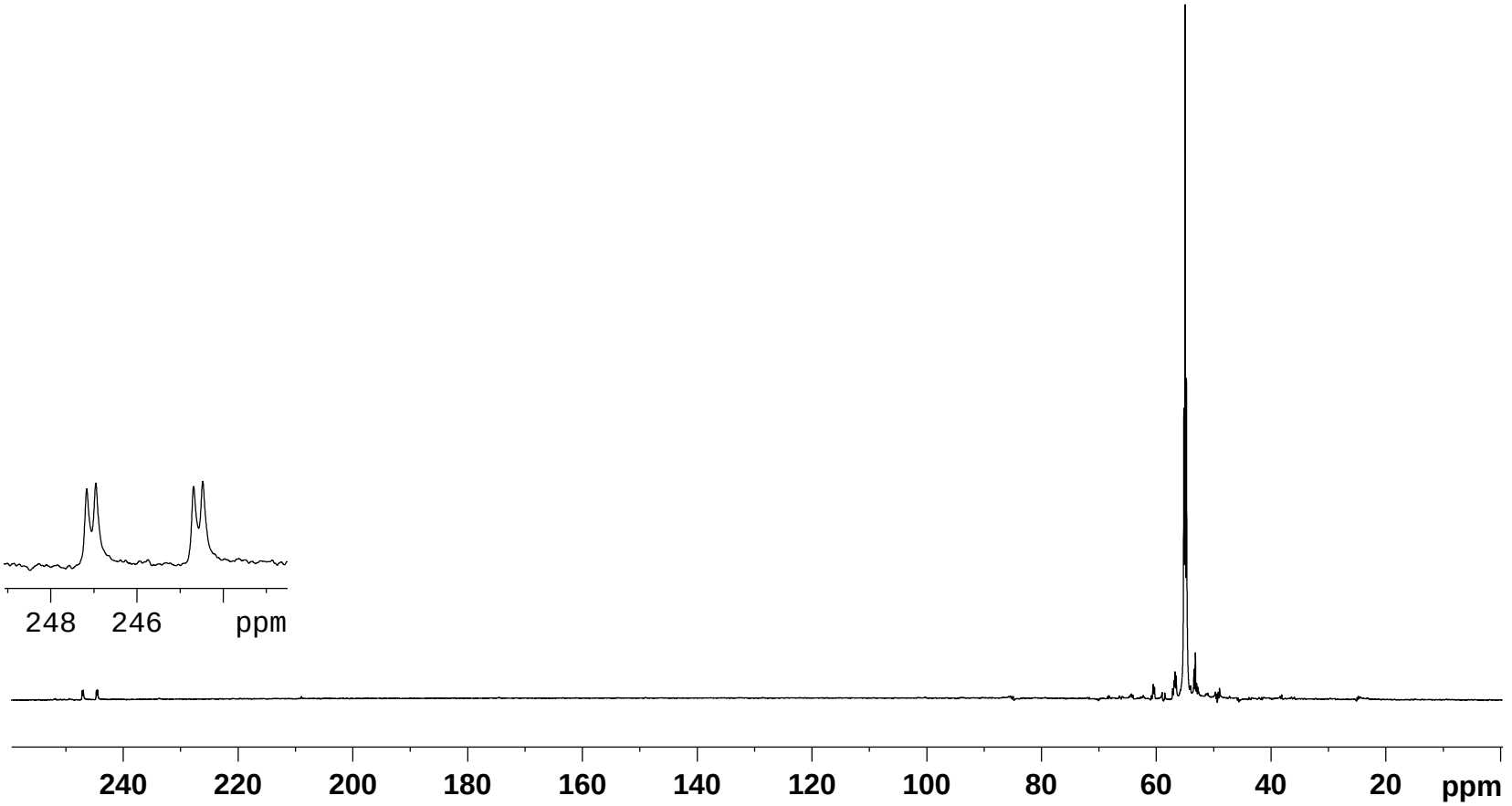
$^{31}P\{^{1}H\}$ NMR spectrum of **1-OTs** recorded at 193 K in dichloromethane



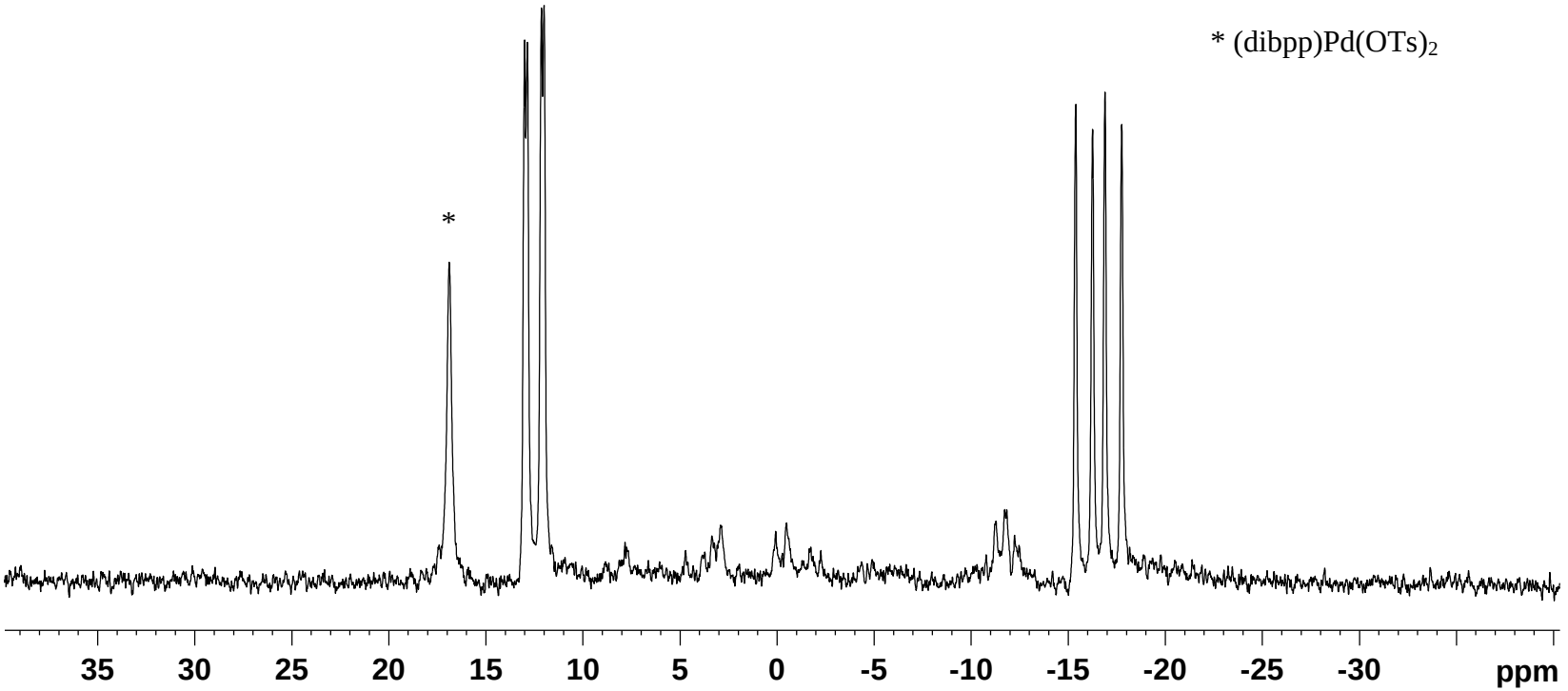
$^{31}P\{^{1}H\}$ NMR spectrum of **2-TFA** recorded at 193 K in dichloromethane



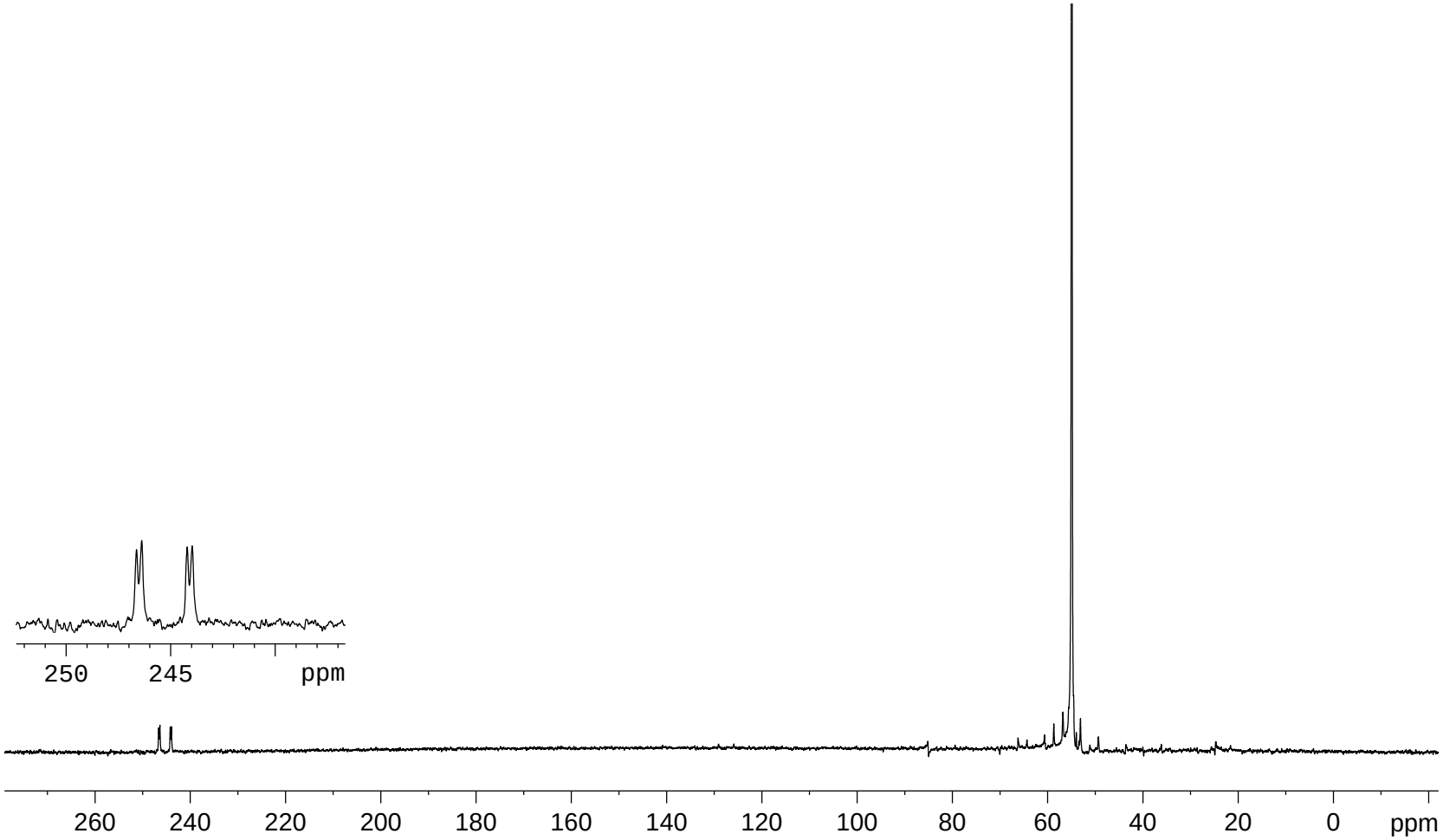
$^{13}C\{^{1}H\}$ NMR spectrum of **2-TFA** recorded at 193 K in dichloromethane



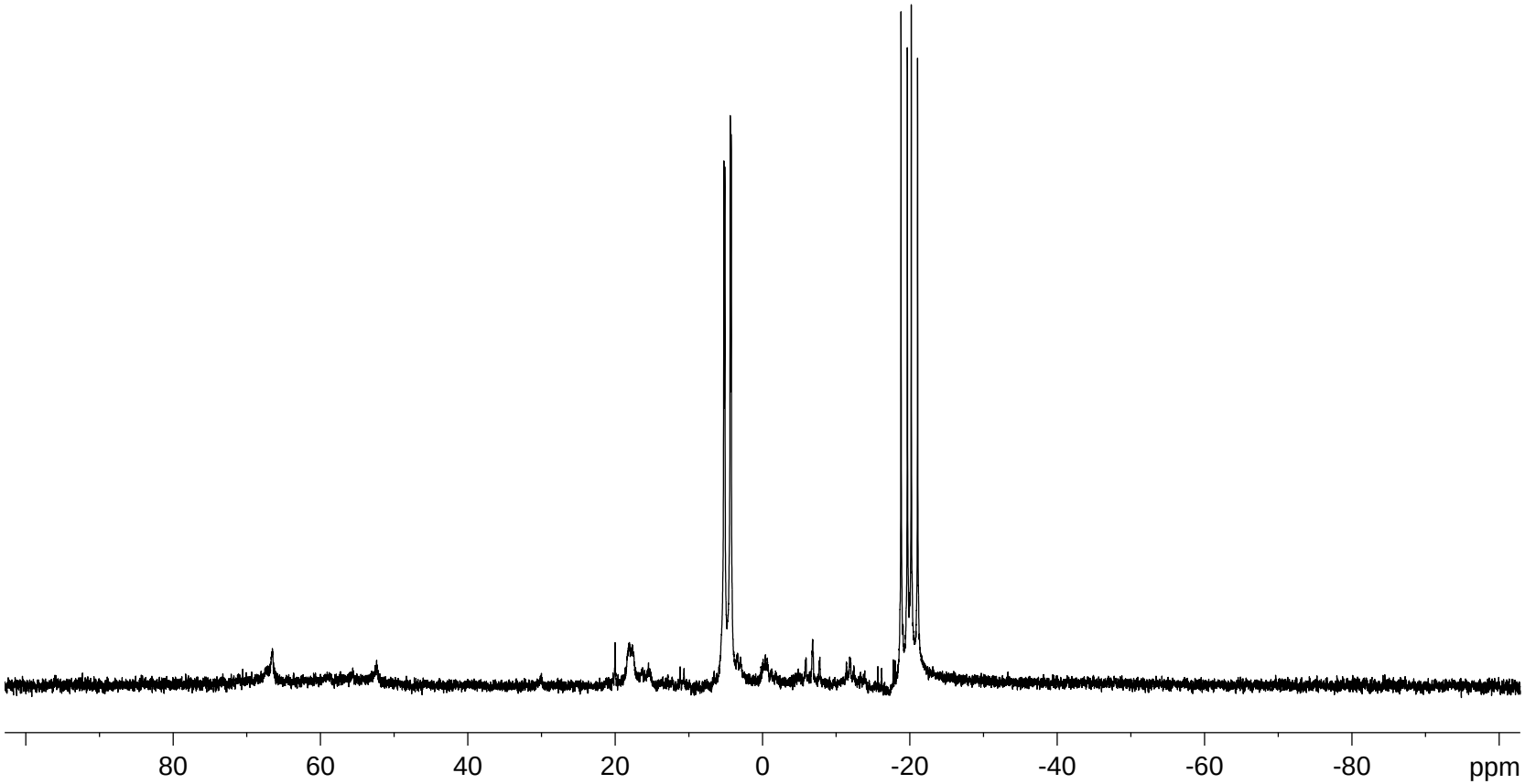
$^{31}P\{^{1}H\}$ NMR spectrum of **2-OTs** recorded at 193 K in dichloromethane



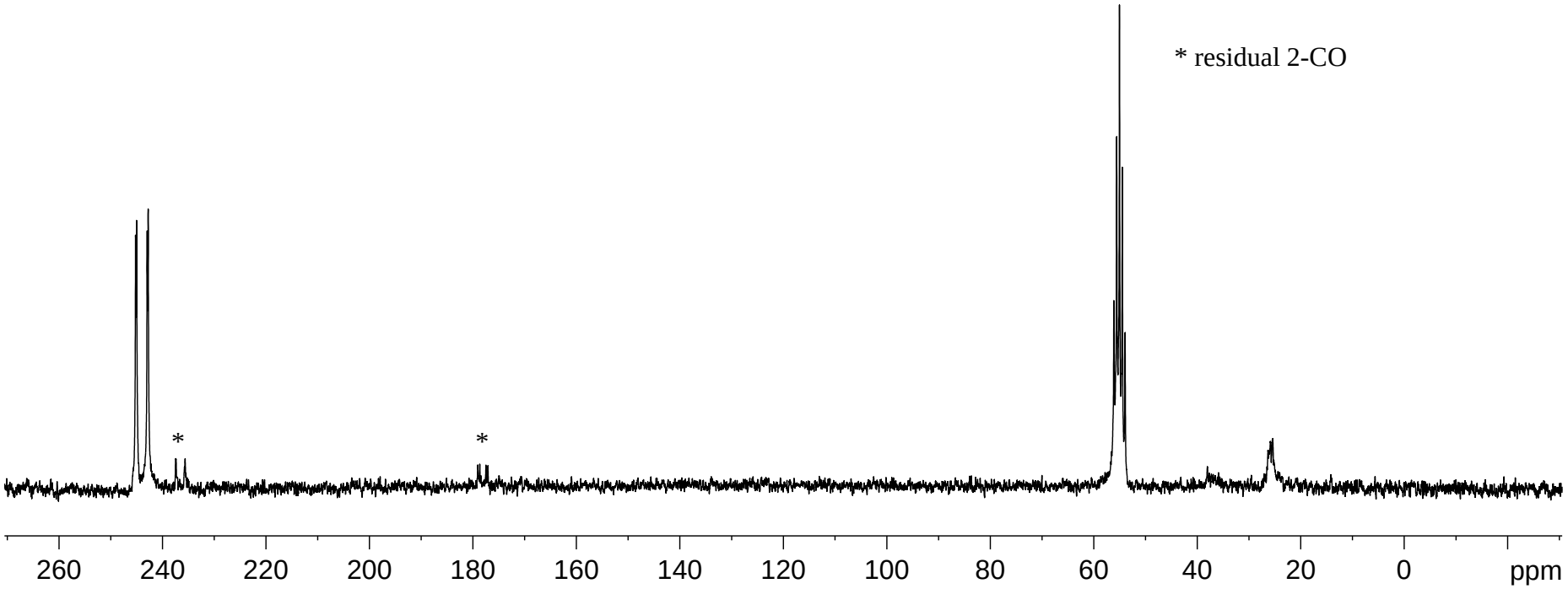
$^{13}C\{^{1}H\}$ NMR spectrum of **2-OTs** recorded at 193 K in dichloromethane



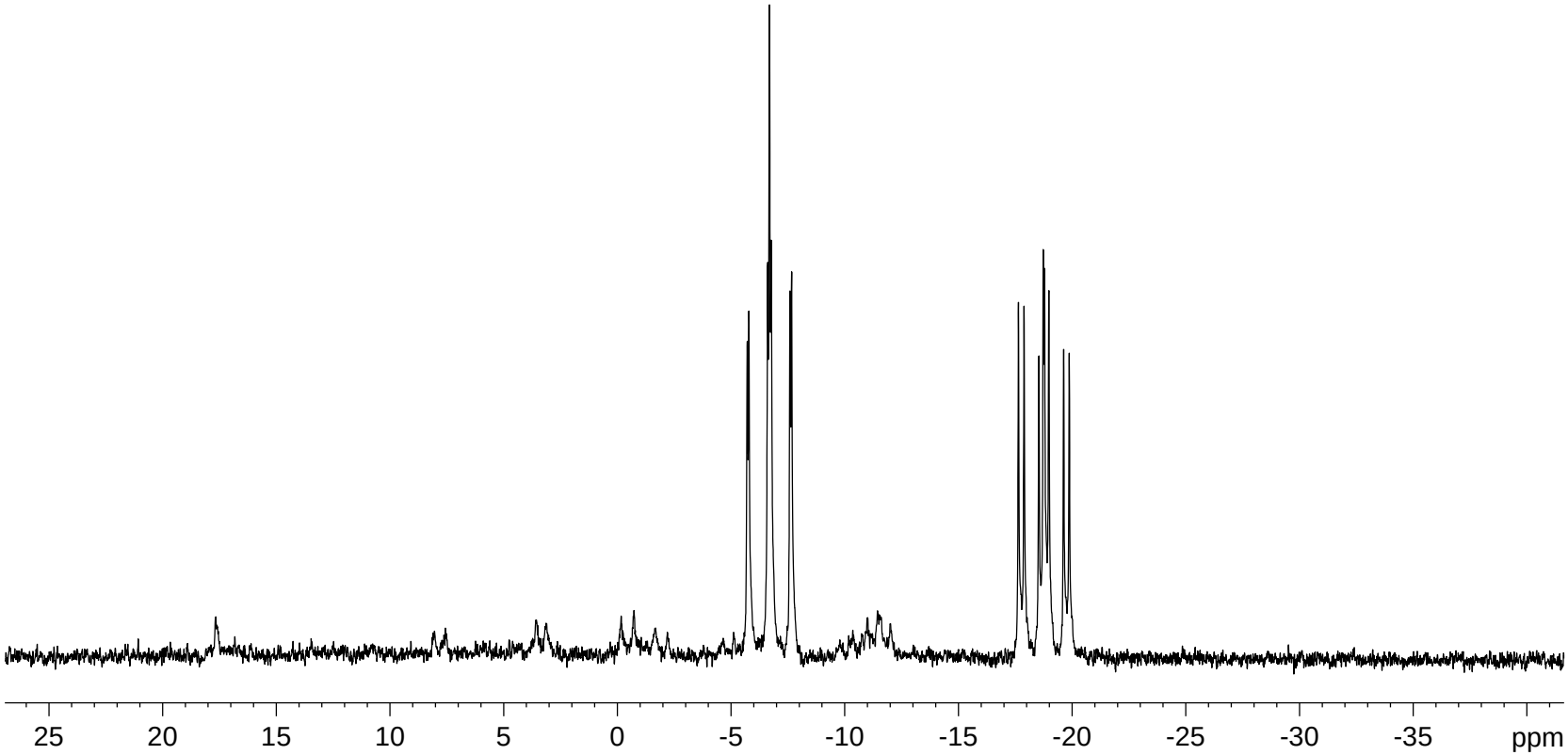
$^{31}P\{^{1}H\}$ NMR spectrum of [**2-CH_3CN](OTf)** recorded at 193 K in dichloromethane



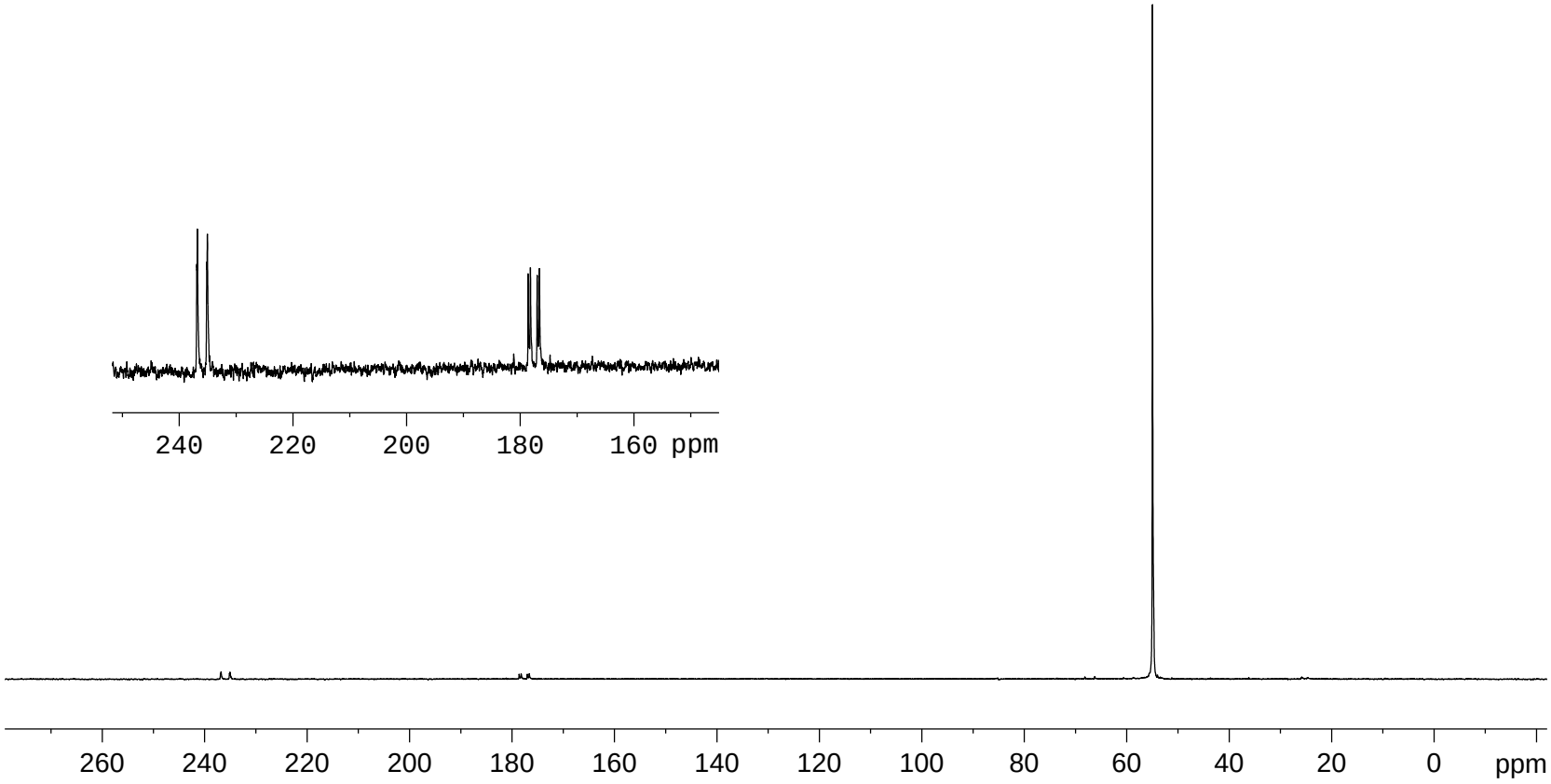
$^{13}C\{^{1}H\}$ NMR spectrum of **[2-CH_3CN](OTf)** recorded at 193 K in dichloromethane



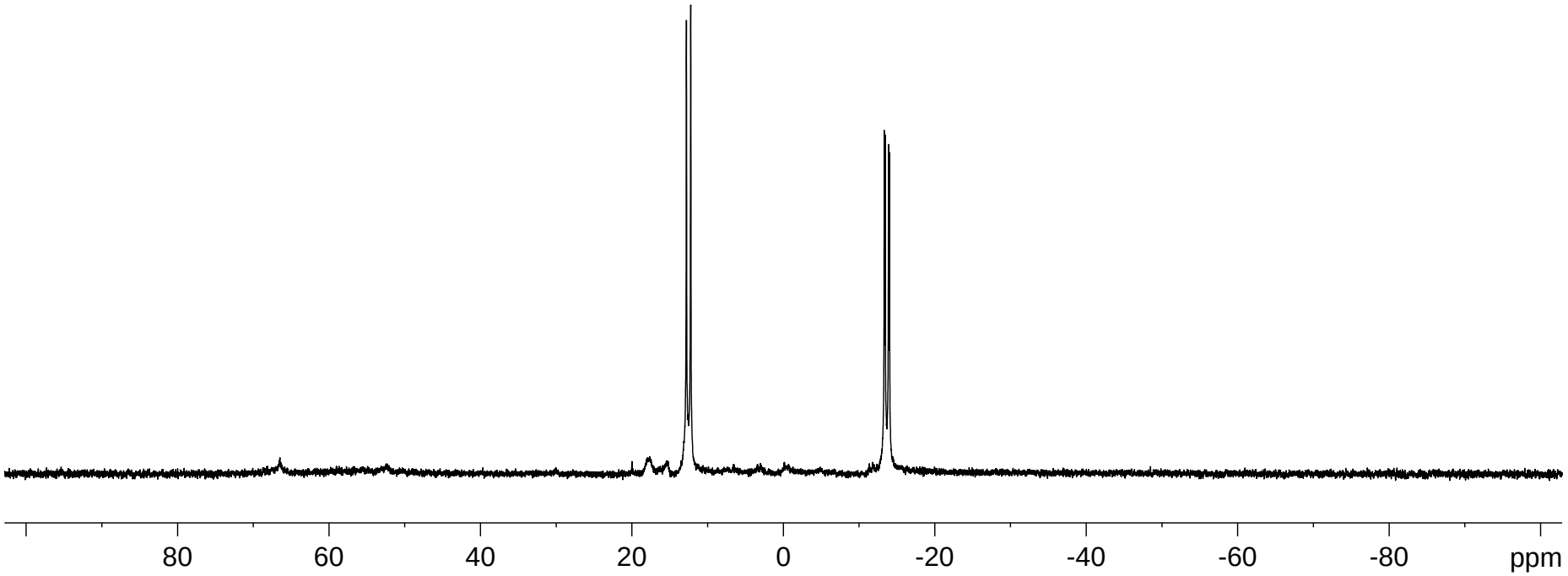
$^{31}P\{^{1}H\}$ NMR spectrum of [**2-CO](OTf)** recorded at 193 K in dichloromethane



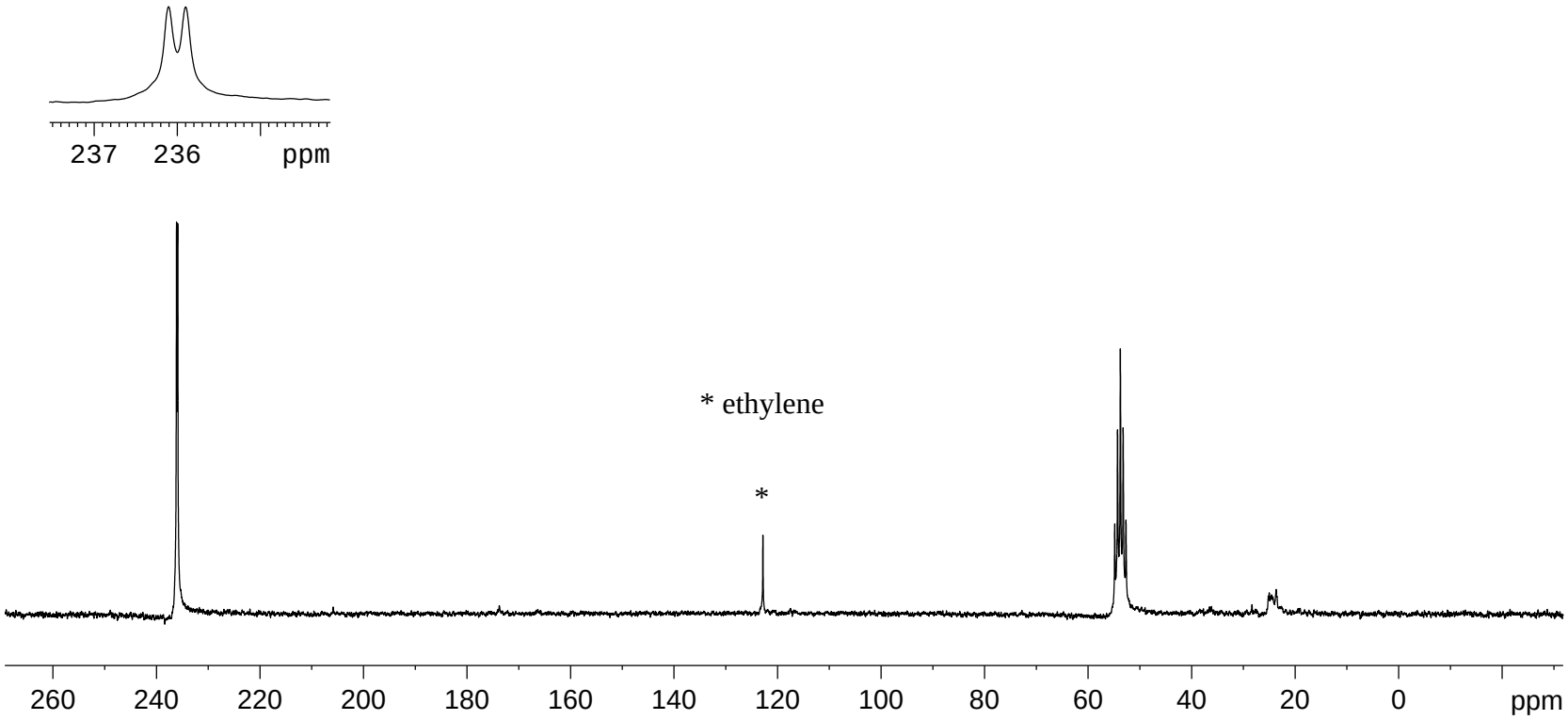
$^{13}C\{^{1}H\}$ NMR spectrum of **[2-CO](OTf)** recorded at 193 K in dichloromethane



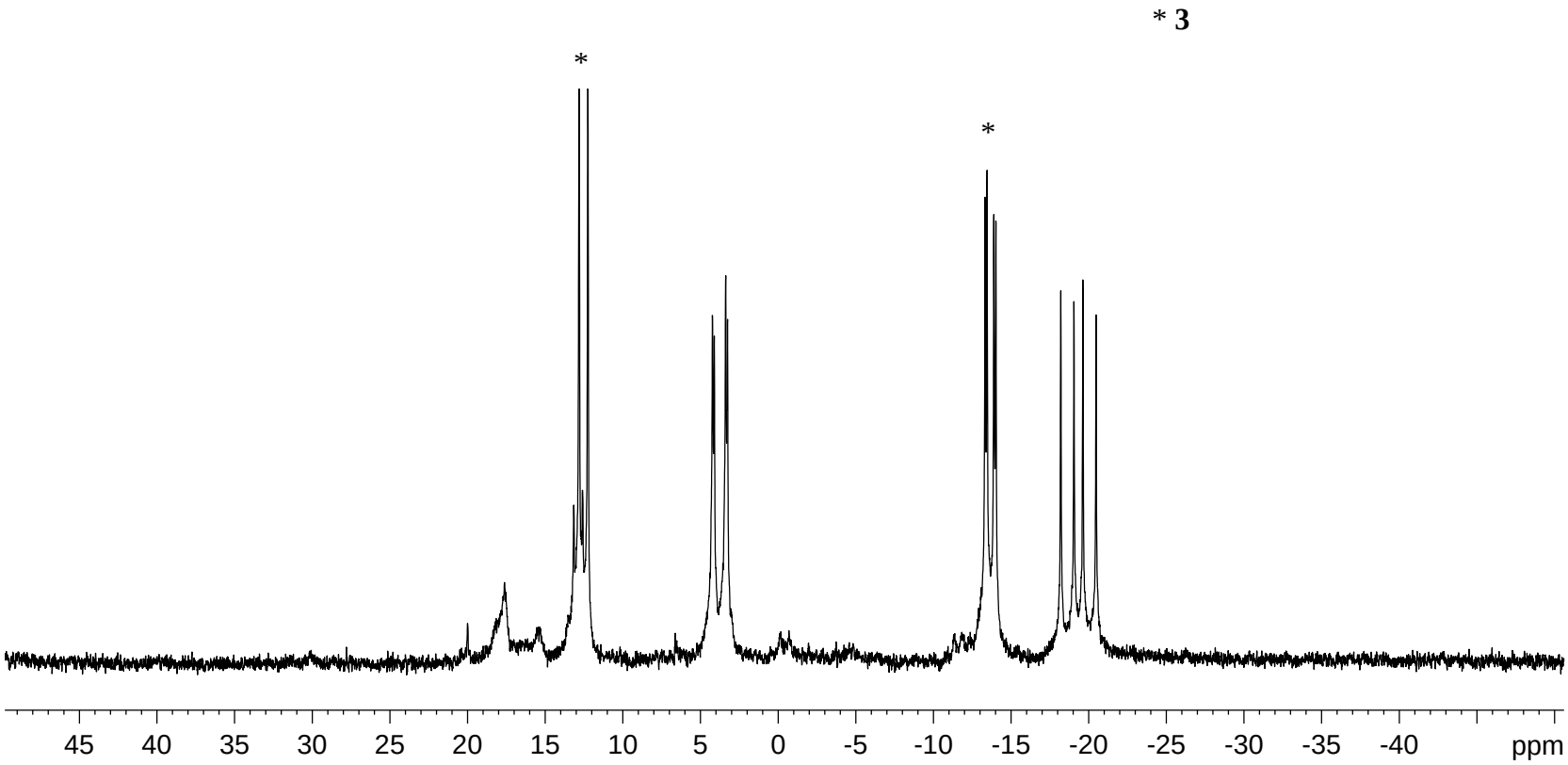
$^{31}P\{^{1}H\}$ NMR spectrum of **3** recorded at 193 K in dichloromethane



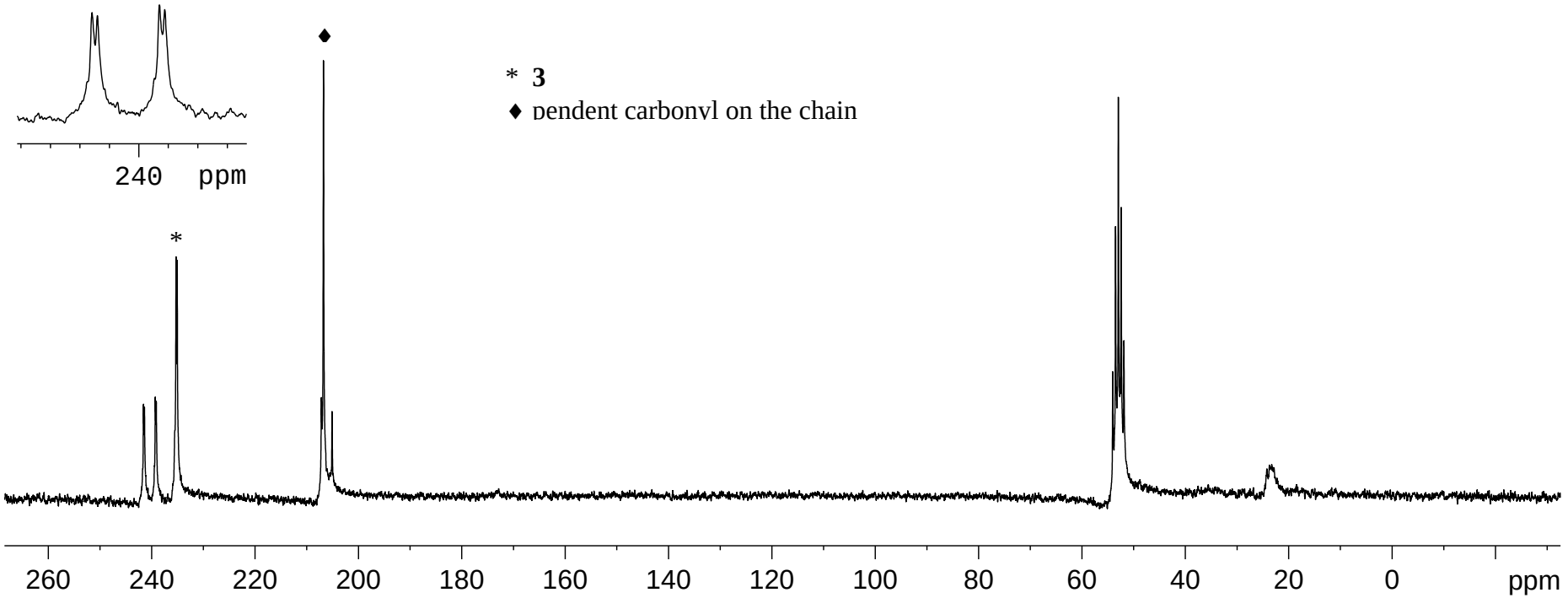
$^{13}C\{^{1}H\}$ NMR spectrum of **3** recorded at 193 K in dichloromethane



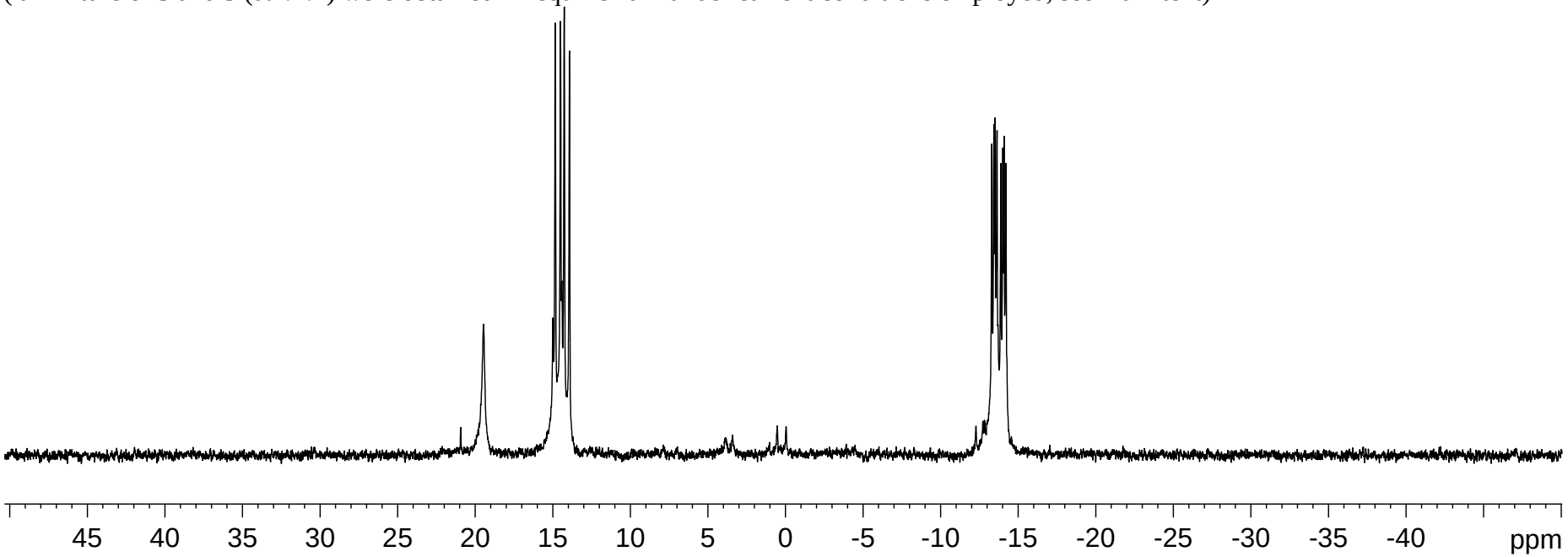
$^{31}P\{^{1}H\}$ NMR spectrum of **3** and **[4-CH_3CN](OTf)** recorded at 193 K in dichloromethane (insertion of CO into **3** can not go to completion under conditions employed)



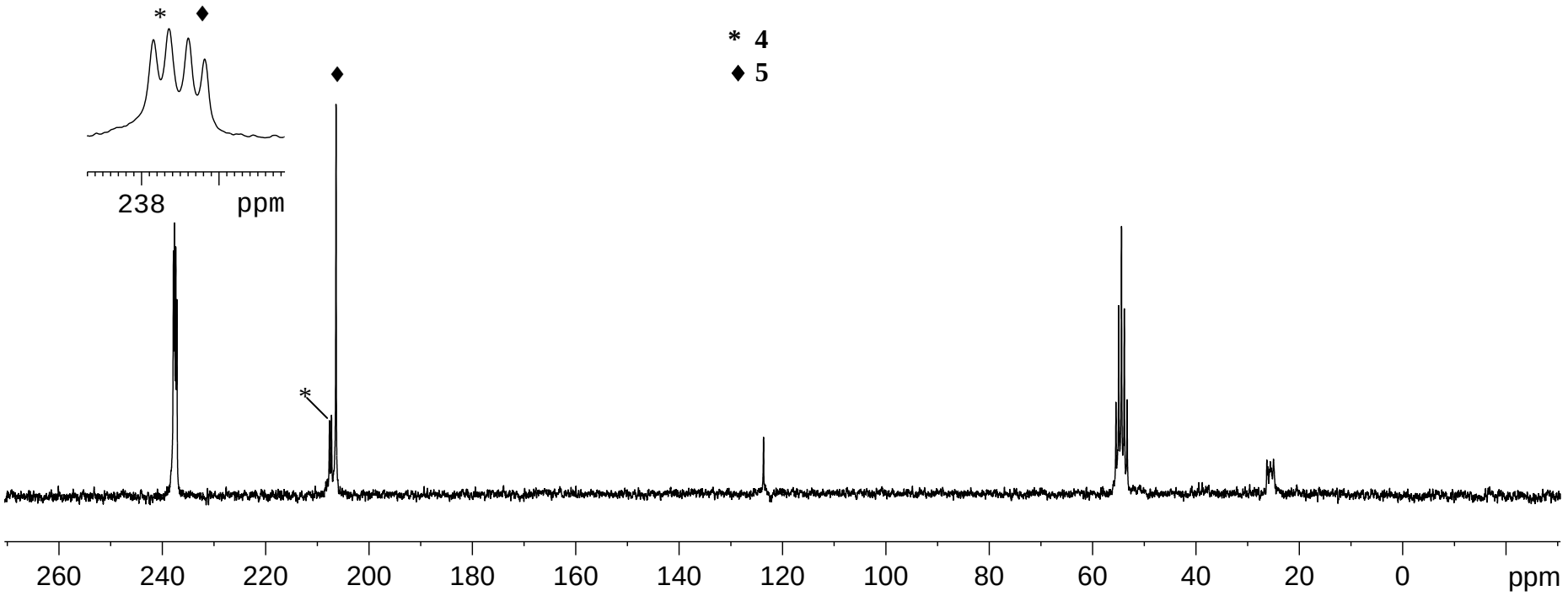
$^{13}C\{^{1}H\}$ NMR spectrum of **[4-CH_3CN](OTf)** recorded at 193 K in dichloromethane



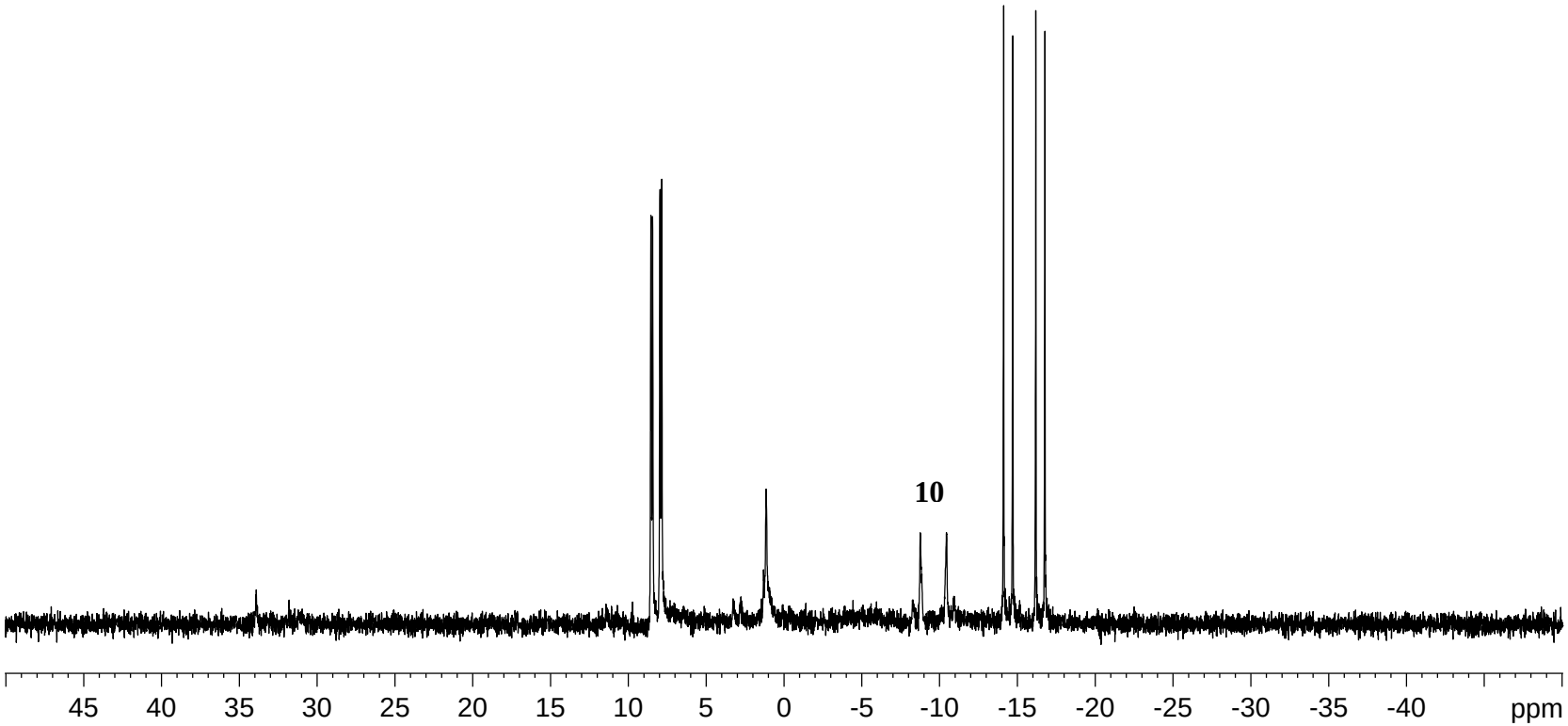
$^{31}P\{^{1}H\}$ NMR spectrum of **3** and **5** recorded at 193 K in dichloromethane
(a mixture of **3** and **5** (*ca* .1:1) were obtained in equilibrium under current conditions employed, see main text)



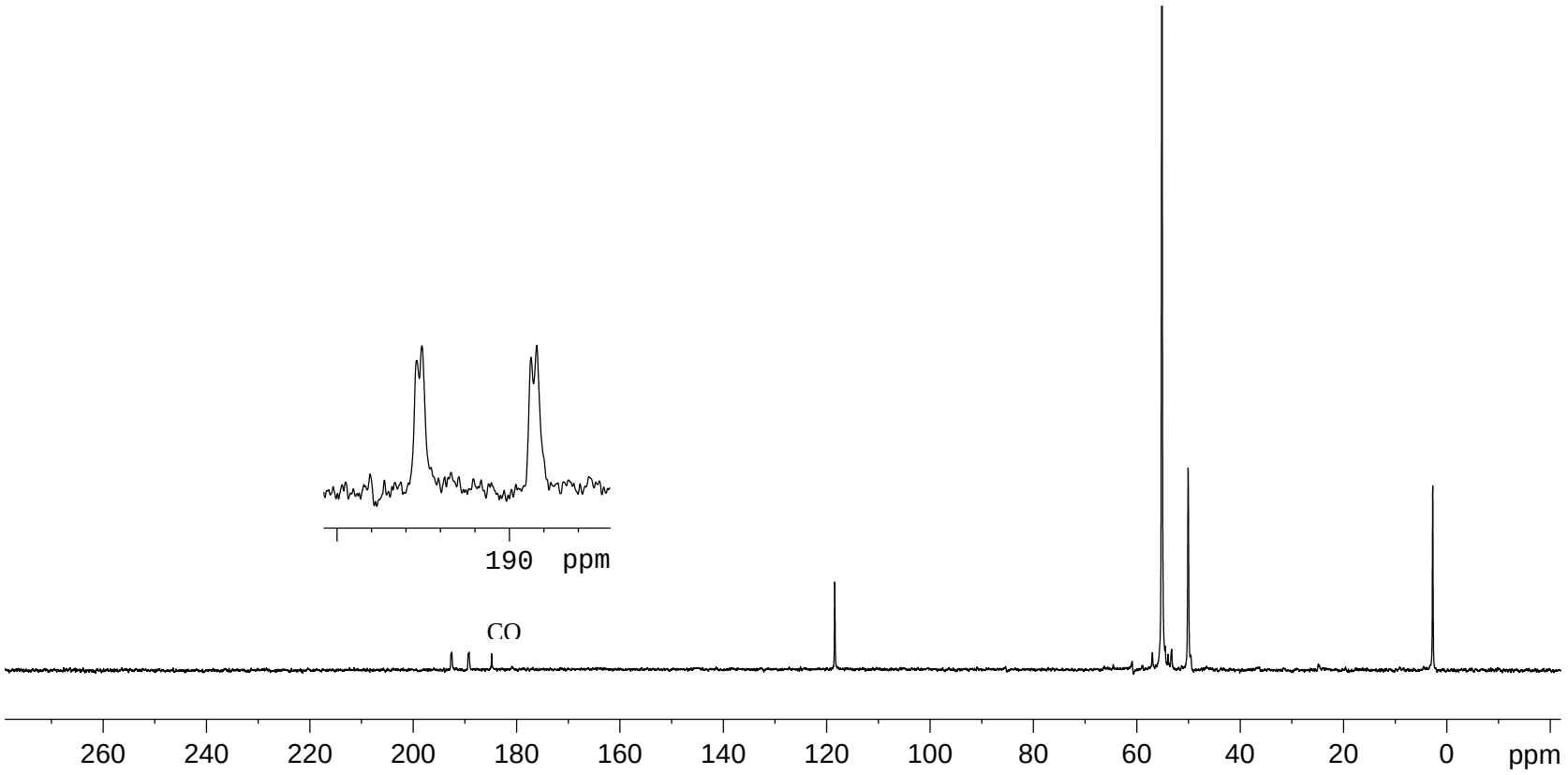
$^{13}C\{^{1}H\}$ NMR spectrum of **5** recorded at 193 K in dichloromethane



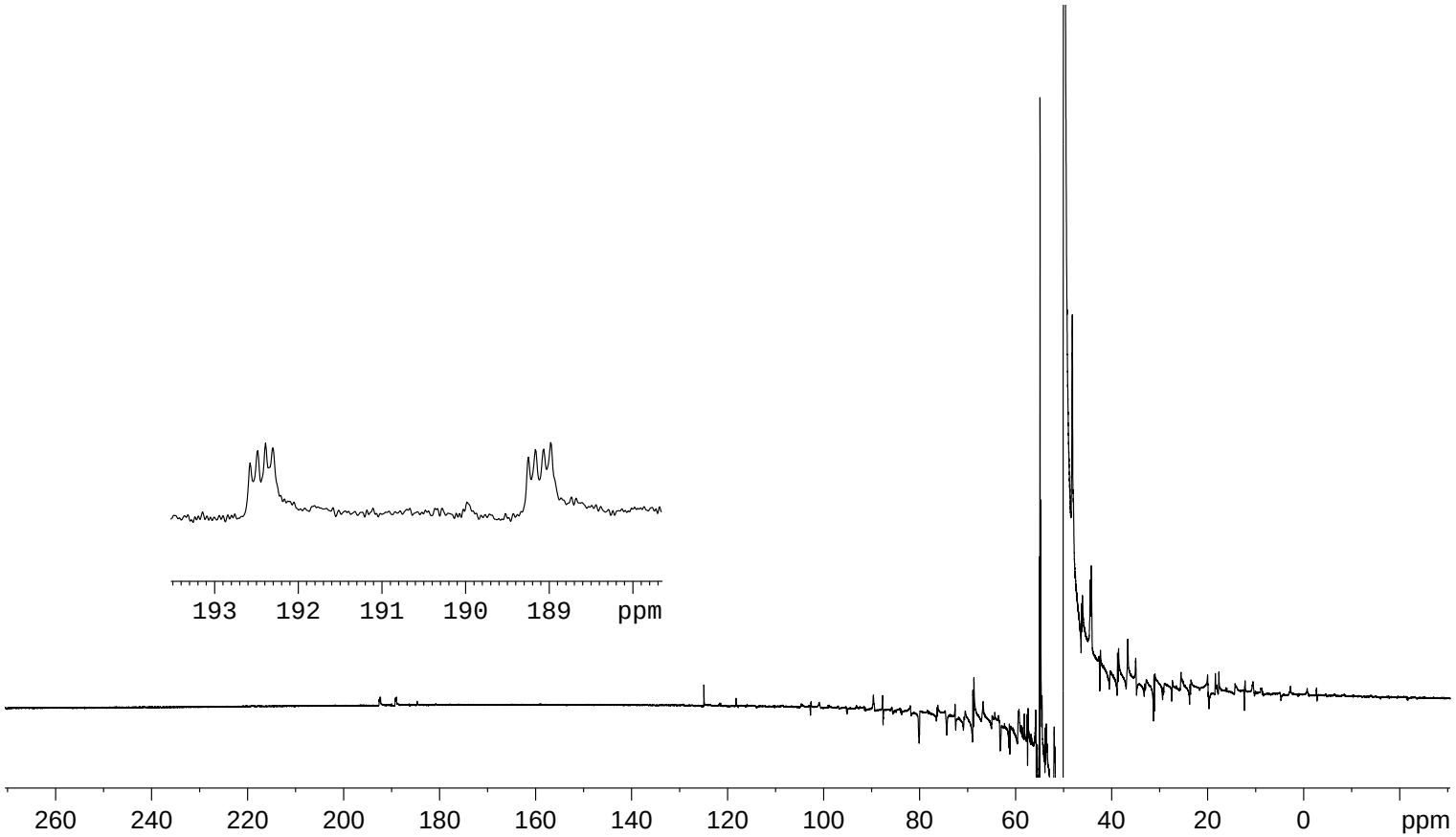
$^{31}P\{^{1}H\}$ NMR spectrum of [**8-CH_3CN](OTf)** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



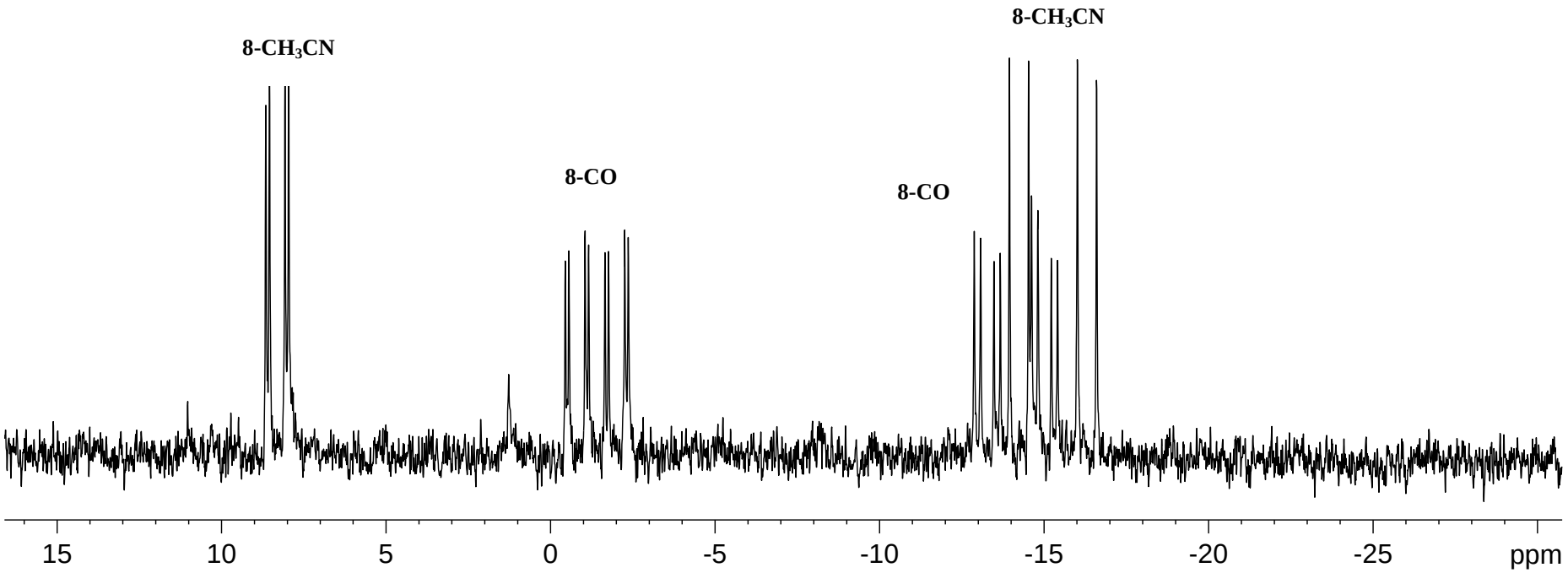
$^{13}C\{^{1}H\}$ NMR spectrum of [**8-CH_3CN](OTf)** recorded at 193 K in $CH_2Cl_2/^{12}CH_3OH/CH_3CN$



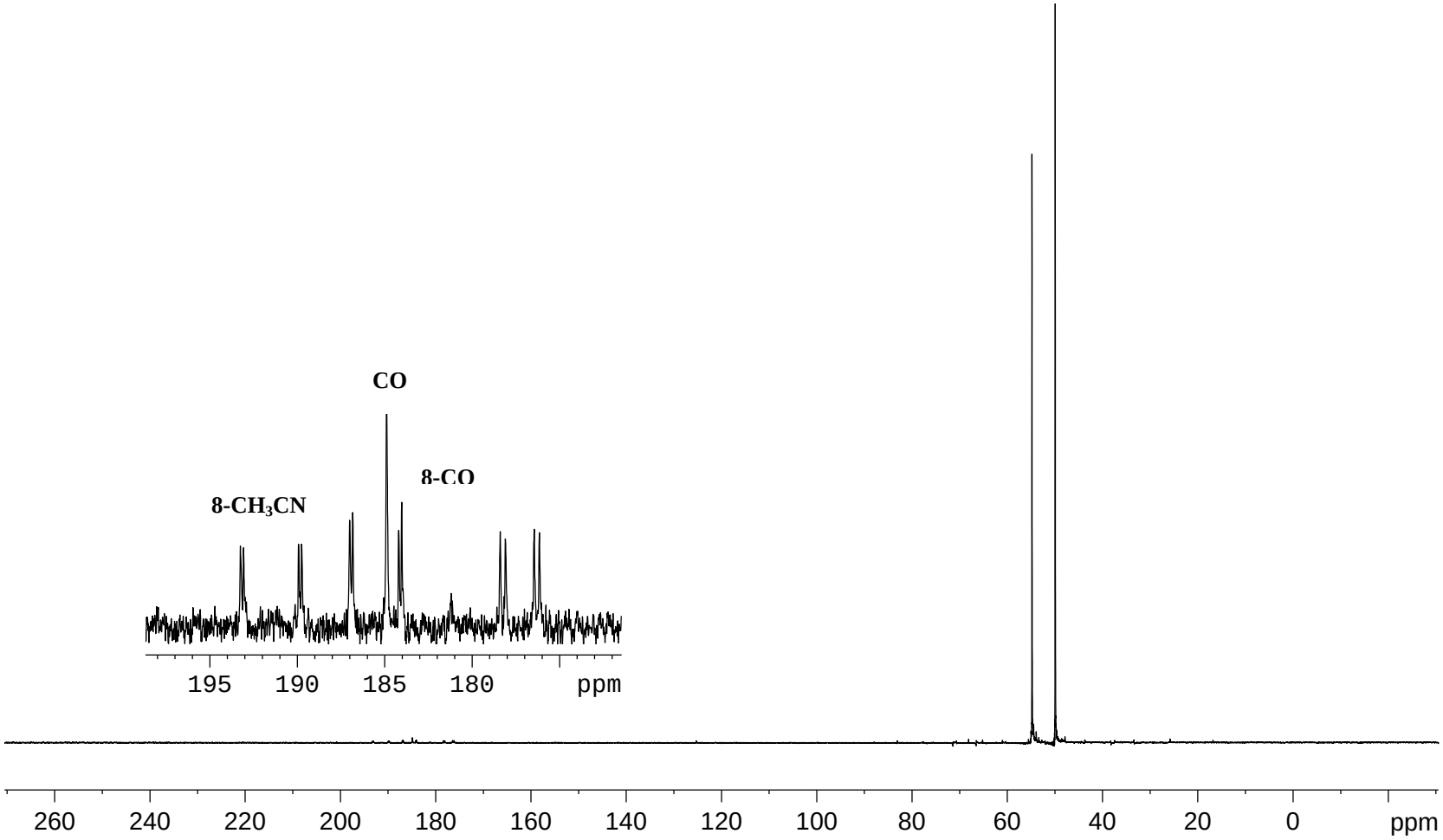
$^{13}C\{^{1}H\}$ NMR spectrum of [**8-CH_3CN](OTf)** recorded at 193 K in $CH_2Cl_2/^{13}CH_3OH/CH_3CN$
($^{13}CH_3O$ resonance is obscured by strong solvent peak, but additional coupling from which to carbonyl is clearly observed in extended carbonyl region)



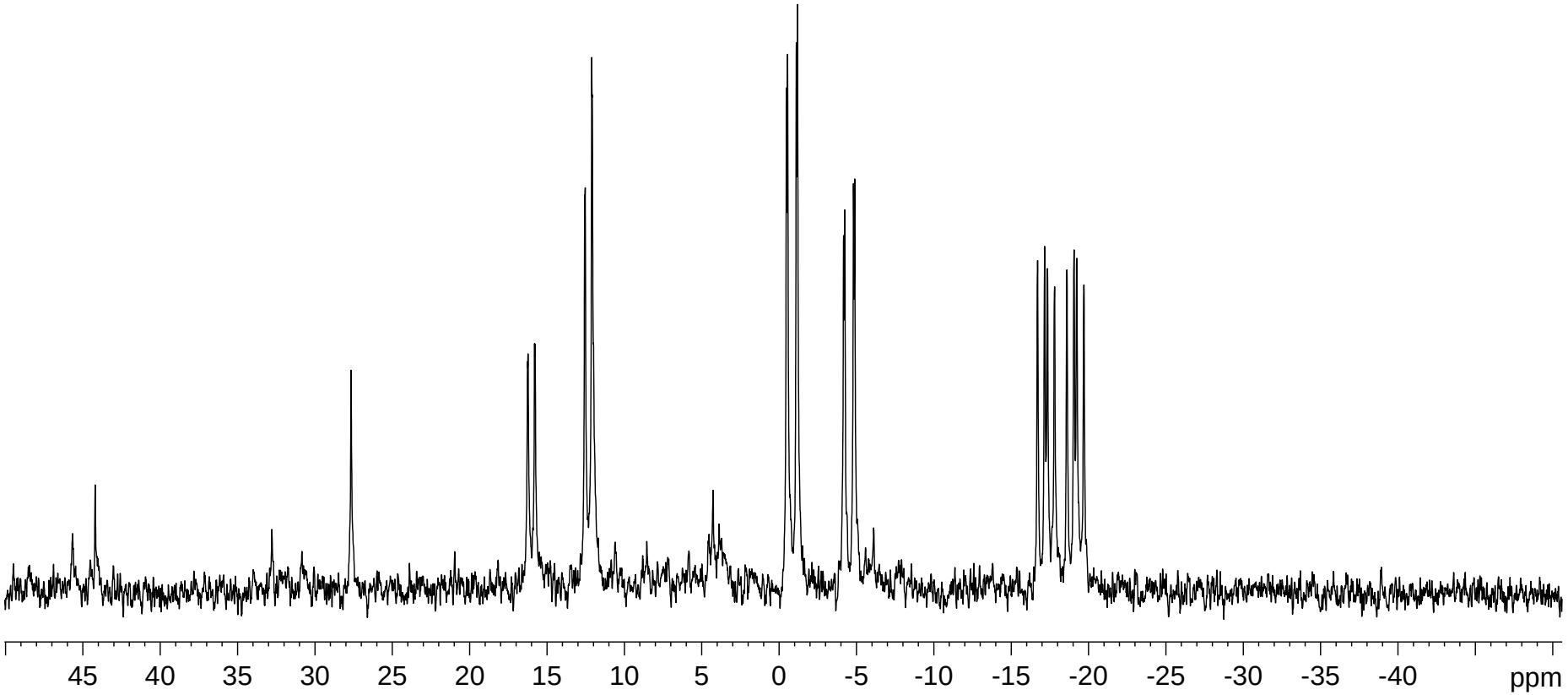
$^{31}P\{^{1}H\}$ NMR spectrum of a mixture of [**8-CO](OTf)** and **[8-CH_3CN](OTf)** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



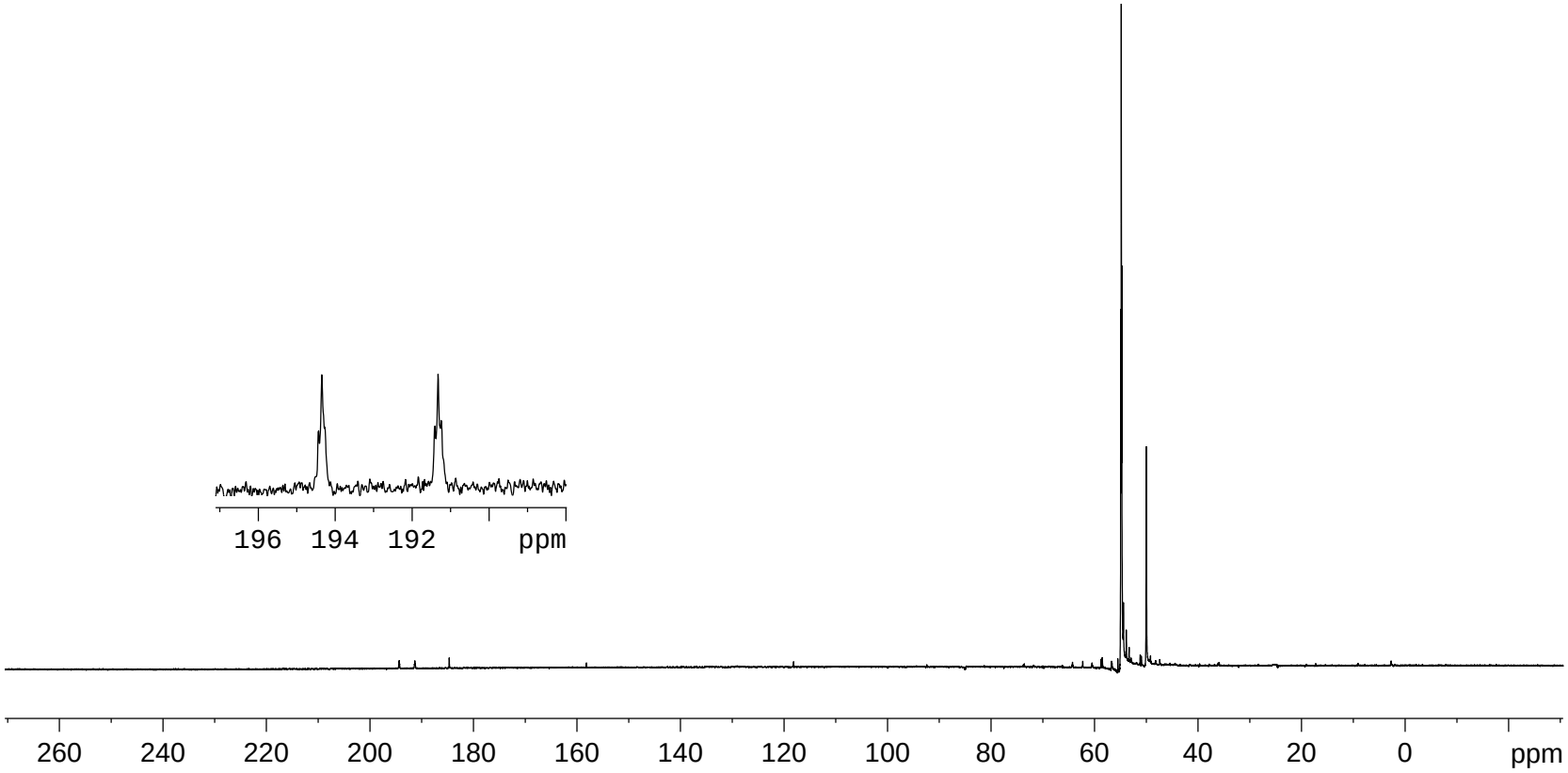
$^{13}C\{^{1}H\}$ NMR spectrum of a mixture of [**8-CO](OTf)** and **[8-CH$_3$CN](OTf)** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



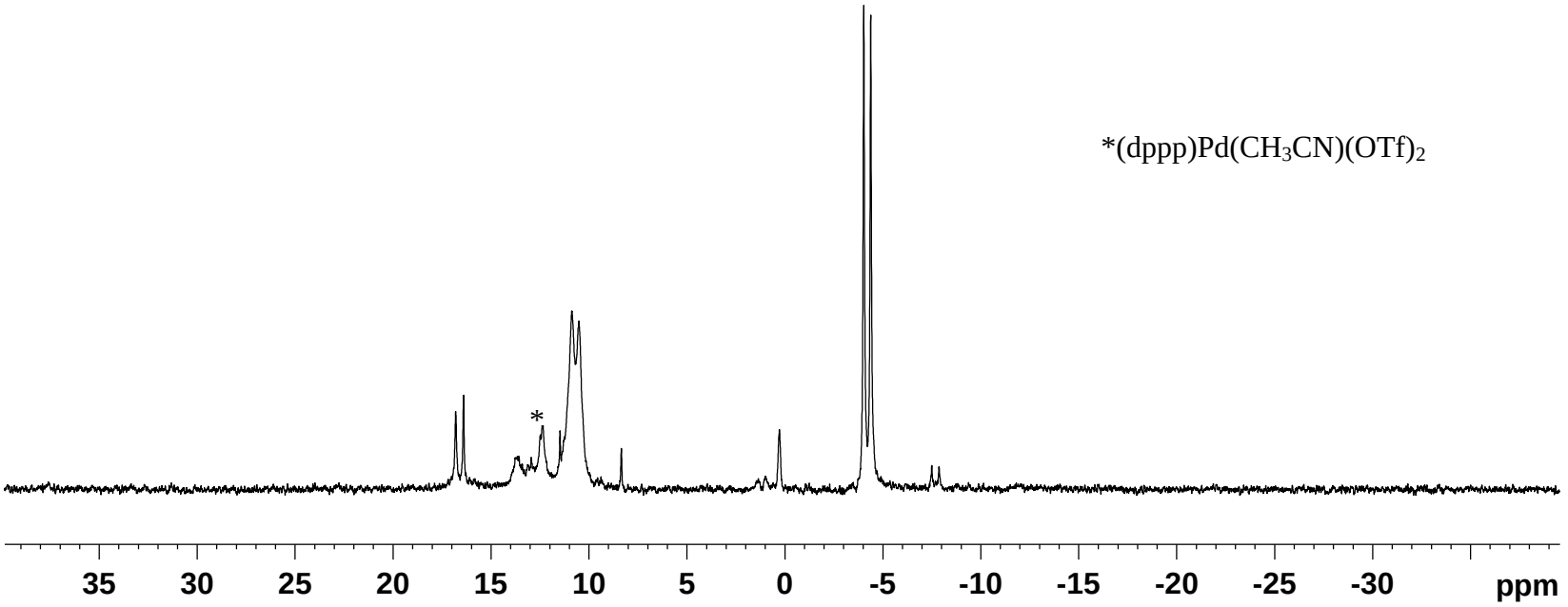
$^{31}P\{^{1}H\}$ NMR spectrum of [**8-PPh$_3$](OTf)** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



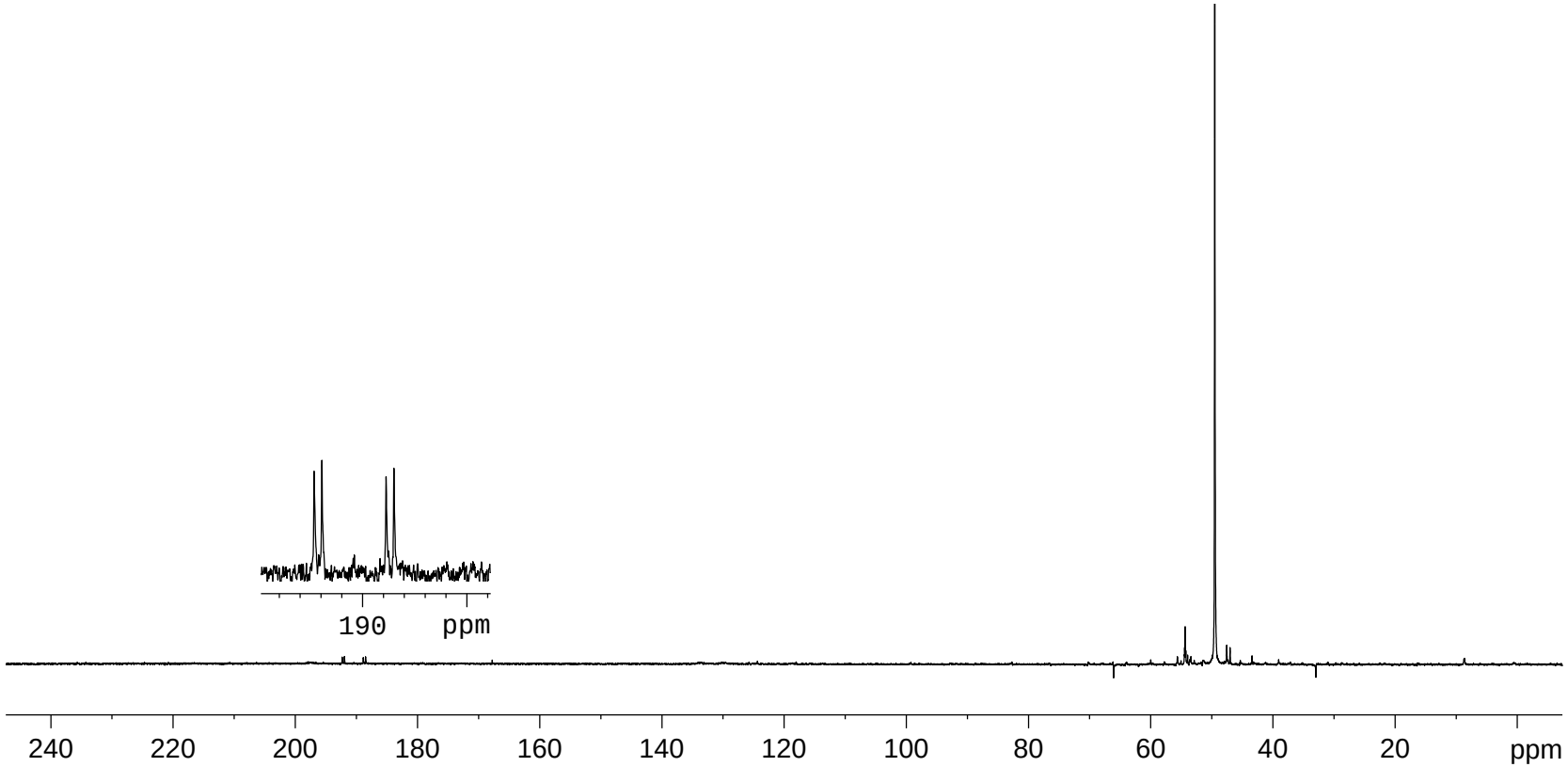
$^{13}C\{^{1}H\}$ NMR spectrum of **[8-PPh$_3$](OTf)** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



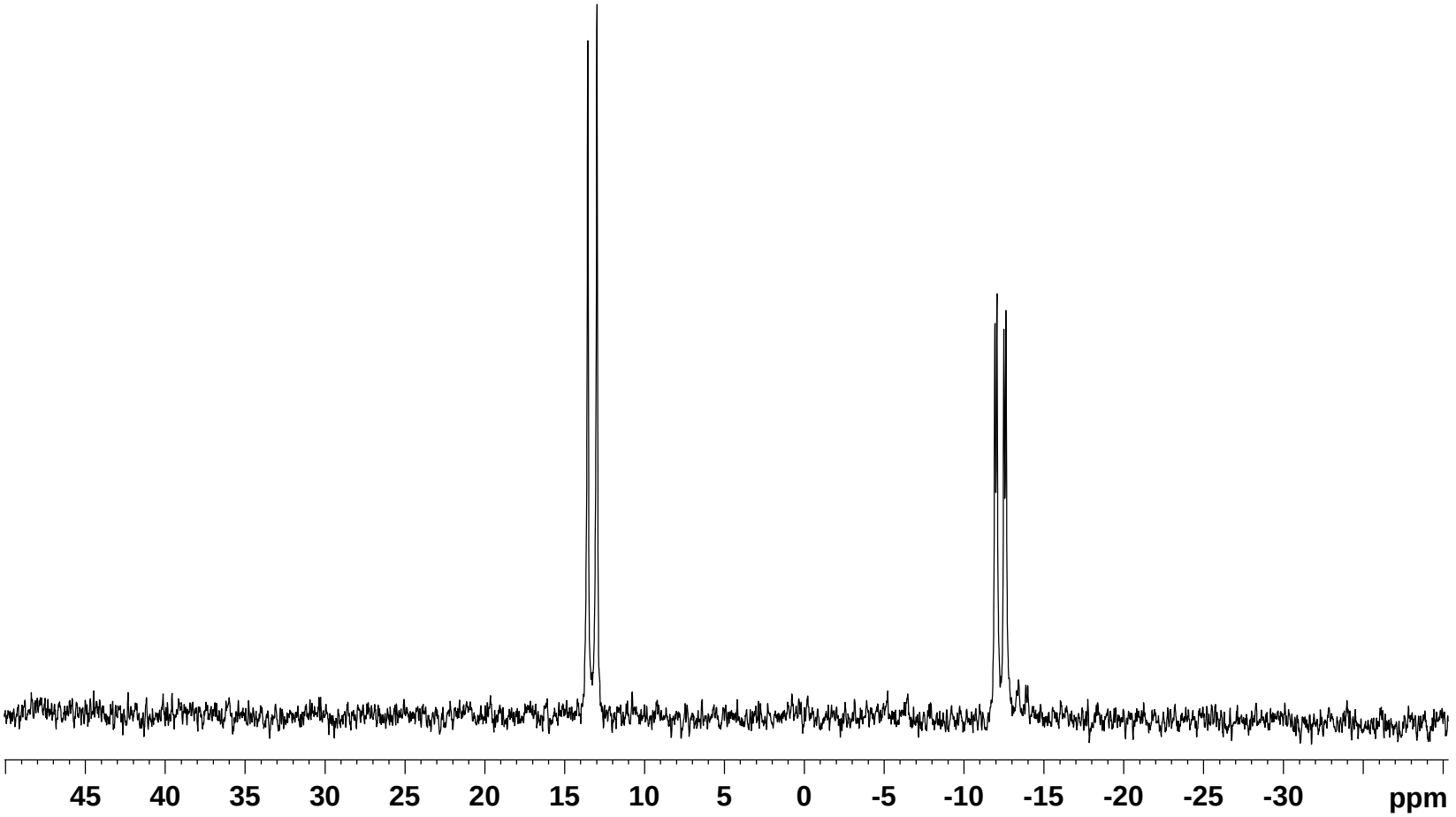
$^{31}P\{^{1}H\}$ NMR spectrum of **9** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



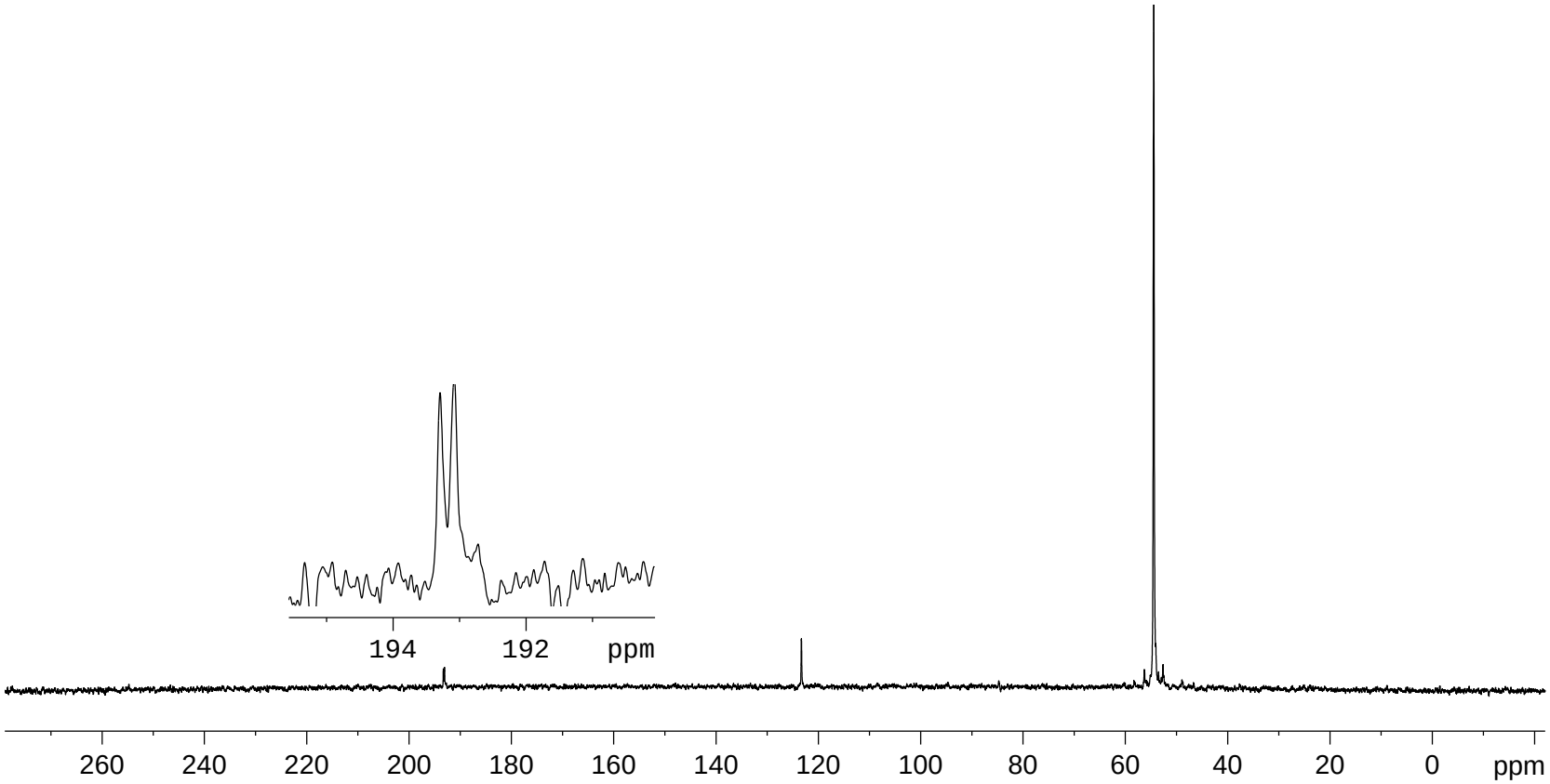
$^{13}C\{^{1}H\}$ NMR spectrum of **9** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



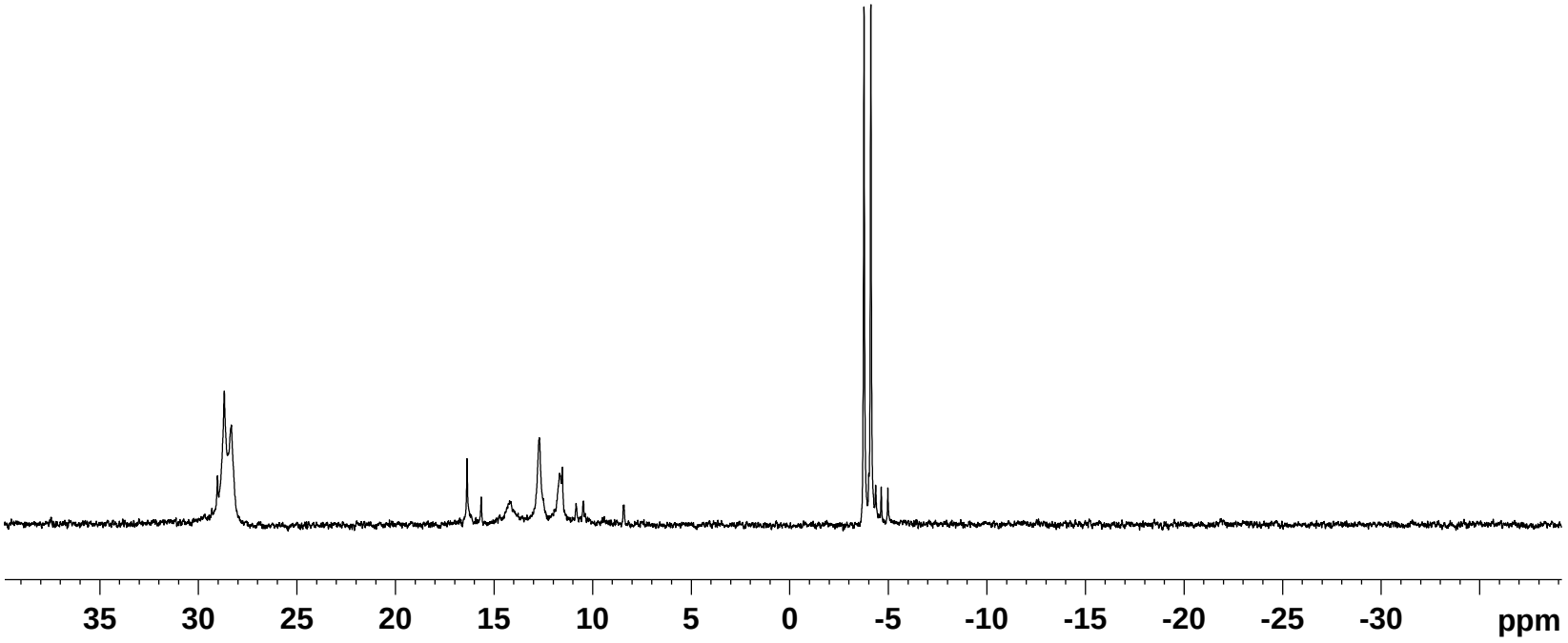
$^{31}P\{^{1}H\}$ NMR spectrum of **11** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



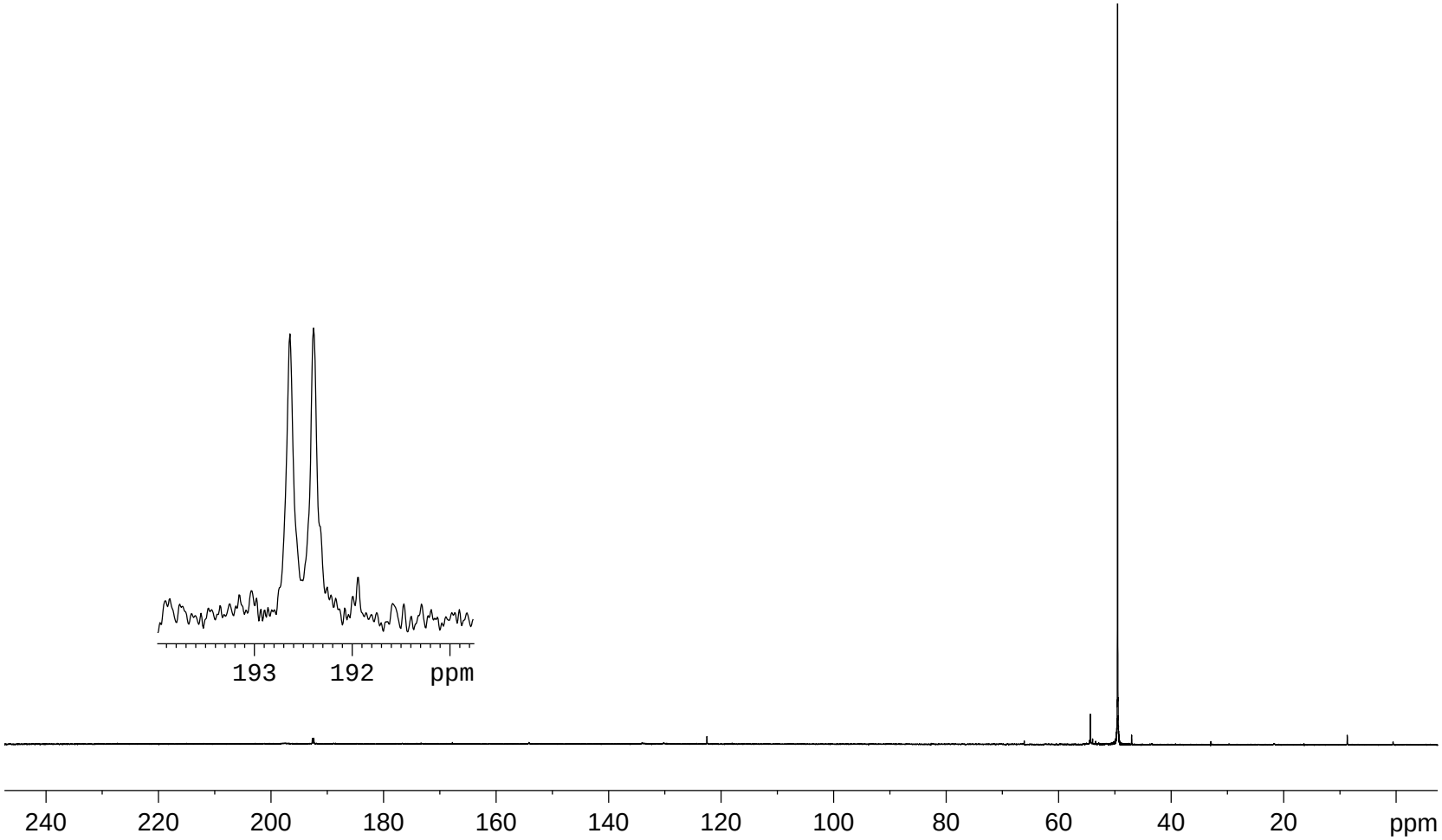
$^{13}C\{^{1}H\}$ NMR spectrum of **11** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



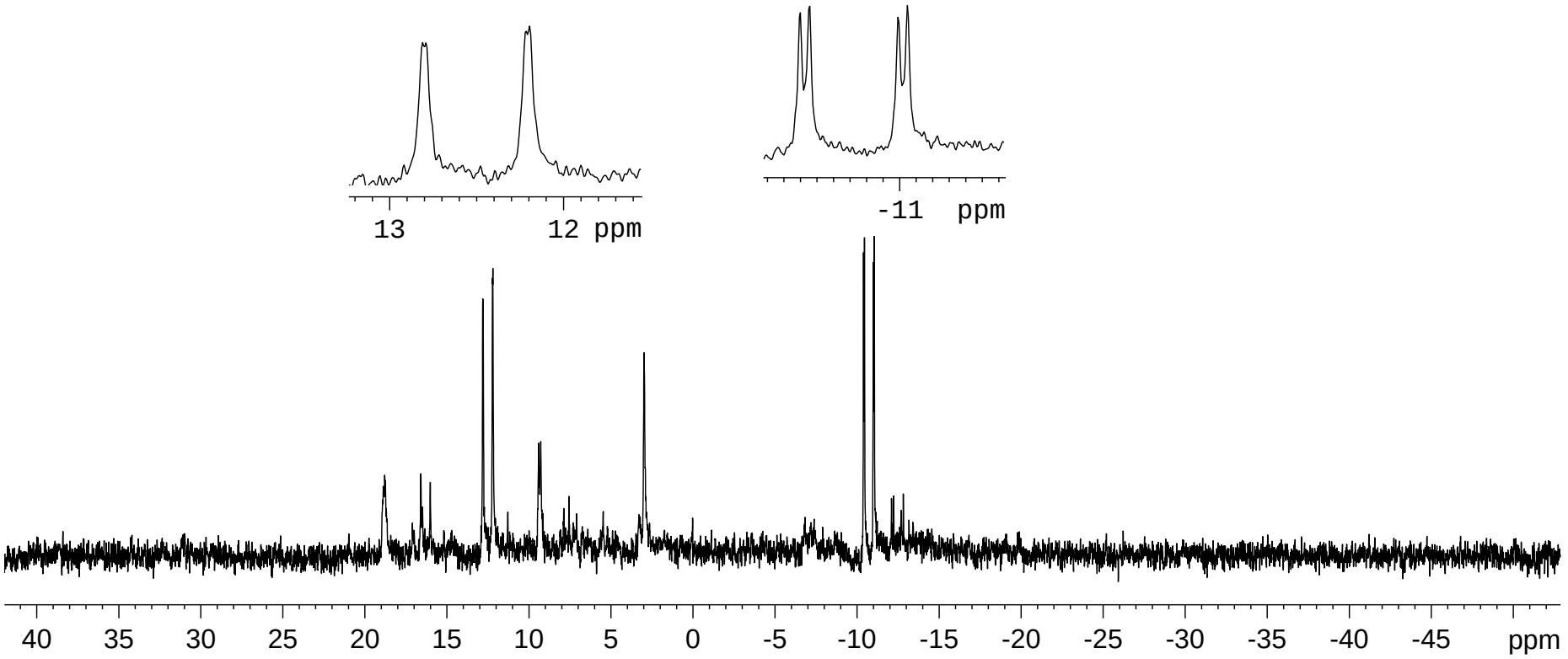
$^{31}P\{^{1}H\}$ NMR spectrum of **12** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



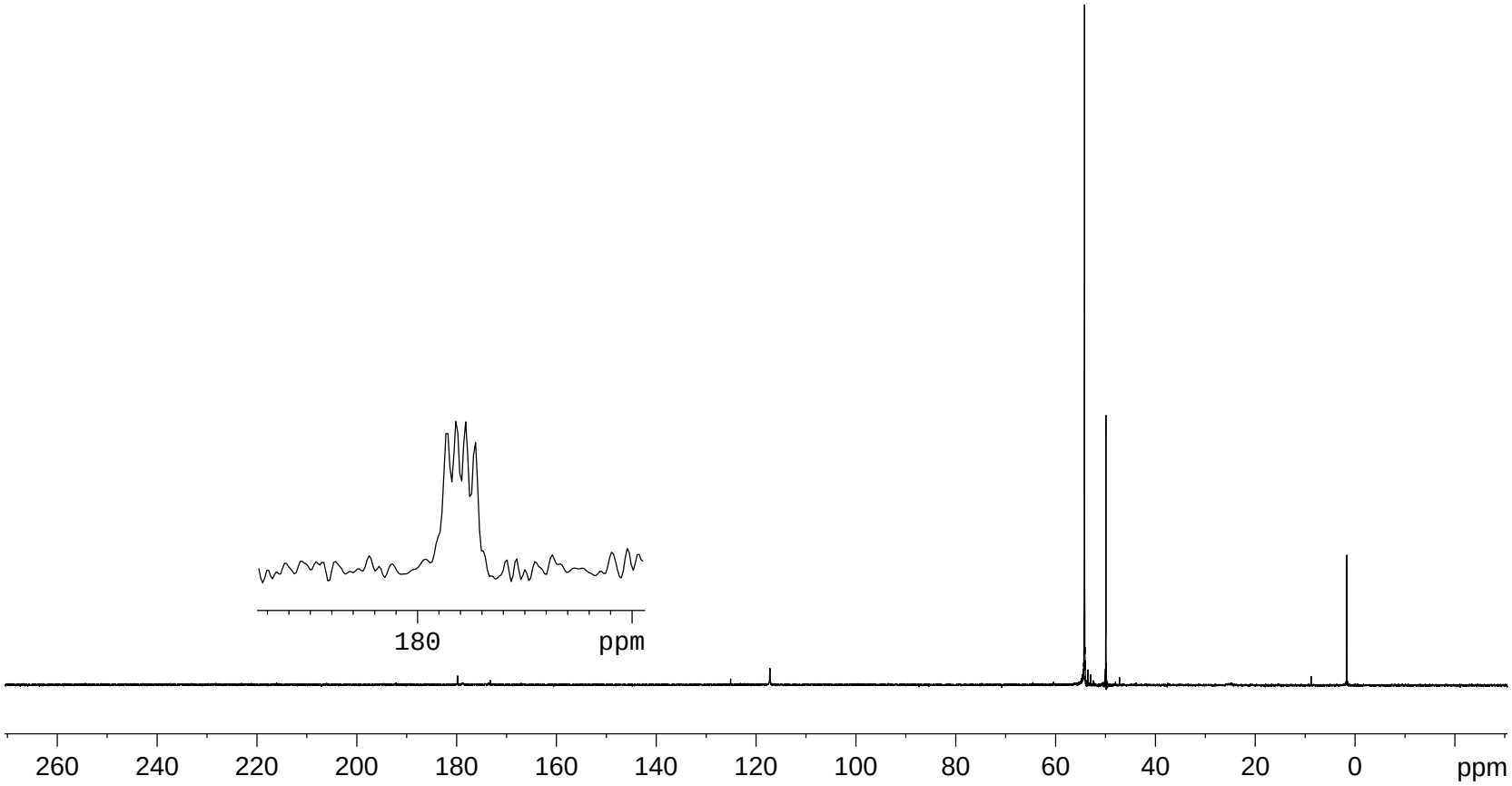
$^{13}C\{^{1}H\}$ NMR spectrum of **12** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



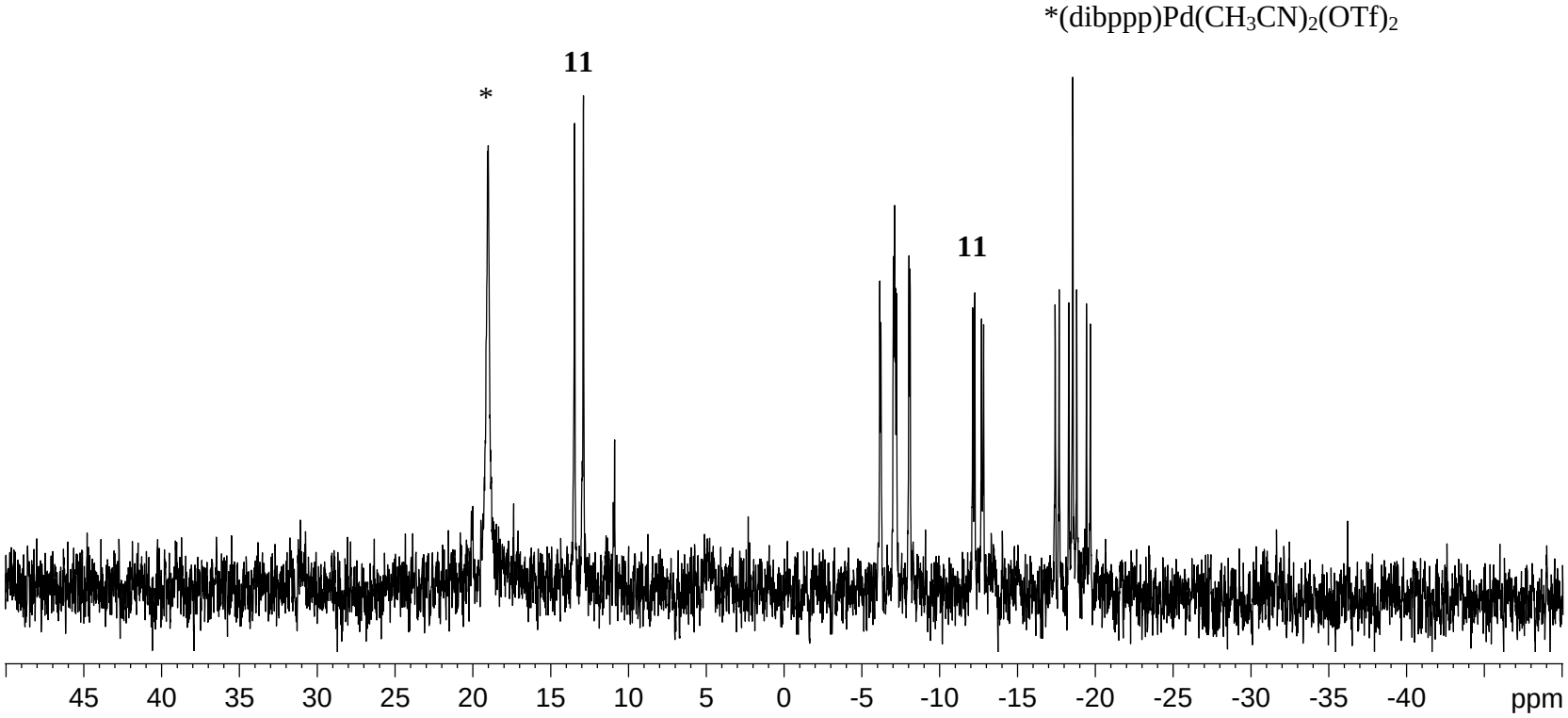
$^{31}P\{^{1}H\}$ NMR spectrum of **13** recorded at 293 K in $CH_2Cl_2/CH_3OH/CH_3CN$



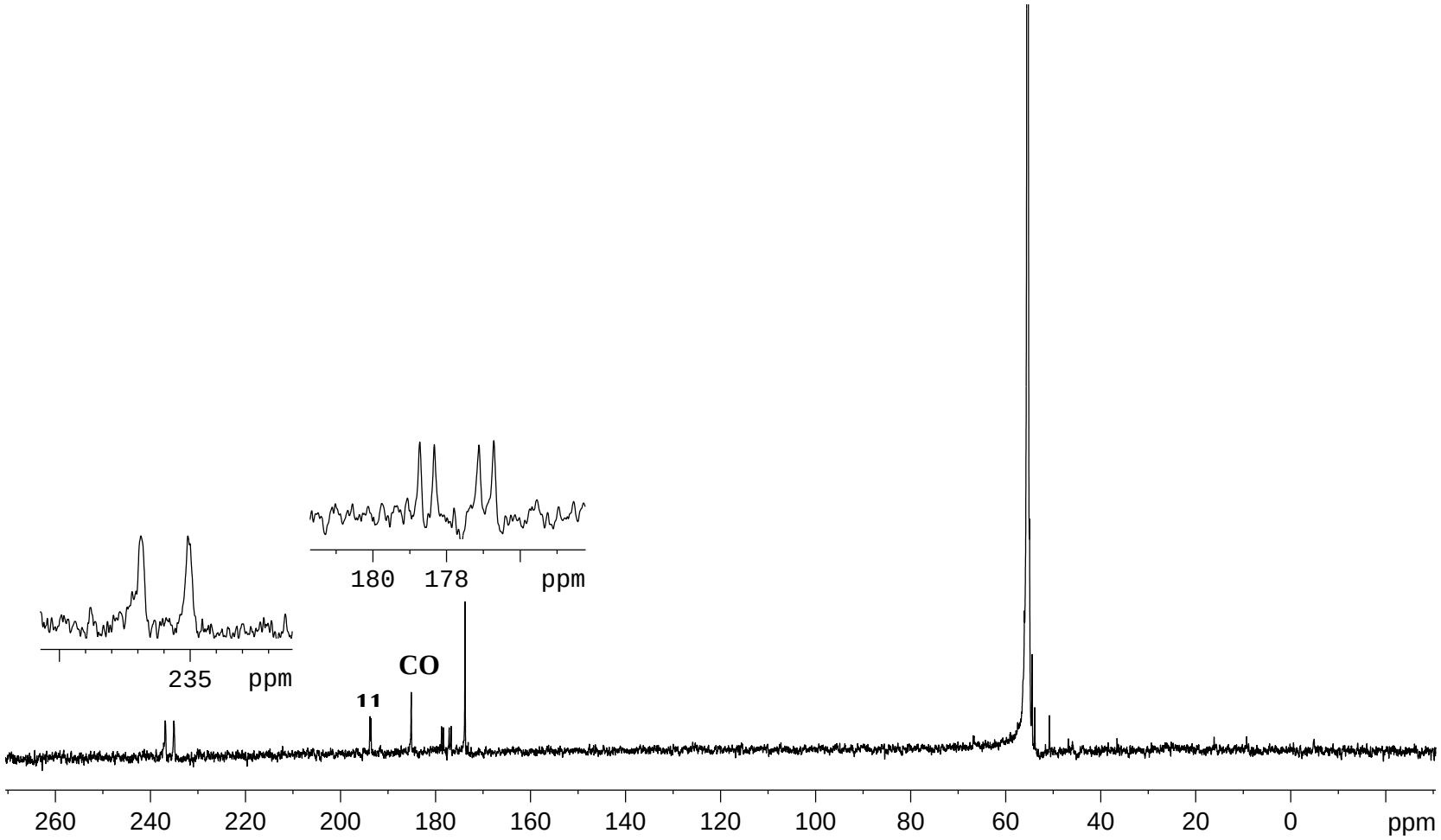
$^{13}C\{^{1}H\}$ NMR spectrum of **13** recorded at 293 K in $CH_2Cl_2/CH_3OH/CH_3CN$



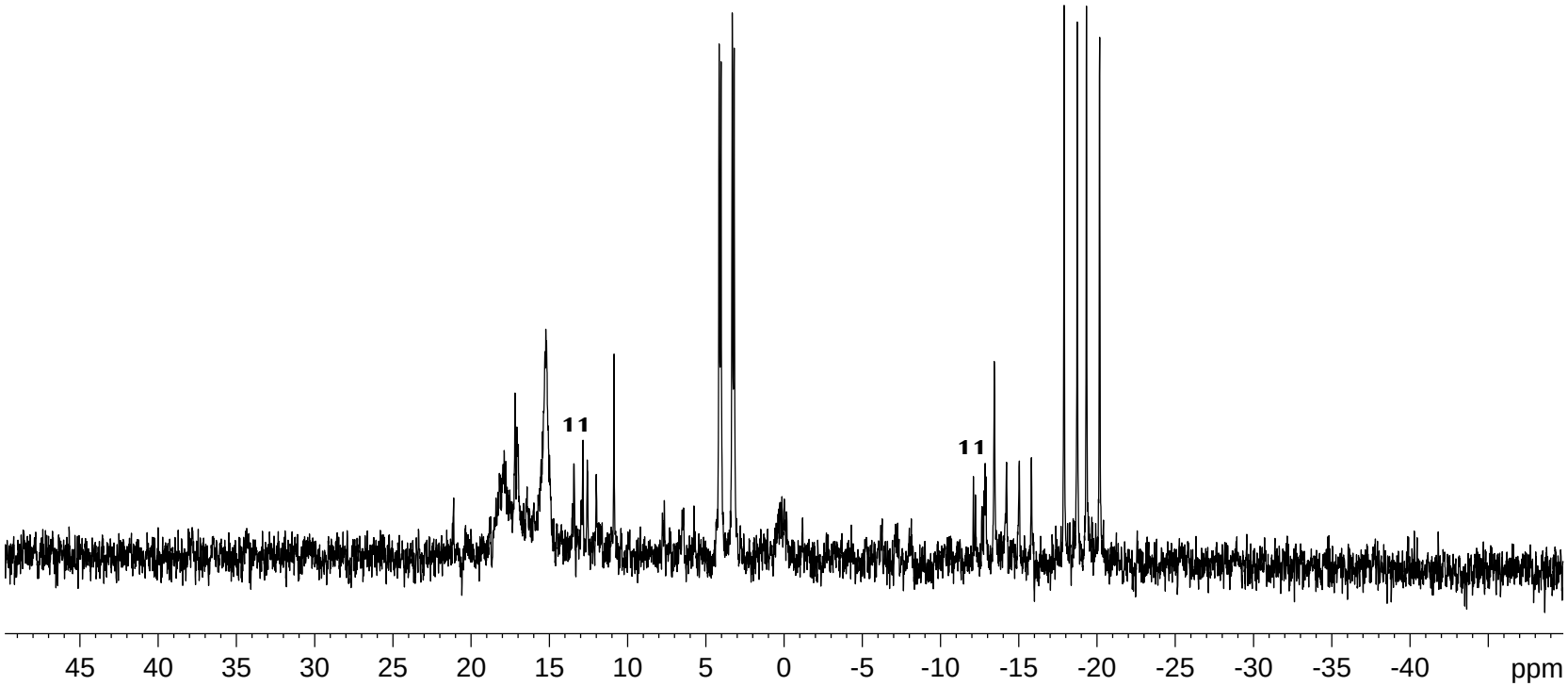
$^{31}P\{^{1}H\}$ NMR spectrum of a mixture of **11** and **14-CO** recorded at 193 K in CH_2Cl_2/CH_3OH



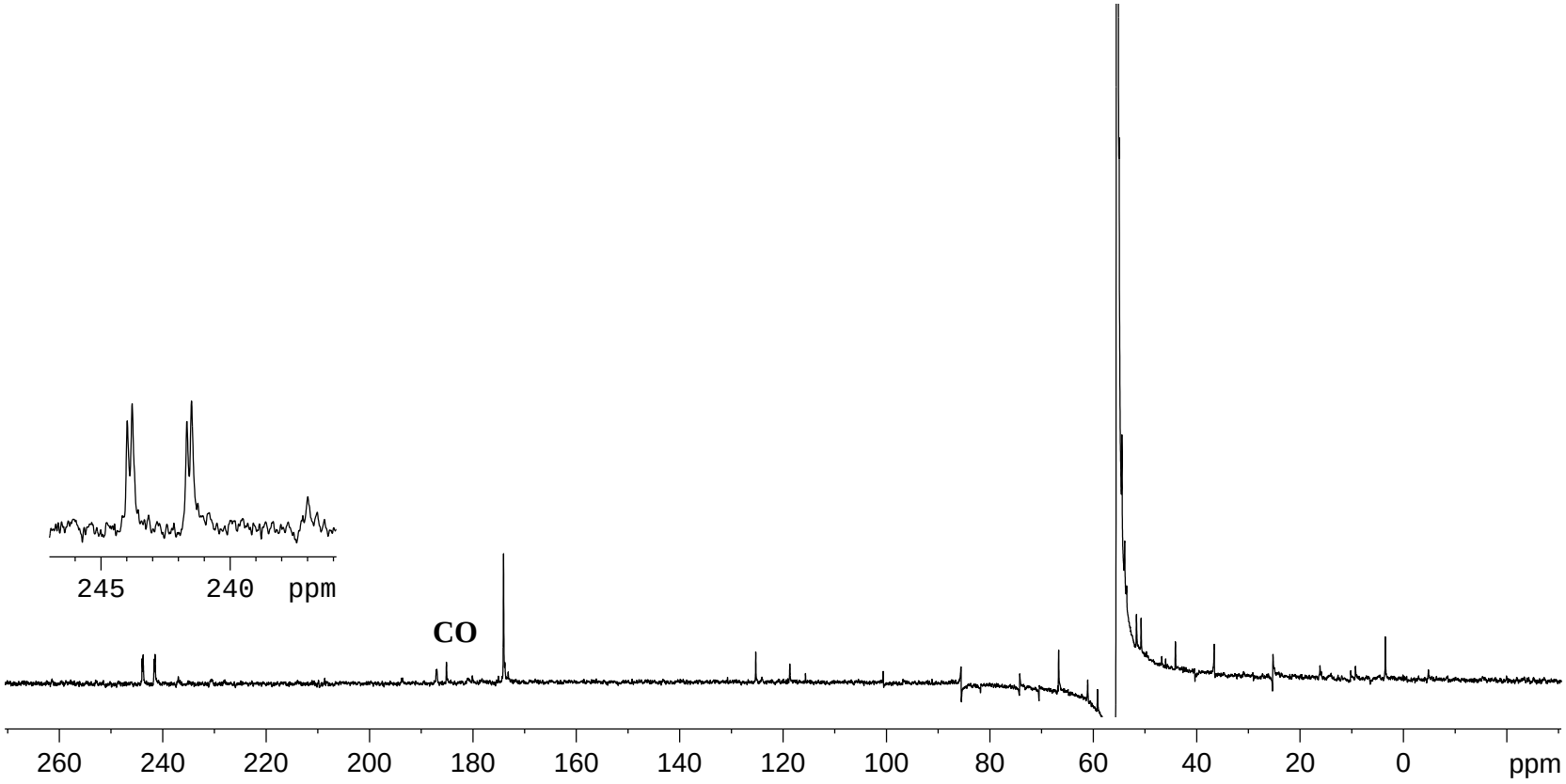
$^{13}C\{^{1}H\}$ NMR spectrum of **14-CO** recorded at 193 K in CH_2Cl_2/CH_3OH



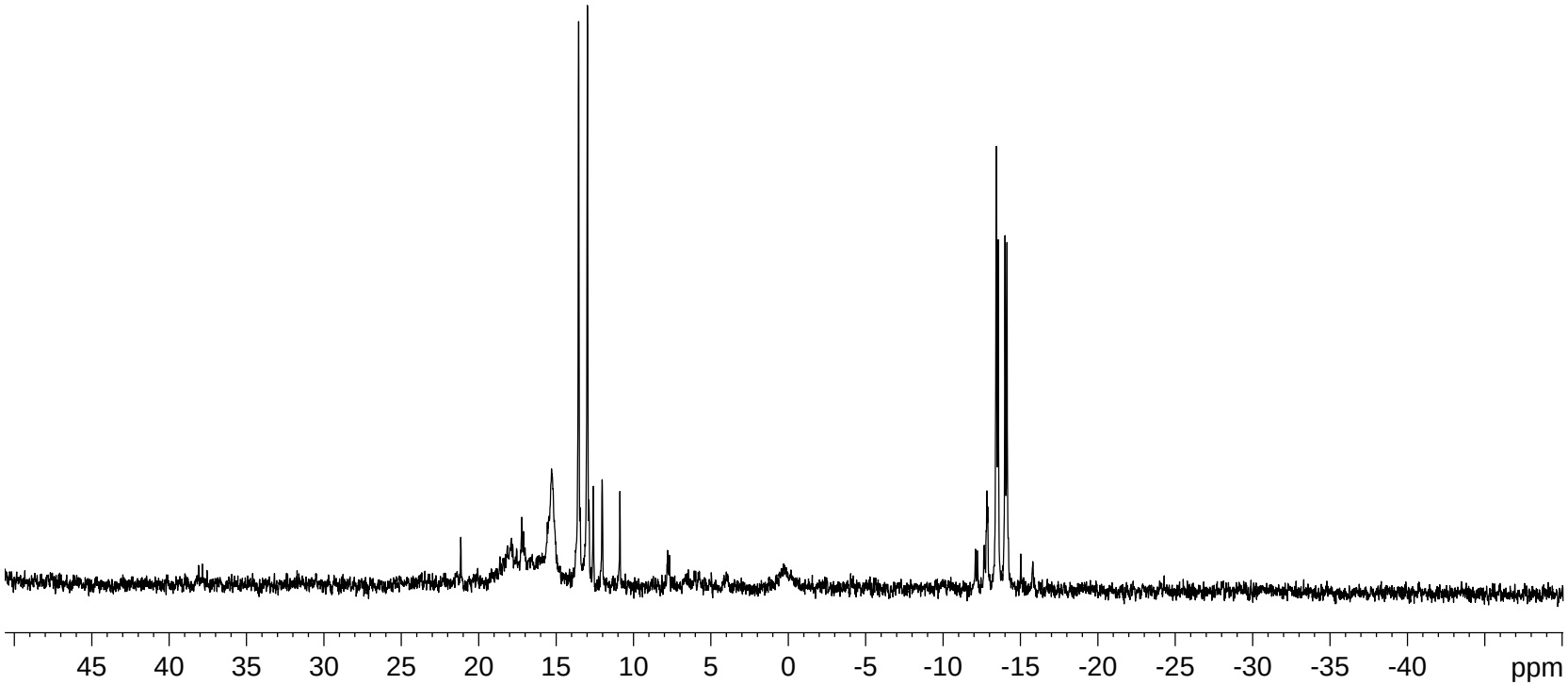
$^{31}P\{^{1}H\}$ NMR spectrum of **14-CH_3CN** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



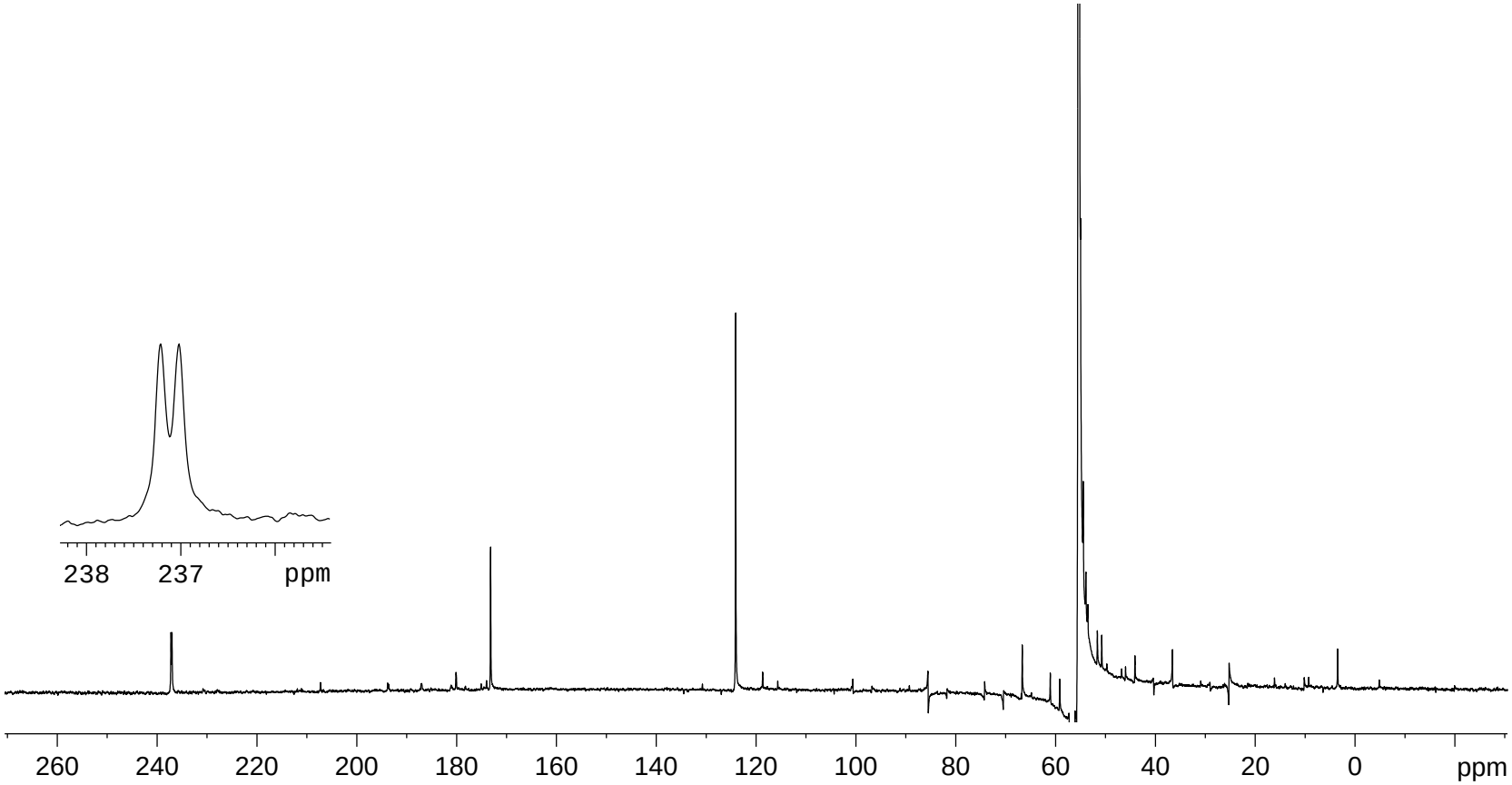
$^{13}C\{^{1}H\}$ NMR spectrum of **14-CH_3CN** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



$^{31}P\{^{1}H\}$ NMR spectrum of **15** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



$^{13}C\{^{1}H\}$ NMR spectrum of **15** recorded at 193 K in $CH_2Cl_2/CH_3OH/CH_3CN$



31P{1H} NMR spectrum of the reaction of [Pd(dibpp)(OTf)2] with Et3N:
(a) in CD2Cl2/CH2Cl2; (b) after addition of Et3N