Supplementary Information

Chiral trifluoromethylphosphines: a new stereoselective synthesis of *Josiphos*-type ligands containing two stereogenic phosphorus atoms

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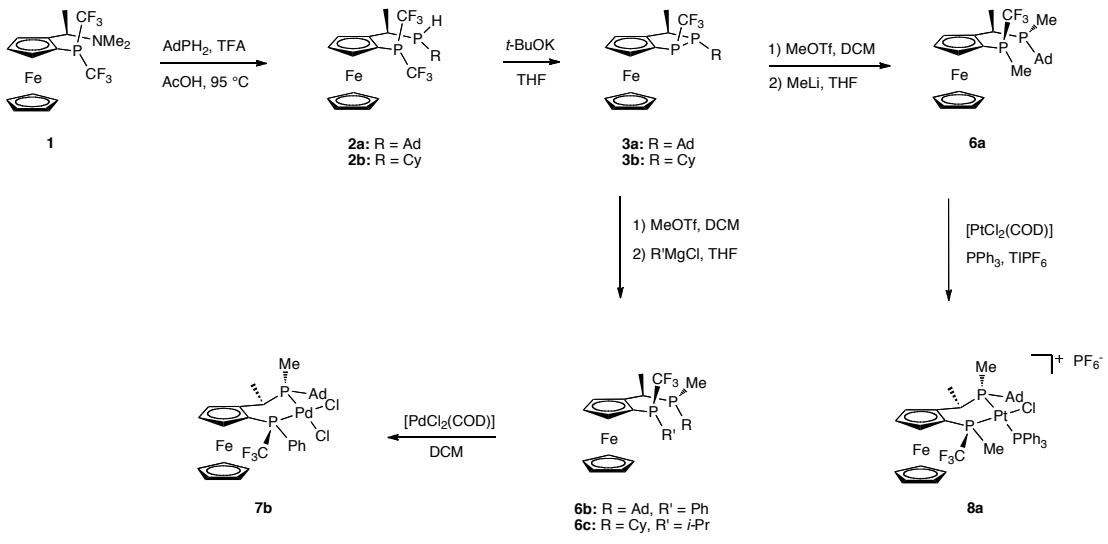
1. Scheme



2. General information

All manipulations were performed under a pure argon atmosphere using common Schlenk technique unless otherwise stated. THF, and diethyl ether were distilled from Na/benzophenone, pentane from Na/benzophenone/diglyme, dichloromethane was dried over CaH_2. Silica gel 60 (230 - 400 mesh) was purchased from *Fluka*. TLC plates were obtained from *Merck* (silica gel 60 F254). NMR spectra were recorded on *Bruker* DPX-250 (^{1}H: 250.13, ^{13}C: 62.90, ^{31}P: 101.25) and DPX-300 (^{1}H: 300.13, ^{13}C: 75.47, ^{19}F: 282.40, ^{31}P: 121.49) instruments operating at the denoted spectrometer frequency given in MHz for the specified nucleus. To specify the signal multiplicity following abbreviations are used: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, ψ quint = pseudo quintet, hept = heptet, m = multiplet. Shifts are reported in ppm relative to tetramethylsilane (TMS) as an external standard for ^{1}H- and ^{13}C-NMR spectra and calibrated against the solvent residual peak. For ^{19}F-NMR spectra $CFCl_3$ and for ^{31}P NMR spectra H_3PO_4 (85%), respectively, were used as an external standard. The following reagents and metal complexes were synthesized according to reported procedures: 1-adamantylphosphine,[1] (R_C, S_p)-1-[bis(trifluoromethyl)-phosphino]-2-[1-(dimethylamino)ethyl]ferrocene,[2] $[PdCl_2(COD)_2]$,[3] $[PtCl_2(COD)_2]$.[3]

The indices Fc and P1/P2 associated with CIP absolute configuration descriptors stand for ferrocene planar chirality and central phosphorus chirality, respectively. P1 is the phosphorus atom directly attached to the ferrocene, P2 the one on the side chain. Note that the cyclopentadiene carbon has a higher CIP priority than to the one of the CF_3 group because it is attached to iron.

3. Experimental procedures

(R,S_{Fc})-1-[Bis(trifluoromethyl)phosphino]-2-{1-[(1-adamantyl)phosphino]ethyl}-ferrocene (**2a**). To a solution of (R,S_{Fc})-1-[bis(trifluoromethyl)phosphino]-2-[1-(dimethylamino)-ethyl]ferrocene (**1**) (2.00 g, 4.70 mmol, 1 eq.) in 4 mL of degassed acetic acid was added trifluoroacetic acid (350 µL, 4.70 mmol, 1 eq.). Then 1-adamantylphosphine (1.58 g, 9.41 mmol, 2 eq.) was added, and the mixture was heated up to 95 °C and the red solution stirred at this temperature for 21 h. The mixture was then cooled down to room temperature, diluted with diethyl ether and saturated aqueous $NaHCO_3$, the organic phase separated, dried over $MgSO_4$ and the solvent removed under reduced pressure. Flash chromatography (silica, pentane:Et_2O 1:0-20:1) gave the product as a mixture of 2 diastereoisomers (6:1). Yield: 2.49 g (96%), orange crystalline solid. Major isomer: **^{1}H NMR** (300 MHz, C_6D_6): δ1.45 (dd, $^3J_{H\text{-}P}$ = 14.8 Hz, ^3J = 6.8 Hz, 3 H, CH*Me*); 1.60 (bs, 6 H, *Ad*); 1.82 (bs, 9 H, *Ad*); 3.02 (d, $J_{H\text{-}P}$ = 204 Hz, 1 H, P*H*); 3.23-3.26 (m, 1 H, C*H*Me); 4.01 (s, 5 H, *Cp'*); 4.08 (t, ^3J = 2.6 Hz, 1 H, *Cp*); 4.18 (s, 1 H, *Cp*); 4.35 (s, 1 H, *Cp*); **^{13}C{^{1}H} NMR** (62.9 MHz, C_6D_6): δ 21.62 (dd, $J_{C\text{-}P}$ = 15.8, 12.1 Hz, *C*HMe); 22.01 (d, $J_{C\text{-}P}$ = 29.3 Hz, CH*Me*); 28.84 (d, $J_{C\text{-}P}$ = 7.4 Hz, *Ad*); 32.72 (d, $J_{C\text{-}P}$ =

14.9 Hz, *Ad*); 36.63 (s, *Ad*); 42.48 (d, $J_{C\text{-}P}$ = 10.3 Hz, *Ad*); 57.04 (d, $J_{C\text{-}P}$ = 6.8 Hz, *Cp*); 70.02 (s, *Cp'*); 70.28 (s, *Cp*); 71.43 (d, $J_{C\text{-}P}$ = 4.4 Hz, *Cp*); 72.23 (d, $J_{C\text{-}P}$ = 2.3 Hz, *Cp*); 103.80 (dd, $J_{C\text{-}P}$ = 35.11, 8.6 Hz, *Cp*); **^{19}F NMR** (282 MHz, C_6D_6): δ -53.94 (dq, $J_{F\text{-}P}$ = 68.4 Hz, $J_{F\text{-}F'}$ = 8.7 Hz, CF_3); -50.80 (dq, $J_{F\text{-}P}$ = 77.0 Hz, $J_{F\text{-}F'}$ = 8.7 Hz, CF_3'); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): δ -2.35 (qq, $J_{P\text{-}F}$ = 77.3 Hz, $J_{P\text{-}F'}$ = 68.6 Hz, *P*$(CF_3)_2$); +4.77 (d, $J_{P\text{-}P}$ = 2.6 Hz, *P*HAd); **^{31}P NMR** (121 MHz, C_6D_6): δ +4.77 (d, $J_{P\text{-}H}$ = 204 Hz, *P*HAd); EA $C_{24}H_{28}F_6FeP_2$ (548.09) calcd C 52.58, H 5.15, F 20.79, P 11.30 found C 52.79, H 5.42, F 20.58, P 11.23; **HRMS** (EI) calcd. (*m/z*) for $C_{24}H_{28}F_6FeP_2$: 548.0914 ($[M]^+$). Found 548.0918 ($[M]^+$); 479.0781 ($[M\text{-}CF_3]^+$); 380.9771 ($[M\text{-}PHAd]^+$)**.** Minor Isomer: **^{19}F NMR** (282 MHz, C_6D_6): δ -53.71 (dq, $J_{F\text{-}P}$ = 67.7 Hz, $J_{F\text{-}F'}$ = 8.5 Hz, CF_3); -50.73 (dq, $J_{F\text{-}P}$ = 76.5 Hz, $J_{F\text{-}F'}$ = 8.4 Hz, CF_3'); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): δ -5.00 - -4.20 (m, *P*$(CF_3)_2$); +12.47 (dq, $J_{P\text{-}P}$ = 39.2 Hz, $J_{P\text{-}F}$ = 15.8 Hz, *P*HAd); **^{31}P NMR** (121 MHz, C_6D_6): δ +12.48 (d, $J_{P\text{-}H}$ = 195 Hz, *P*HAd).

(*R*,*S*$_{Fc}$)-1-[Bis(trifluoromethyl)phosphino]-2-[1-(cyclohexylphosphino)ethyl]ferrocene (2b). To a solution of (R_C, S_{Fc})-1-[bis(trifluoromethyl)phosphino]-2-[1-(dimethylamino)ethyl]ferrocene (**1**) (2.00 g, 4.70 mmol, 1 eq.) in 5 mL of degassed acetic acid was added trifluoroacetic acid (350 µL, 4.70 mmol, 1 eq.). Then cyclohexylphosphine (1.29 mL, 9.41 mmol, 2 eq.) was added and the mixture was heated up to 90 °C and the red solution stirred at this temperature for 18 h. The mixture was then cooled to 60 °C and the acetic acid removed under reduced pressure. The residue was then diluted with diethyl ether and saturated aqueous $NaHCO_3$ and the organic phase separated and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by flash chromatography (silica, pentane:Et_2O 1:0-20:1) to yield the product as a mixture of 2 diastereoisomers (10:7). Yield: 1.99 g (85%), dark red oil. Major isomer: **^{1}H NMR** (300 MHz, C_6D_6): *d* 1.03-1.24 (m, 5 H, *Cy*); 1.28-1.75 (m, 5 H, *Cy*); 1.34 (dd, $^3J_{H\text{-}P}$ = 13.3 Hz, ^3J = 7.0 Hz, 3 H, CH*Me*); 2.99-3.09 (m, 1 H, C*H*Me); 3.19 (dd, $^1J_{H\text{-}P}$ = 199.1 Hz, *J* = 5.4 Hz, 1 H, P*H*); 4.00 (s, 5 H, *Cp'*); 4.06 (s, 1 H, *Cp*); 4.14 (s, 1 H, *Cp*); 4.36 (s, 1 H, *Cp*); **^{19}F NMR** (282 MHz, C_6D_6): *d* -54.05 (dqd, $^2J_{F\text{-}P}$ = 63.7 Hz, $^4J_{F\text{-}F'}$ = 8.5 Hz, $J_{F\text{-}P'}$ = 4.0 Hz, CF_3); -50.78 (dq, $^2J_{F\text{-}P}$ = 76.6 Hz, $^4J_{F\text{-}F'}$ = 8.6 Hz, CF_3'); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): *d* -15.79 (d, $J_{P\text{-}P}$ = 12.1 Hz, *P*HCy); -4.62 – -0.97 (m, *P*$(CF_3)_2$); **^{31}P NMR** (121 MHz, C_6D_6): *d* -15.78 (d, $^1J_{P\text{-}H}$ = 201 Hz, *P*HAd); **HRMS** (EI) calcd. (*m/z*) for $C_{20}H_{24}F_6FeP_2$: 496.0602 ($[M]^+$). Found: 496.0607 ($[M]^+$); 427.0652 ($[M\text{-}CF_3]^+$); 380.9930 ($[M\text{-}PHCy]^+$)**.** Minor Isomer: **^{19}F NMR** (282 MHz, C_6D_6): *d* -53.83 (ddq, $^2J_{F\text{-}P}$ = 66.6 Hz, $J_{F\text{-}P'}$ = 17.0 Hz, $^4J_{F\text{-}F'}$ = 8.5 Hz, CF_3); -50.93 (dq, $^2J_{F\text{-}P}$ = 76.4 Hz, $^4J_{F\text{-}F'}$ = 8.5 Hz, CF_3'); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): *d* -10.48 (dq, $J_{P\text{-}P}$ = 33.5 Hz, $^2J_{P\text{-}F}$ = 16.5 Hz, *P*HCy); -4.62 – -0.97 (m, *P*$(CF_3)_2$); **^{31}P NMR** (121 MHz, C_6D_6): *d* -10.47 (d, $^1J_{P\text{-}H}$ = 200 Hz, *P*HAd).

(1*S*,2*R*,3*R*,*S*$_{Fc}$)-2-(1-Adamantyl)-3-methyl-1-(trifluoromethyl)-2,3-dihydro-1*H*-ferroceno[*c*][1,2]diphosphole (3a). To a solution of (R,S_{Fc})-2-{1-[(1-adamantyl)phosphino]ethyl}-1-[bis(trifluoromethyl)phosphino]ferrocene (**2a**) (400 mg, 0.730 mmol, 1 eq.) in 2 mL of THF was added a solution of *t*-BuOK (81.9 mg, 0.730 mmol, 1 eq.) and 18-crown-6 (212 mg, 0.803 mmol, 1.2 eq.) in 6 mL of THF. The orange solution immediately turned dark. The mixture was allowed to stir for ten minutes, quenched with 1 mL of saturated aqueous NH_4Cl and diluted with 2 mL of distilled water and 20 mL of diethyl ether. The organic phase was separated, dried over $MgSO_4$ and the solvent removed under reduced pressure. Flash column chromatography (SiO_2, pentane:EtOAc = 100:1 – 20:1) gave the

product as an orange crystalline solid. Yield: 274 mg (79%); **^{1}H NMR** (300 MHz, C_6D_6): δ 1.33 (dd, $^3J_{H\text{-}P}$ = 21.0 Hz, ^3J = 7.2 Hz, 3 H, CH*Me*); 1.61 (b s, 6 H, Ad); 1.88 (bs, 9 H, Ad); 3.43 (ψ quint, J = 6.9 Hz, 1 H, C*H*Me); 3.95 (s, 5 H, Cp'); 3.98-4.00 (m, 2 H, *Cp*); 4.20 (s, 1 H, *Cp*); **^{13}C{^{1}H} NMR** (62.9 MHz, C_6D_6): δ 23.87 (d, $J_{C\text{-}P}$ = 34.9 Hz, PCH*Me*); 28.54 (d, $J_{C\text{-}P}$ = 29.3 Hz, *Ad*); 29.05 (dd, $J_{C\text{-}P}$ = 26.0, 2.9 Hz, P*C*HMe); 32.89 (dd, $J_{C\text{-}P}$ = 20.1, 10.4 Hz, *Ad*); 36.53 (s, *Ad*); 42.13 (dd, $J_{C\text{-}P}$ = 11.0, 7.7 Hz, *Ad*); 66.7 (s, *Cp*); 68.11 (d, $J_{C\text{-}P}$ = 11.2 Hz, *Cp*); 70.09 (s, *Cp'*); 73.15 (d, J = 2.6 Hz, *Cp*); 76.12 (dd, $J_{C\text{-}P}$ = 10.3, 4.5 Hz, *Cp*); 103.08 (s, *Cp*); **^{19}F NMR** (282 MHz, C_6D_6): δ -55.30 (dd, $^2J_{F\text{-}P}$ = 57.0 Hz, $^3J_{F\text{-}P}$ = 19.3 Hz, CF_3); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): δ -2.35 (dq, $^1J_{P\text{-}P}$ = 207.8 Hz, $^2J_{P\text{-}F}$ = 57.2 Hz, *P*CF_3); +68.33 (dq, $^1J_{P\text{-}P}$ = 207.4 Hz, $^3J_{P\text{-}F}$ = 19.3 Hz, *P*Ad); **EA:** Anal. calcd. for $C_{23}H_{27}F_3FeP_2$ (478.26): C 57.76, H 5.69, F 11.92, P 12.95. Found: C 57.58, H 5.56, F 12.17, P 12.87; **HRMS** (EI) calcd. (*m/z*) for $C_{23}H_{27}F_3FeP_2$: 478.0884 ($[M]^+$). Found: 478.0887 ($[M]^+$)**.**

(1*S*,2*R*,3*R*,*S*$_{Fc}$)-2-Cyclohexyl-3-methyl-1-(trifluoromethyl)-2,3-dihydro-1*H*-ferroceno[*c*]-[1,2]diphosphole (3b). To a solution of (*R*$_C$, *S*$_{Fc}$)-1-[bis(trifluoromethyl)phosphino]-2-[1-(cyclohexyl-phosphino)ethyl]ferrocene **(2b)** (1060 mg, 2.136 mmol, 1 eq.) in 4 mL of THF was added a solution of *t*-BuOK (240 mg, 2.136 mmol, 1 eq.) and 18-crown-6 (621 mg, 2.350 mmol, 1.2 eq.) in 4 mL of THF. The orange solution immediately turned dark. The mixture was allowed to stir for ten minutes, was then quenched with 1 mL of saturated aqueous NH_4Cl and diluted with 2 mL of distilled water and 20 mL of diethyl ether. The organic phase was separated, dried over $MgSO_4$ and the solvent removed under reduced pressure. Flash column chromatography (SiO_2, pentane:EtOAc = 100:1 – 20:1) gave the impure product in the first coloured fraction. Recrystallization from hot ethanol gave the pure product as an orange crystalline solid. Yield: 364 mg (40%); **^{1}H NMR** (300 MHz, C_6D_6): *d* 1.09-1.39 (m, 5 H, *Cy*); 1.33 (dd, $^3J_{H\text{-}P}$ = 20.8 Hz, ^3J = 7.5 Hz, 3 H, CH*Me*); 1.55 (bs, 1 H, *Cy*); 1.66 (bs, 3 H, *Cy*); 2.08-2.23 (m, 2 H, *Cy*); 2.88 (q, ^3J = 6.9 Hz, 1 H, C*H*Me); 3.87 (s, 5 H, Cp'); 3.93 (bs, 1 H, *Cp*); 4.07 (t, J = 62.2 Hz, 1 H, *Cp*); 4.16 (bs, 1 H, *Cp*); **^{19}F NMR** (282 MHz, C_6D_6): *d* -54.87 (dd, $^2J_{F\text{-}P}$ = 52.7 Hz, $^3J_{F\text{-}P}$ = 16.7 Hz, CF_3); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): *d* -16.13 (dq, $^1J_{P\text{-}P}$ = 229.5 Hz, $^2J_{P\text{-}F}$ = 52.7 Hz, *P*CF_3); +47.87 (dq, $^1J_{P\text{-}P}$ = 229.5 Hz, $^3J_{P\text{-}F}$ = 16.7 Hz, *P*Cy); **EA:** Anal. calcd. for $C_{19}H_{23}F_3FeP_2$ (426.18): C 53.55, H 5.44, F 13.37, P 14.54. Found: C 53.46, H 5.45, F 13.43, P 14.57; **HRMS** (EI) calcd. (*m/z*) for $C_{19}H_{23}F_3FeP_{22}$: 426.0571 ($[M]^+$). Found: 426.0574 ($[M]^+$); 357.0614 ($[M\text{-}CF_3]^+$); 342.9710 ($[M\text{-}C_2H_3F_3]^+$); 273.9756 ($[M\text{-}C_7H_{11}F_3]^+$).

(*R*$_{P1}$,*R*$_{P2}$,*R*,*S*$_{Fc}$)-1-[Methyl(trifluoromethyl)phosphino]-2-{1-[(1-adamantyl)methyl-phosphino]ethyl}ferrocene (6a). To a solution of (1*R*,2*S*,3*R*,*S*$_{Fc}$)-2-(1-adamantyl)-3-methyl-1-(trifluoromethyl)-2,3-dihydro-1*H*-ferroceno-[*c*][1,2]diphosphole (**3a)** (300 mg, 0.627 mmol, 1 eq.) in 5 mL of dichloromethane was added methyl triflate (71 µL, 0.627 mmol, 1 eq.) and the solution was stirred for one hour. The solvent was then removed under reduced pressure and the residue was washed with 5 mL of diethyl ether. The residue was dissolved in 2 mL of THF and the solution was cooled down to -78 °C. Then a 1.6 M solution of methyl lithium in diethyl ether (470 µL, 0.753 mmol, 1.2 eq.) was added and the mixture was allowed to warm up to room temperature. The reaction mixture was then quenched with 1 mL of saturated aqueous NH_4Cl and diluted with 2 mL of distilled water and 20 mL of diethyl ether. The organic phase was separated, dried over $MgSO_4$ and the solvent removed

under reduced pressure. Flash column chromatography (SiO_2, pentane:EtOAc:Et_3N = 50:1:1) gave the product as an orange crystalline solid. Yield: 173 mg (54%); **^{1}H NMR** (300 MHz, C_6D_6): δ 0.79 (d, $^2J_{H\text{-}P}$ = 5.4 Hz, 3 H, PAd*Me*); 1.35 (d, $^2J_{H\text{-}P}$ = 4.8 Hz, 3 H, PCF_3*Me*); 1.41 (dd, ^3J = 6.9 Hz, $^3J_{H\text{-}P}$ = 4.5 Hz, 3 H, CH*Me*); 1.75 (s, 6 H, *Ad*); 1.87 (s, 6 H, *Ad*); 1.98 (s, 3 H, *Ad*); 3.12 (qd, ^3J = 7.2 Hz, $J_{H\text{-}P}$ = 2.7 Hz, 1 H, C*H*Me); 3.90 (s, 5 H, *Cp'*); 4.05 (d, *J* = 2.4 Hz, 1 H, *Cp*); 4.11 (s, 1 H, *Cp*); 4.14 (s, 1 H, *Cp*); **^{13}C{^{1}H} NMR** (62.9 MHz, C_6D_6): δ 0.05 (d, $J_{C\text{-}P}$ = 27.6 Hz, PAd*Me*); 7.07-7.29 (m, PCF_3*Me*); 18.02 (s, CH*Me*); 24.20 (dd, $J_{C\text{-}P}$ = 24.7, 7.5 Hz, *C*HMe); 28.71 (d, $J_{C\text{-}P}$ = 8.0 Hz, *Ad*); 32.78 (d, $J_{C\text{-}P}$ = 20.6 Hz, *Ad*); 37.11 (s, *Ad*); 39.54 (d, $J_{C\text{-}P}$ = 11.6 Hz, *Ad*); 66.27-66.54 (m, *Cp*); 69.28 (s, *Cp'*); 69.63-69.87 (m, *Cp*); 104.31 (dd, $J_{C\text{-}P}$ = 28.9, 23.0 Hz, *Cp*); 131.55 (qd, $^1J_{C\text{-}F}$ = 323.5 Hz, $^1J_{C\text{-}P}$ = 33.3, *C*F_3); **^{19}F NMR** (282 MHz, C_6D_6): δ -59.10 (dd, $^2J_{F\text{-}P}$ = 57.9, $J_{F\text{-}P}$ = 25.4 Hz, C*F*$_3$); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): δ -31.16 (qd, $^2J_{P\text{-}F}$ = 57.8 Hz, $J_{P\text{-}P}$ = 20.4 Hz, *P*CF_3Me); +4.10 (qd, $J_{P\text{-}F}$ = 25.4 Hz, $J_{P\text{-}P}$ = 20.5 Hz, *P*AdMe); **EA**: Anal. calcd. for $C_{25}H_{33}F_3FeP_2$ (508.33): C 59.07, H 6.54, F 11.21, P 12.19. Found: C 59.16, H 6.72, F 11.35, P 12.21; **HRMS** (EI) calcd. (*m/z*) for $C_{23}H_{27}F_3FeP_2$: 508.1354 ($[M]^+$). Found: 508.1350 ($[M]^+$); 469.1302 ($[M\text{-}Me]^+$); 439.1402 ($[M\text{-}CF_3]^+$)**.**

(*R*$_{P1}$,*S*$_{P2}$*R*,*S*$_{Fc}$)-1-[Phenyl(trifluoromethyl)phosphino]-2-{1-[(1-adamantyl)methyl-phosphino]ethyl}ferrocene (6b). To a solution of (1*R*,2*S*,3*R*,*S*$_{Fc}$)-2-(1-adamantyl)-3-methyl-1-(trifluoromethyl)-2,3-dihydro-1*H*-ferroceno-[*c*][1,2]diphosphole (**3a)** (200 mg, 0.418 mmol, 1 eq.) in 3 mL of dichloromethane was added methyl triflate (57 µL, 0.502 mmol, 1.2 eq.) and the solution was stirred for one hour. After removal of the solvent under reduced pressure, the residue was dissolved in 4 mL of THF and the solution cooled down to -78 °C. A 2 M solution of phenylmagnesiumchloride in THF (251 µL, 0.502 mmol, 1.2 eq.) was added and the mixture was stirred for one hour at -78 °C and for another hour at room temperature. The solvent was removed under reduced pressure and the residue diluted with 5 mL of saturated aqueous NH_4Cl, 10 mL of distilled water and 20 mL of diethyl ether. The organic phase was separated, dried over $MgSO_4$ and the solvent removed under reduced pressure. Flash column chromatography (SiO_2, pentane:EtOAc:Et_3N = 50:1:1) gave the product as an orange crystalline solid. Yield: 143 mg (60%); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 0.89 (d, $^2J_{H\text{-}P}$ = 4.8 Hz, 3 H, PAd*Me*); 1.53 (dd, ^3J = 6.8 Hz, $^3J_{P\text{-}H}$ = 4.9 Hz, 3 H, CH*Me*); 1.74 (s, 12 H, *Ad*); 1.98 (s, 3 H, *Ad*) 3.10-3.18 (m 1 H, C*H*Me); 3.76 (s, 5 H, *Cp'*); 4.33 (s, 1 H, *Cp*); 4.42 (s, 1 H, *Cp*); 4.51 (s, 1 H, *Cp*); 7.50-7.53 (m, 3 H, *Ph*); 8.01 (t, $^3J_{H\text{-}P}$ = 8.2 Hz, *Ph*); **^{13}C{^{1}H} NMR** (62.9 MHz, $CDCl_3$): δ 0.14 (d, $J_{C\text{-}P}$ = 26.4 Hz, PAd*Me*); 18.46 (s, CH*Me*); 23.56 (dd, $J_{C\text{-}P}$ = 22.6, 10.5 Hz, *C*HMe); 28.26 (d, $J_{C\text{-}P}$ = 8.0 Hz, *Ad*); 32.75 (d, $J_{C\text{-}P}$ = 18.8 Hz, *Ad*); 37.09 (s, *Ad*); 39.40 (d, $J_{C\text{-}P}$ = 11.0 Hz, *Ad*); 64.36-64.68 (m, *Cp*); 68.92 (dd, $J_{C\text{-}P}$ = 7.3, 6.4 Hz, *Cp*); 69.37 (s, *Cp'*); 70.22 (s, *Cp*); 71.58 (d, $J_{C\text{-}P}$ = 4.6 Hz, *Cp*); 105.05 (dd, $J_{C\text{-}P}$ = 32.4, 23.3 Hz, *Cp*); 128.11 (d, $J_{C\text{-}P}$ = 10.0 Hz, *Ph*); 130.23 (qd, $^1J_{C\text{-}F}$ = 323.2 Hz, $^1J_{C\text{-}P}$ = 26.3 *C*F_3); 130.99 (d, $J_{C\text{-}P}$ = 1.3 Hz, *Ph*); 131.46-131.68 (m, *Ph*); 135.35 (d, $J_{C\text{-}P}$ = 25.7 Hz, *Ph*); **^{19}F NMR** (282 MHz, $CDCl_3$): δ -54.72 (dd, $^2J_{F\text{-}P}$ = 67.5 Hz, *J* = 20.4 Hz, C*F*$_3$); **^{31}P{^{1}H} NMR** (121 MHz, $CDCl_3$): δ -16.16 (qd, $^2J_{P\text{-}F}$ = 67.3 Hz, $J_{P\text{-}P}$ = 14.5 Hz, *P*CF_3Ph); +4.83 (qd, $^2J_{P\text{-}F}$ = 20.4 Hz, $J_{P\text{-}P}$ = 14.8 Hz, *P*AdMe); **EA**: Anal. calcd. for $C_{25}H_{33}F_3FeP_2$ (570.40): C 63.17, H 6.18, F 9.99, P 10.86. Found C 62.88, H 6.28, F 10.20, P 10.64; **HRMS** (EI) calcd. (*m/z*) for $C_{30}H_{35}F_3FeP_2$: 570.1510 ($[M]^+$). Found: 570.1497 ($[M]^+$); 501.1554 ($[M\text{-}CF_3]^+$)**.**

(R_{P1},$S_{P2}R$,S_{Fc})-1-[Isopropyl(trifluoromethyl)phosphino]-2-[1-(cyclohexylmethyl-phosphino)ethyl]ferrocene (6c). To a solution of (1*R*,2*S*,3*R*,S_{Fc})-2-cyclohexyl-3-methyl-1-(trifluoromethyl)-2,3-dihydro-1*H*-ferroceno-[*c*][1,2]diphosphole **(3b)** (200 mg, 469 mmol, 1 eq.) in 3 mL of dichloromethane was added methyl triflate (63 mL, 563 mmol, 1.2 eq.) and the solution was stirred for one hour. After removal of the solvent under reduced pressure, the residue was dissolved in 3 mL of THF and cooled down to -78 °C. A 2 M solution of isopropylmagnesiumchloride in tetrahydrofuran (282 mL, 502 mmol, 1.2 eq.) was added and the mixture was stirred for one hour at -78 °C and for another two hours at room temperature. The solvent was removed under reduced pressure and the residue diluted with 3 mL of degased water and 10 mL of diethyl ether. The organic phase was concentrated and the residue crystallized from hot ethanol to give the oxidation sensitive product as an orange crystalline material. Yield: 140 mg (62%); **^{1}H NMR** (300 MHz, $CDCl_3$): *d* 0.81 (d, $^{2}J_{H-P}$ = 3.5 Hz, 3 H, PCy*Me*); 1.08-1.50 (m, 15 H, CH*Me*, CH*Me*$_2$, *Cy*); 1.55-1.83 (m, 5 H, *Cy*); 2.46-2.61 (m 1 H, C*H*Me$_2$); 2.87 (q, ^{3}J = 6.8 Hz, 1 H, C*H*Me); 4.21 (s, 5 H, *Cp'*); 4.35 (bs, 2 H, *Cp*); 4.40 (s, 1 H, *Cp*); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): *d* 3.83 (d, $^{1}J_{C-P}$ = 23.3 Hz, PCy*Me*); 15.69 (s, CH*Me*); 20.02 (d, $^{2}J_{C-P}$ = 5.0 Hz, CH*Me*$_2$); 21.59 (d, $^{2}J_{C-P}$ = 25.5 Hz, CH*Me*$_2$); 24.87-26.01 (m, *C*HMe, *C*HMe$_2$); 26.41 (s, *Cy*); 26.77 (s, *Cy*); 26.90 (d, J_{C-P} = 3.6 Hz, *Cy*); 28.92 (d, J_{C-P} = 12.8 Hz, *Cy*); 29.24 (d, J_{C-P} = 16.0 Hz, *Cy*); 36.25 (d, J_{C-P} = 14.9 Hz, *Cy*); 67.57-68.34 (m, *Cp*); 68.78-69.18 (m, *Cp*); 69.43 (s, *Cp*); 69.51 (s, *Cp'*); 72.47 (d, J_{C-P} = 6.7 Hz, *Cp*); 100.56 (dd, J_{C-P} = 21.4, 16.4 Hz, *Cp*); 130.16 (qd, $^{1}J_{C-F}$ = 322.9 Hz, $^{1}J_{C-P}$ = 39.9, *C*F_3); **^{19}F NMR** (282 MHz, $CDCl_3$): *d* -50.31 (dd, $^{2}J_{F-P}$ = 58.0 Hz, $J_{F-P'}$ = 19.3 Hz, C*F*$_3$); **^{31}P{^{1}H} NMR** (121 MHz, $CDCl_3$): *d* -10.52 (qd, J_{P-F} = 19.1 Hz, $J_{P-P'}$ = 18.9 Hz, *P*CyMe); +0.84 (qd, $^{2}J_{P-F}$ = 57.9 Hz, $J_{P-P'}$ = 17.5 Hz, *P*CF_3^{i}Pr); **HRMS** (EI) calcd. (*m/z*) for $C_{23}H_{33}F_3FeP_2$: 484.1354 ($[M]^+$). Found: 484.1364 ($[M]^+$); 441.0808 ($[M-^{i}Pr]^+$); 415.1402 ($[M-CF_3]^+$).

[$PdCl_2$(6b)] (7b). (R_{P1},S_{P2},*R*, S_{Fc})-1-[Phenyl(trifluoromethyl)phosphino]-2-{1-[(1-adamantyl)-methylphosphino]ethyl}ferrocene **(6b)** (18.0 mg, 32 µmol, 1.1 eq.) and [$PdCl_2$(COD)] (8.2 mg, 29 µmol, 1 eq.) were dissolved in dichloromethane and the deep red solution stirred for 10 minutes. The solvent was then removed and the red residue washed with pentane (5 mL) and diethyl ether (5 mL). The dark red crystalline solid was dried under reduced pressure. Yield: 18 mg (84%); **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 1.53 (d, $^{2}J_{H-P}$ = 11.1 Hz, 3 H, PAd*Me*); 1.60-1.91 (m, 18 H, P*Ad*Me, CH*Me)*; 2.69 (bs, 1 H, C*H*Me); 4.52 (s, 5 H, *Cp'*); 4.65 (s, 1 H, *Cp*); 4.80 (s, 1 H, *Cp*); 4.82 (s, 1 H, *Cp*); 7.76 (s, 3 H, *Ph*); 8.63-8.69 (m, 2 H, *Ph*); **^{19}F NMR** (282 MHz, CD_2Cl_2): δ -53.58 (d, $^{2}J_{F-P}$ = 68.7, C*F*$_3$); **^{31}P{^{1}H} NMR** (121 MHz, CD_2Cl_2): δ +49.26 (q, $^{2}J_{P-F}$ = 68.6 Hz, *P*CF_3Ph); +85.01 (s, *P*AdMe); **HRMS** (MALDI) calcd. (*m/z*) for $C_{30}H_{35}ClF_3FeP_2Pd$: 711.0243 ($[M-Cl]^+$). Found: 711.0250 ($[M-Cl]^+$).

[$PtCl_2$(6a)] (7a) and **[PtCl(6a)PPh_3]PF_6 (8).** To (R_{P1},S_{P2},*R*, S_{Fc})-1-[methyl(trifluoromethyl)-phosphino]-2-{1-[(1-adamantyl)methylphosphino]ethyl}ferrocene **(6a)** (50 mg, 98 mmol, 1 eq.) and [$PtCl_2$(COD)] (37 mg, 98 mmol, 1 eq.) was added 8 mL of dichloromethane. Immediately a yellow precipitate was observed. The solvent was removed and the residue dried under vacuum. **(7a):** (No spectroscopic data were measured due to the poor solubility of the product). **EA**: Anal. calcd. for $C_{25}H_{33}Cl_2F_3FeP_2Pt$ (774.31): C 38.78, H 4.30, Cl 9.16, F 7.36, P 8.00. Found: C 38.65, H 4.43, Cl 9.31,

F 7.42, P 7.90; **HRMS** (MALDI) calcd. (*m/z*) for $C_{25}H_{33}ClF_3FeP_2Pt$ ($[M\text{-}Cl]^+$): 739.0689. Found: 739.0683 ($[M\text{-}Cl]^+$).

Part of the residue (30 mg, 36 mmol, 1eq.) and triphenylphosphine (9.4 mg, 36 µmol, 1 eq.) were suspended in 5 mL of THF. A solution of thallium(I) hexafluorophosphate (12.5 mg, 36 µmol, 1 eq.) in 1 mL of THF was then added and the mixture stirred for 2 hours during which a red solution and a white precipitate was obtained. The mixture was filtered over celite, the solvent removed under reduced pressure and the red residue washed with pentane (5 mL) and diethyl ether (5 mL). The red crystalline solid was dried under reduced pressure. **(8):** Yield: 30 mg (70%); **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 1.51 (dd, $^2J_{H\text{-}P}$ = 10.5 Hz, J = 1.8 Hz, 3 H, PAd*Me*); 1.81 (dd, $^3J_{H\text{-}P}$ = 12.0 Hz, ^3J = 6.8 Hz, 3 H, CH*Me*); 1.88 (bs, 6 H, P*Ad*Me); 2.19 (bs, 9 H, P*Ad*Me); 2.49 (d, $^2J_{H\text{-}P}$ = 10.4 Hz, 3 H, PCF_3*Me*); 3.43 (bs, 1 H, C*H*Me,); 4.44 (s, 5 H, *Cp'*); 4.48 (bs, 1 H, *Cp*); 4.67 (bs, 2 H, *Cp*); 7.55-7.60 (m, 9 H, P*Ph$_3$*); 7.69-7.75 (m, 6 H, P*Ph$_3$*); **^{19}F NMR** (282 MHz, CD_2Cl_2): δ -72.80 (d, $^1J_{F\text{-}P}$ = 711.2 Hz, P*F*$_6$); -58.02 (dd, $^2J_{F\text{-}P}$ = 74.7 Hz, $^3J_{F\text{-}Pt}$ = 39.6 Hz, PC*F*$_3$Me); **^{31}P{^{1}H} NMR** (121 MHz, C_6D_6): δ -144.22 (hept, $^1J_{P\text{-}F}$ = 711.1 Hz, *P*F$_6$); +19.64 (dqdd, $^1J_{P\text{-}Pt}$ = 3613.9 Hz, $^2J_{P\text{-}F}$ = 74.7 Hz, $^2J_{P\text{-}P}$ = 26.6, 15.4 Hz, *P*CF_3Me); +20.24 (ddd, $^1J_{P\text{-}Pt}$ = 2304.5 Hz, $^2J_{P\text{-}P}$ = 367.8, 14.9 Hz, *P*Ph_3); +60.08 (ddd, $^1J_{P\text{-}Pt}$ = 2333.7 Hz, $^2J_{P\text{-}P}$ = 368.4, 26.7 Hz, *P*AdMe); **HRMS** (MALDI) calcd. (*m/z*) for $C_{43}H_{48}ClF_3FeP_3Pt$: 1001.1607 ($[M]^+$). Found: 1001.1588 ($[M]^+$); 966.1964 ($[M\text{-}Cl]^+$); 881.1933 ($[MH\text{-}FeCp]^+$); 739.0681 ($[M–PPh_3]^+$).

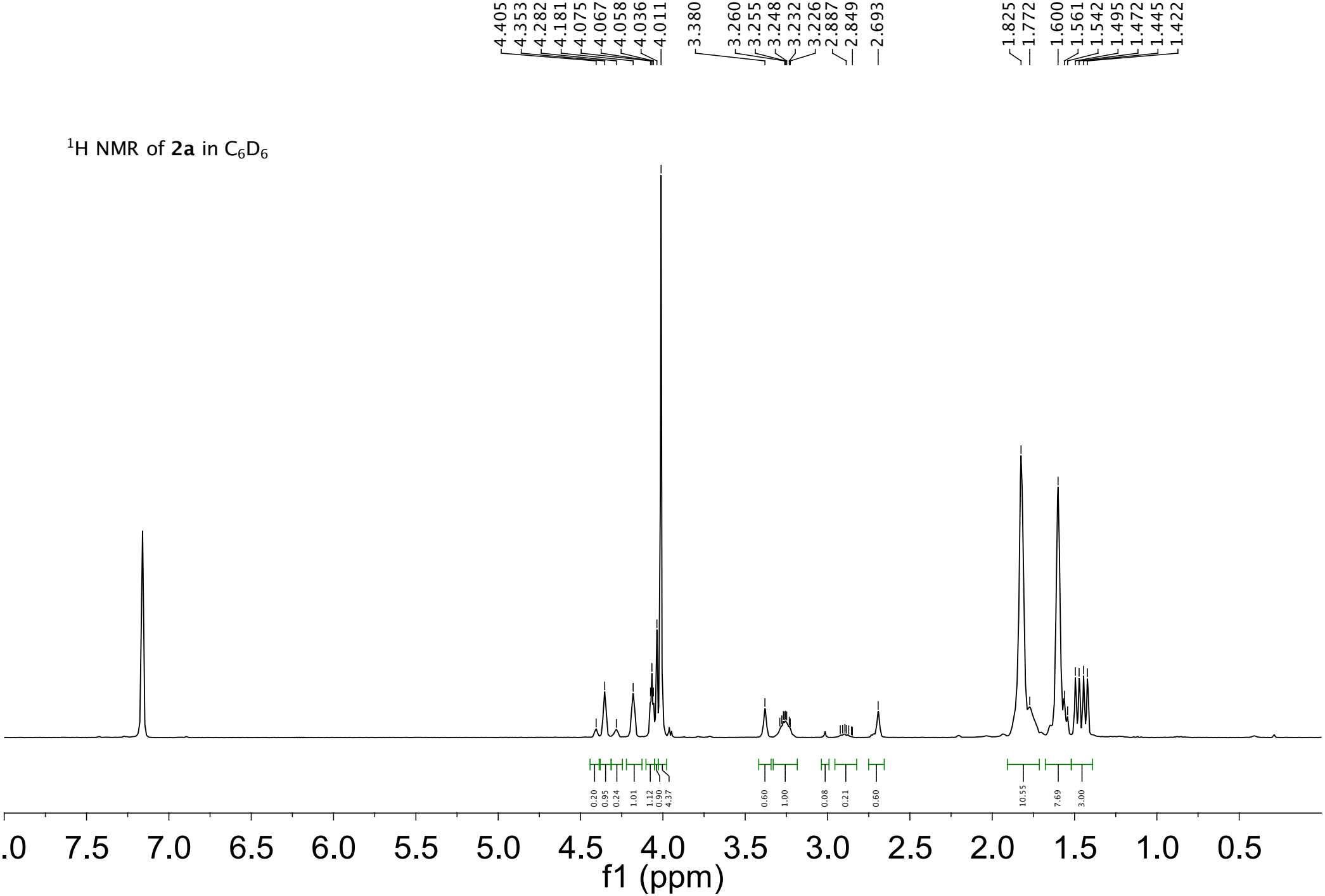
4. References

[1] a) H. Stetter and W. D. Last, *Chem Ber-Recl*, 1969, **102**, 3364; b) M. Gouygou, G. Etemadmoghadam and M. Koenig, *Synthesis-Stuttgart*, 1987, 508.

[2] R. Koller and A. Togni, unpublished results. Compound **1** has been prepared using the method reported by Caffyn and co-workers, see: E. J. Velazco, A. J. M. Caffyn, X. F. Le Goff and L. Ricard, Organometallics, 2008, 27, 2402.

[3] D. Drew and J. R. Doyle, *Inorg. Synth.*, 1990, **28**, 346.

^{1}H NMR of **2a** in C_6D_6



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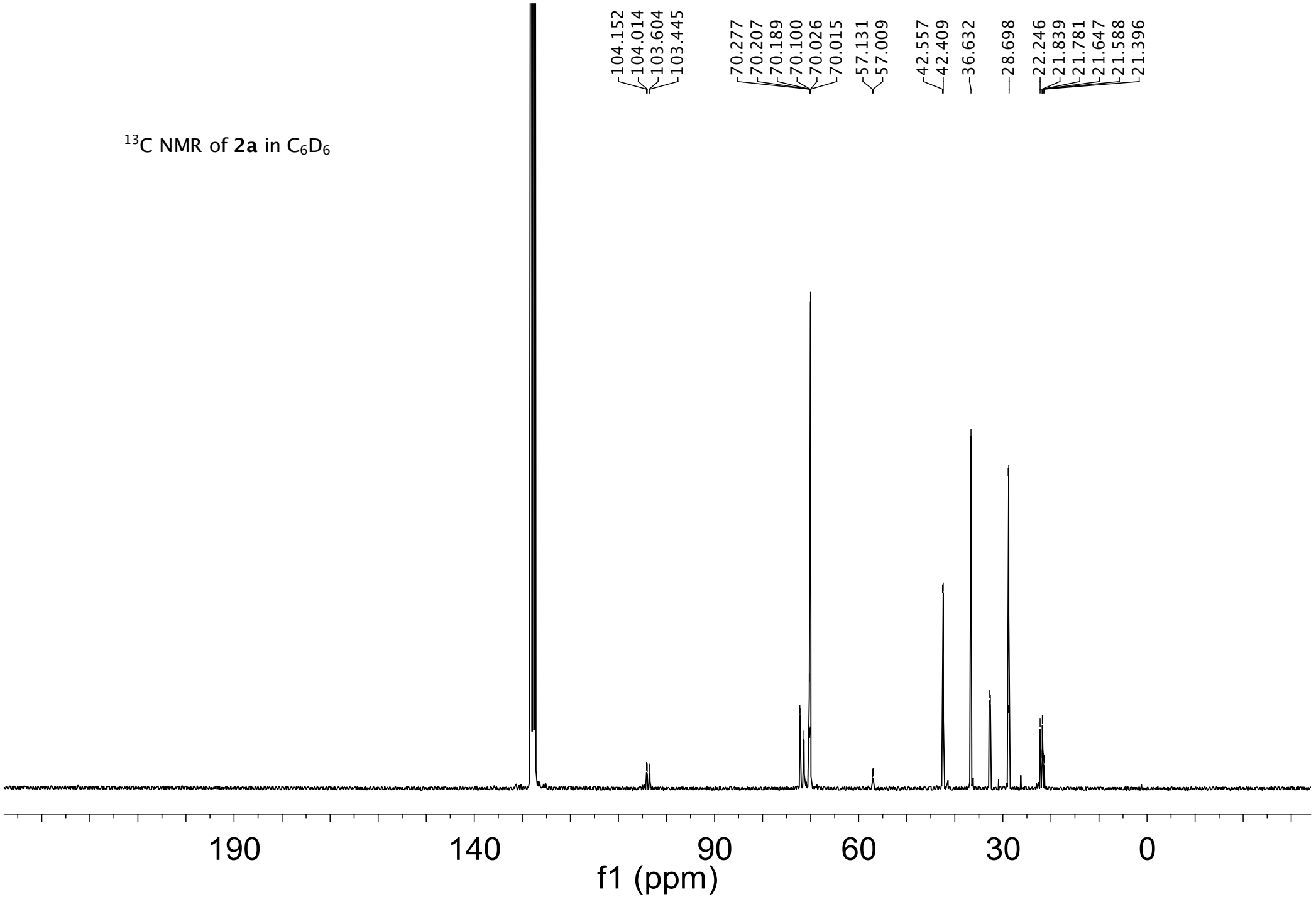

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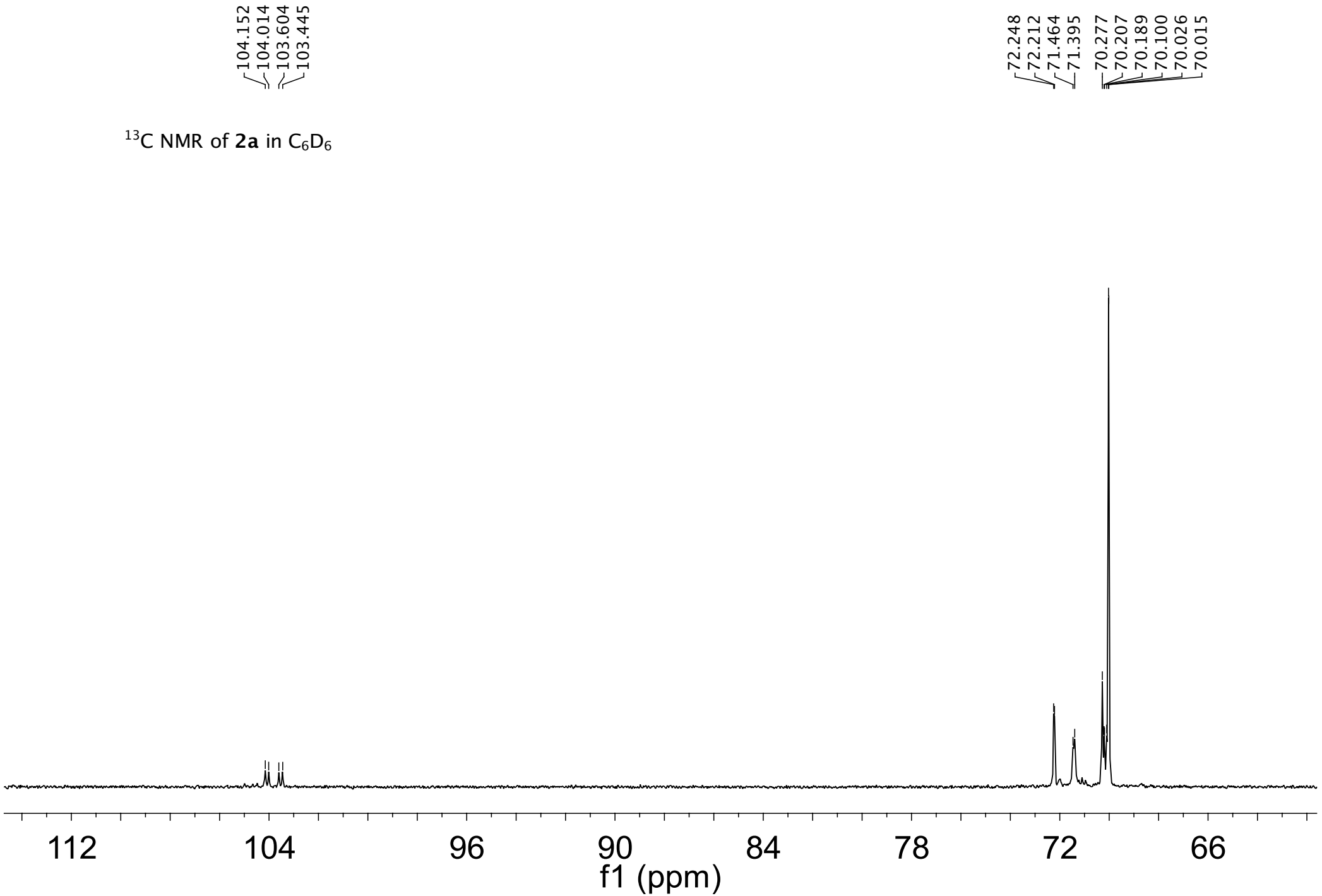

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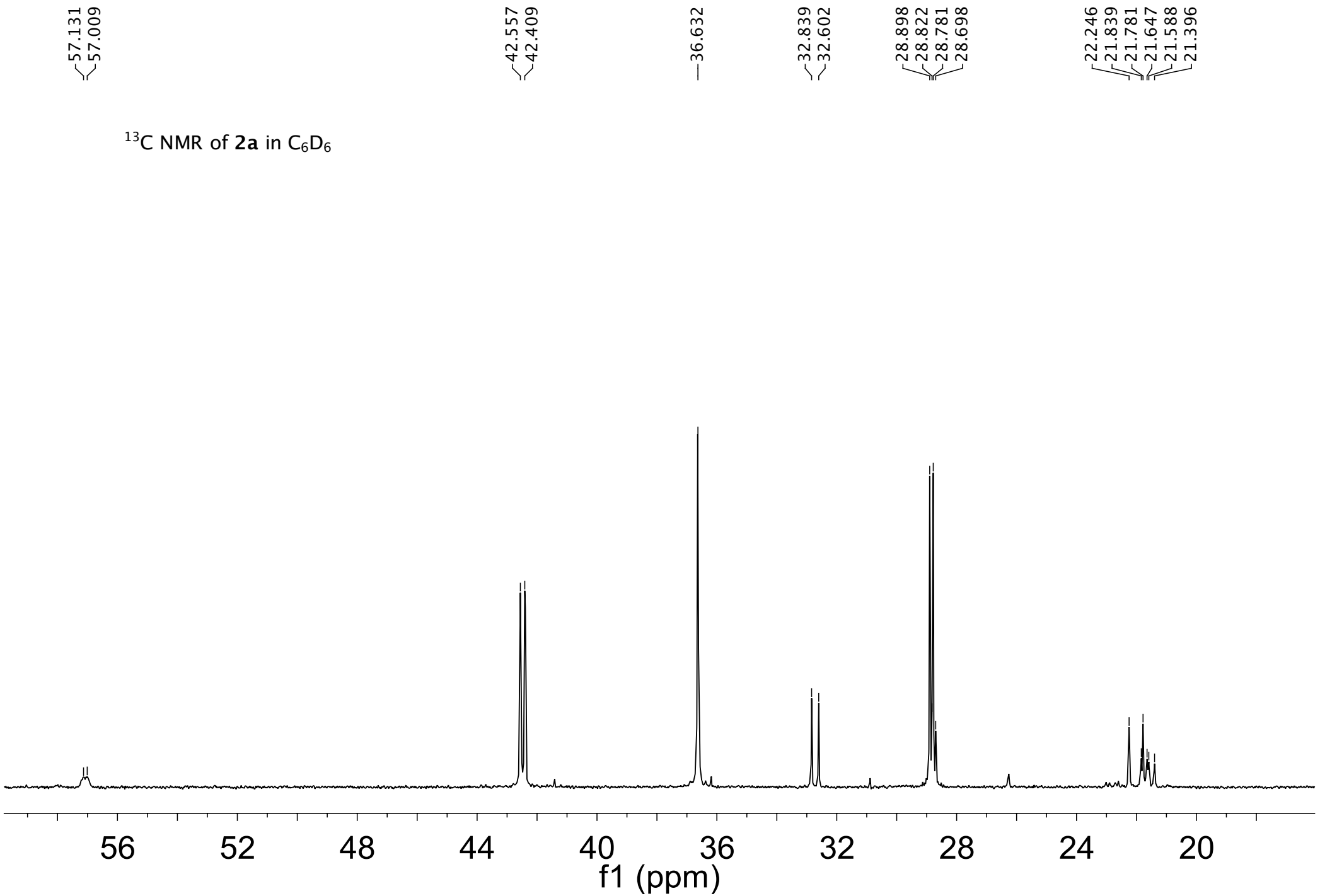

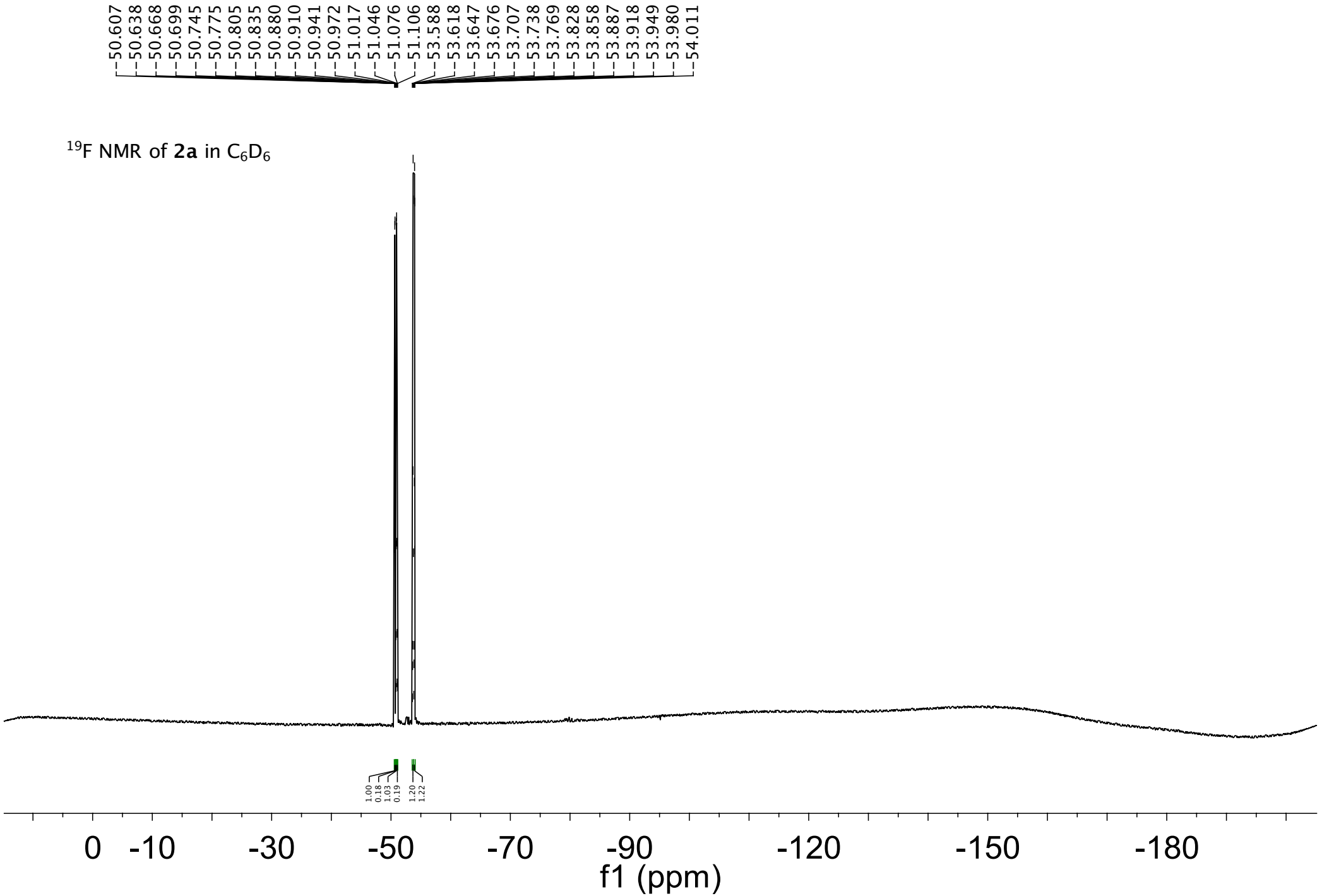
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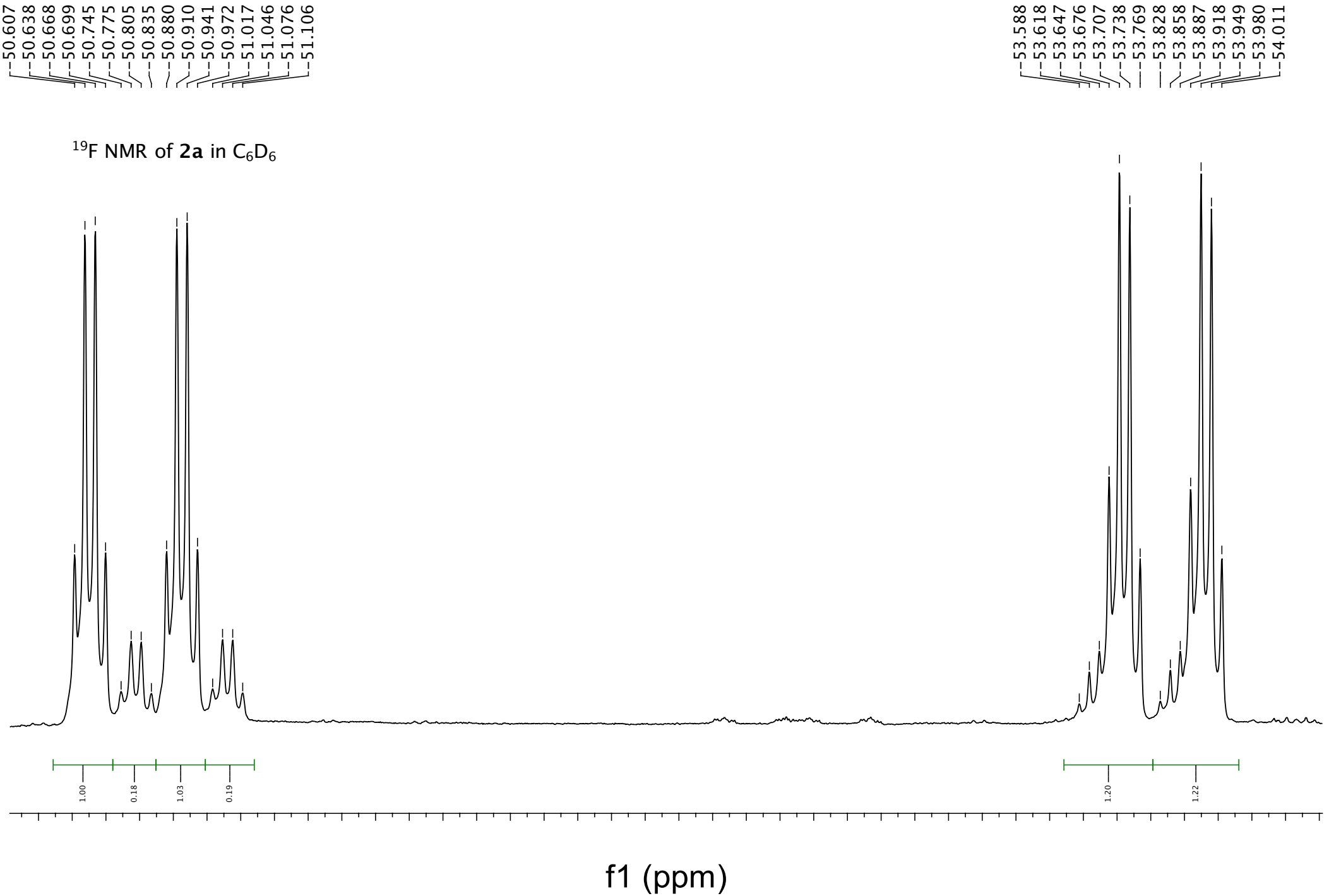
f1 (ppm)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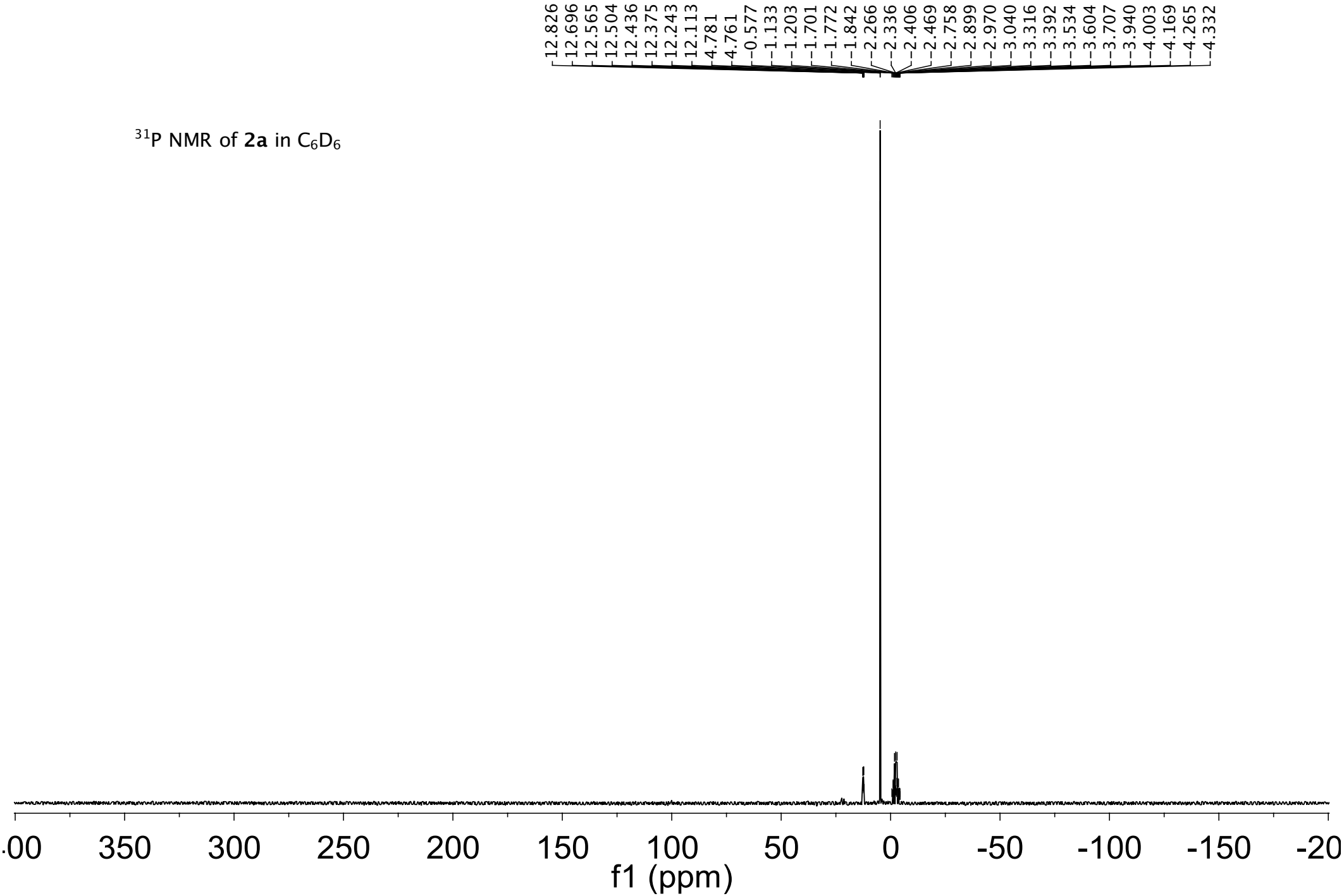
1.22
f1 (ppm)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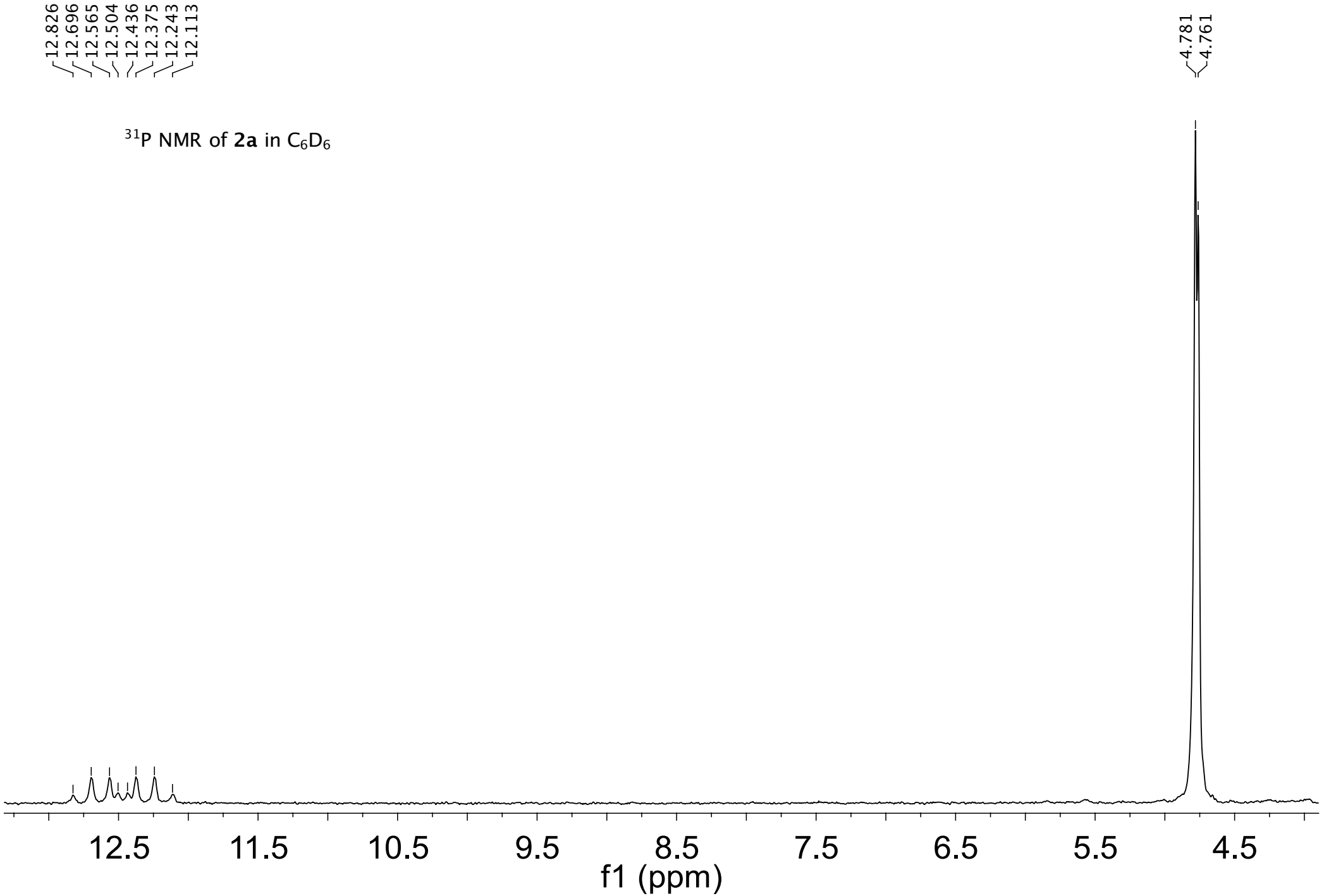
f1 (ppm)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4.5
f1 (ppm)

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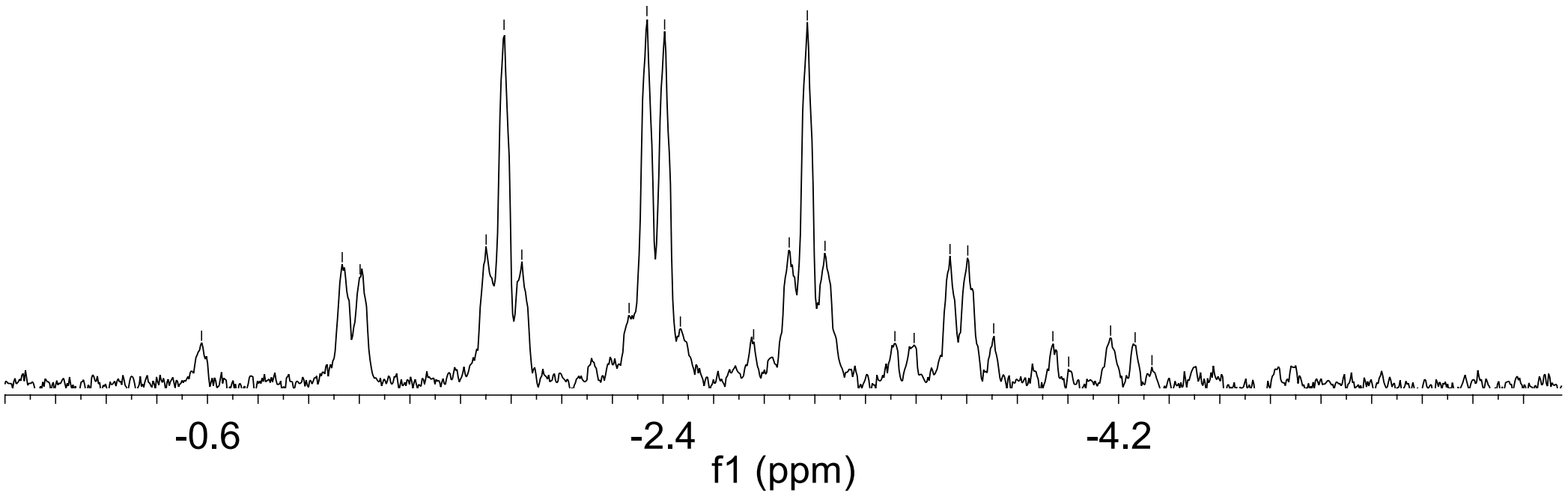
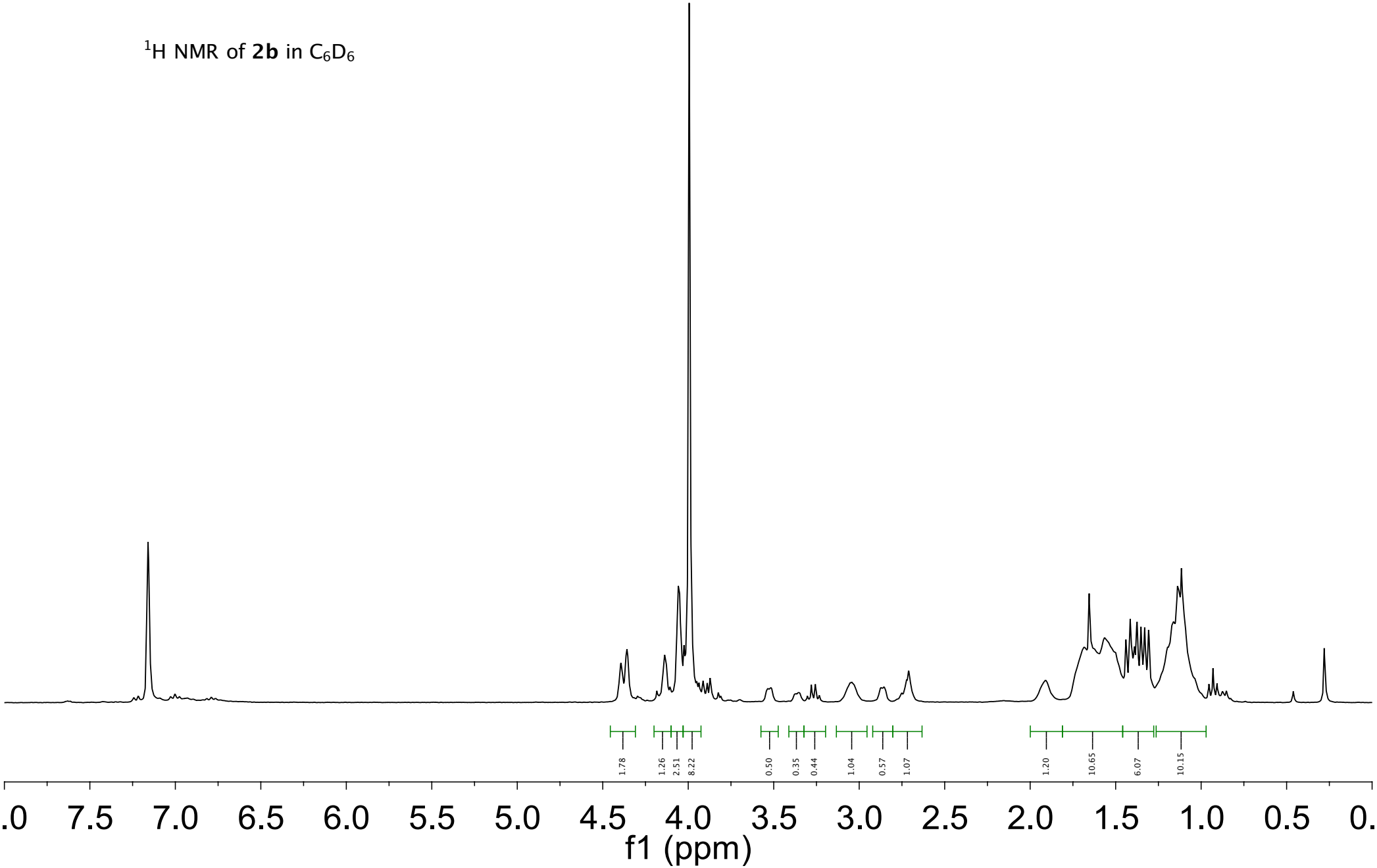
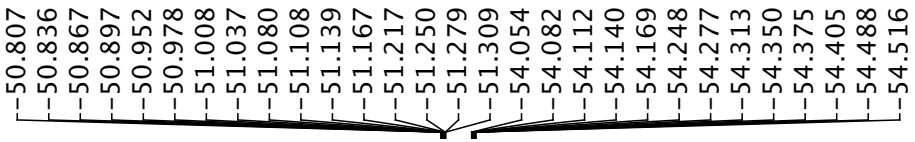
^{31}P NMR of **2a** in C_6D_6

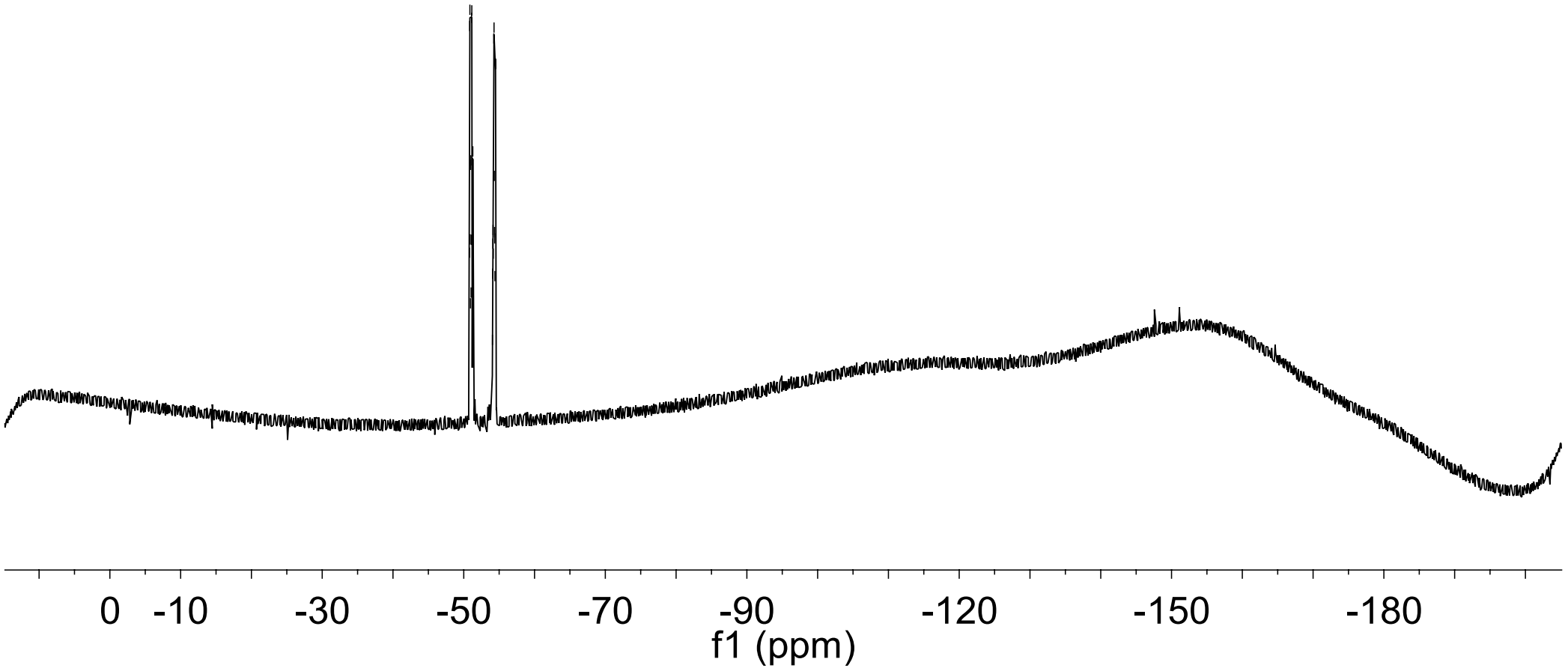


^{1}H NMR of **2b** in C_6D_6

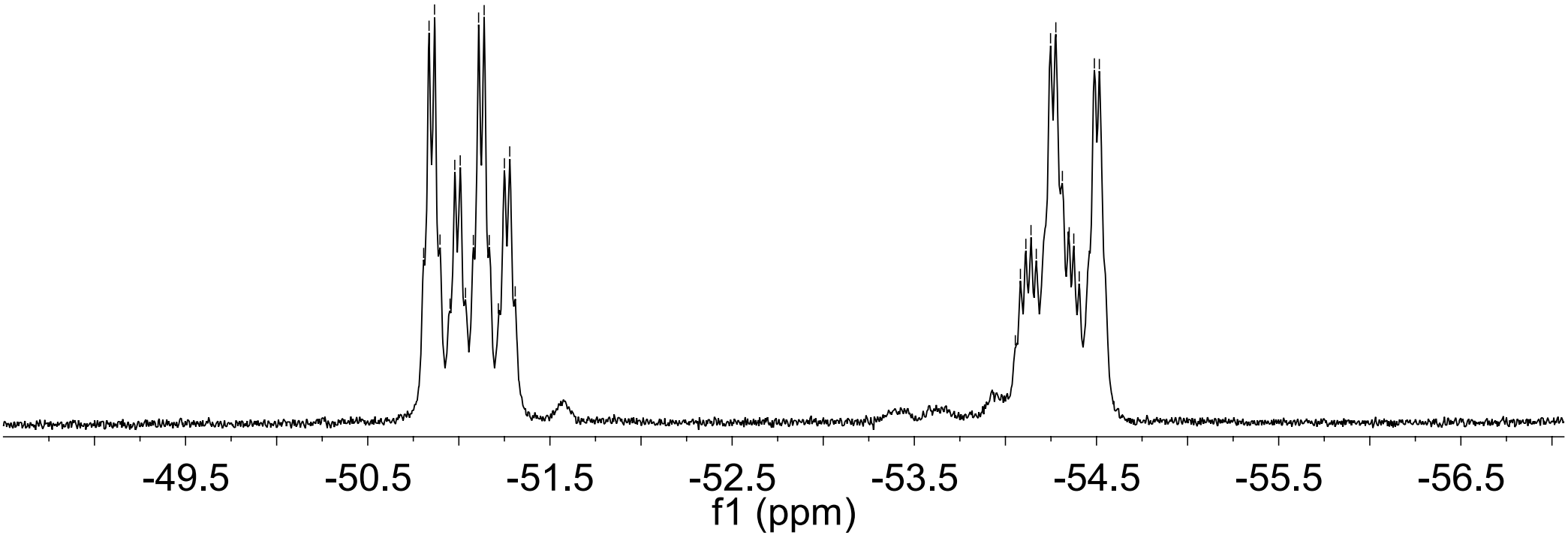




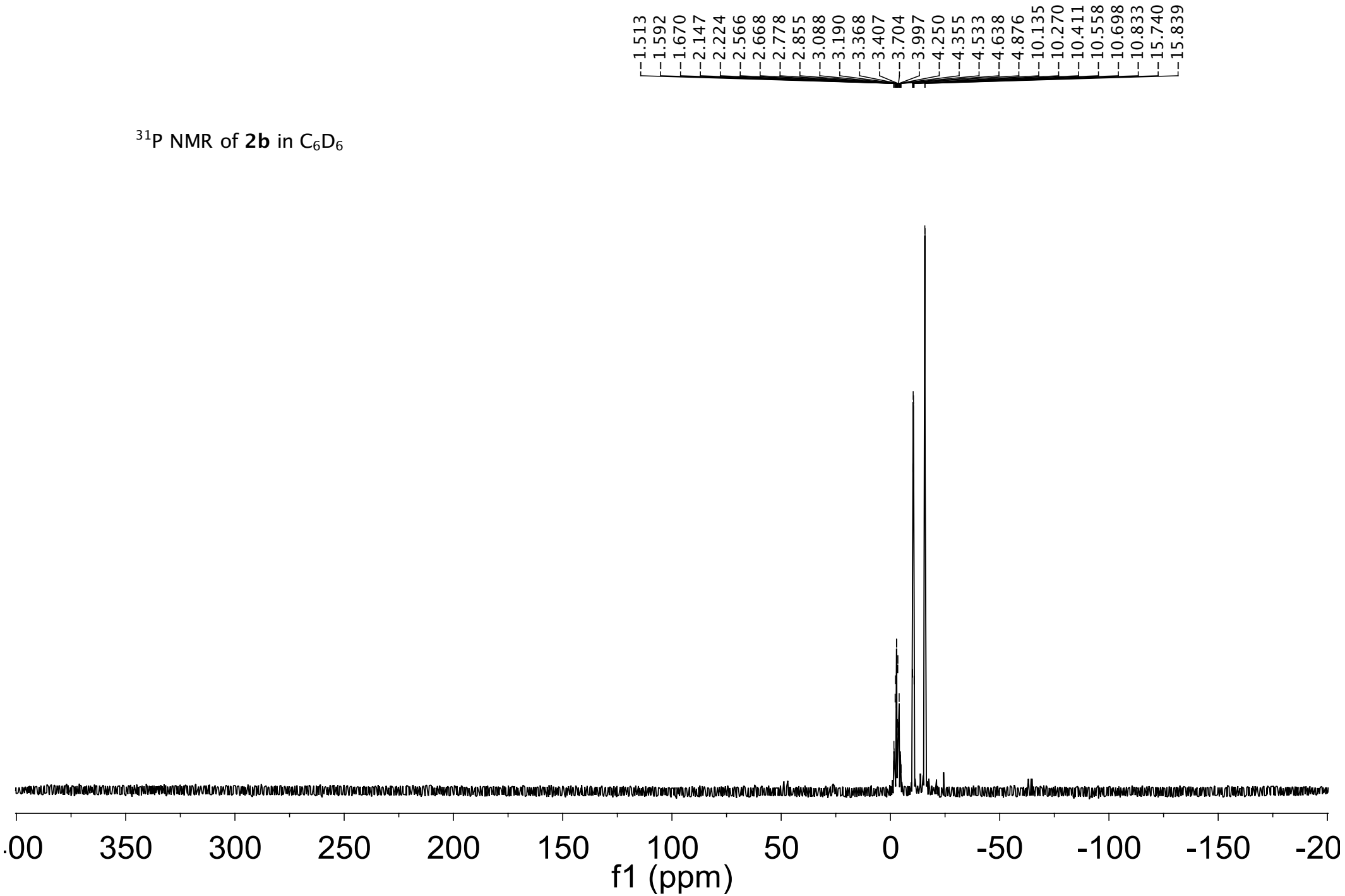
^{19}F NMR of **2b** in C_6D_6

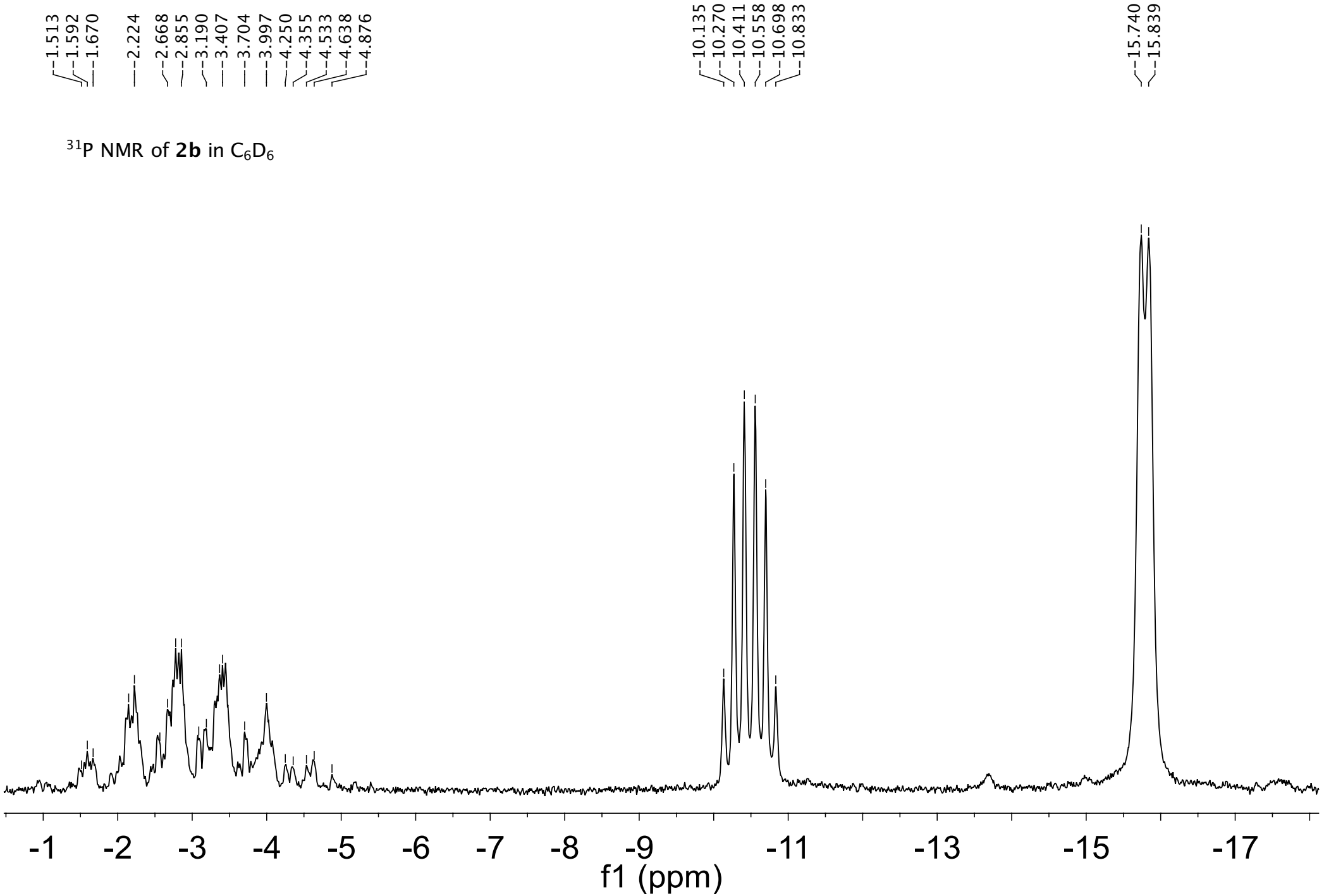


^{19}F NMR of **2b** in C_6D_6



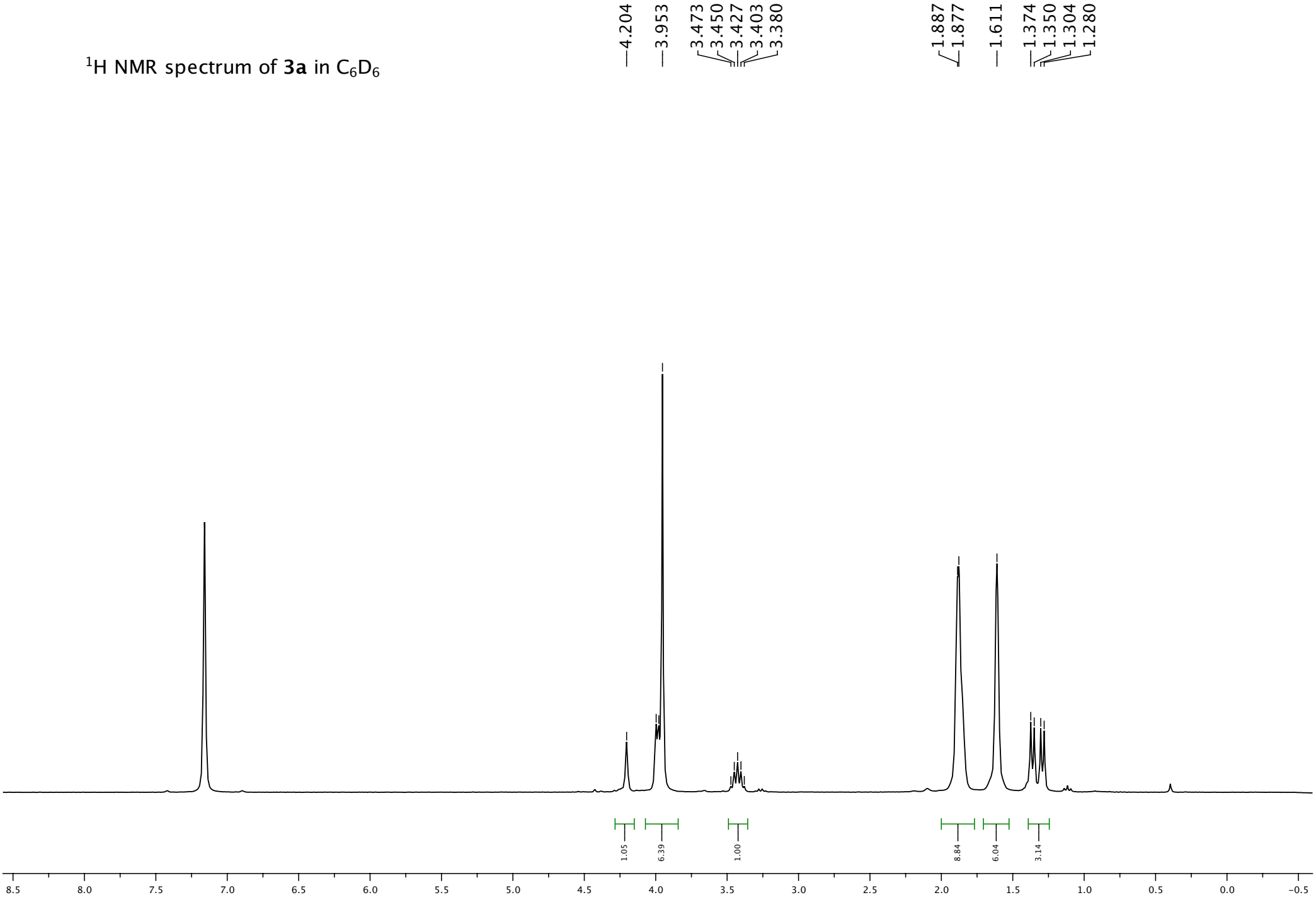
^{31}P NMR of **2b** in C_6D_6



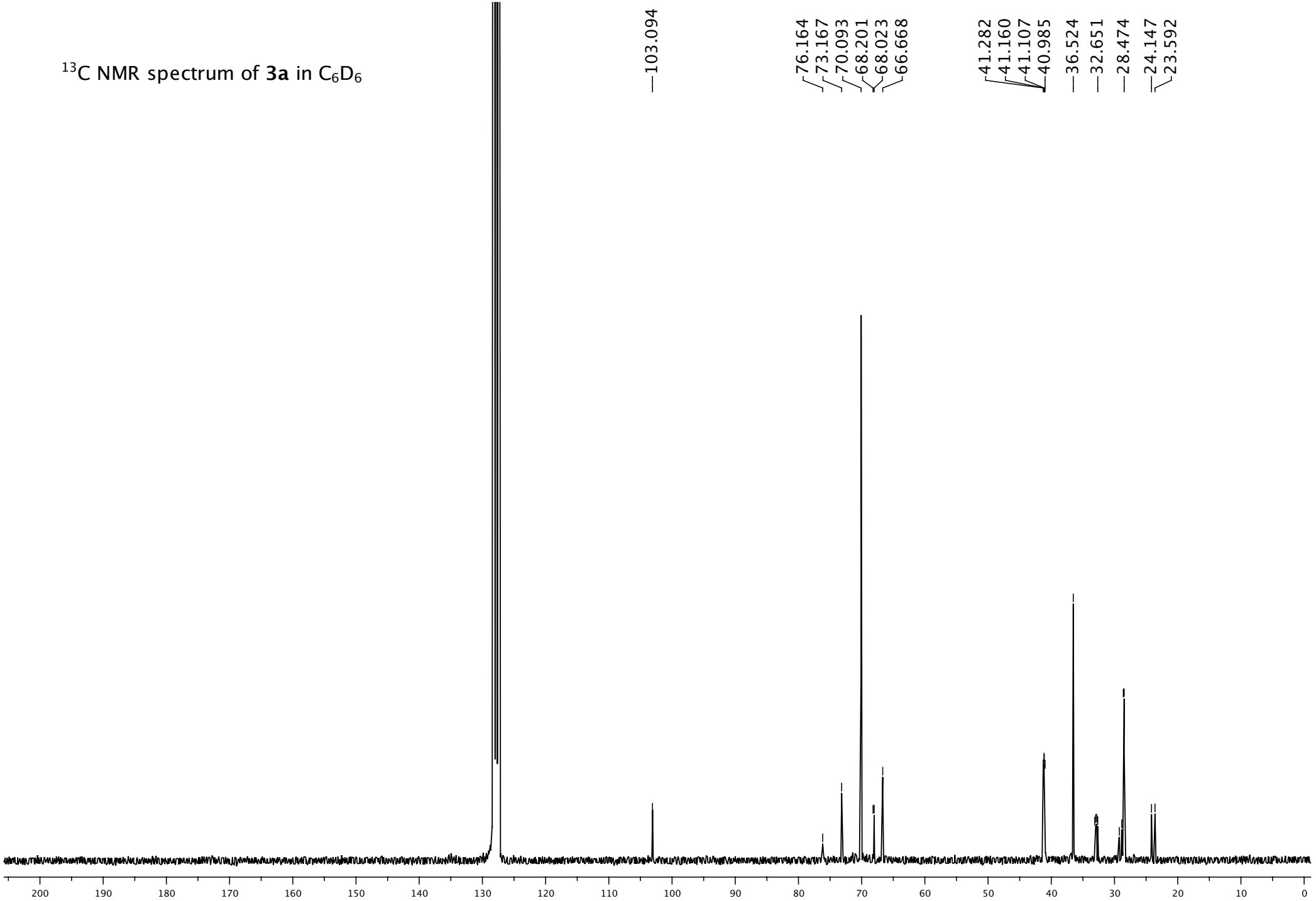


^{31}P NMR of **2b** in C_6D_6

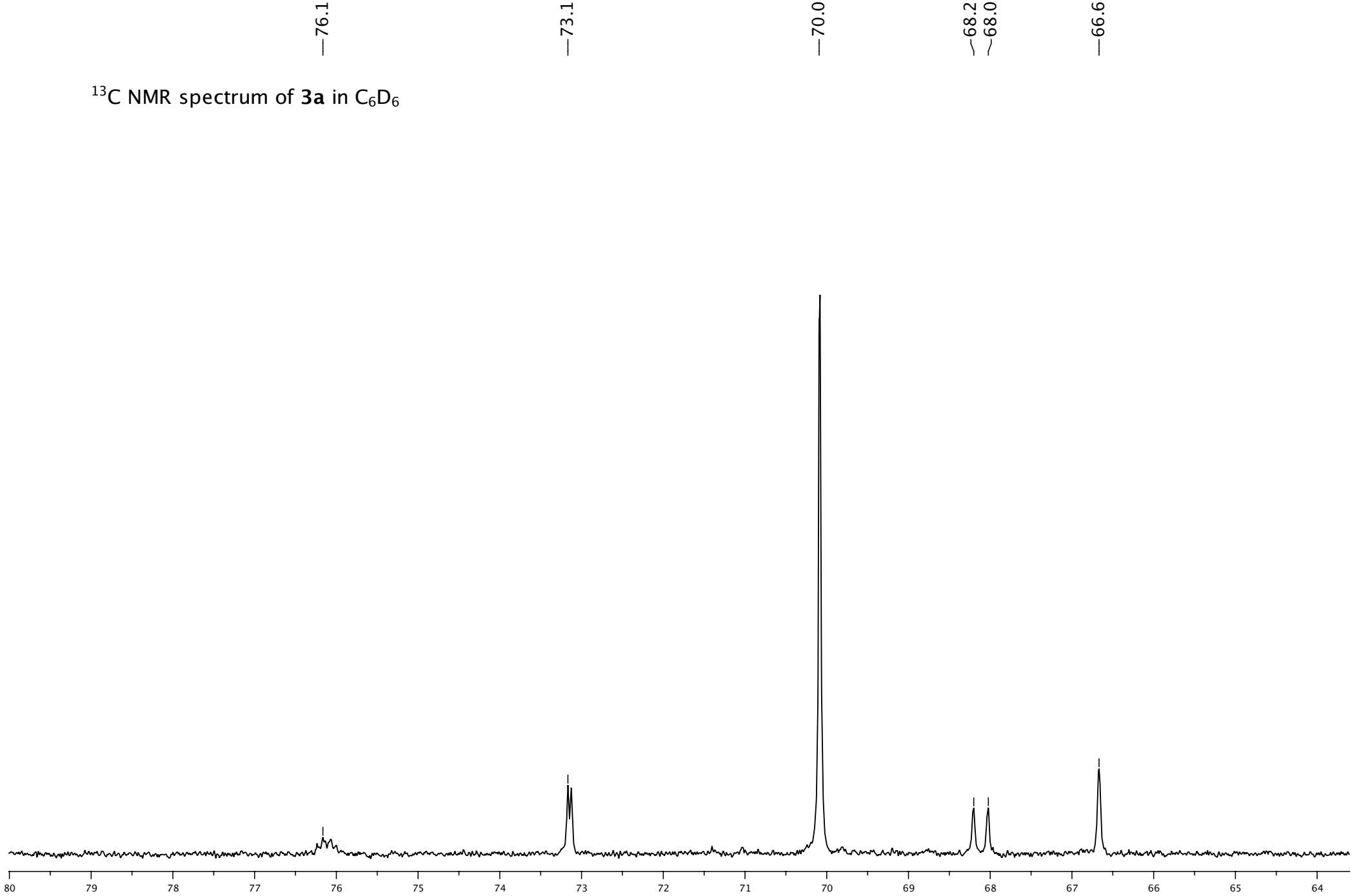
^{1}H NMR spectrum of **3a** in C_6D_6



^{13}C NMR spectrum of **3a** in C_6D_6

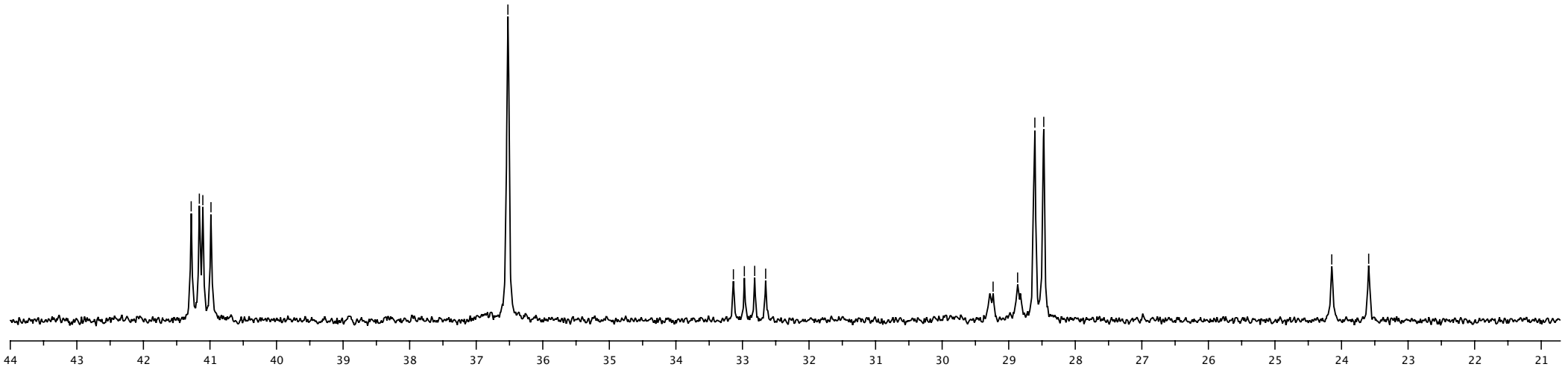


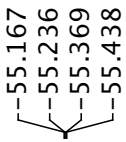
^{13}C NMR spectrum of **3a** in C_6D_6



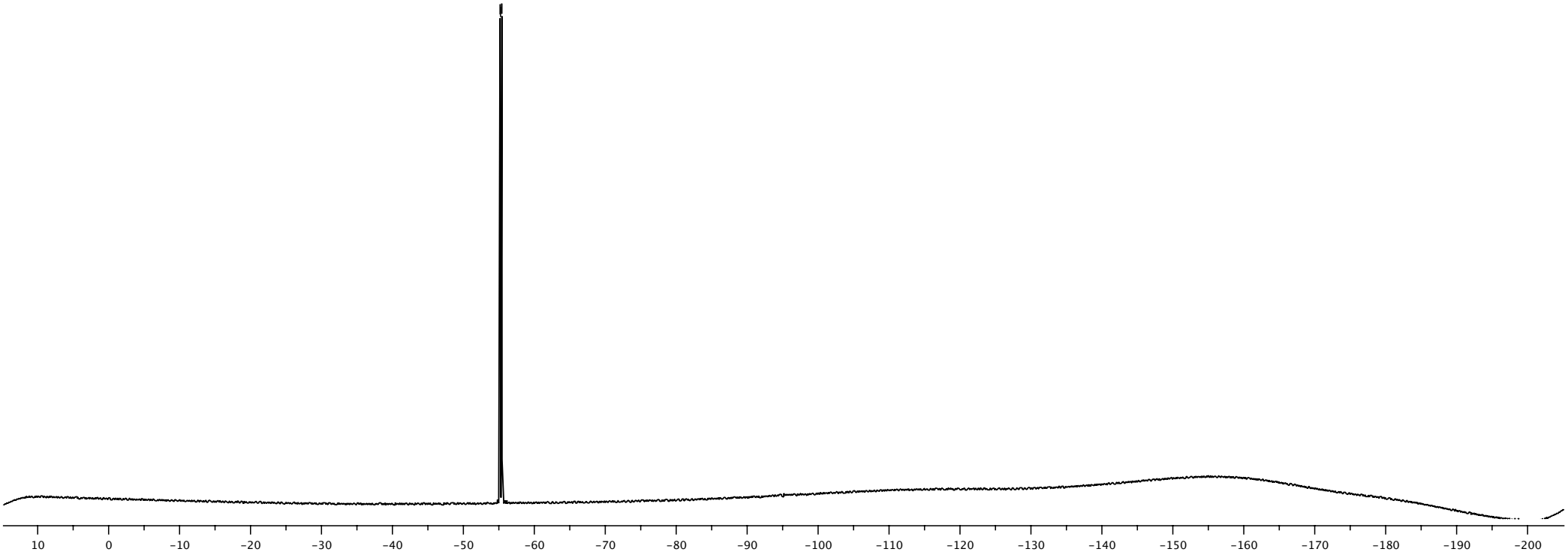
41.282
41.160
41.107
40.985
36.524
33.136
32.972
32.816
32.651
29.234
28.866
28.607
28.474
24.147
23.592

^{13}C NMR spectrum of **3a** in C_6D_6

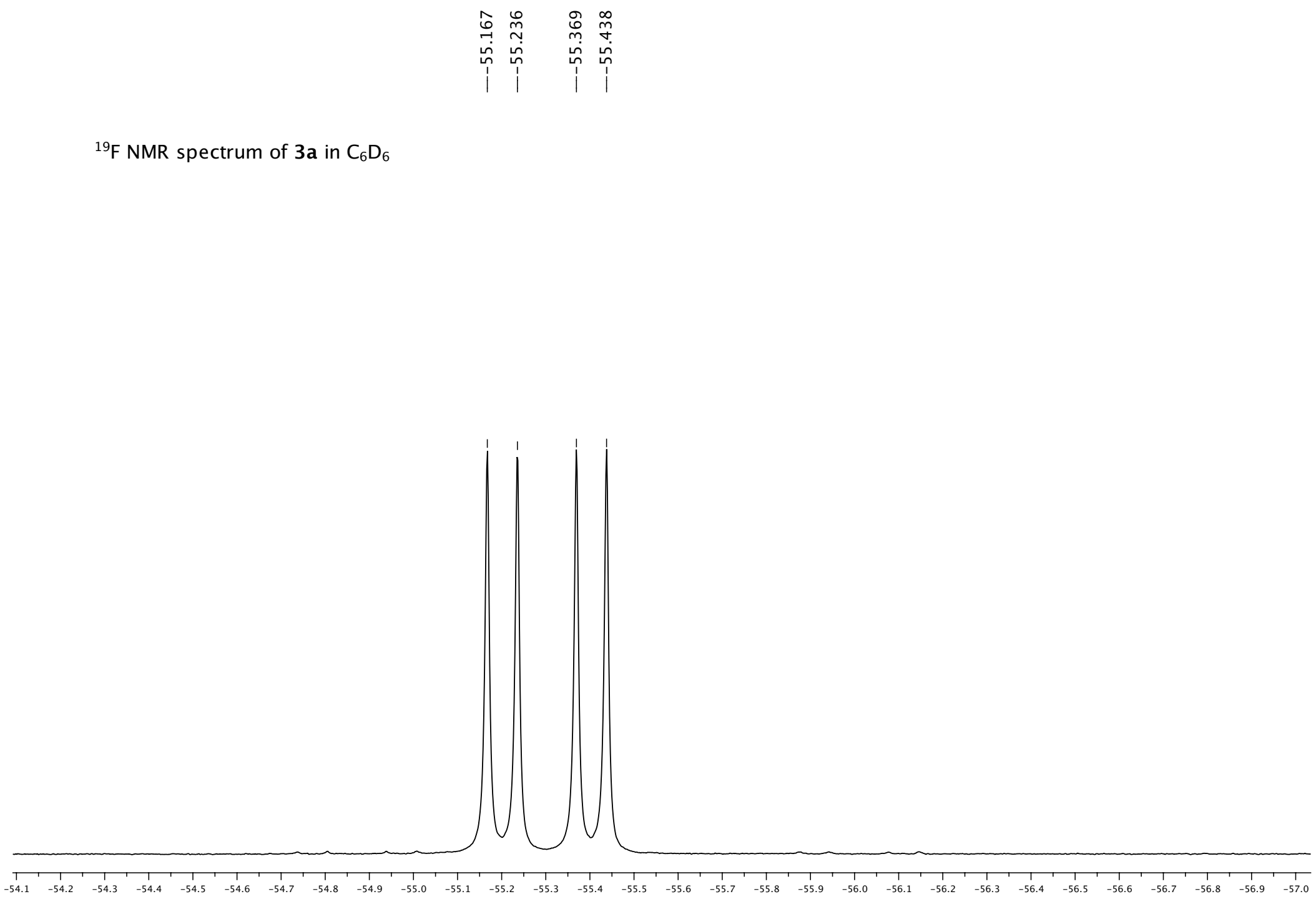




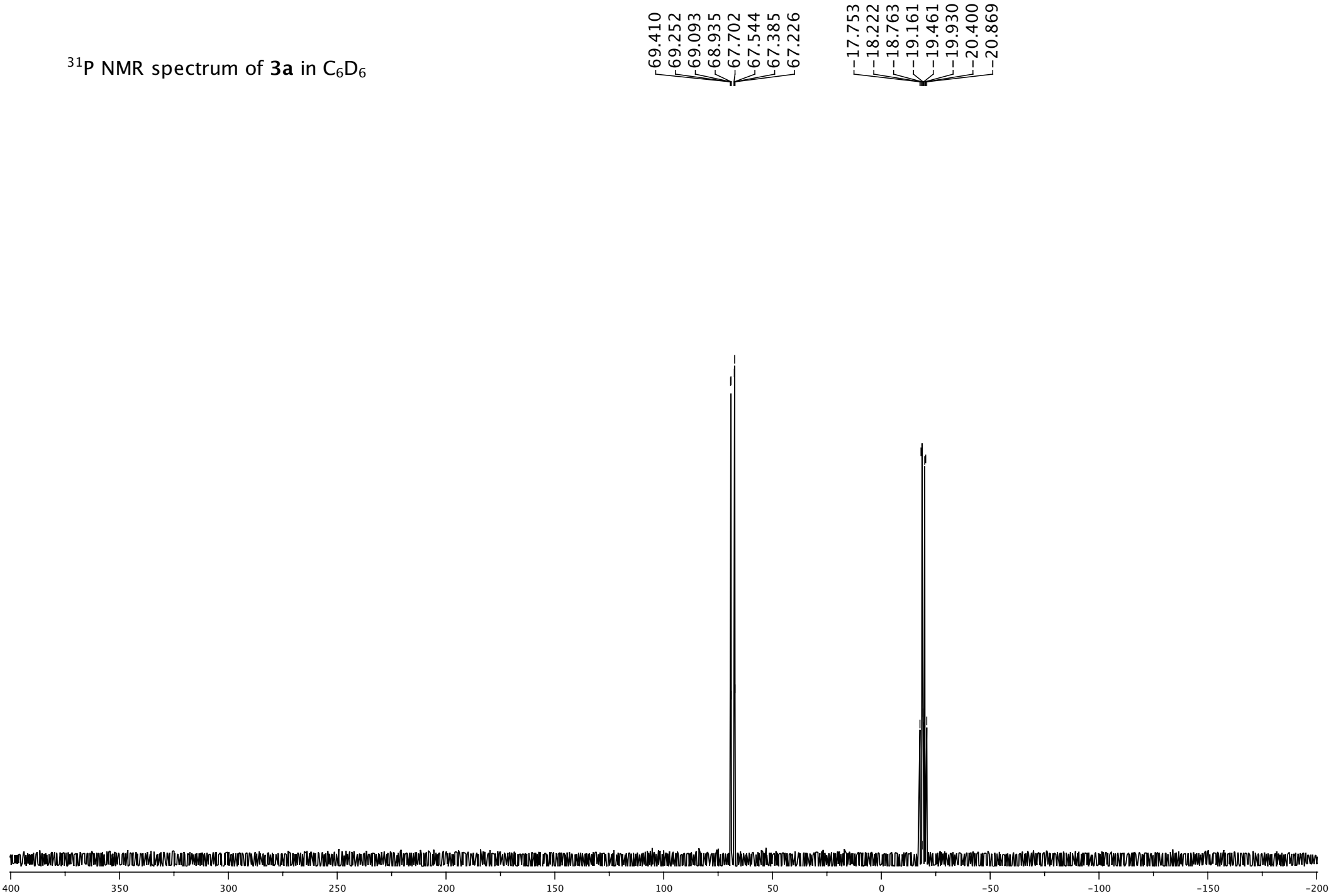
^{19}F NMR spectrum of **3a** in C_6D_6



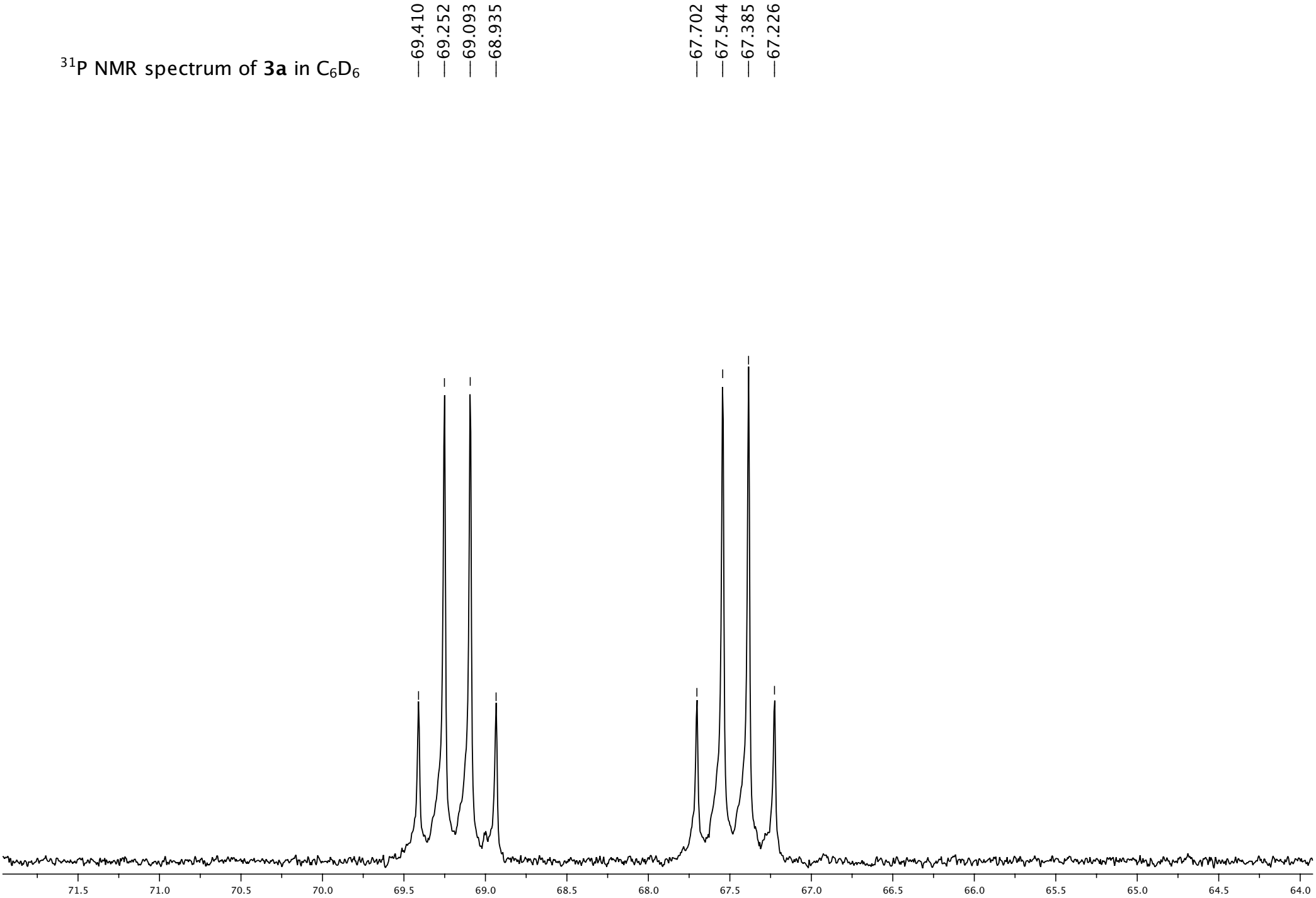
^{19}F NMR spectrum of **3a** in C_6D_6



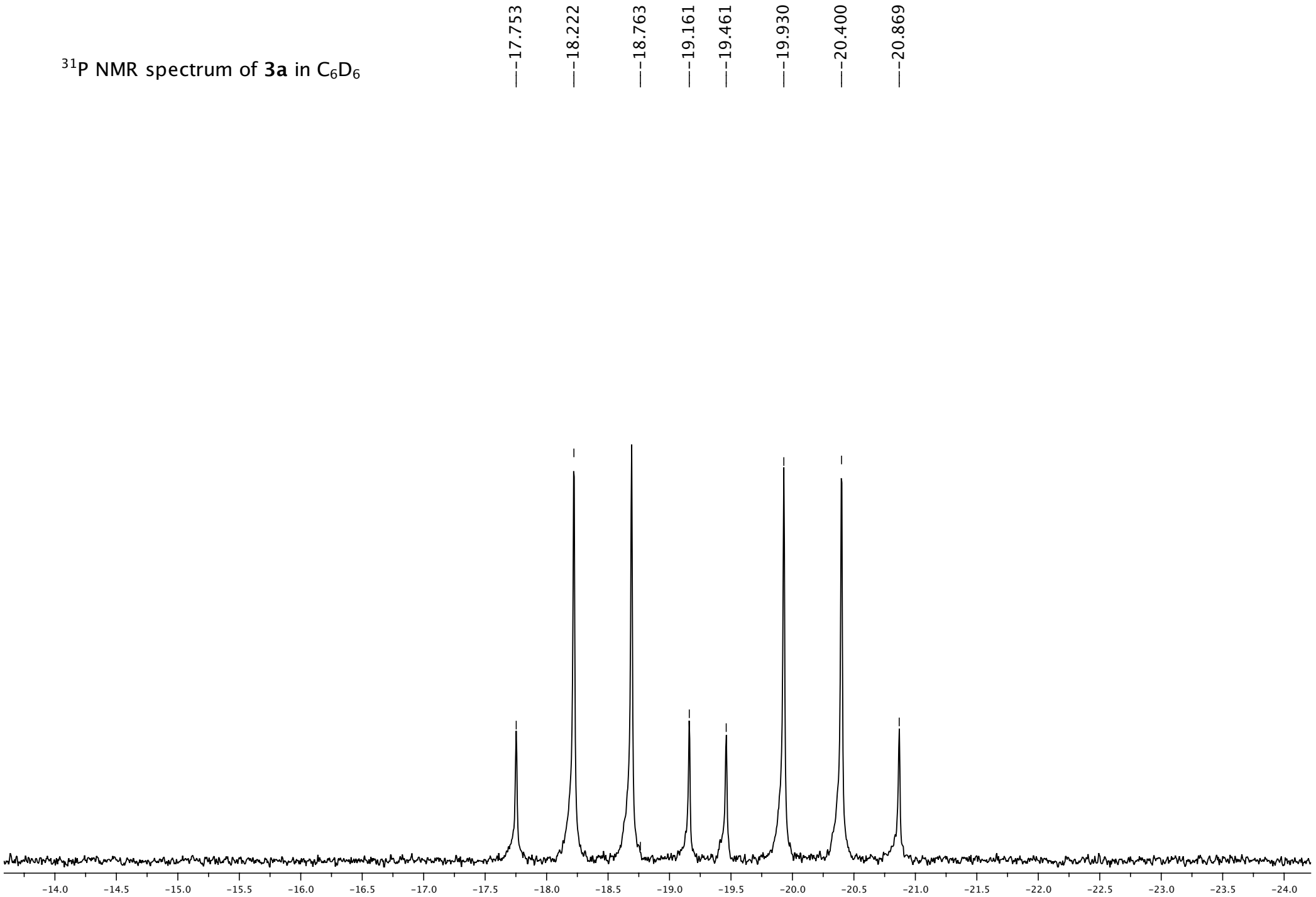
^{31}P NMR spectrum of **3a** in C_6D_6



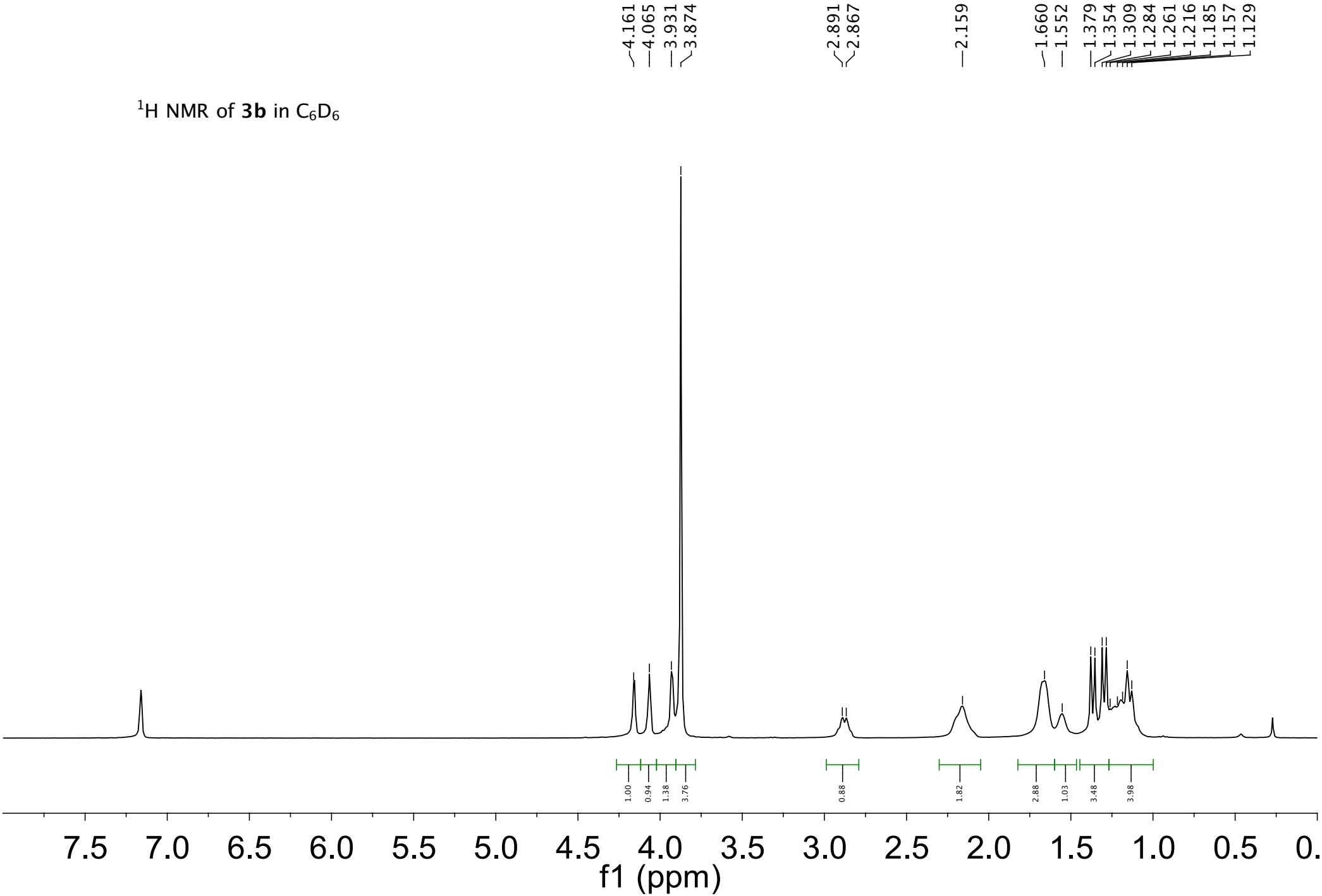
^{31}P NMR spectrum of **3a** in C_6D_6



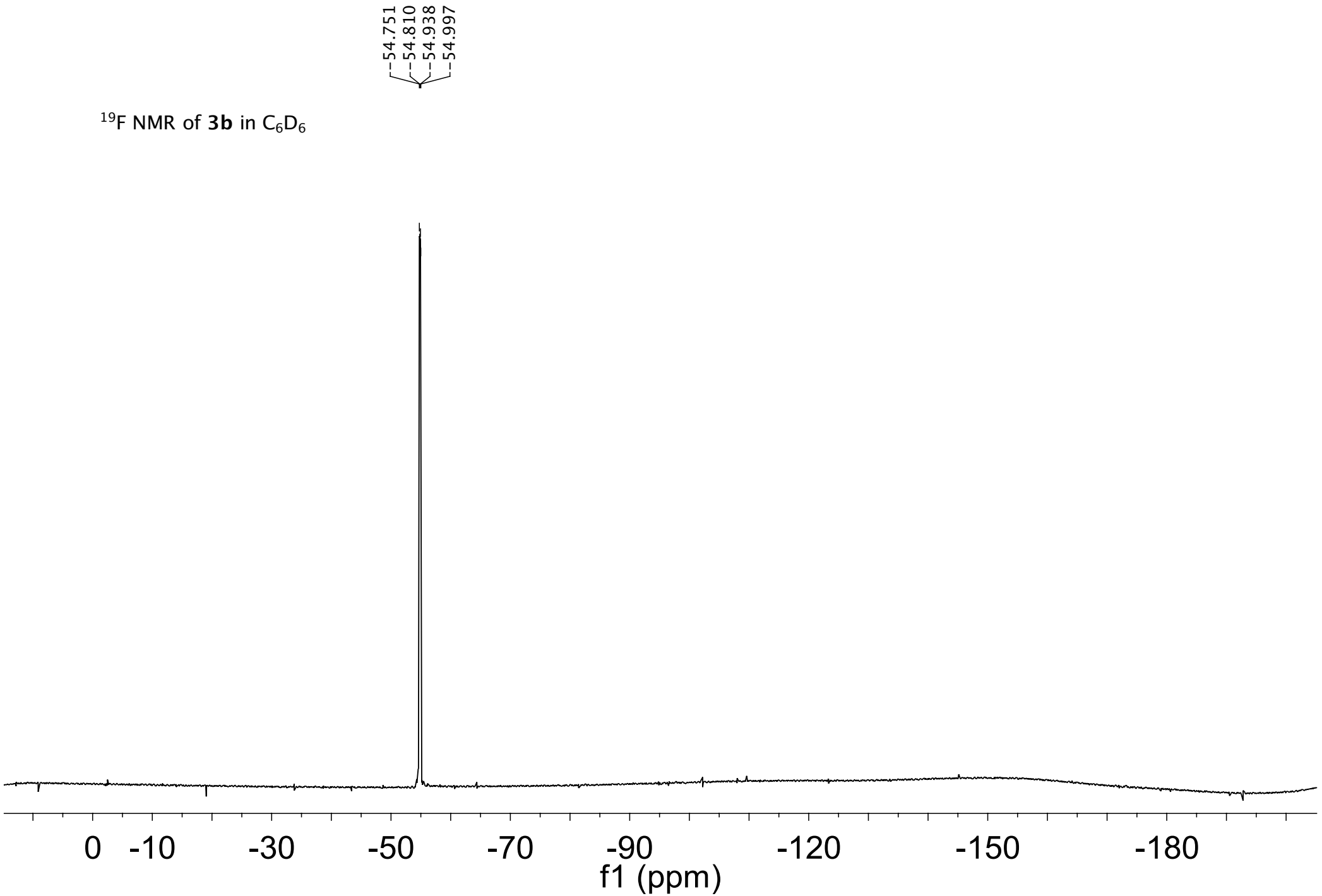
^{31}P NMR spectrum of **3a** in C_6D_6



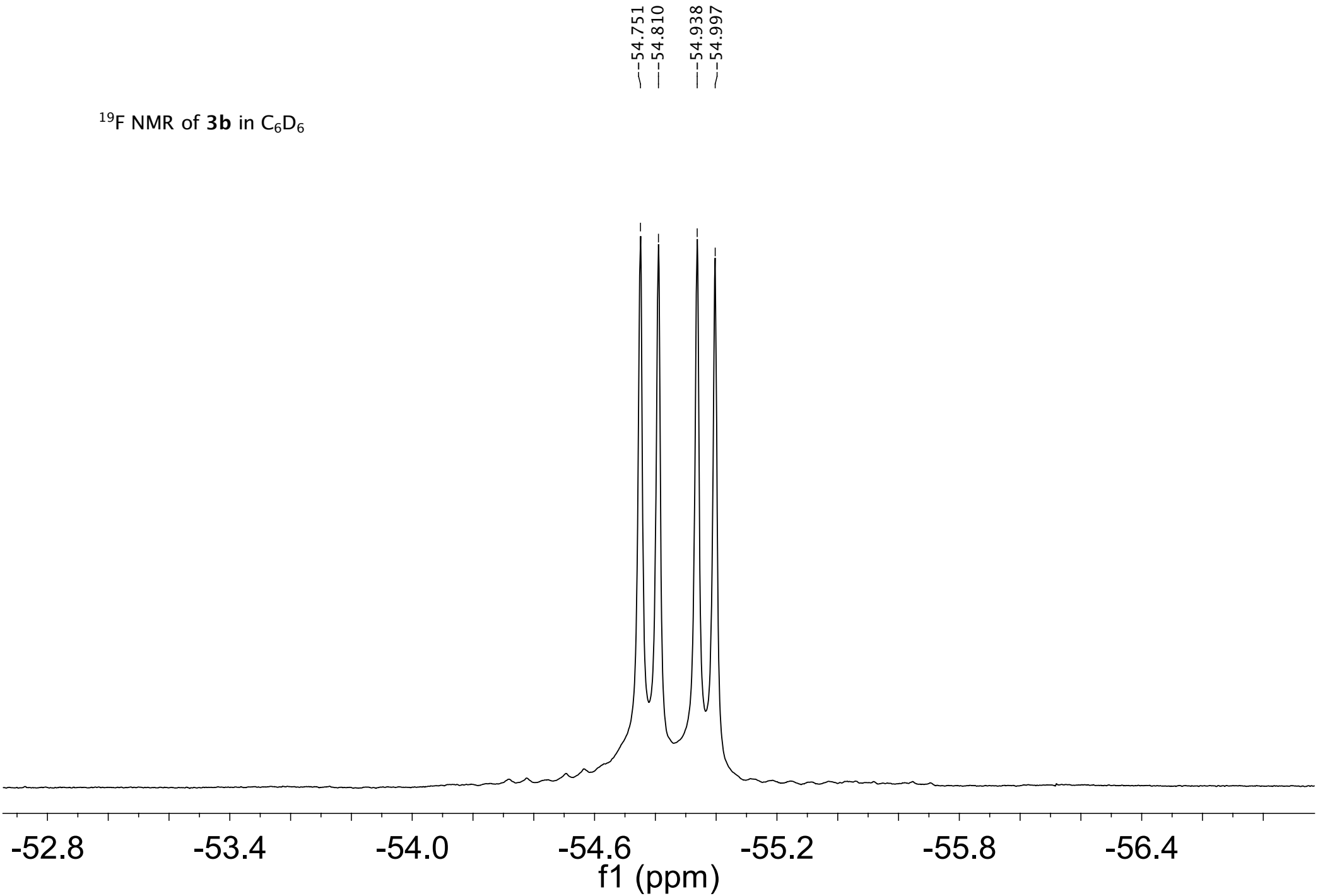
^{1}H NMR of **3b** in C_6D_6



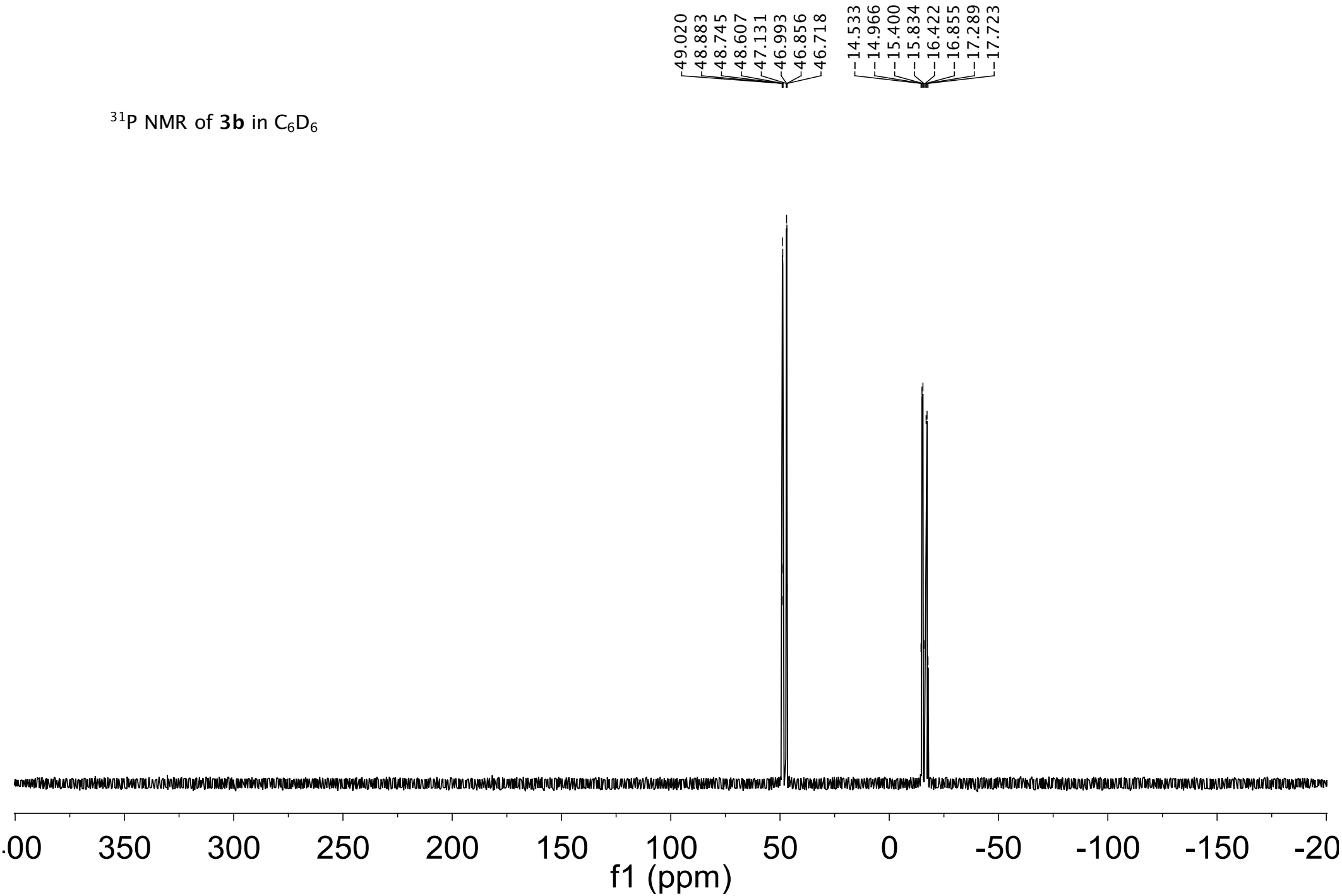
^{19}F NMR of **3b** in C_6D_6



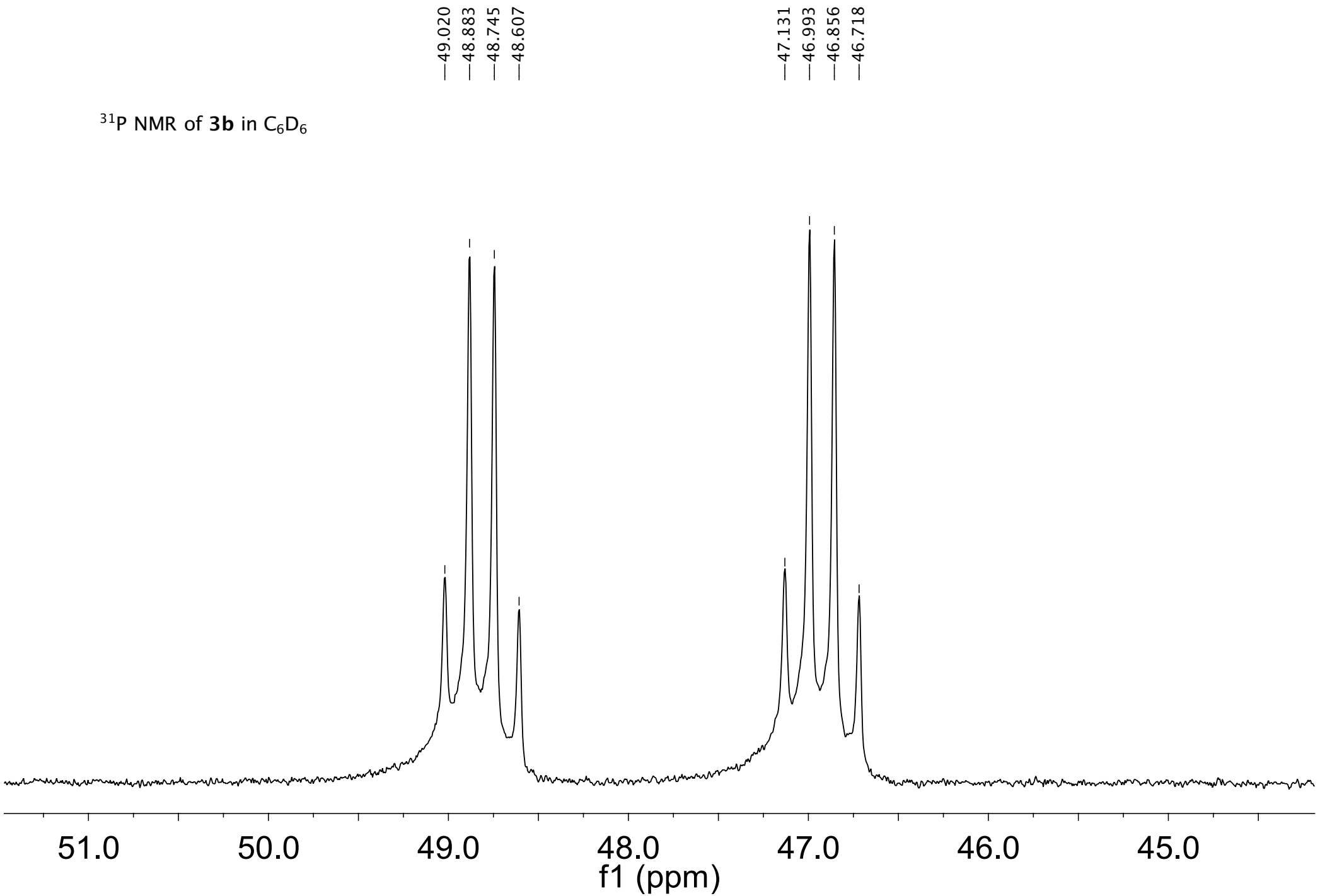
^{19}F NMR of **3b** in C_6D_6



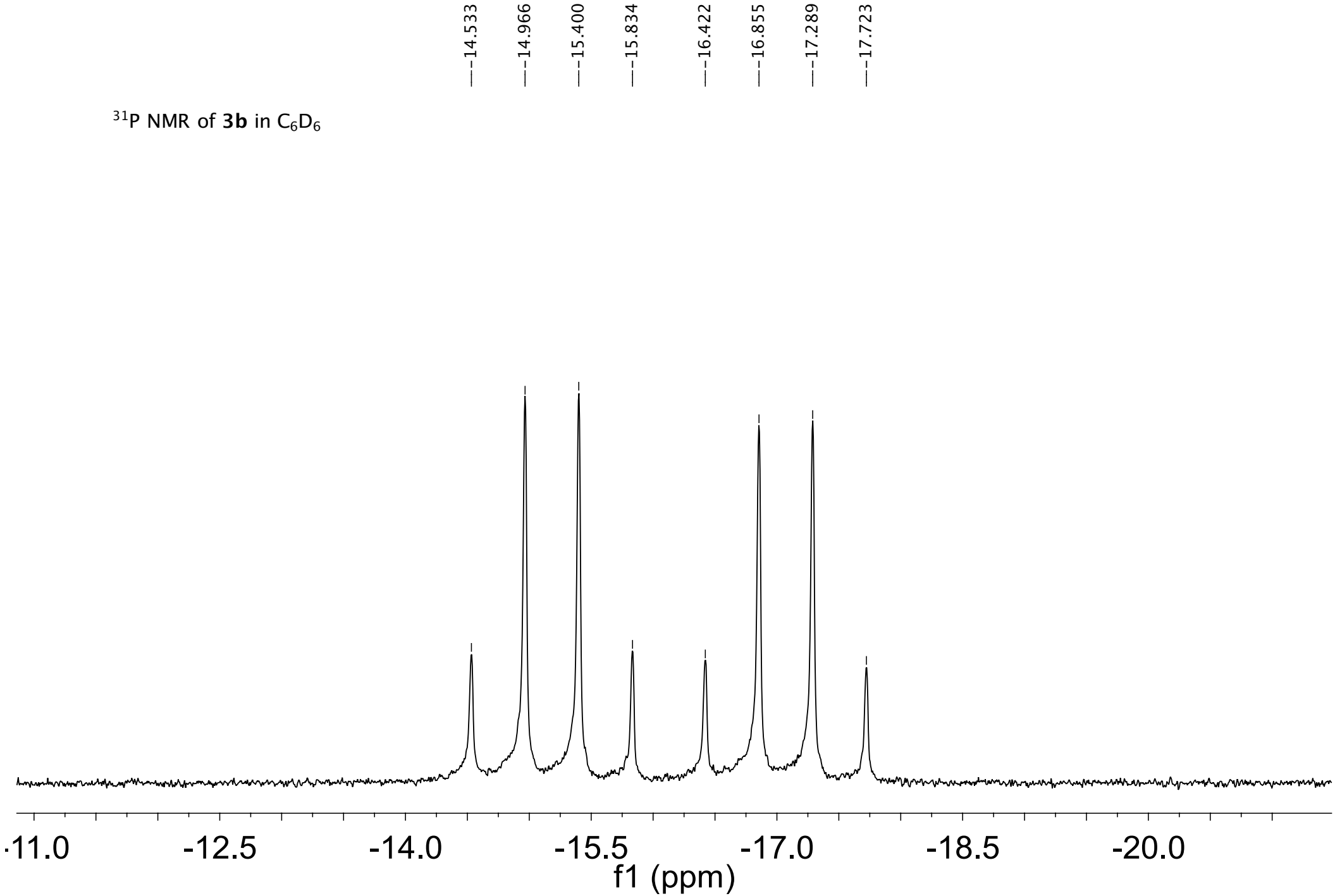
^{31}P NMR of **3b** in C_6D_6



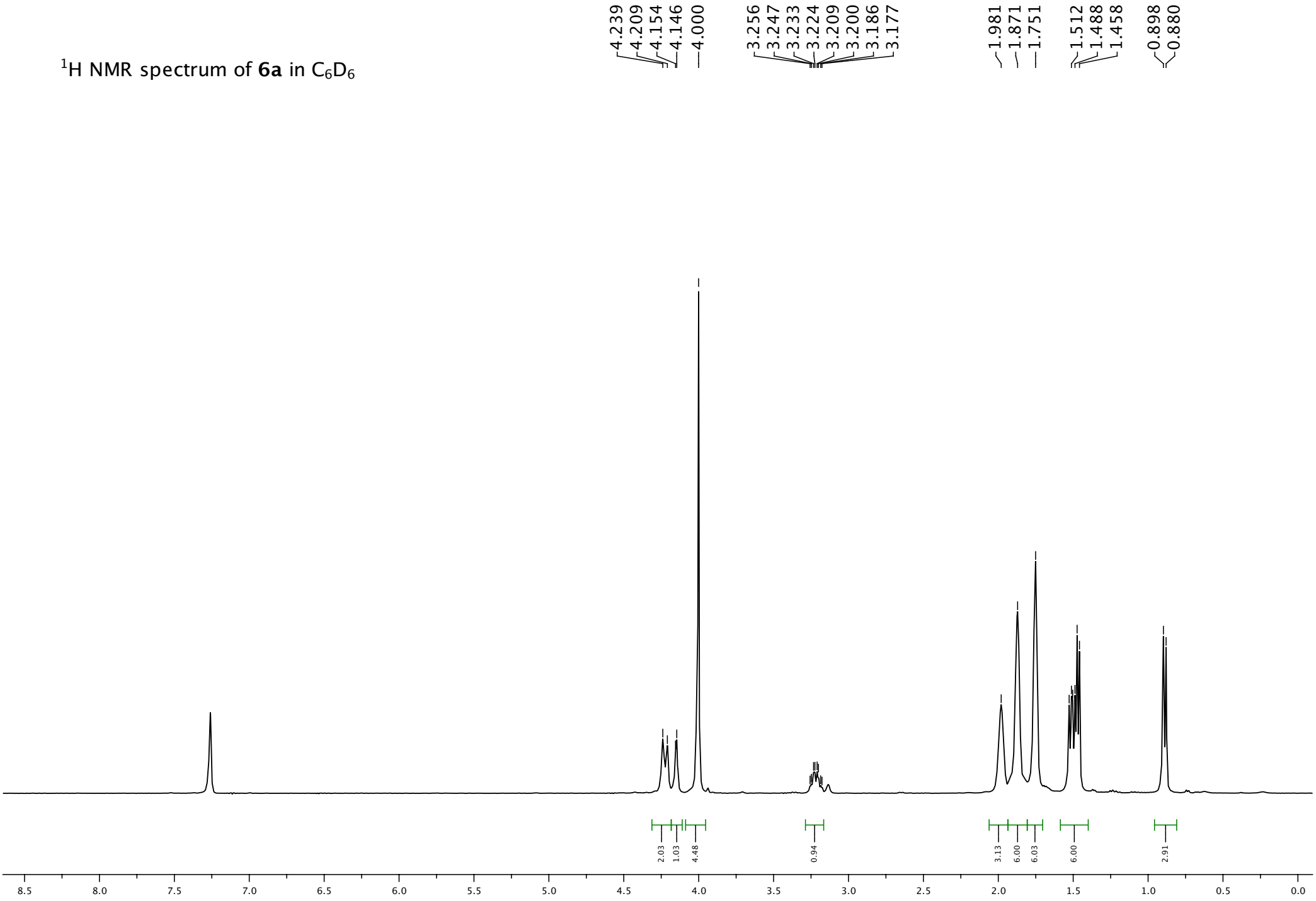
^{31}P NMR of **3b** in C_6D_6



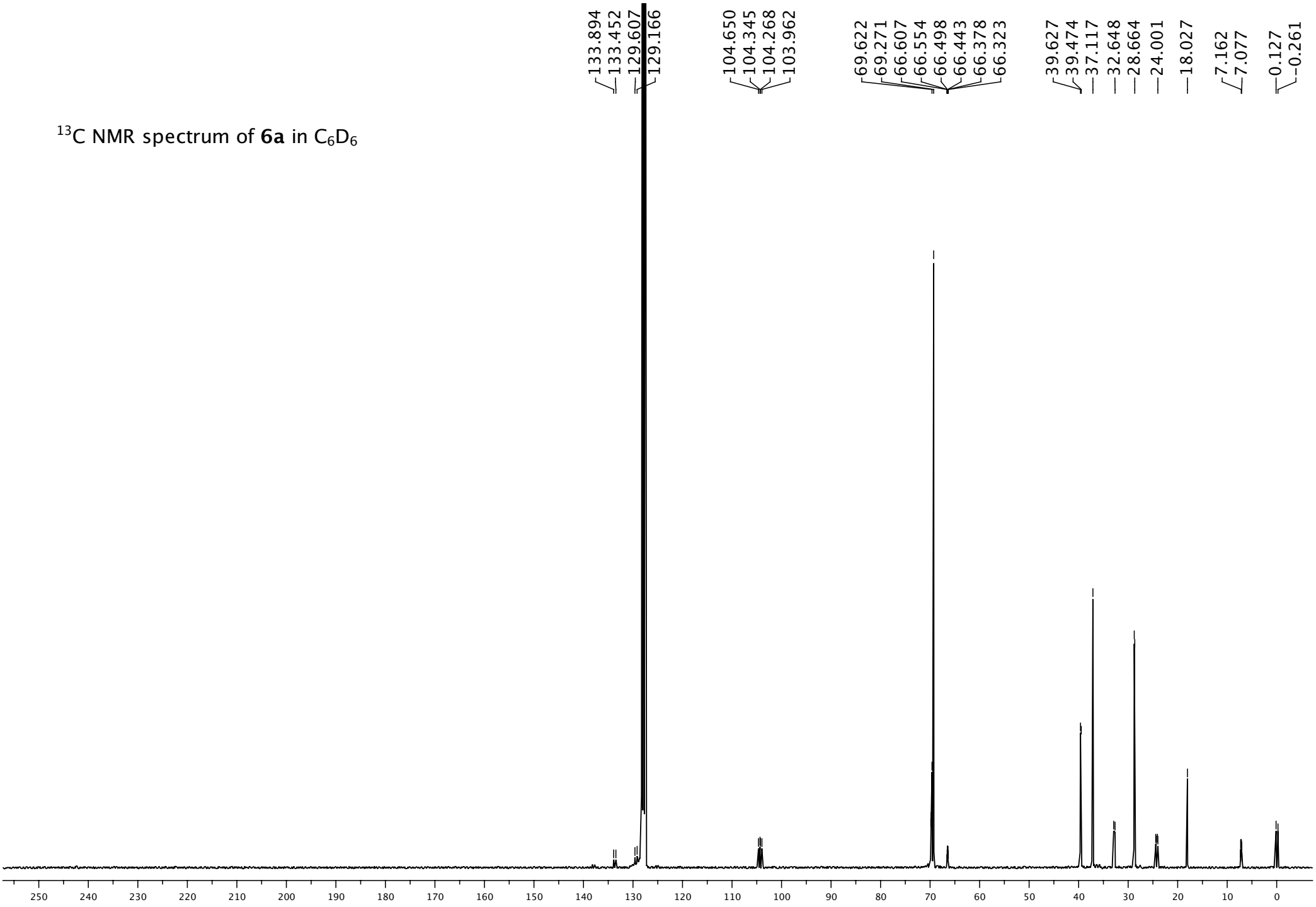
^{31}P NMR of **3b** in C_6D_6



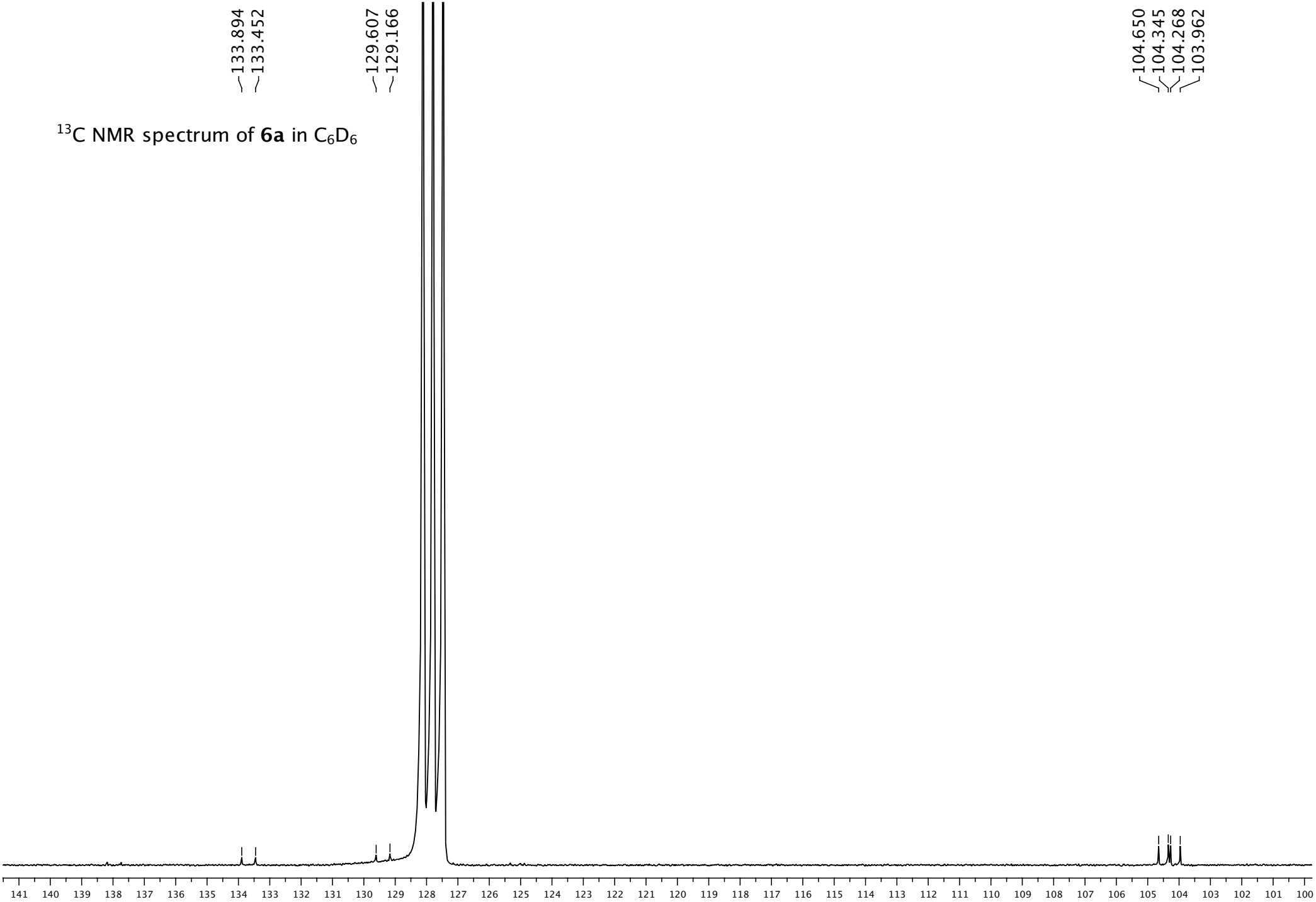
^{1}H NMR spectrum of **6a** in C_6D_6



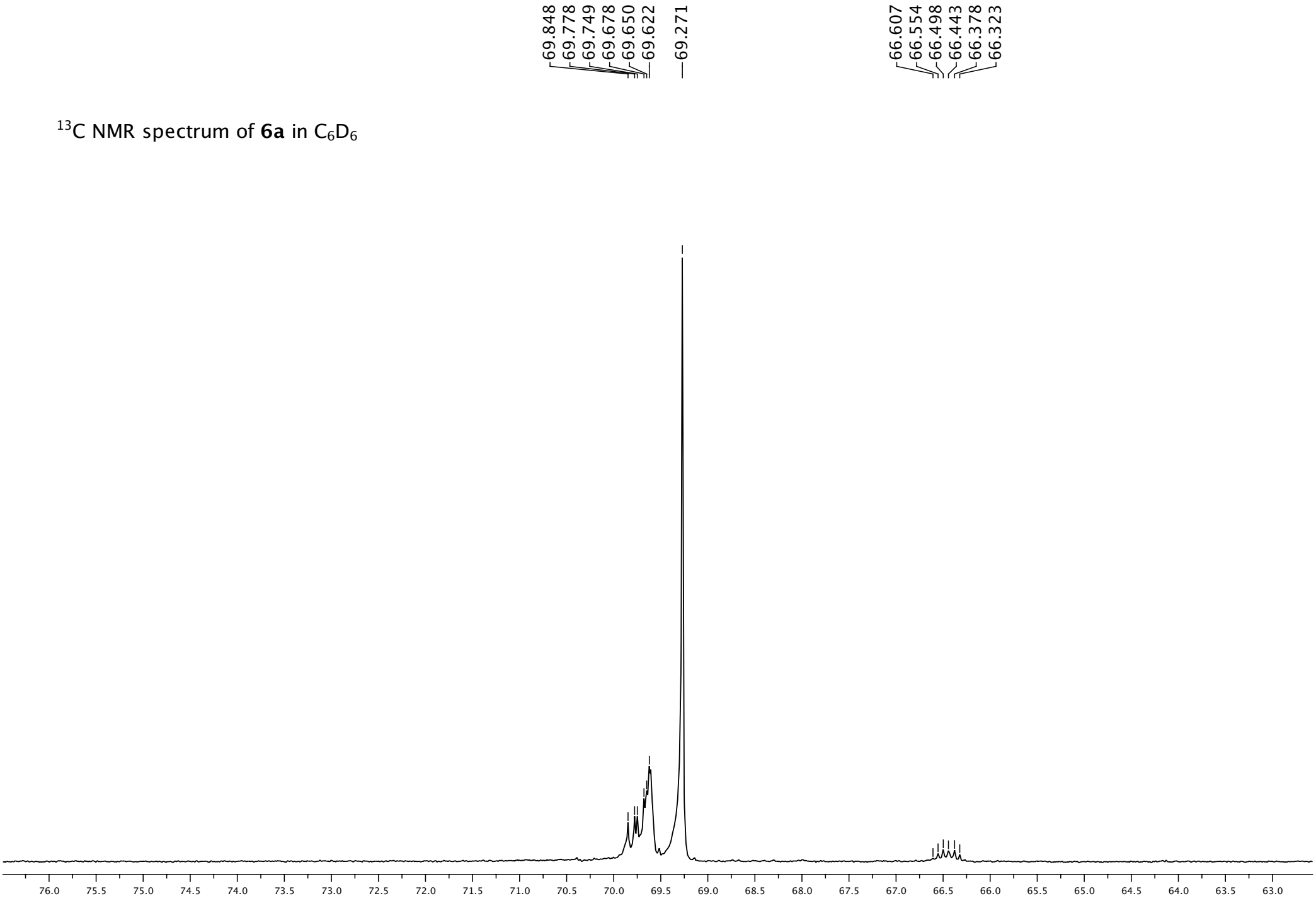
^{13}C NMR spectrum of **6a** in C_6D_6



^{13}C NMR spectrum of **6a** in C_6D_6

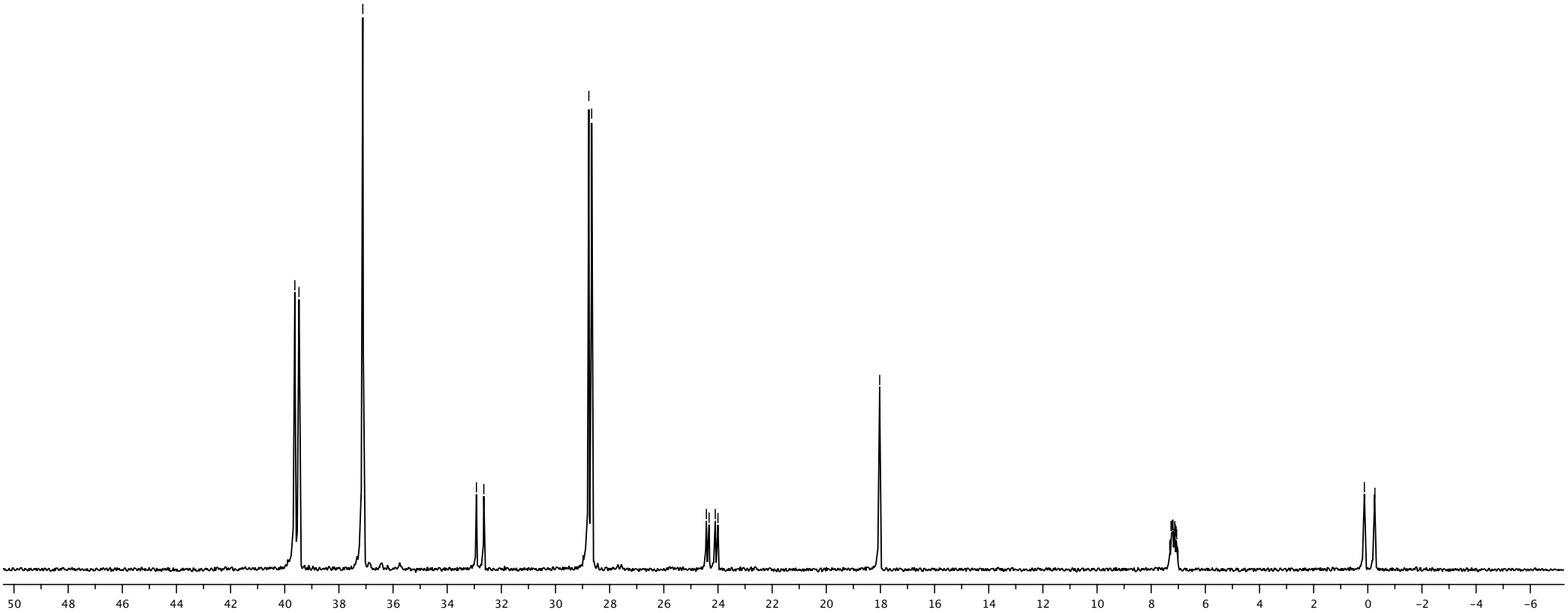


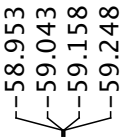
^{13}C NMR spectrum of **6a** in C_6D_6



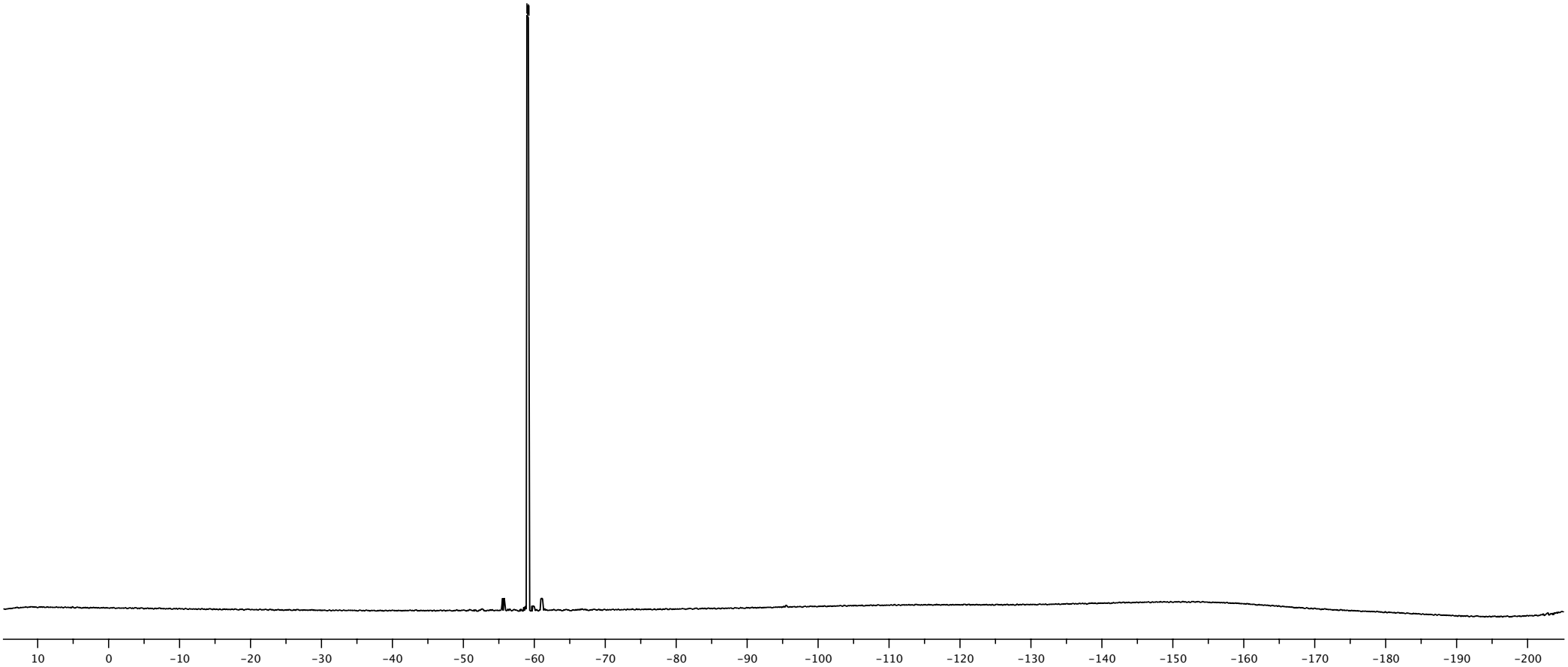
39.627
39.474
37.117
32.921
32.648
28.769
28.664
24.428
24.328
24.101
24.001
18.027
7.266
7.248
7.214
7.196
7.162
7.130
7.111
7.077
7.060
7.026
7.010
0.127
-0.261

^{13}C NMR spectrum of **6a** in C_6D_6

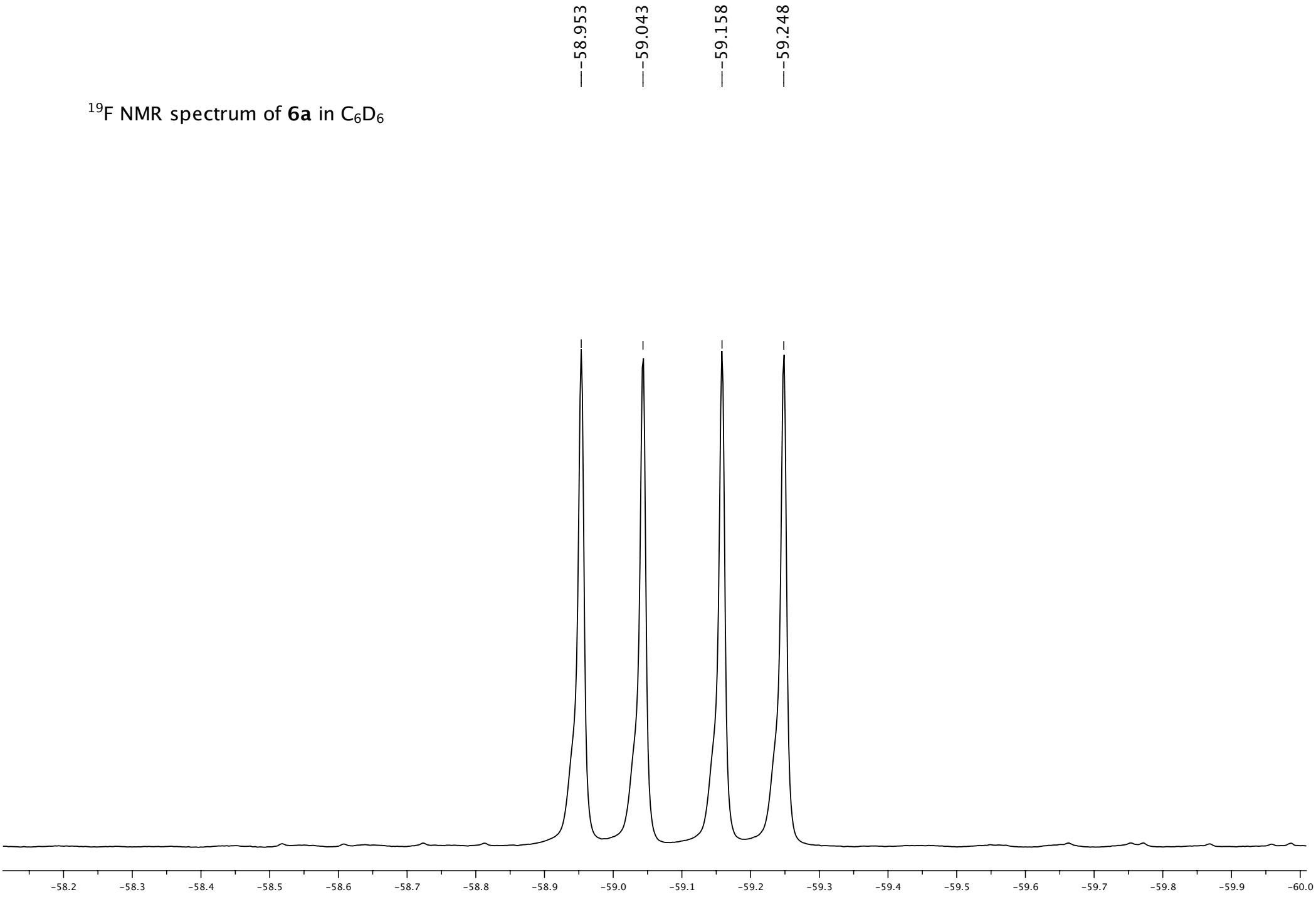




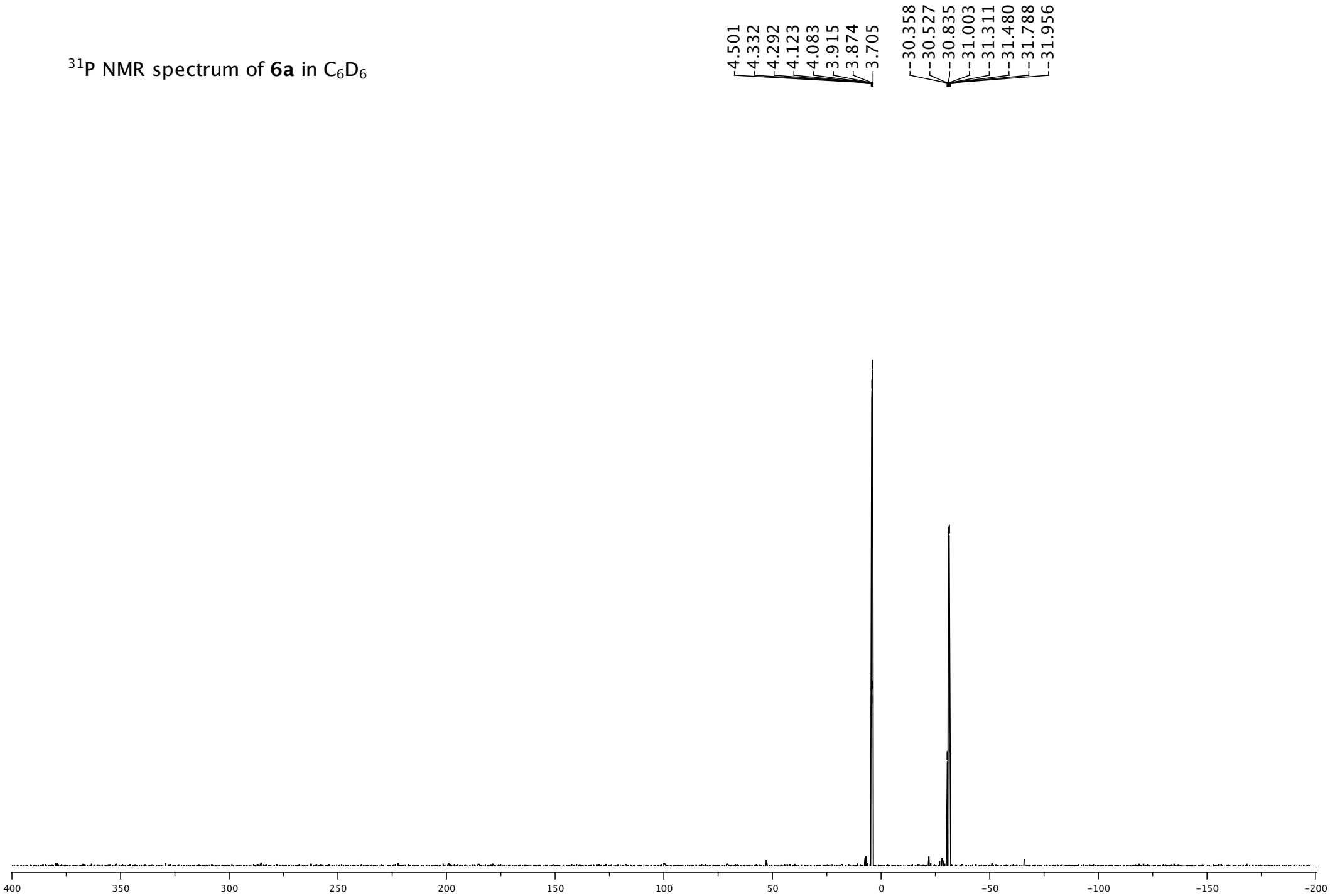
^{19}F NMR spectrum of **6a** in C_6D_6



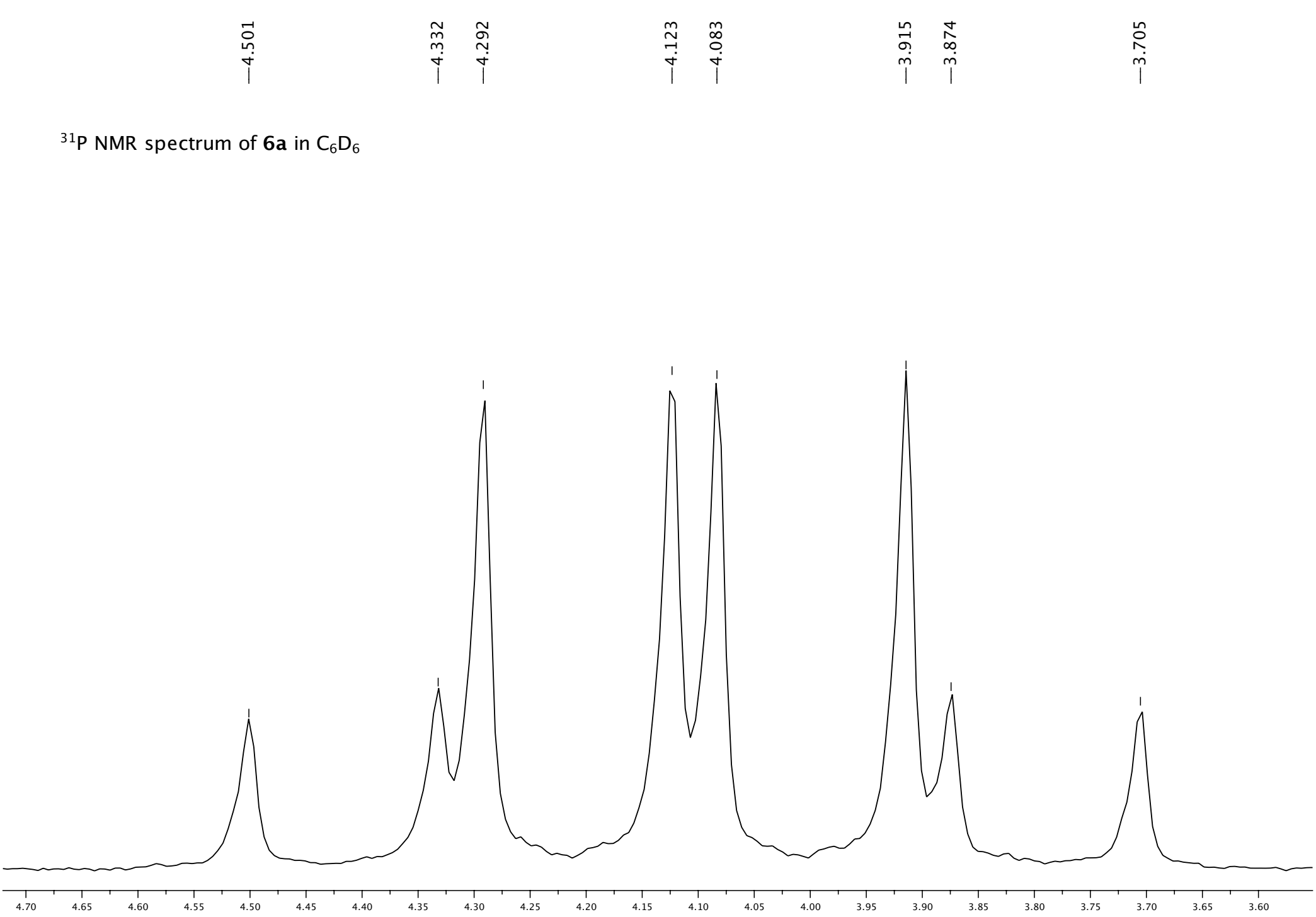
^{19}F NMR spectrum of **6a** in C_6D_6



^{31}P NMR spectrum of **6a** in C_6D_6

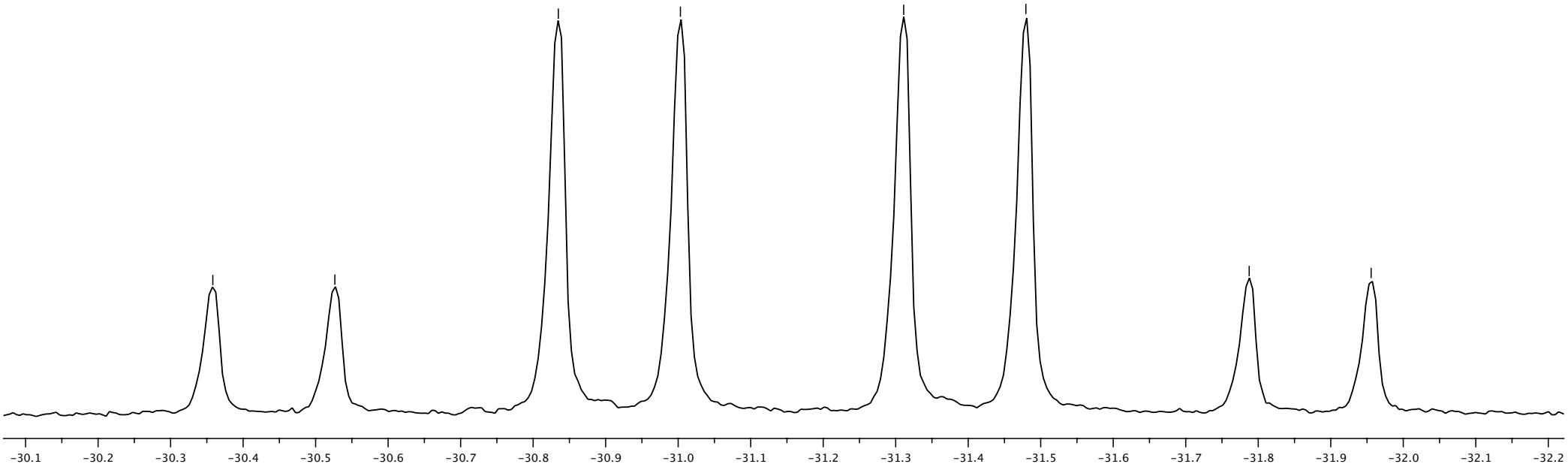


^{31}P NMR spectrum of **6a** in C_6D_6

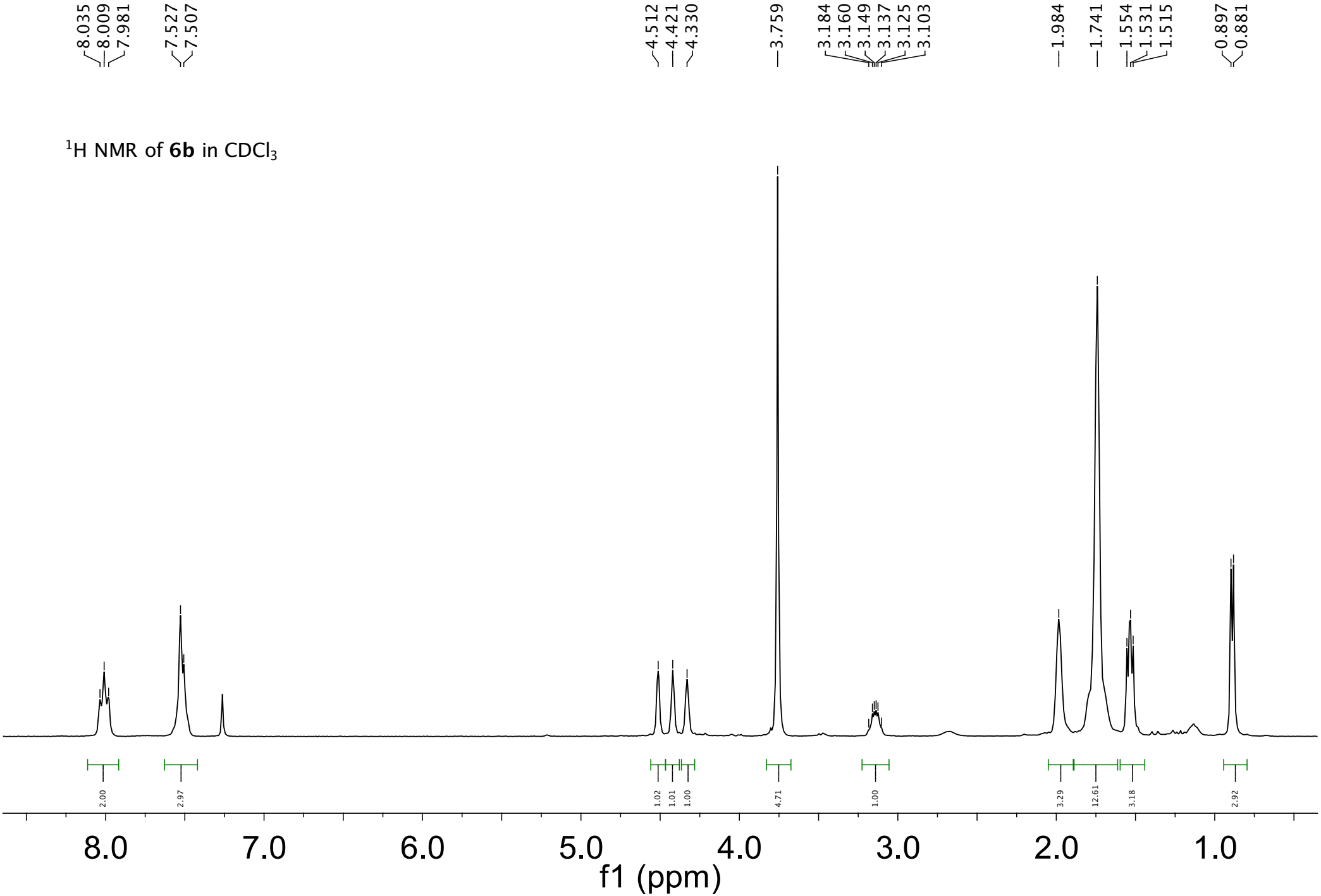


—-30.358
—-30.527
—-30.835
—-31.003
—-31.311
—-31.480
—-31.788
—-31.956

^{31}P NMR spectrum of **6a** in C_6D_6

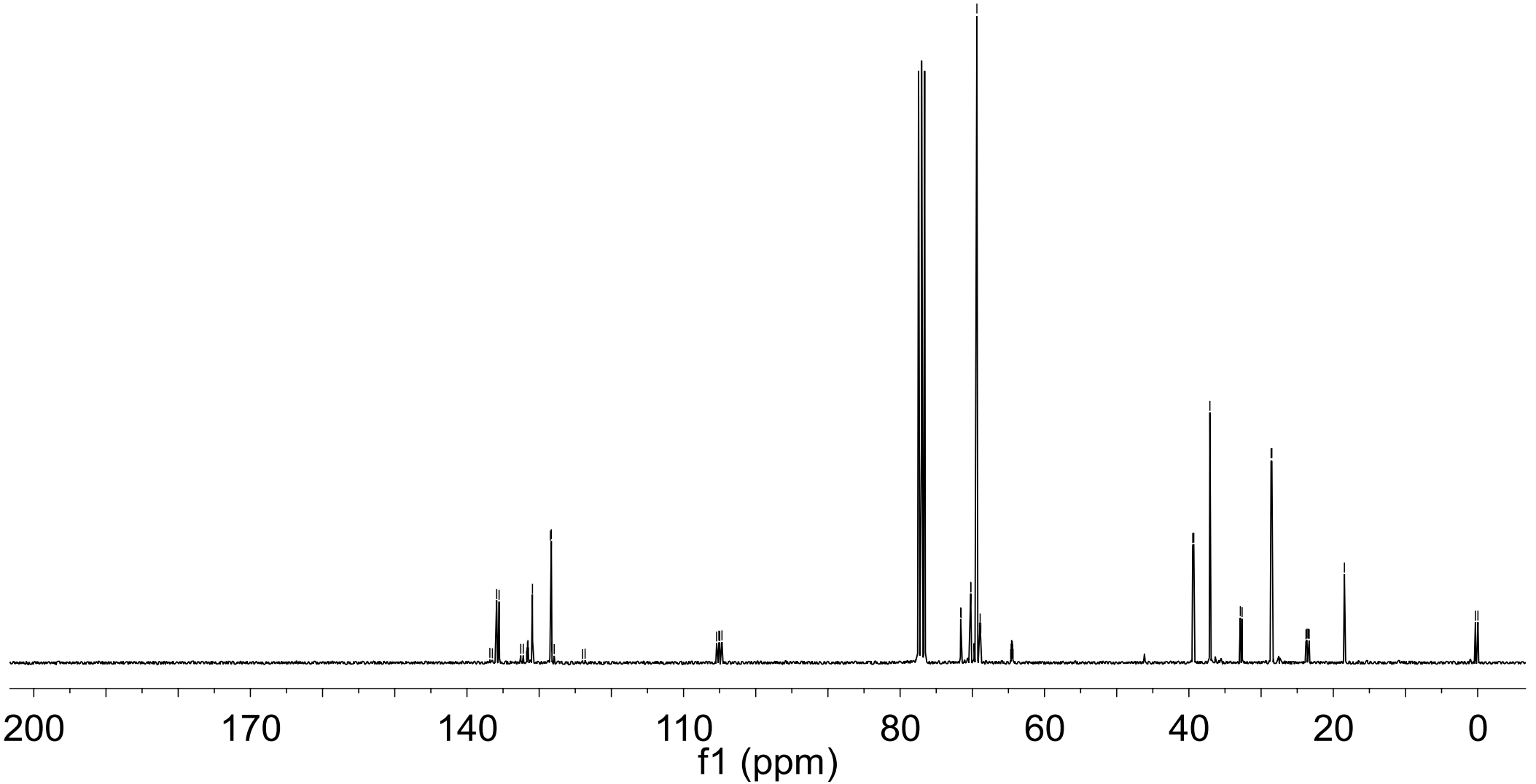


^{1}H NMR of **6b** in $CDCl_3$



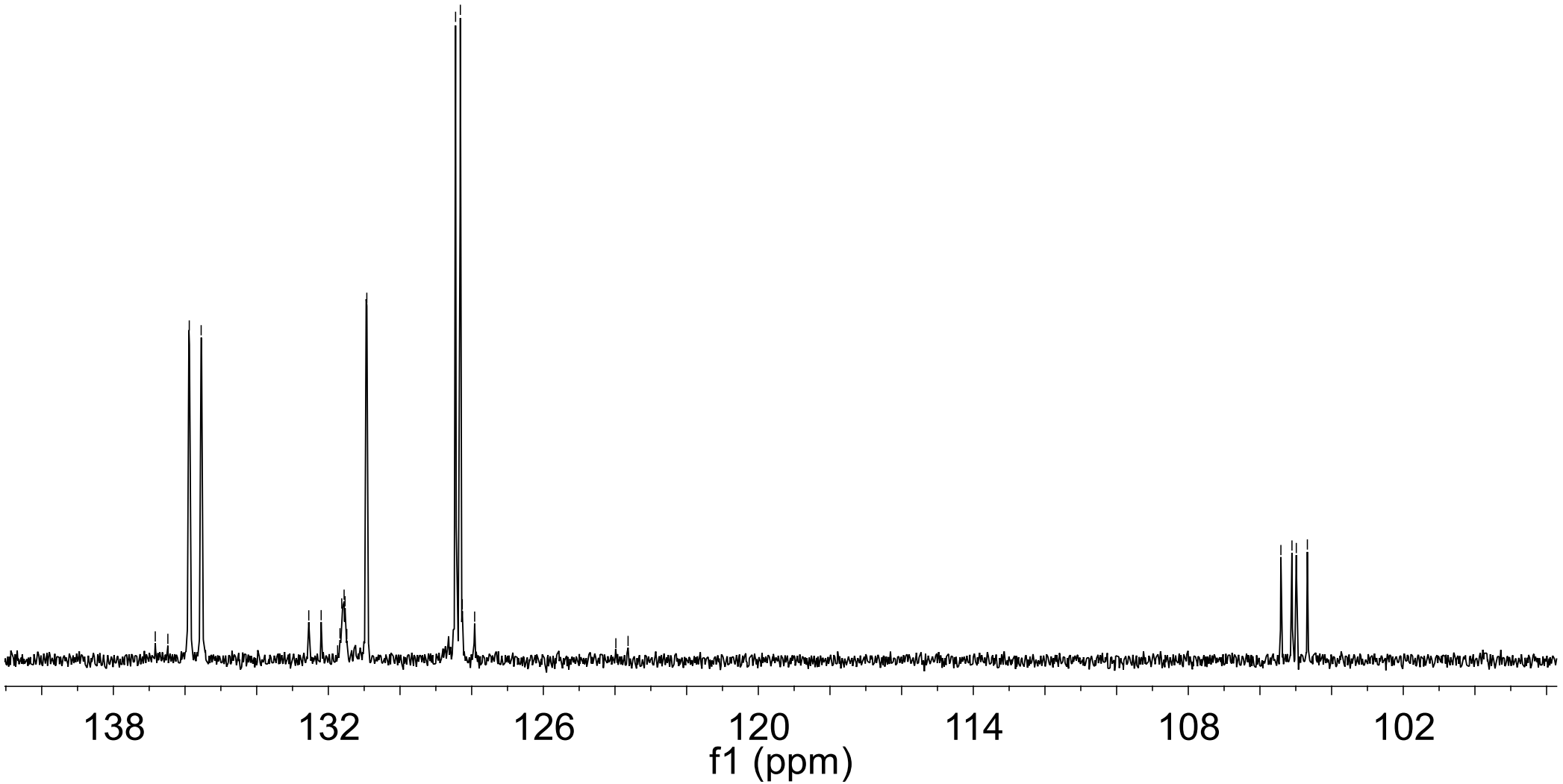
136.830
136.479
135.881
135.550
132.546
132.200
131.741
131.675
131.626
131.560
131.534
131.485
130.926
128.449
128.316
128.263
127.917
123.976
123.635
105.415
105.106
104.985
104.676
71.610
70.219
70.203
69.368
69.010
68.913
68.828
64.647
64.568
64.455
64.356
39.469
39.323
37.093
32.628
28.510
23.342
18.464
0.314
-0.036

^{13}C NMR of **6b** in $CDCl_3$

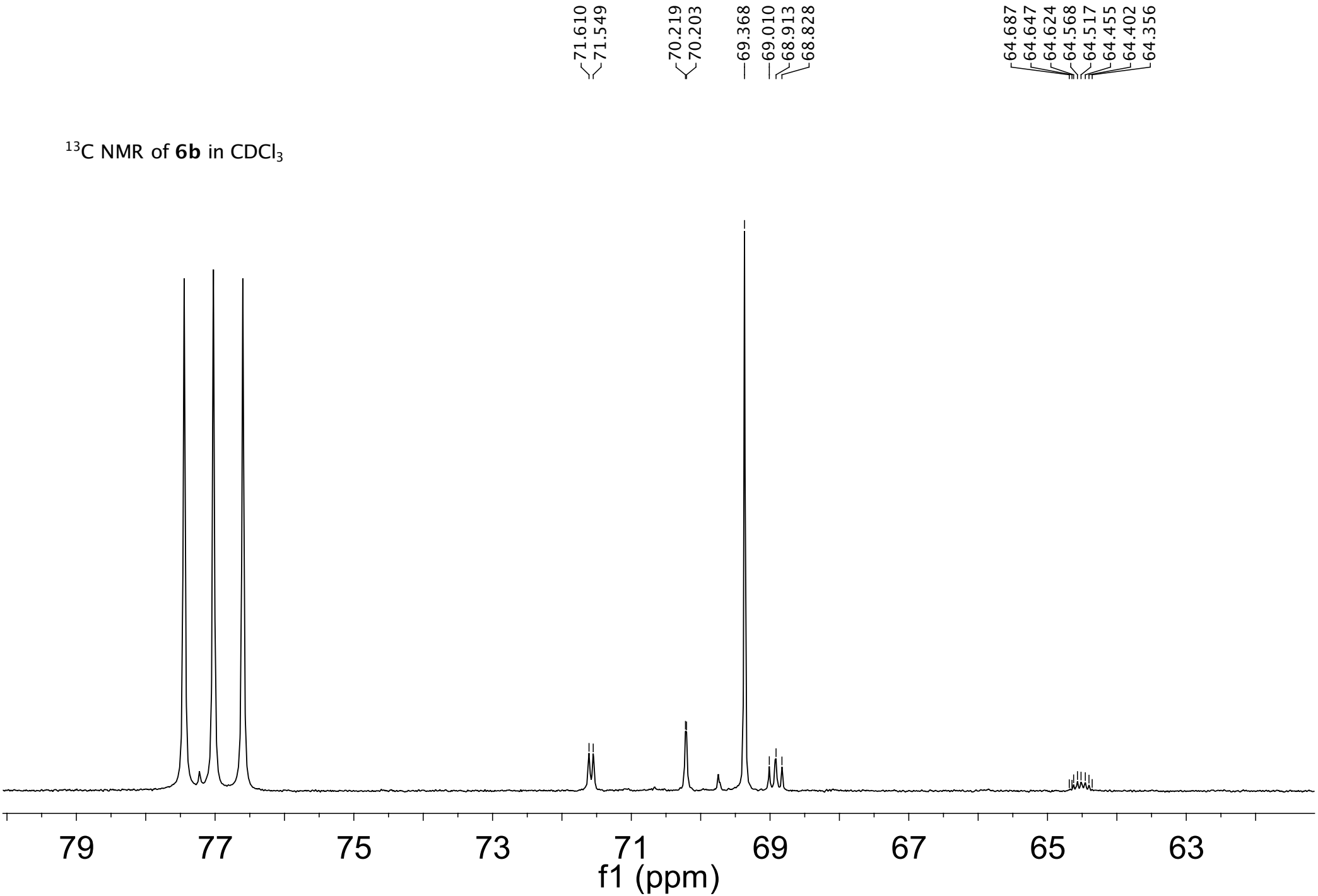


136.830
136.479
135.881
135.550
132.200
131.675
131.626
131.560
131.534
131.485
130.926
128.449
128.316
128.263
127.917
123.976
123.635
105.415
105.106
104.985
104.676

^{13}C NMR of **6b** in $CDCl_3$

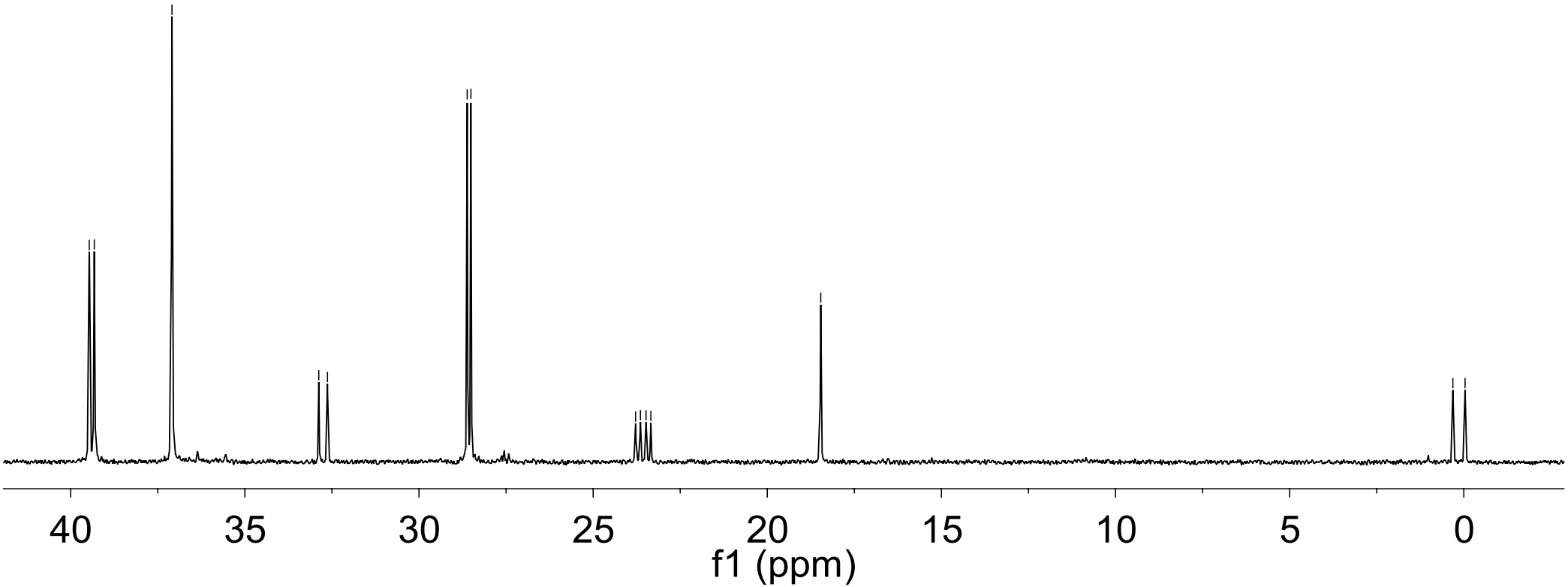


^{13}C NMR of **6b** in $CDCl_3$

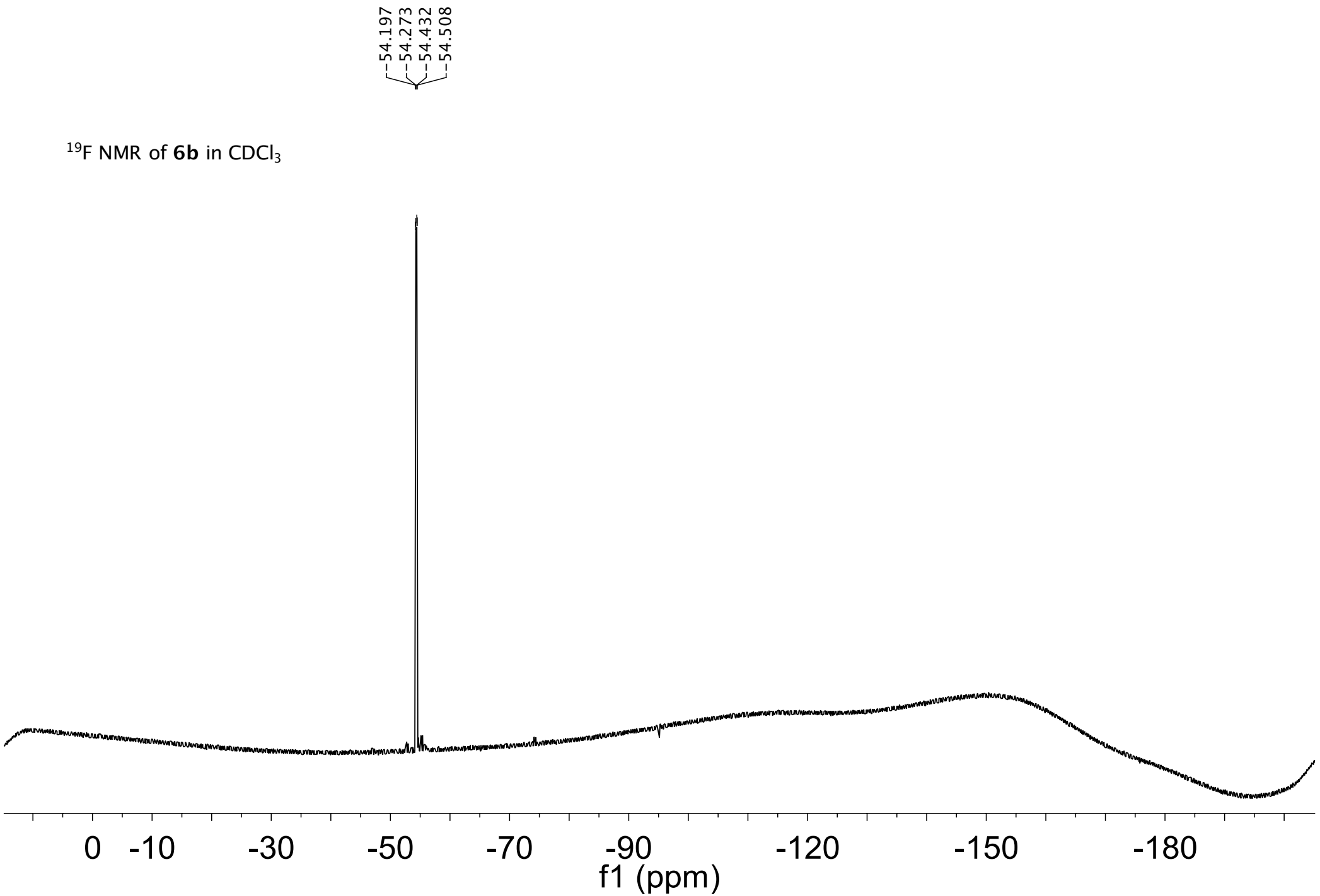


39.469
39.323
37.093
32.877
32.628
28.616
28.510
23.781
23.641
23.481
23.342
18.464
0.314
-0.036

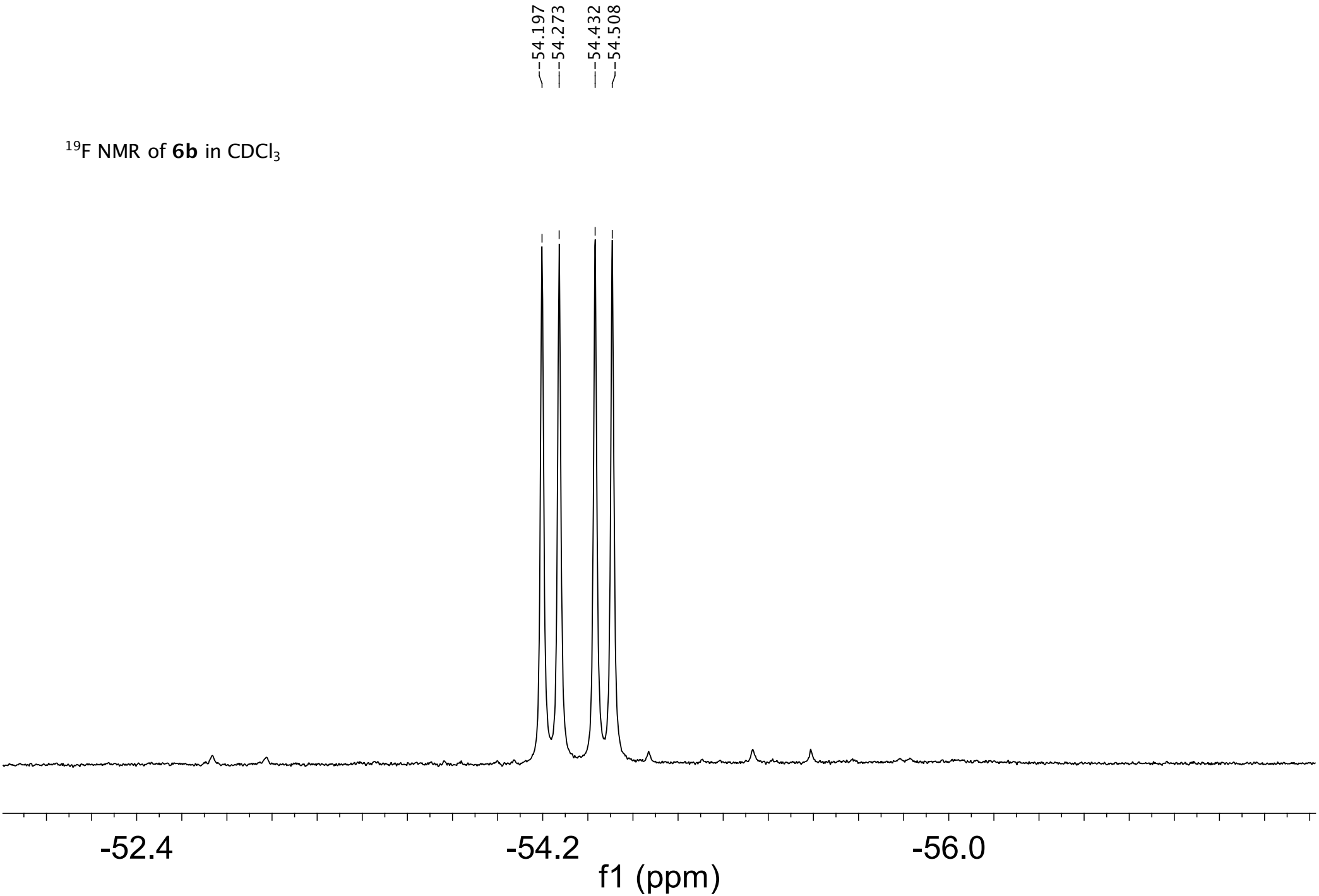
^{13}C NMR of **6b** in $CDCl_3$



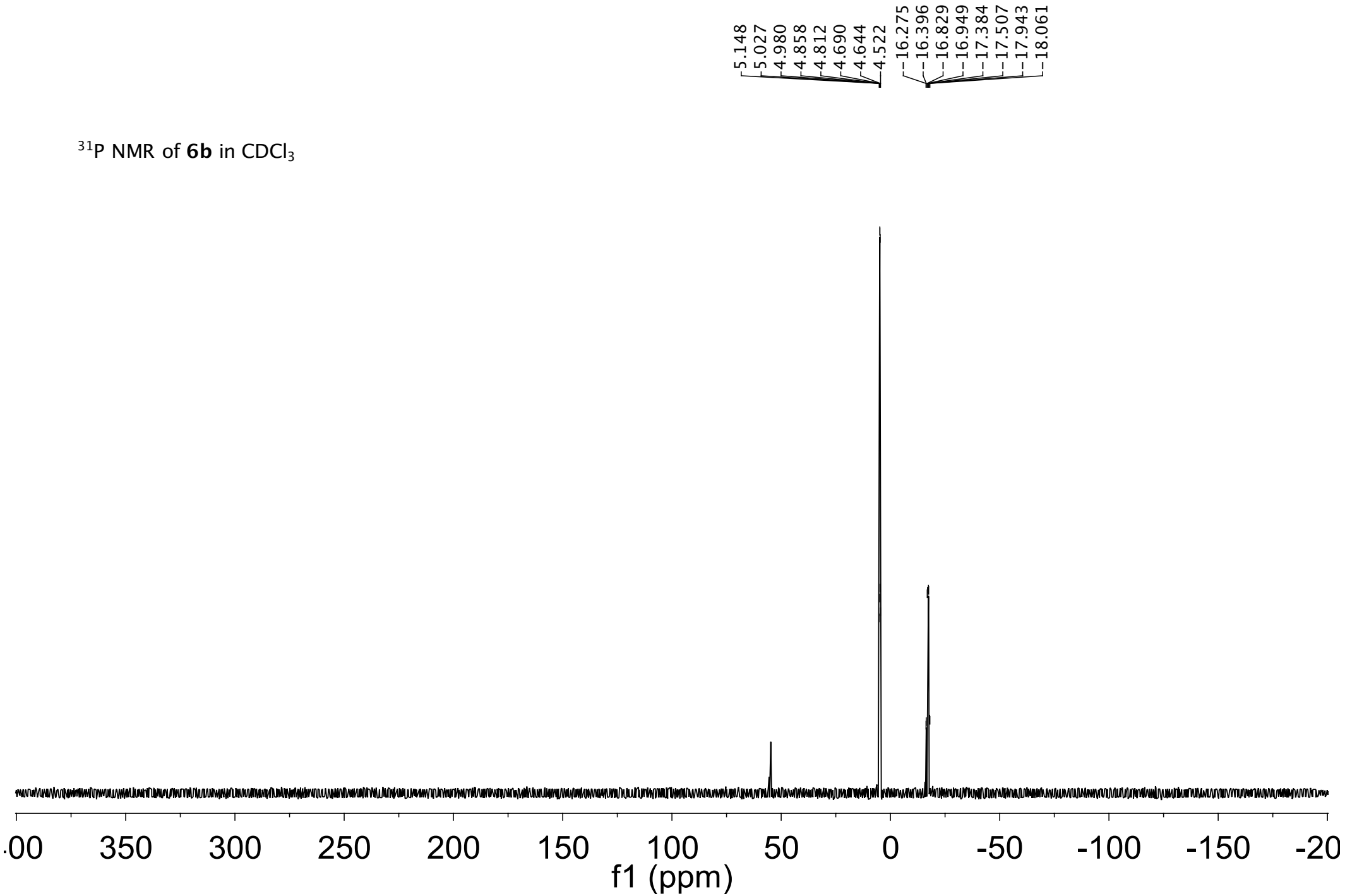
^{19}F NMR of **6b** in $CDCl_3$



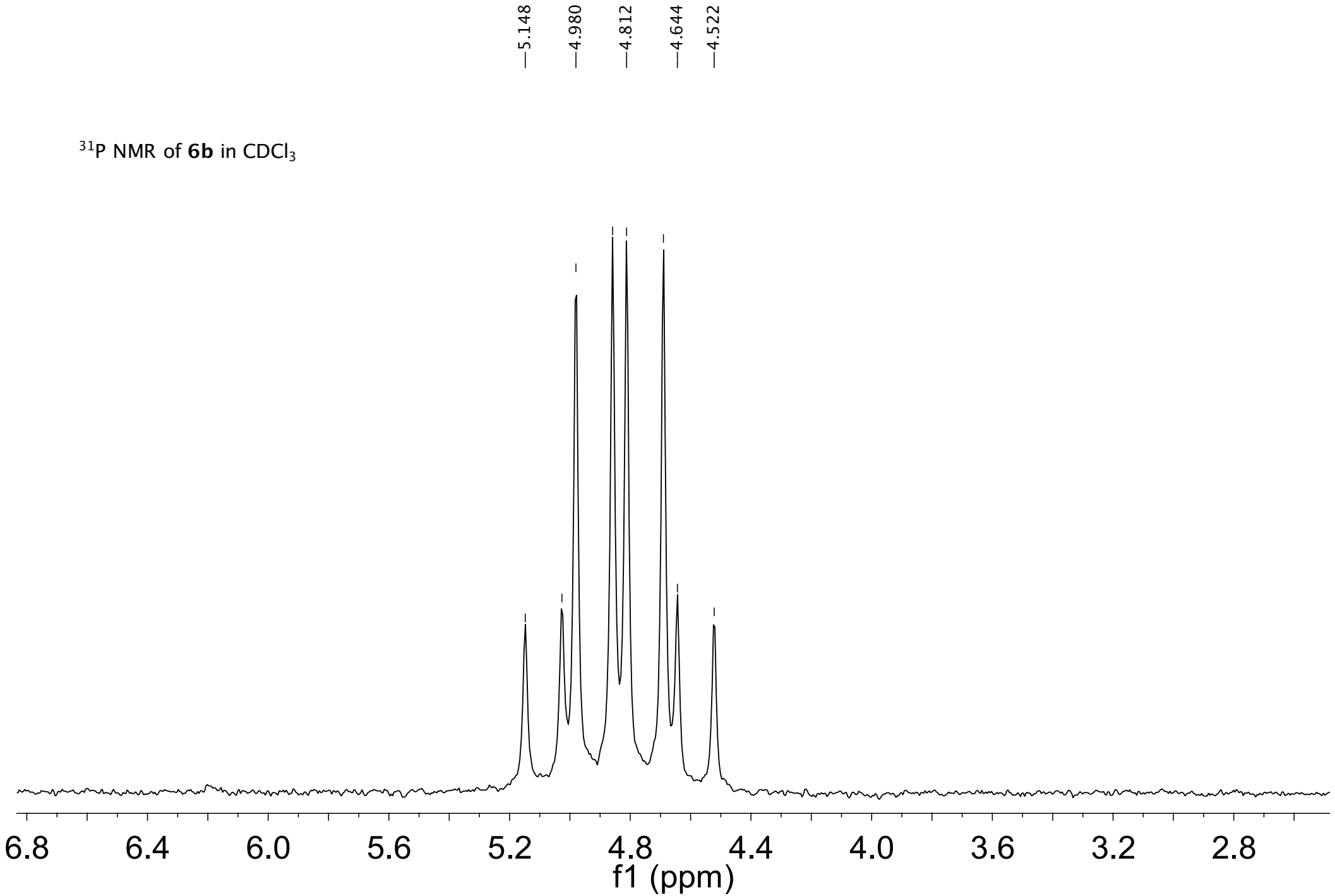
^{19}F NMR of **6b** in $CDCl_3$



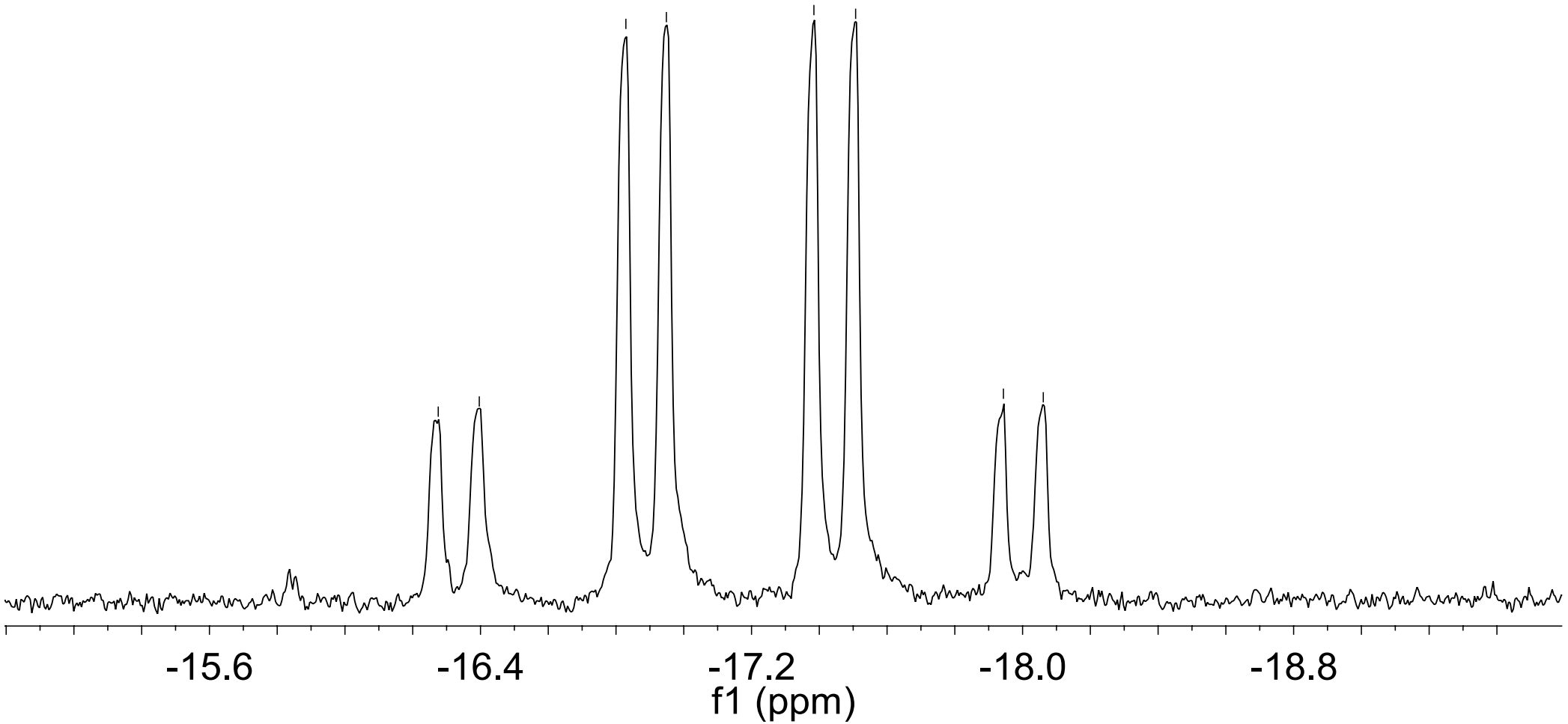
^{31}P NMR of **6b** in $CDCl_3$

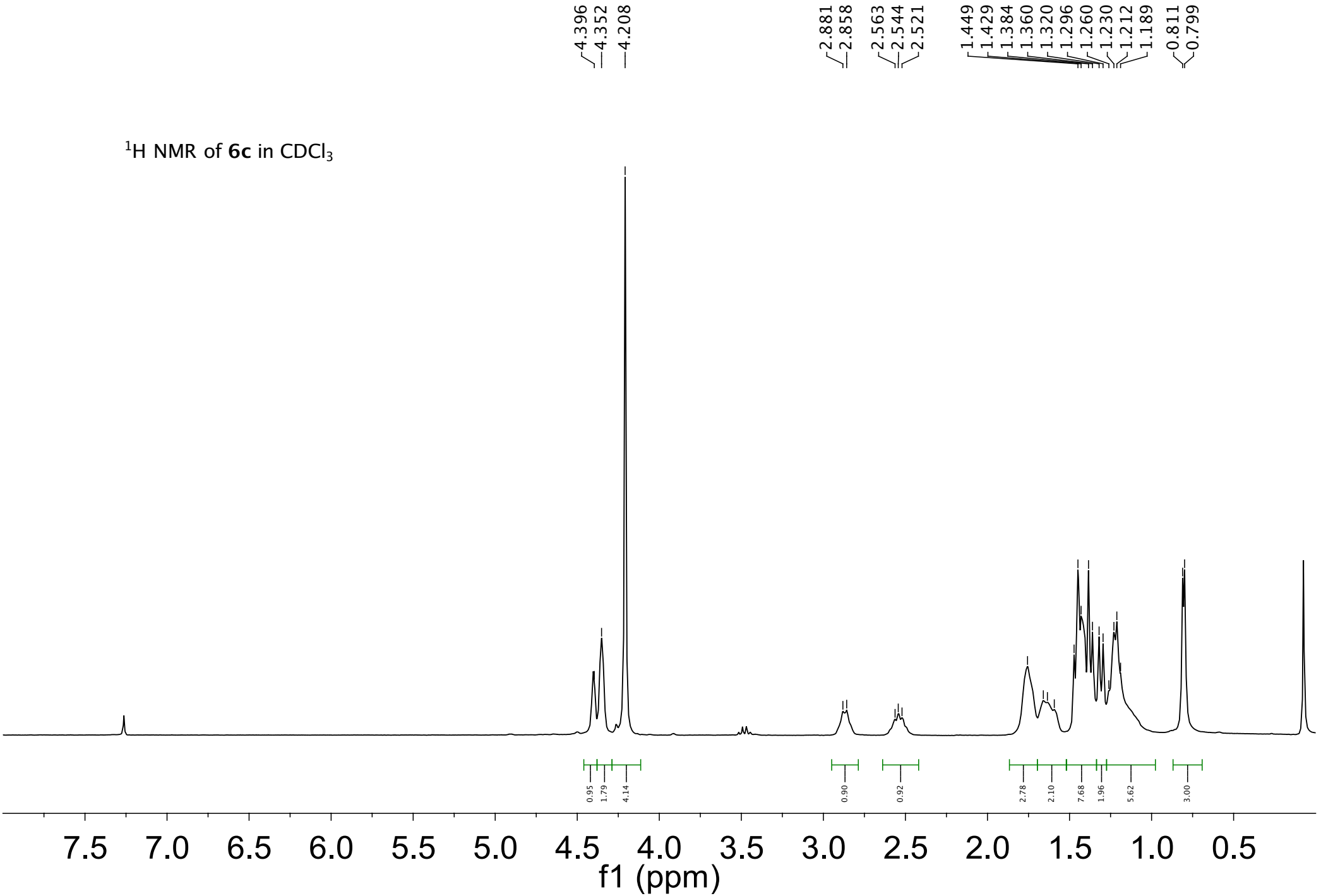


^{31}P NMR of **6b** in $CDCl_3$



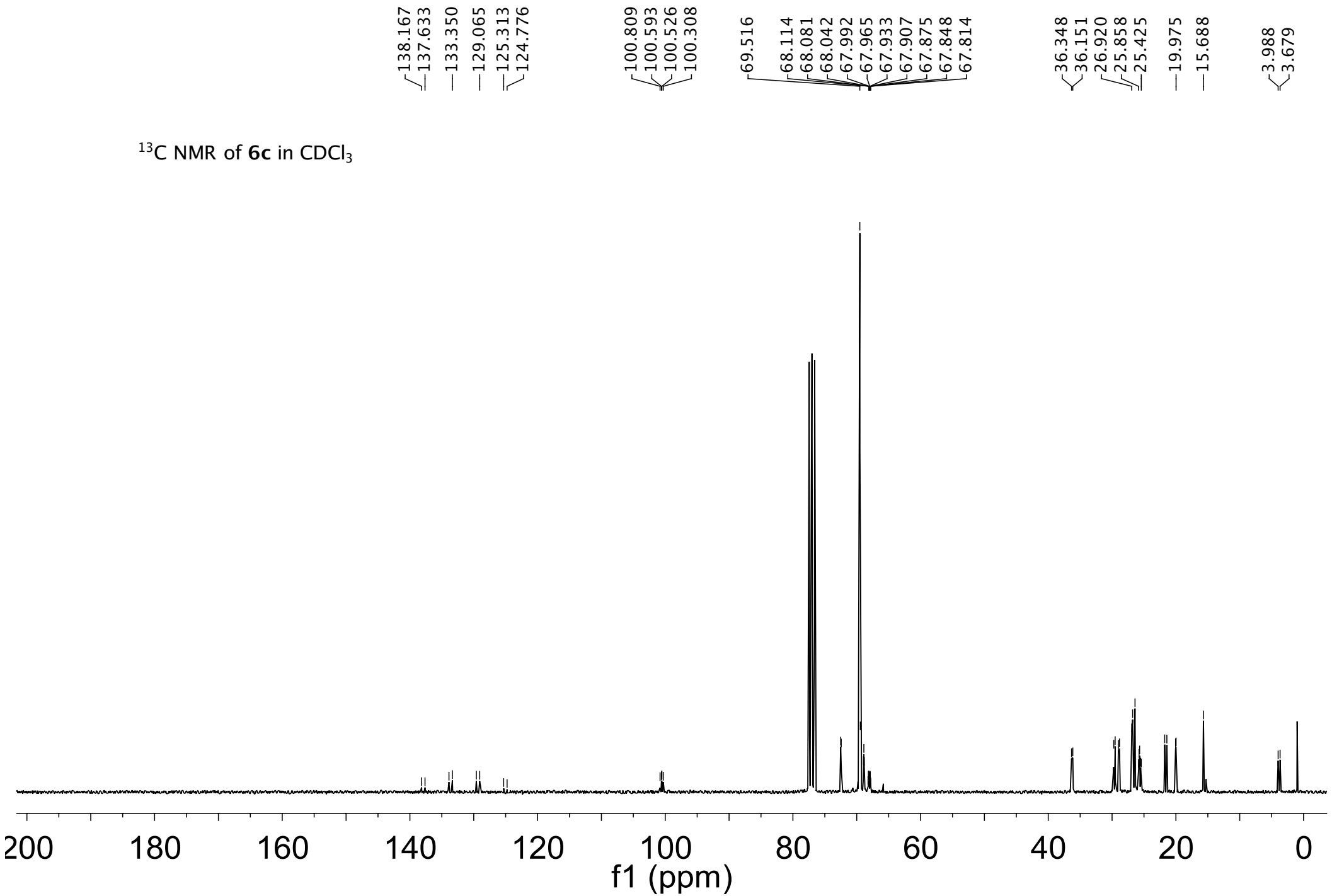
^{31}P NMR of **6b** in $CDCl_3$



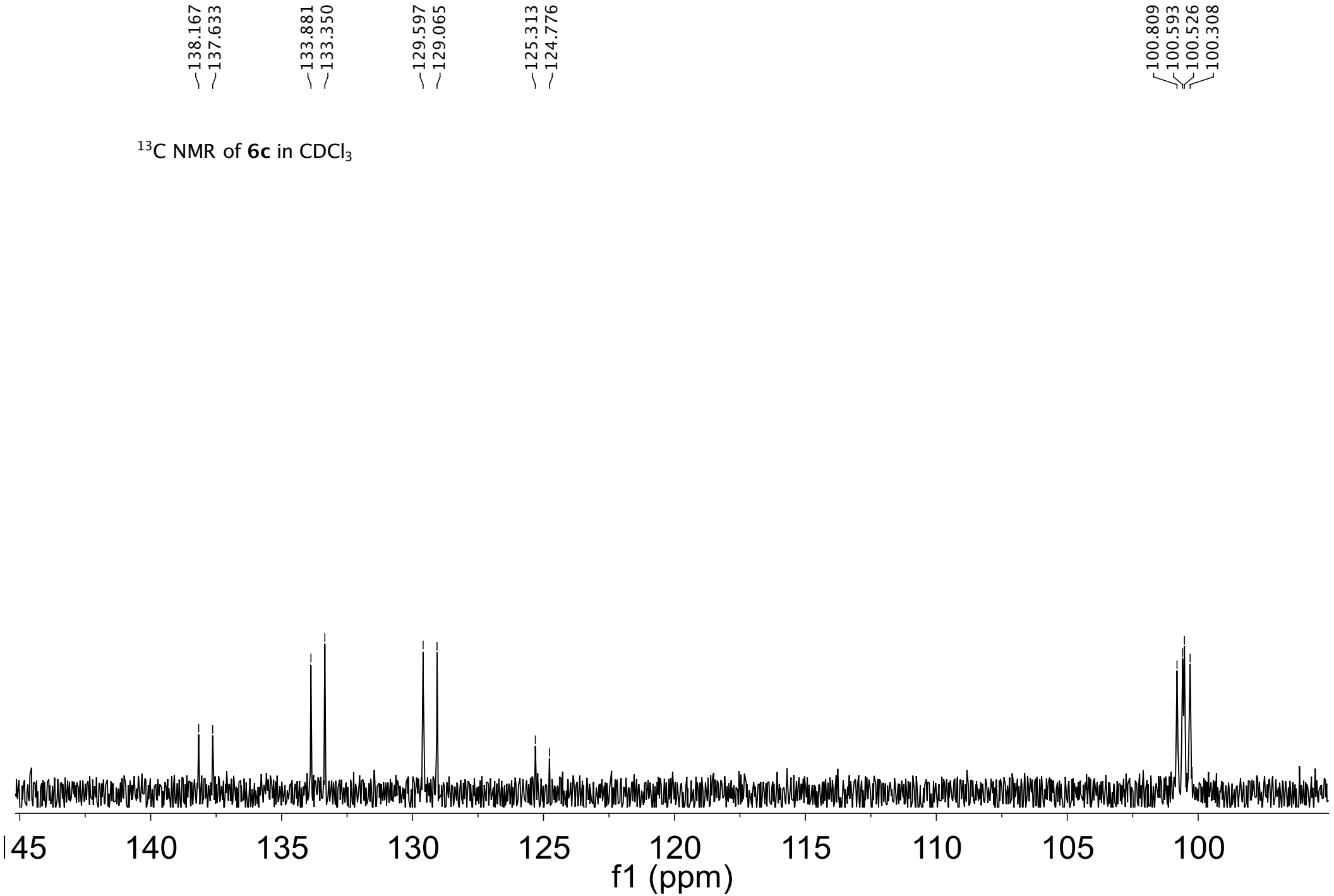


^{1}H NMR of **6c** in $CDCl_3$

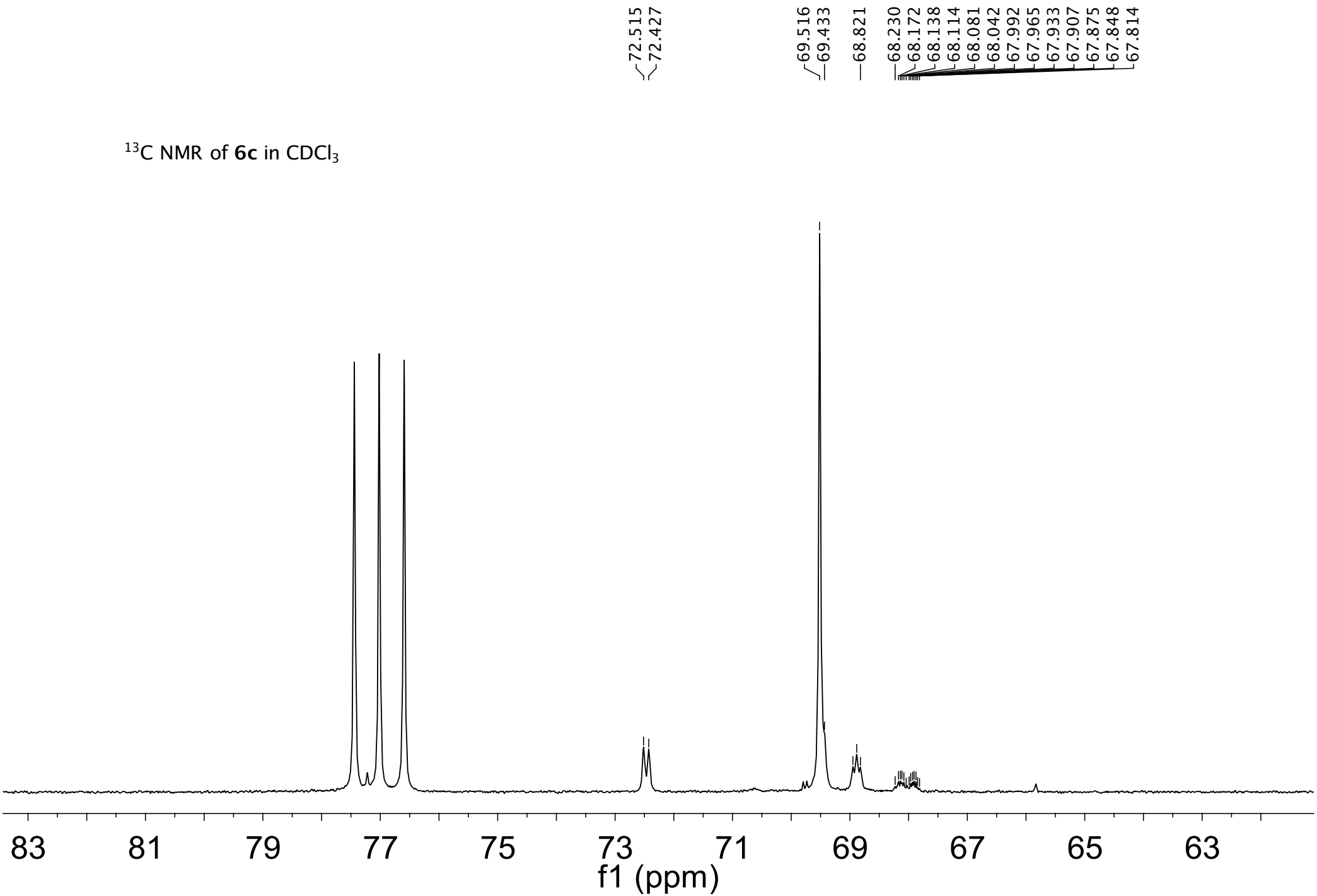
^{13}C NMR of **6c** in $CDCl_3$



^{13}C NMR of **6c** in $CDCl_3$

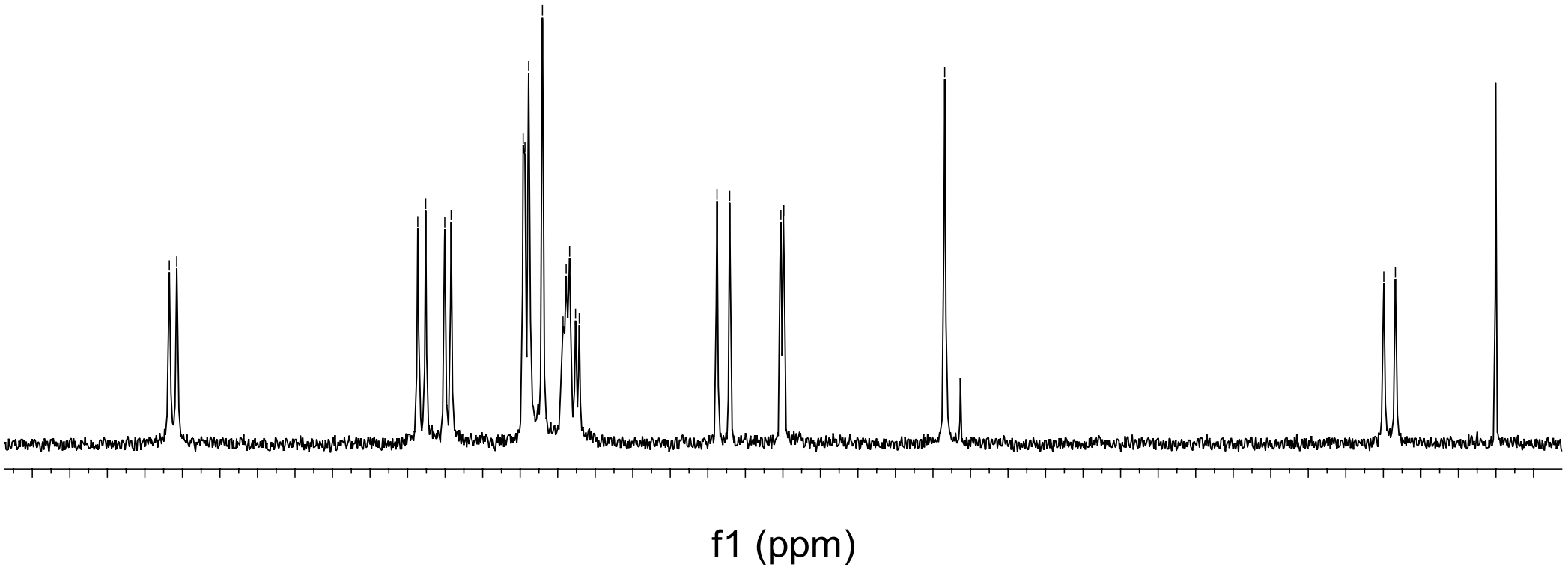


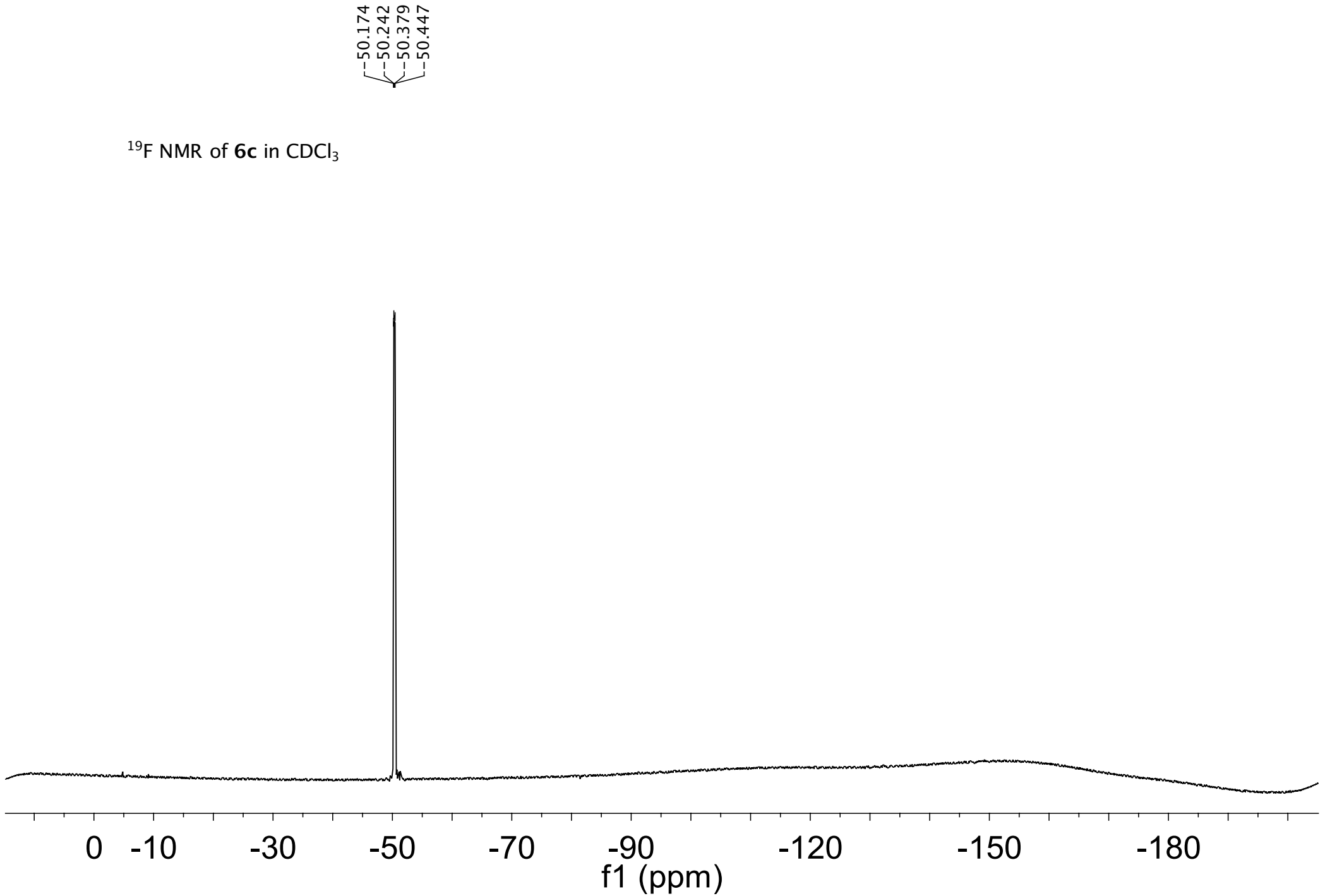
^{13}C NMR of **6c** in $CDCl_3$



36.348
36.151
29.729
29.518
29.009
28.839
26.774
26.407
25.858
25.774
25.683
25.525
25.425
21.755
21.417
20.053
19.975
15.688
3.988
3.679

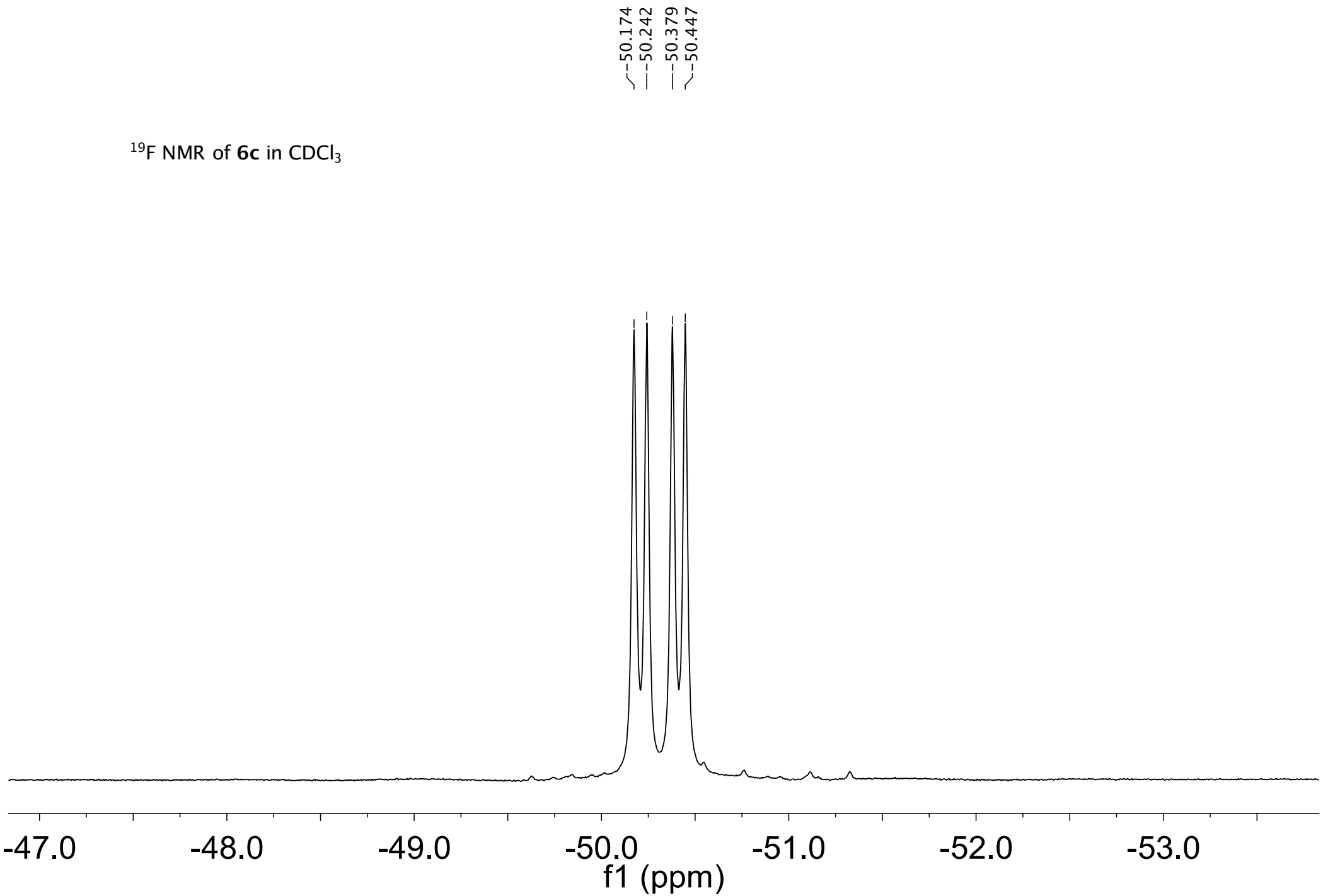
^{13}C NMR of **6c** in $CDCl_3$

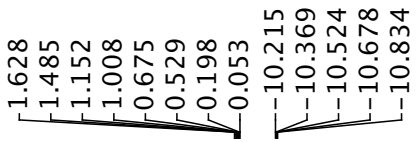




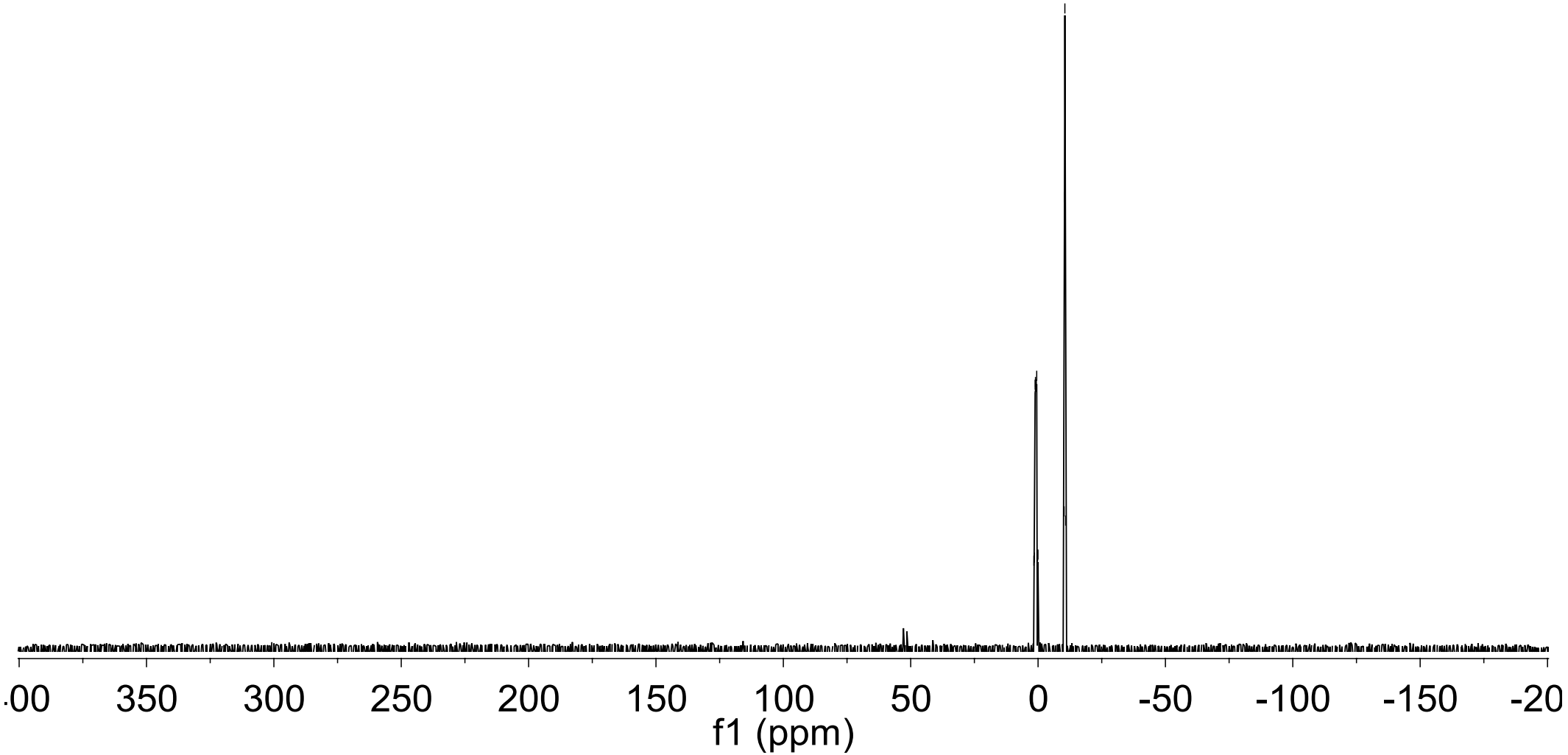
^{19}F NMR of **6c** in $CDCl_3$

^{19}F NMR of **6c** in $CDCl_3$

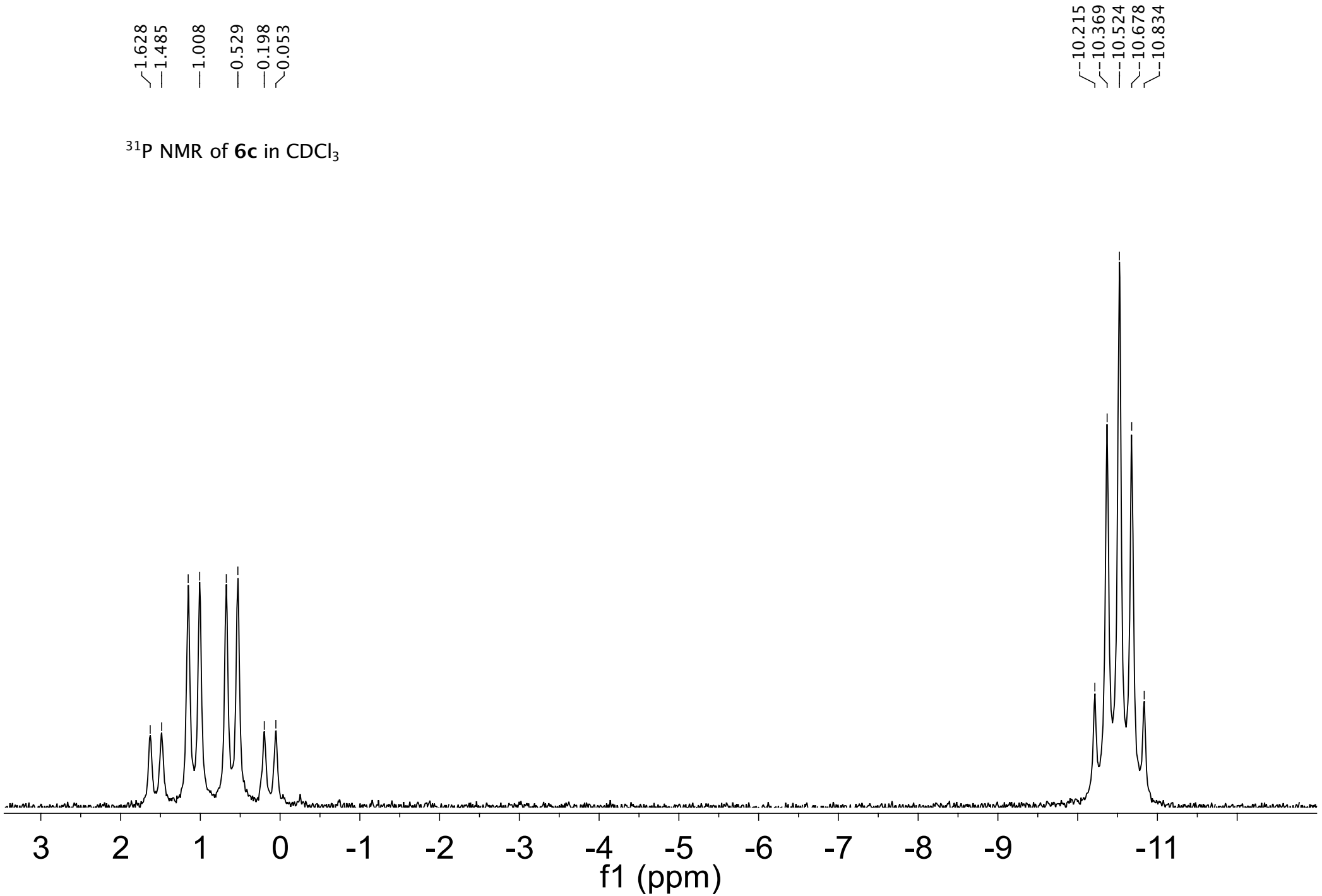




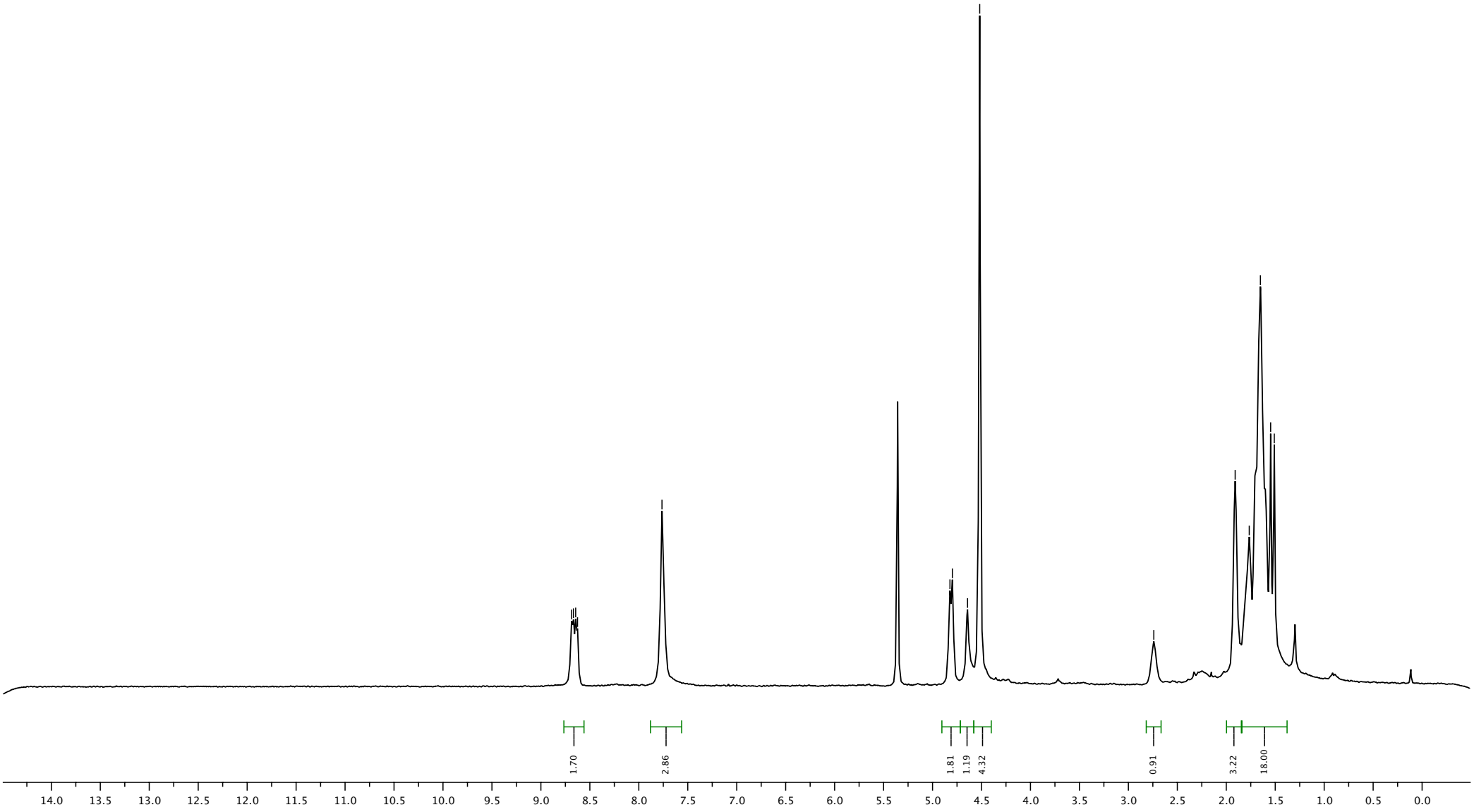
^{31}P NMR of **6c** in $CDCl_3$



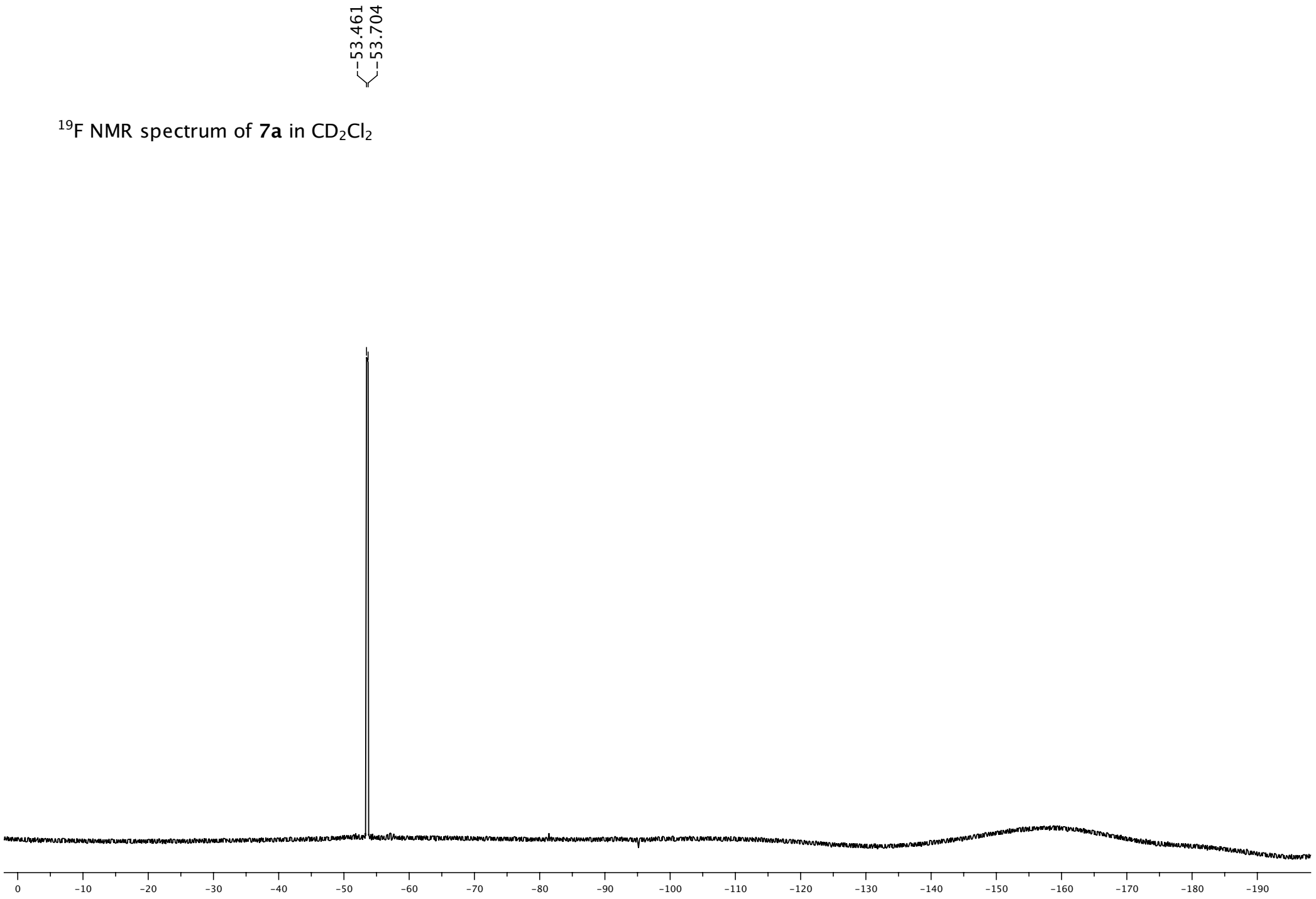
^{31}P NMR of **6c** in $CDCl_3$



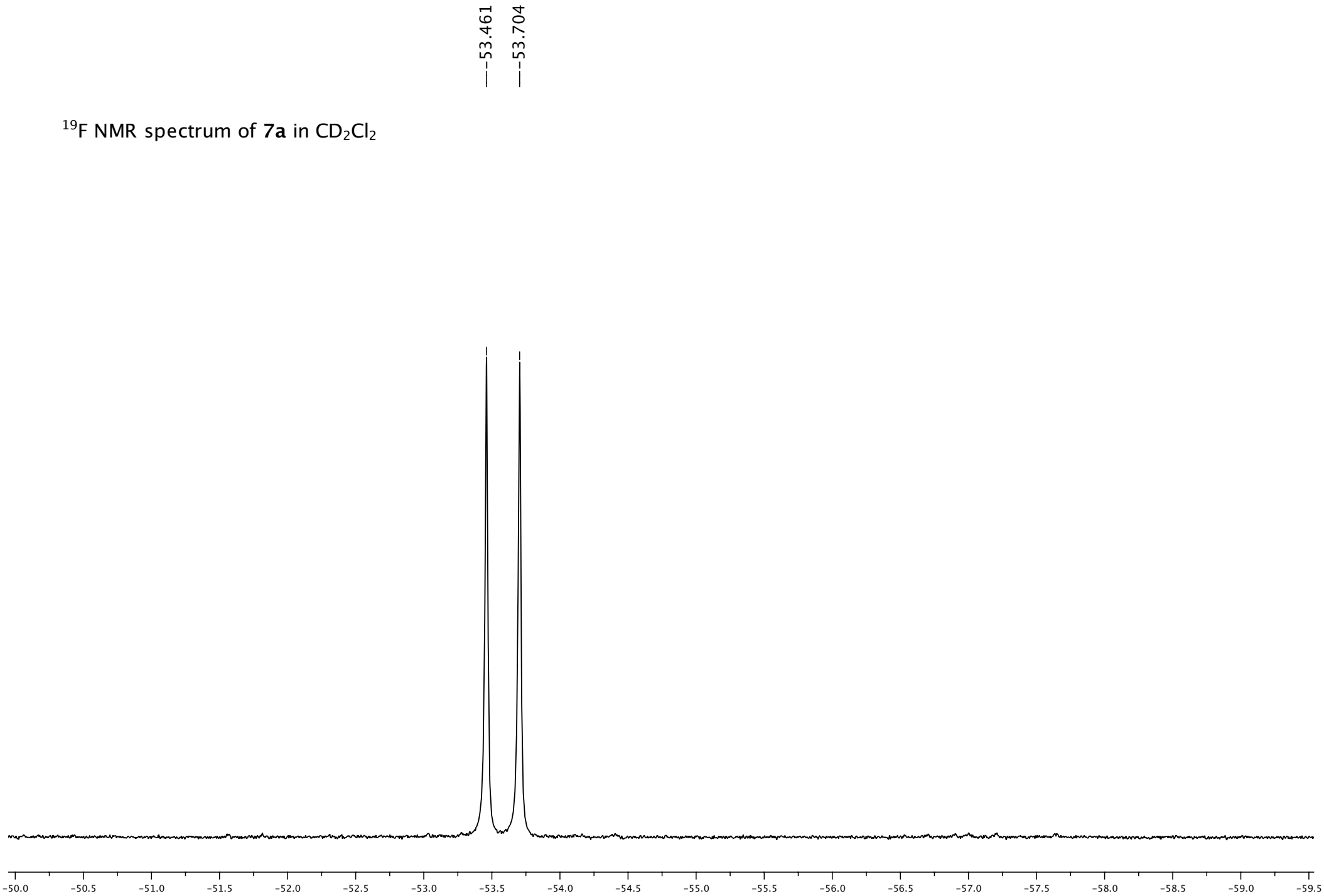
^{1}H NMR spectrum of **7a** in CD_2Cl_2



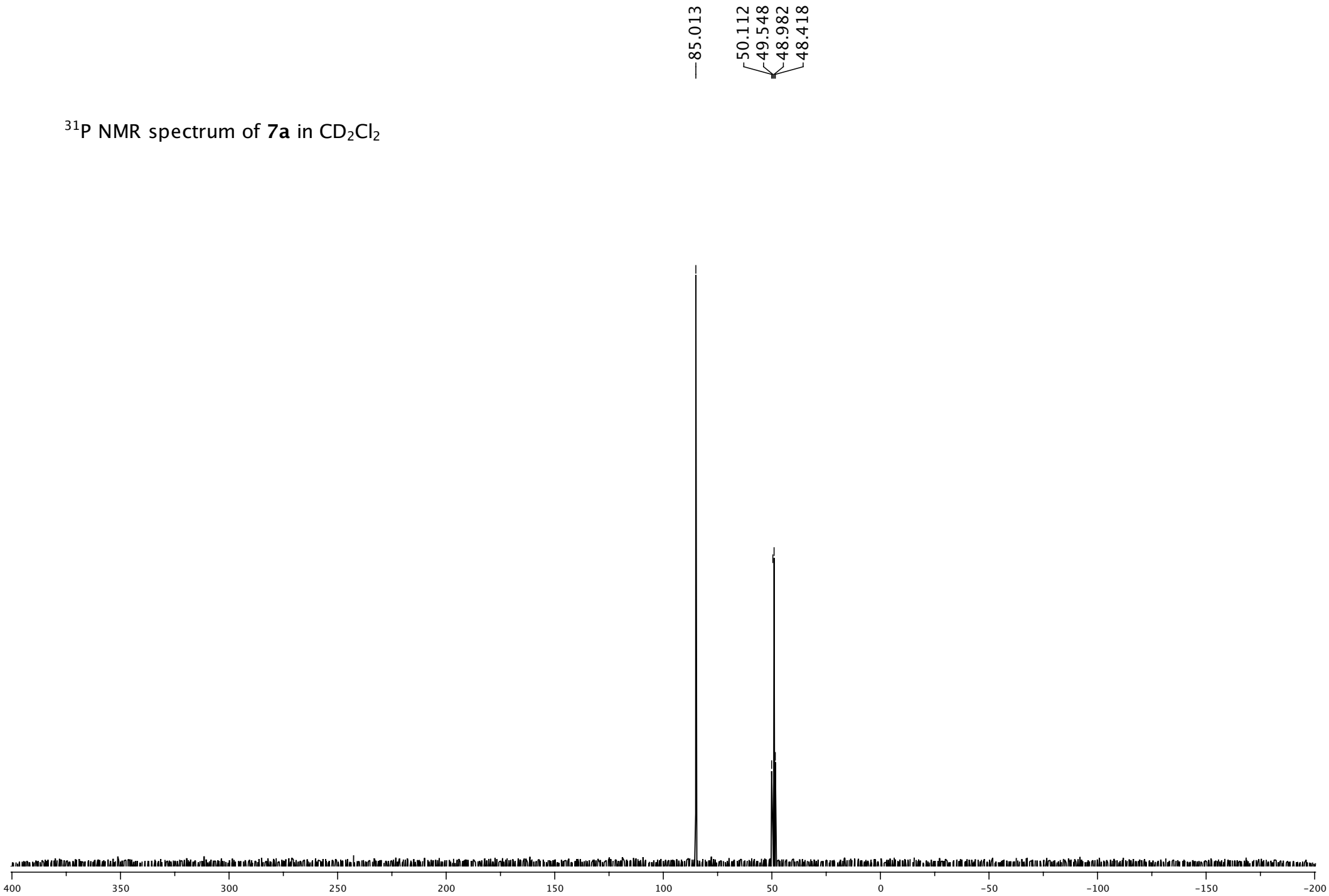
^{19}F NMR spectrum of **7a** in CD_2Cl_2



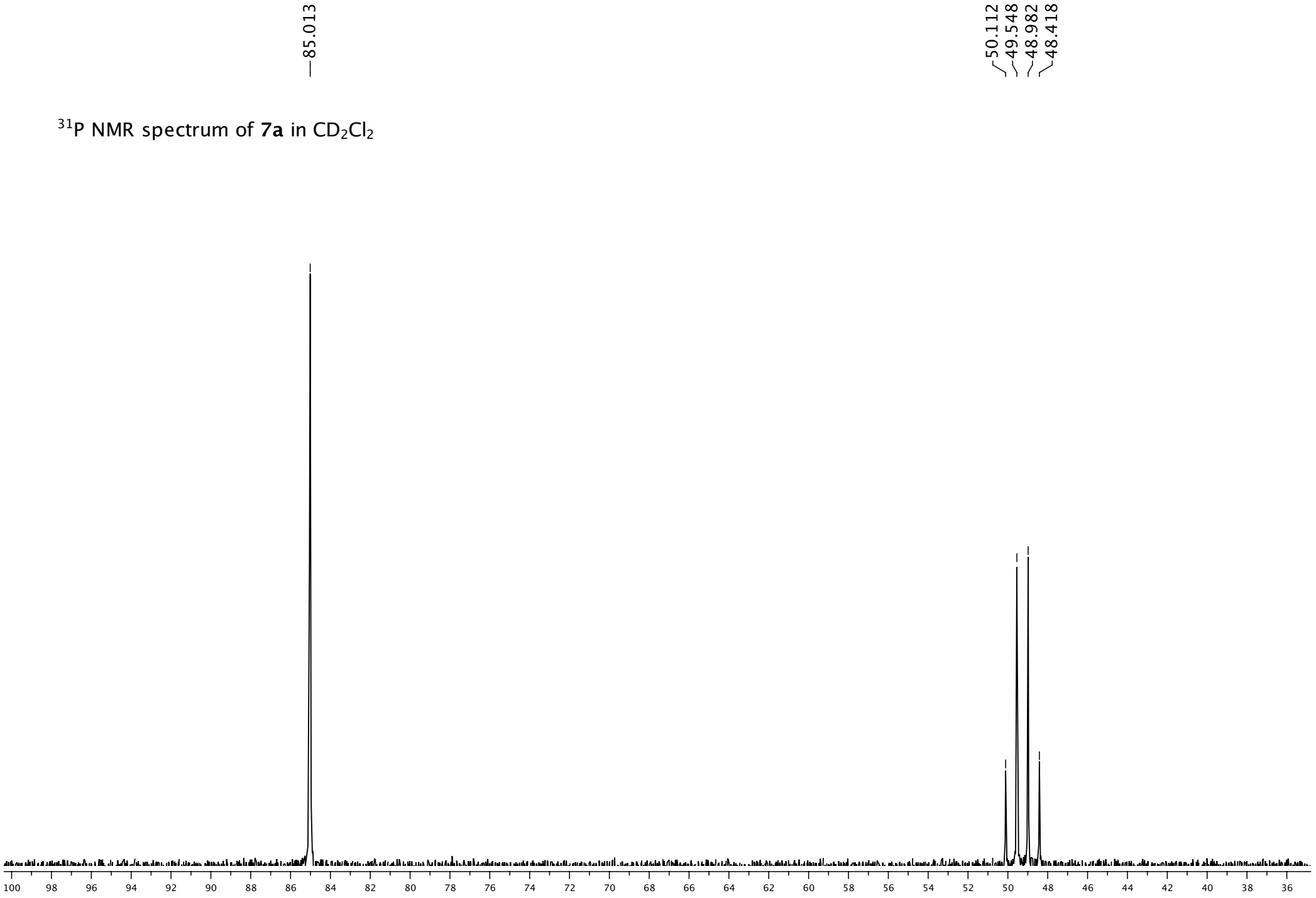
^{19}F NMR spectrum of **7a** in CD_2Cl_2



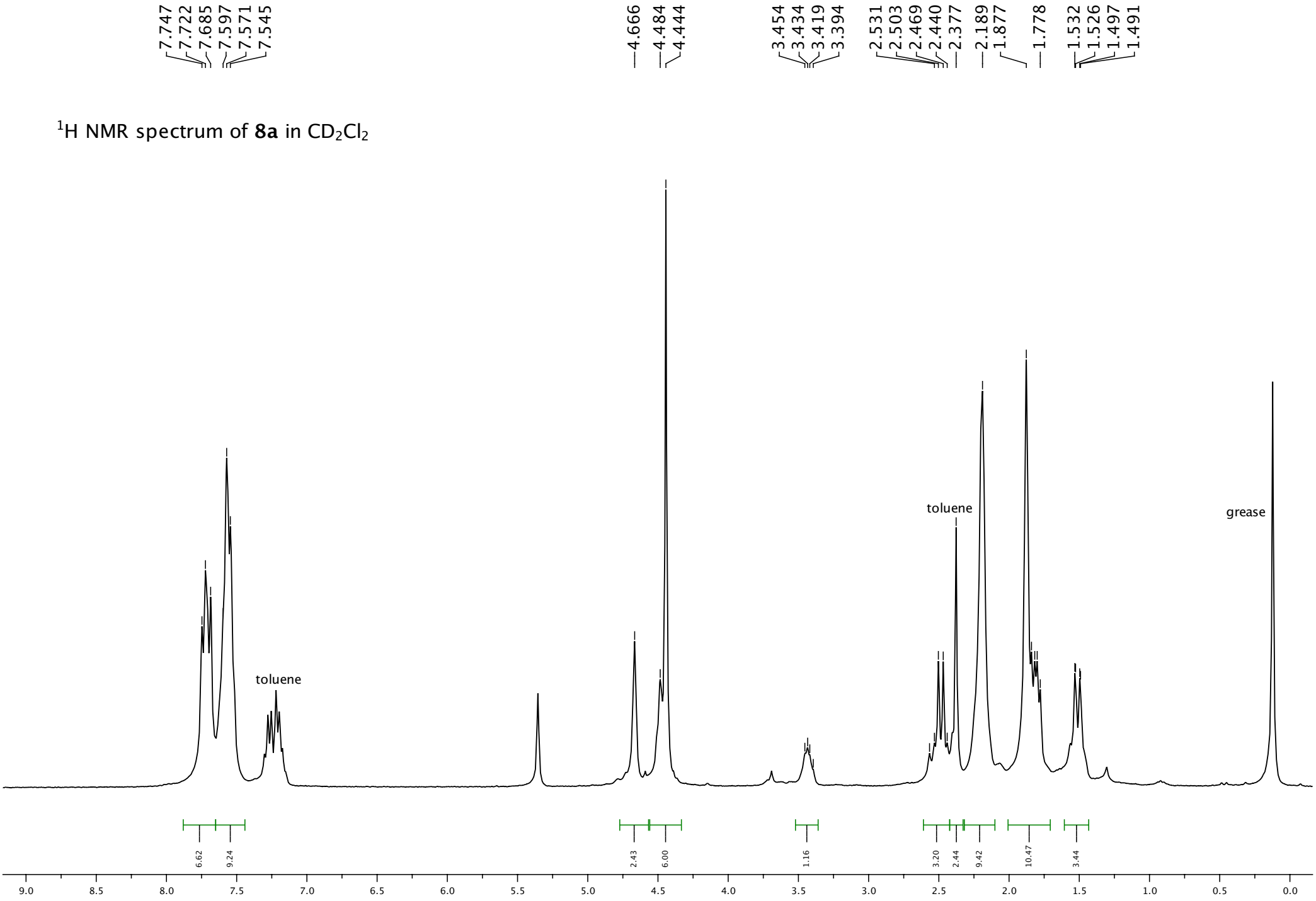
^{31}P NMR spectrum of **7a** in CD_2Cl_2

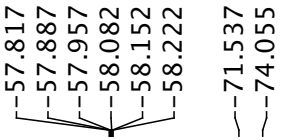


^{31}P NMR spectrum of **7a** in CD_2Cl_2

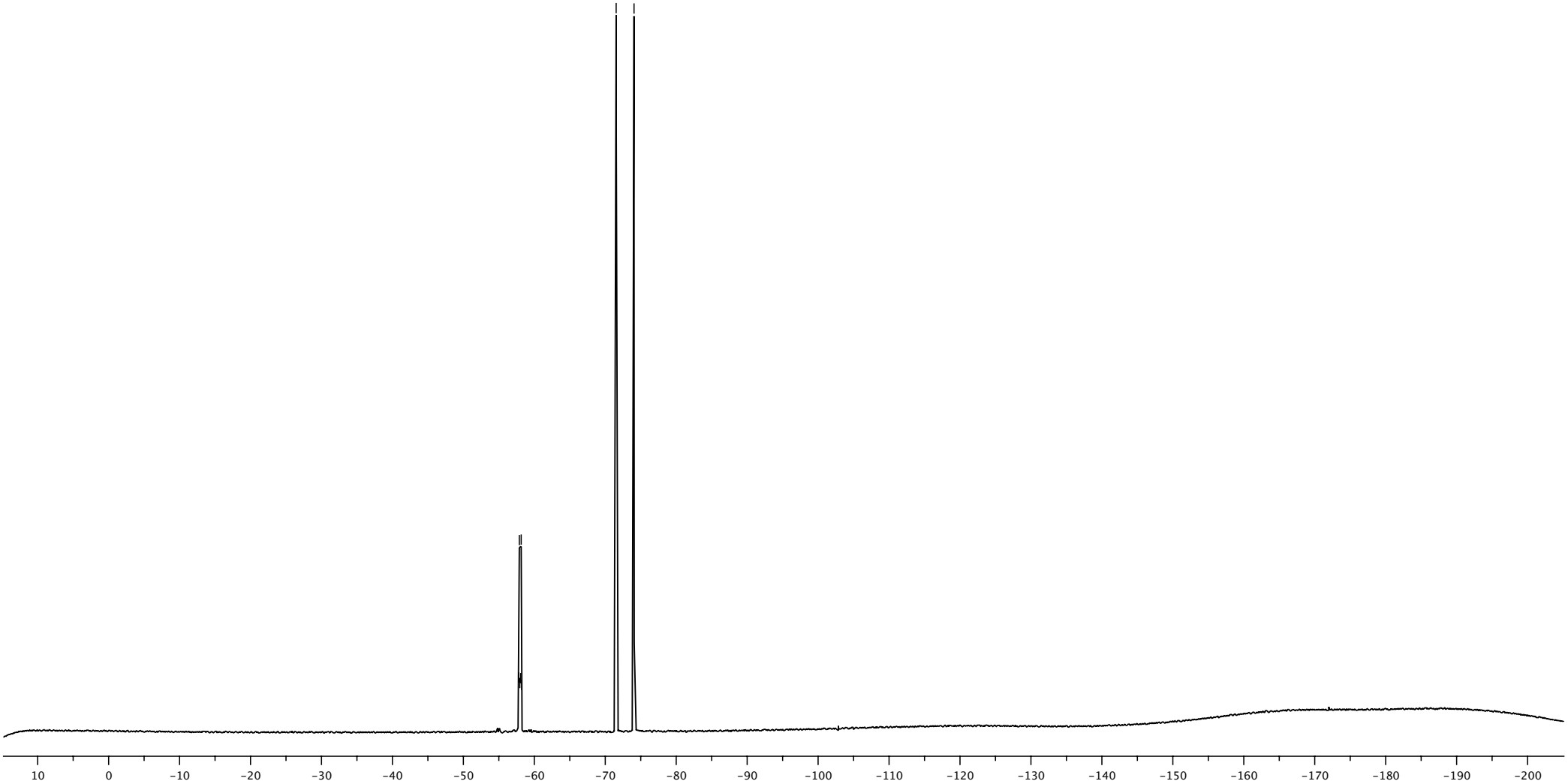


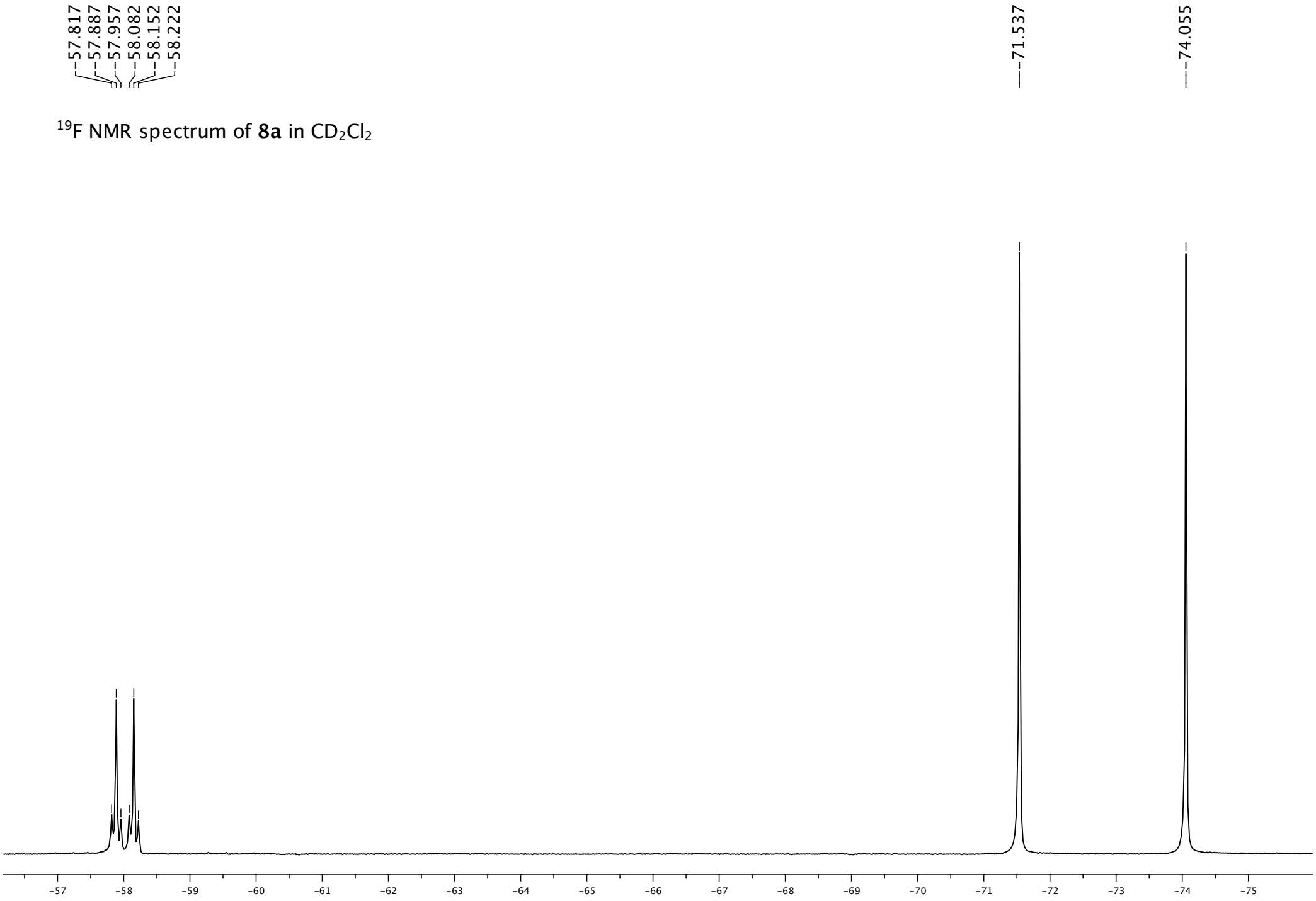
^{1}H NMR spectrum of **8a** in CD_2Cl_2





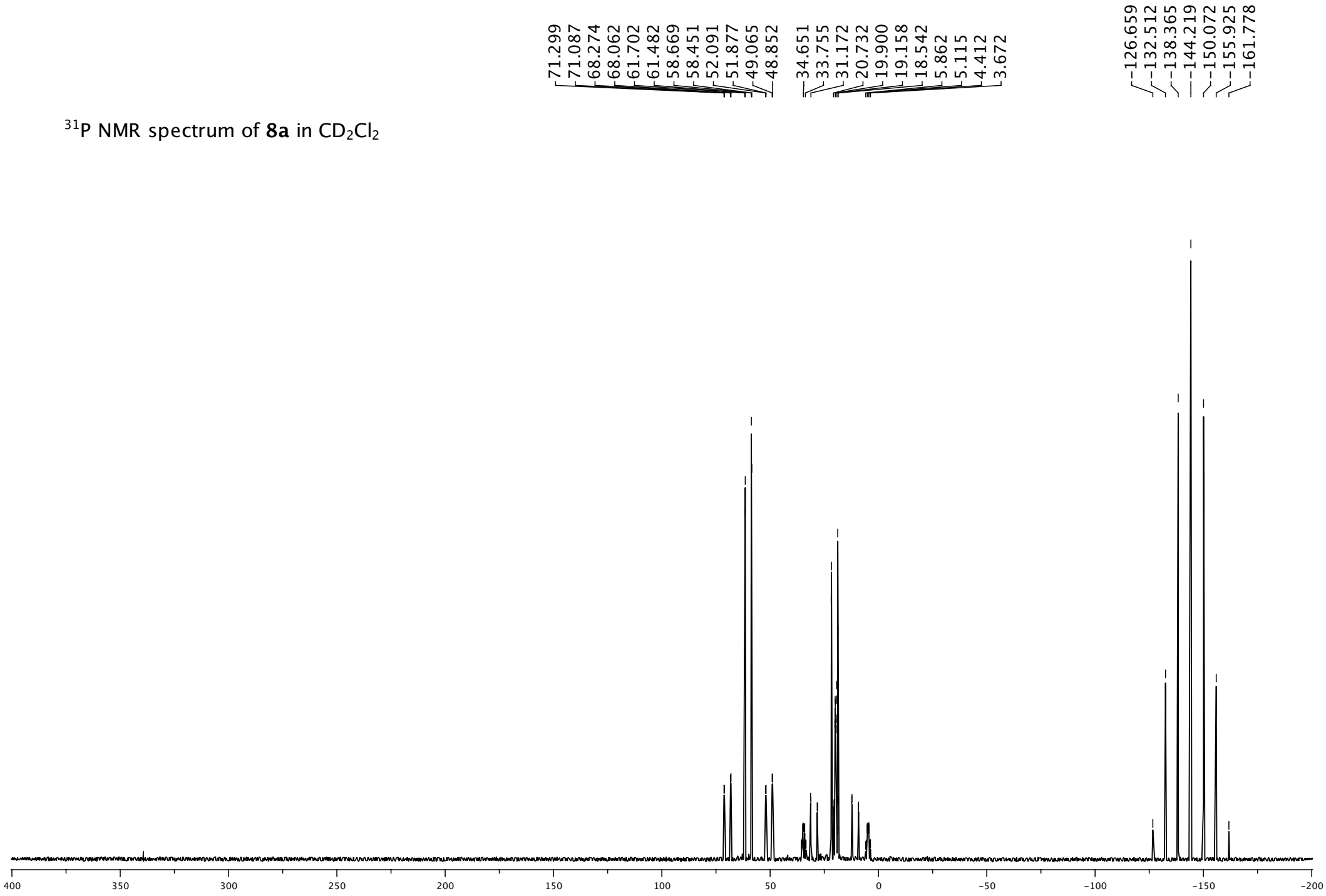
^{19}F NMR spectrum of **8a** in CD_2Cl_2





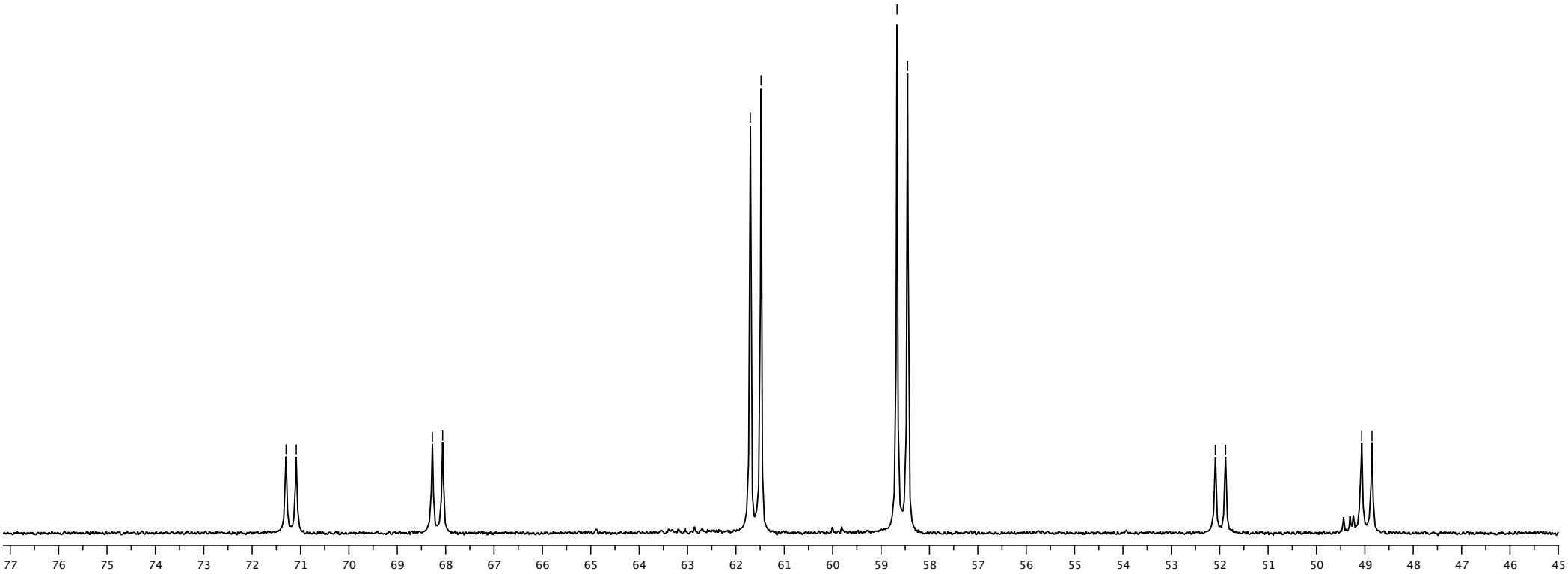
^{19}F NMR spectrum of **8a** in CD_2Cl_2

^{31}P NMR spectrum of **8a** in CD_2Cl_2



71.299
71.087
68.274
68.062
61.702
61.482
58.669
58.451
52.091
51.877
49.065
48.852

^{31}P NMR spectrum of **8a** in CD_2Cl_2



^{31}P NMR spectrum of **8a** in CD_2Cl_2