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A Generic Route to Fluoroalkyl-containing Phosphanes†

Alan K. Brisdon,*[a] Christopher J. Herbert[a]

[a]School of Chemistry
The University of Manchester
Oxford Road
Manchester
UK
M13 9PL

Materials and Methods:

All syntheses were carried out using Schlenk techniques under an inert (N_2) atmosphere, unless otherwise stated. Air/moisture sensitive compounds were handled under an argon atmosphere in a dry box (Belle Technology, UK) fitted with a recirculatory drying column. Low temperature reactions were carried out in an ethanol bath in a silvered Dewar vessel equiped with a closed-cycle 2-stage dip chiller unit (L.P. Technology, Leeds, UK).

Diethyl ether and THF (Fisher) were dried over sodium/benzophenone for *ca*. 1 day and then freshly distilled prior to use. Hexane (Fisher) was dried over sodium wire for *ca*. 1 day and then freshly distilled prior to use. Solvents were thoroughly degassed prior to use. CF_3I, C_2F_5I, *i*-C_3F_7, *s*-C_4F_9I, *t*-C_4F_9I, $C_6F_{11}I$ (all Apollo Scientific), Ph_2PH (Strem), Li (3.2 mm diam. wire), MeLi (1.6 M in Et_2O) (all Acros), PPh_3, Me_3SiCl and $CDCl_3$, (all Aldrich) were used as supplied after verification of their purity by spectroscopic methods. Ph_2PSiMe_3 was synthesized based on literature methods.[1]

NMR data was recorded as $CDCl_3$ solutions in 5mm tubes unless otherwise stated. $^{31}P\{^1H\}$, ^{31}P, and ^1H NMR spectra were recorded on either Bruker Avance III 400 MHz or Bruker DPX200 spectrometers operating at 161.967 or 81.013 MHz (^{31}P), and 400.130 or 200.131 MHz (^1H) respectively. Quoted chemical shift values are given using the high frequency positive convention and are referenced to external 85% H_3PO_4 and either $SiMe_4$ or residual proton signals from the solvent respectively. ^{19}F, ^{13}C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer operating at 376.461 and 100.622 MHz and referenced to either external $CFCl_3$, $SiMe_4$, or solvent signals. $^{29}Si\{^1H\}$ NMR spectra were recorded on a Varian Inova 400 operating at 79.5 MHz and referenced with respect to external $SiMe_4$. Coupling constants are given in Hz and are measured directly from spectra, or obtained by modelling and iterative fitting of the NMR data using the SPINWORKS program.[2] Elemental analyses were performed by The School of Chemistry's microanalysis section.

The X-ray crystallography measurements were recorded on a Bruker-Nonius Kappa CCD machine using MoKα radiation (λ= 0.71073 Å) at 150 K. Data were corrected for Lorentz, polarisation and absorption using the multi-scan method. The X-ray structural data was solved by direct methods and refined by Full Matrix Least Squares using SHELXL.[3] Hydrogen atoms were placed in idealized locations all other atoms were refined isotropically.

Table S1: Crystallographic Data for 4

	4
Formula	$C_{15}H_{10}F_7P$
Formula Weight	354.12
Crystal System	Monoclinic
Space Group	$P2_1/c$
a (Å)	8.9091(2)
b (Å)	26.2430(6)
c (Å)	6.3928(1)
α (°)	90
β (°)	99.406(1)
γ (°)	90
V (Å^3)	1474.55(5)
Z	4
T/ K	150
D_c (g cm^{-1})	1.595
Crystal Size (mm)	0.15 x 0.15 x 0.15
μ (mm^{-1})	0.257
2Θ range (°)	3.1→25.5
Total reflections	2736
Unique reflections (R_{int})	2736 (0.047)
Obs. reflections [I>2σ (I)]	1979
Parameters	208
Final R indices I>2σ(I)]	R_1 0.0796 wR_2 0.2488
Max., min. Δρ (eÅ^{-3})	-0.42, 0.92
Goodness of fit on F^2	1.08

Preparation of Ph_2PSiMe_3,

In a dried 3-necked round-bottomed flask maintained under a nitrogen atmosphere was placed thf (200 cm^3) into which Ph_3P (65.8g, 0.25 mol) was dissolved. Lithium wire (6.18 g, 0.90 mol) was added and the solution stirred rapidly for 24 hours. The excess of lithium wire was removed from the deep red solution which was cooled to 0 °C. Me_3SiCl (65.6 cm^3, 0.51 mol) was added slowly and the solution left to stir for 2 hours. The volatiles were removed under vacuum and hexane (200 cm^3) was added. The solution was filtered and the solvent removed under vacuum to give a pale yellow liquid which was vacuum distilled twice (154 °C, 5 mmHg) to yield pure Ph_2PSiMe_3 (43.6 g, 68%).

Preparation of *i*-Pr_2PSiMe_3

A dried 3-necked flask was charged with thf (100 cm^3) under nitrogen, *i*-Pr_2PCl (10.4 cm^3, 65 mmol) with Me_3SiCl (8.6 cm^3, 67 mmol) and the solution cooled to 0°C. Lithium wire (1.00 g, 144 mmol) was added and the mixture stirred and allowed to warm to room temperature over 24 h. The mixture was concentrated and filtered through Celite. The volatiles were removed under vacuum and the residue distilled (34-35 °C, 5 mmHg) to yield the title compound as a clear pyrophoric liquid (5.7g, 46%).

Preparation of $PhMePSiMe_3$

Using a similar protocol Ph_2PMe (1.0 cm^3, 1.08 g, 5.4 mmol) was dissolved in thf (30 cm^3). Lithium wire (0.185 g, 27 mmol) was added, and left to stir for 24 h at room temperature. The excess of lithium was removed, and the mixture cooled to 0 °C. Me_3SiCl (1.95g, 10.8 mmol) was added slowly. This was allowed to stir and warm to room temperature over a period of 2 h, then filtered through Celite and the volatiles were removed. The resulting pale yellow liquid was used without further purification.

General Procedure for non-optimised NMR Scale Experiments 1-9.

Ph_2PSiMe_3 (0.1 cm^3, 0.39 mmol) was dissolved in $CDCl_3$ (0.75 cm^3) in an NMR tube in a glove box. One equivalent of perfluoroalkyl iodide was then added, and the tube sealed. Spectra were recorded after 30 minutes and periodically until no further change in the spectra could be observed. The products were identified on the basis of their multinuclear NMR spectra. A repeat of all reactions were undertaken in the presence of 0.25 cm^3 of an internal NMR standard which was prepared from $CH_2FCH_2CH_2F$ (0.32 g, 4.1 mmol) made upto 5 cm^3 with $CDCl_3$ in a volumetric flask.

Ph_2PCF_3, 1

Using the procedure set out above and CF_3I (0.03 cm^3, 0.4 mmol) a slow reaction was observed. After a period of 6 days no further change to the NMR spectra were observed:
$^{31}P\{^1H\}$ NMR: δ 2.5 ppm (q, $^2J_{PF}$ = 73.8 Hz) ^{19}F NMR: δ -55.1 ppm (d, $^2J_{PF}$ = 73.9 Hz. ^1H NMR: δ 7.4-7.7 (m). The identity of the product was verified by comparison with published data. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ2.8 ppm [^2J(PF) = 73.5 Hz], ^{19}F NMR: δ-55.0 ppm [J = 73 Hz].[4]

$Ph_2PC_2F_5$, 2

Using the procedure described above and CF_3CF_2I (0.05 cm^3, 0.4 mmol) a slow reaction was observed. After a period of 5 days no further change to the NMR spectra were observed:
$^{31}P\{^1H\}$ NMR: δ -1.9 ppm (tq, $^2J_{PF}$ = 56.8 Hz, $^3J_{PF}$ = 16.7 Hz). ^{19}F NMR: δ -113.0 ppm (2F, dq, $^2J_{PF}$ = 56.8 Hz, $^3J_{FF}$ = 3.0, CF_2), -81.0 ppm (3F, dt, $^3J_{PF}$ = 16.7 Hz, $^3J_{FF}$ = 3.0 Hz, CF_3). ^1H NMR: δ 7.4-7.7 (m). The identity of the product was verified by comparison with published data. $^{31}P\{^1H\}$ NMR (C_6D_6): δ-1.4 ppm [J = 58, 17], ^{19}F NMR: δ-80.7 ppm [J = 16.5, 3.1], -112.6 [J = 57.0, 3.1 Hz].[5]

$Ph_2PC_8F_{17}$, 3

Using the procedure described above $CF_3(CF_2)_7I$ (0.22 g, 0.4 mmol) was reacted with Ph_2PSiMe_3 when a slow reaction ensued. After a period of 6 days no further changes to the NMR spectra were observed:
$^{31}P\{^1H\}$ NMR: δ 1.1 ppm (m, $^2J_{PF}$ = 56.0 Hz). ^{19}F NMR: δ -81.7 (3F, t, J_{FF} = 7.8 Hz, CF_3), -109.4 (2F, dt, $^2J_{PF}$ = 56.0 Hz, J_{FF} = 13.3 Hz, PCF_2), -122.1 (2F, m), -122.6 (6F, m), -123.5 (2F, m), -127.0 (2F, m). ^1H NMR: δ 7.4-7.7 (m).

$Ph_2PCF(CF_3)_2$, 4

Reaction with $(CF_3)_2CFI$ (0.06 cm^3, 0.4 mmol) as described above, resulted in a rapid reaction, which was complete within 30 minutes according to NMR spectroscopy. For the relevant NMR data see later.

$Ph_2PCF(CF_3)(CF_2CF_3)$, 5

Using the procedure set out above and *s*-C_4F_9I (0.07 cm^3, 0.4 mmol) a rapid reaction (complete within 30 minutes) was observed to occur.
$^{31}P\{^1H\}$ NMR: δ 3.7 ppm (dddqq, $^2J_{PFb}$ = 78.0 Hz, $^3J_{PFd}$ = 44.6 Hz, $^3J_{PFc}$ = 33.2 Hz, $^3J_{PFa}$ = 16.9 Hz, $^4J_{PFe}$ = 12.0 Hz). ^{19}F NMR: δ_{Fa} -67.8 ppm (3F, ddddq, $^3J_{PFa}$ = 16.9 Hz, $^3J_{FaFb}$ = 12.1 Hz, $^4J_{FaFc}$ = 12.3 Hz, $^4J_{FaFd}$ = 5.5 Hz, $^5J_{FaFe}$ = 8.6 Hz), δ_{Fe} -80.0 (3F, ddddq, $^4J_{PFe}$ = 12.0 Hz, $^4J_{FeFa}$ = 8.6 Hz, $^4J_{FeFb}$ = 12.0 Hz, $^3J_{FeFc}$ = 0.1 Hz, $^3J_{FeFd}$ = 0.6 Hz), δ_{Fc} -110.6 ppm (1F, ddqdq, $^1J_{FcFd}$ = 295.6 Hz, $^3J_{PFc}$ = 33.2 Hz,

$^4J_{FcFa}$ = 12.3 Hz, $^3J_{FcFb}$ = 12.0 Hz, $^3J_{FcFe}$ = 0.1 Hz) δ_{Fd} -114.5 ppm (1F, dddqq, $^1J_{FdFc}$ = 295.6 Hz, $^3J_{FdP}$ = 44.6 Hz, $^3J_{FdFb}$ = 11.9 Hz, $^4J_{FdFa}$ = 5.5 Hz, $^3J_{FdFe}$ = 0.6 Hz), δ_{Fb} -183.4 ppm (1F, dqdqd, $^2J_{FbP}$ = 78.0 Hz, $^3J_{FbFa}$ = 12.1 Hz, $^3J_{FbFc}$ = 12.0 Hz, $^4J_{FbFe}$ = 12.0, $^3J_{FbFd}$ = 11.9 Hz). ^{1}H NMR: δ 7.4-7.7 (m).

$Ph_2P(c\text{-}C_6F_{11})$, 6

Using the procedure described above and c-$C_6F_{11}I$ (0.16 g, 0.4 mmol) a rapid reaction was observed. $^{31}P\{^1H\}$ NMR: δ -3.4 ppm (td, 3JPF2ax = 84.0 Hz, 2JPF1 = 68.0 Hz). Fluorine NMR data are assigned based on that previously reported for mono-substituted perfluorocyclohexyl systems.[6] ^{19}F NMR: δ -110.5 (2F, $^3J_{PF}$ = 84.0 Hz,$^2J_{FF}$ = 298.3 Hz, 2a,6a), -122.6 (2F, d, $^2J_{FF}$ = 280.0 Hz, 3a,5a), -124.4 ppm (1F, d, $^2J_{FF}$ = 288.8 Hz, 4a) -124.5 (2F, d, $^2J_{FF}$ = 298.3 Hz, 2e,6e), -138.2 (2F, d, $^2J_{FF}$ = 280.0 Hz, 3e,5e), -142.0 (1F, d, $^2J_{FF}$ = 285.5 Hz, 4e), and -185.8 (1F, dm, $^2J_{PF}$ = 68.0 Hz, 1a).

$Ph_2P(t\text{-}C_4F_9)$, 7

Using the procedure set out above and *t*-C_4F_9I (0.14 g, 0.45 mmol) a rapid reaction was observed. $^{31}P\{^1H\}$ NMR: δ 15.2 ppm (dectet, $^3J_{PF}$ = 12.3 Hz), ^{19}F NMR: δ –60.0 ppm (d, $^3J_{PF}$ = 12.2 Hz). ^{1}H NMR: δ 7.4-7.7 (m). Some decomposition was observed to give $(CF_3)_3CH$ and $(CF_3)_2C{=}F_2$ (CARE: perfluoroisobutene is highly toxic).[7]

***i*-$Pr_2PC_2F_5$ (8).**

Reaction of CF_3CF_2I (0.05 cm^3, 0.4 mmol) with *i*-Pr_2PSiMe_3 in an NMR tube, as described above, resulted in a reaction which was complete after 2 hours.
$^{31}P\{^1H\}$ NMR: δ 24.5 (tq, $^2J_{PF}$ = 41.7, $^3J_{PF}$ = 14.8 Hz) ^{19}F NMR: δ –82.4 (dt, $^3J_{PF}$ = 14.8, $^3J_{PF}$ = 2.9 Hz), -111.7 (dq, $^2J_{PF}$ = 41.7, $^3J_{PF}$ = 2.9 Hz). ^{1}H NMR: δ 1.16 (6H, m, C*H*$_3$), 2.2 (1H, dsept, $^2J_{PH}$ = 2.4, $^3J_{HH}$ = 7.1 Hz, C*H*).

$PhMePCF(CF_3)_2$ (9).

Reaction of $(CF_3)_2CFI$ (0.06 cm^3, 0.4 mmol) with $PhMePSiMe_3$ in an NMR tube, as outlined above, resulted in a rapid reaction, which was complete within 30 minutes.
$^{31}P\{^1H\}$ NMR: δ -12.0 (dsept, $^2J_{PF}$ = 61.1, $^3J_{PF}$ = 16.4 Hz) ^{19}F NMR: δ –70.2 [3F, ddq, $^2J_{PF}$ = 16.4, $^3J_{FF}$ = 11.2, $^4J_{FF}$ = 9.3 Hz, CF_3], –71.2 [3F, ddqq, $^2J_{PF}$ = 16.4, $^3J_{FF}$ = 11.2, $^4J_{FF}$ = 9.3, $^5J_{FH}$ = 1.5 Hz, CF_3'],-190.3 [1F, dsept, ^2JPF = 61.1, $^3J_{FF}$ = 11.0, CF] ^{1}H NMR: δ 7.28-7.40 (6H, m), 1.63 (3H, d, $^2J_{PH}$ = 6.0 Hz, CH_3).

Synthesis of $Ph_2PCF(CF_3)_2$, 4

A dried Schlenk vessel was charged with Ph_2PSiMe_3 (2.2 cm^3, 8.5 mmol) and hexane (20 cm^3). This

was cooled to *ca*. -30°C and $(CF_3)_2CFI$ (1.2 cm^3, 8.5 mmol) added slowly. The solution was allowed to warm to 0°C and stirred overnight. The solution was recooled to -20°C, and MeLi (1.6 M in Et_2O, 5.2 cm^3, 8.5 mmol) was added slowly. The solution was then allowed to stir for *ca.* 30 mins, and warmed to room temperature. The solution was filtered, and the volatiles removed under vacuum. The resulting yellowish solid was redissolved in hexane (15 cm^3) and DCM (5 cm^3), and filtered. Removal of the solvents *in vacuo* afforded **1** as a white solid (2.28 g, 75 %). $C_{15}F_7H_{10}P$ requires: C 50.84, H 2.85, P 8.75%, found: C 50.88, H 2.71, P 8.04%. $^{31}P\{^1H\}$ NMR: δ -0.8 ppm (dsept, $^2J_{PF}$ = 74.0 Hz, $^3J_{PF}$ = 18.0 Hz), ^{19}F NMR: δ -69.6 ppm (6F, dd, $^3J_{PF}$ = 18.0 Hz, $^3J_{FF}$ = 11.9 Hz, CF_3), -184.9 ppm (1F, dsept, $^2J_{PF}$ = 74.0 Hz, $^3J_{FF}$ = 11.9 Hz, CF_2), $^{13}C\{^1H\}$ NMR: δ 135.8 ppm (d, $^2J_{PC}$ = 26.0 Hz, *ortho*), 131.2 ppm (s, *para*), 130.0 ppm (dd, $^1J_{PC}$ = 12.3 Hz, $^3J_{CF}$ = 6.8 Hz, *ipso*), 128.9 (d, $^3J_{PC}$ = 10.3 Hz, *meta*), ^1H NMR: δ 7.24-7.45 ppm (6H, m), 7.65-7.85 (4H, m).

References

1.

2. Spinworks, version 2.55, Kirk Marat, University of Manitoba, 2006.

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4. P. Eisenberger, I. Kieltsch, N. Armanio and A. Togni *Chem. Commun*., 2008, 1575

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6. G. Gurato, L. Cavalli, G. G. Troilo, *Org. Mag. Res*., 1975, **7**, 532.

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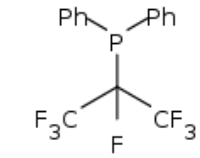
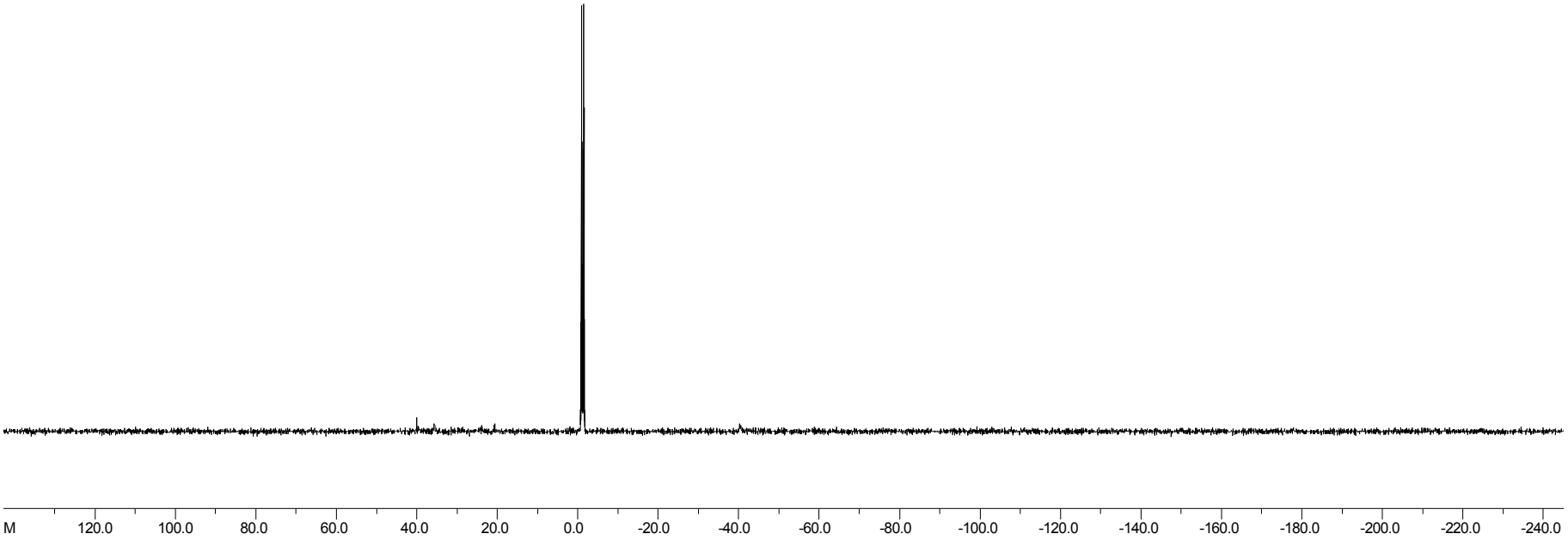
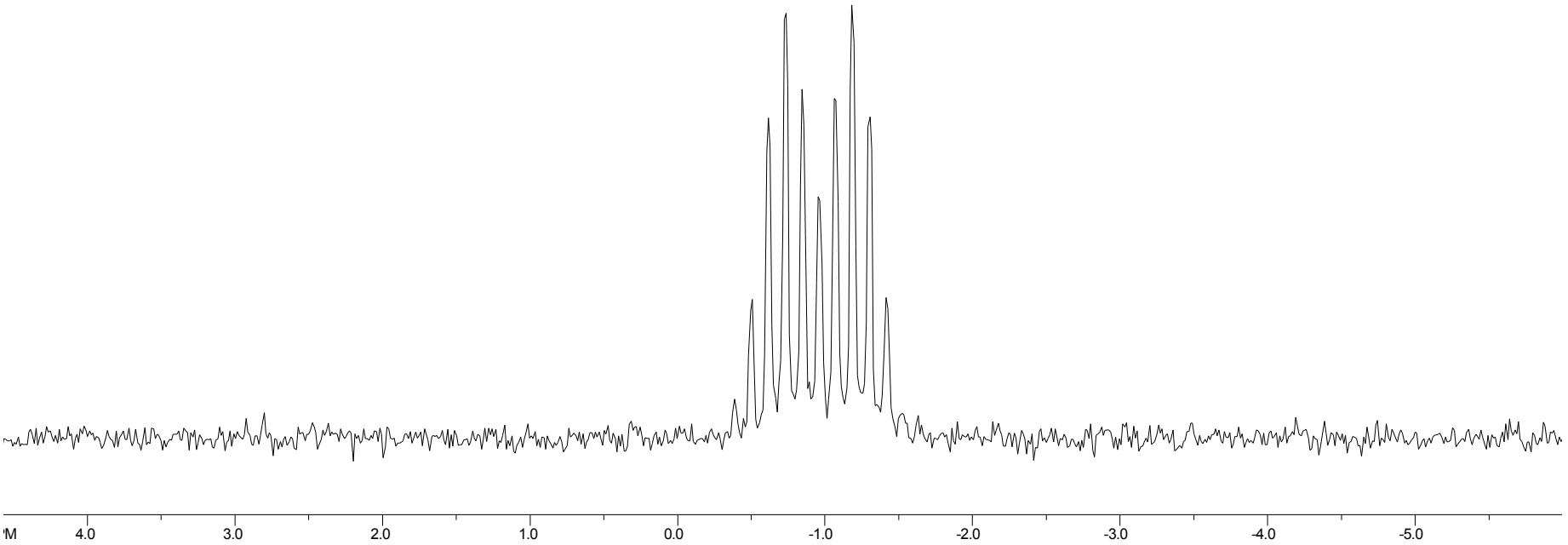
$^{31}P\{^{1}H\}$ NMR spectrum of $Ph_2PCF(CF_3)_2$, **4**

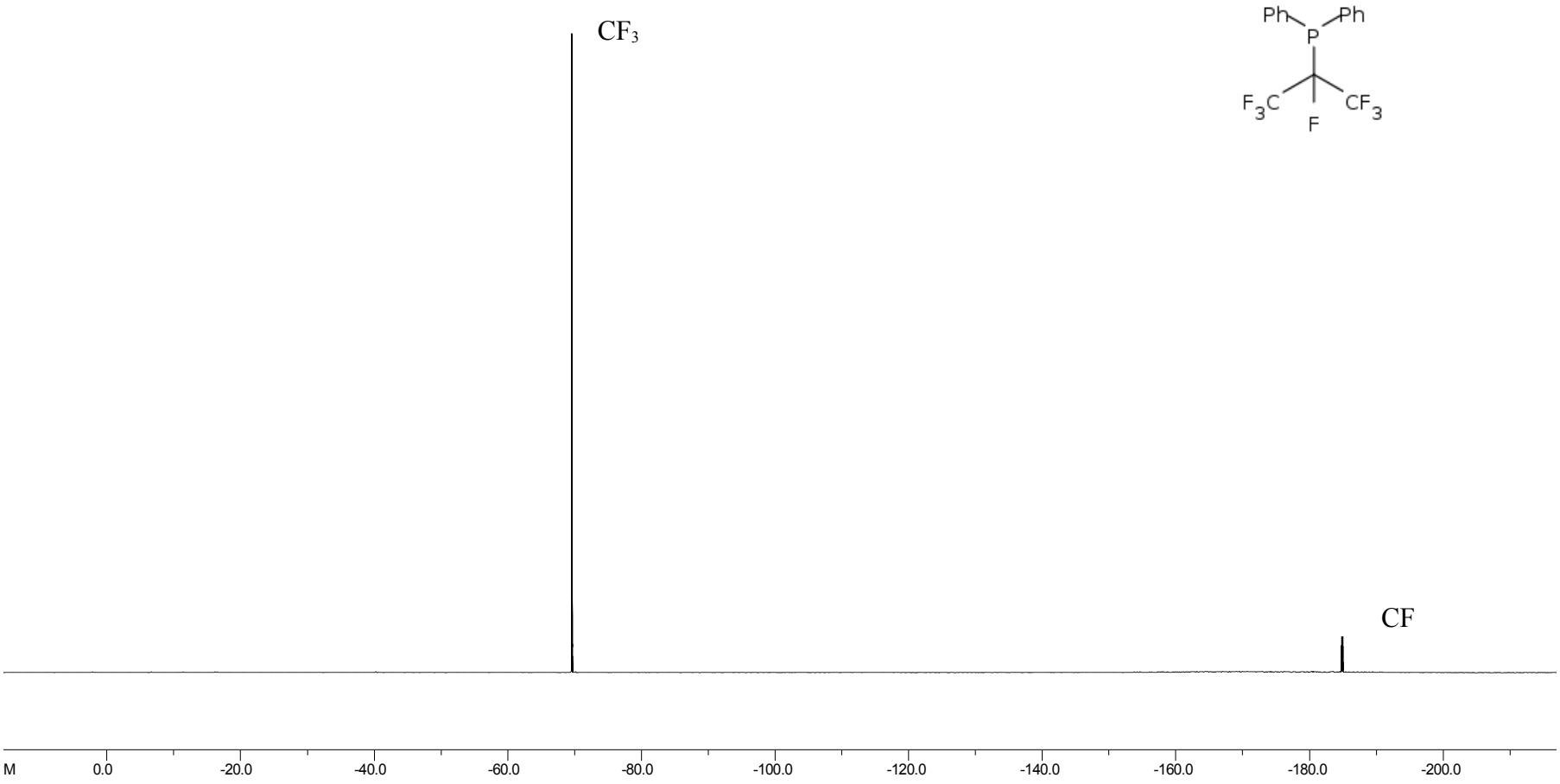




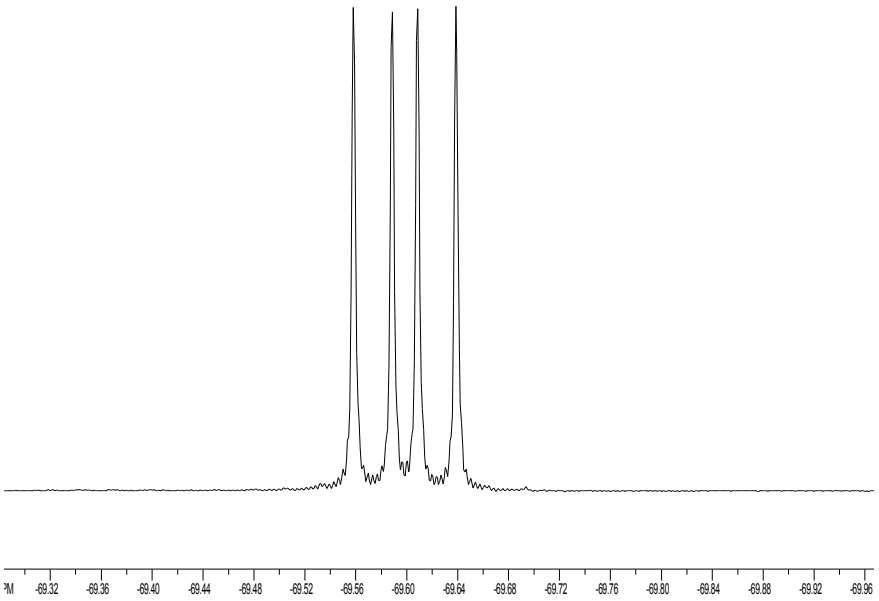
Expansion of $^{31}P\{^{1}H\}$ NMR spectrum of $Ph_2PCF(CF_3)_2$, **4**



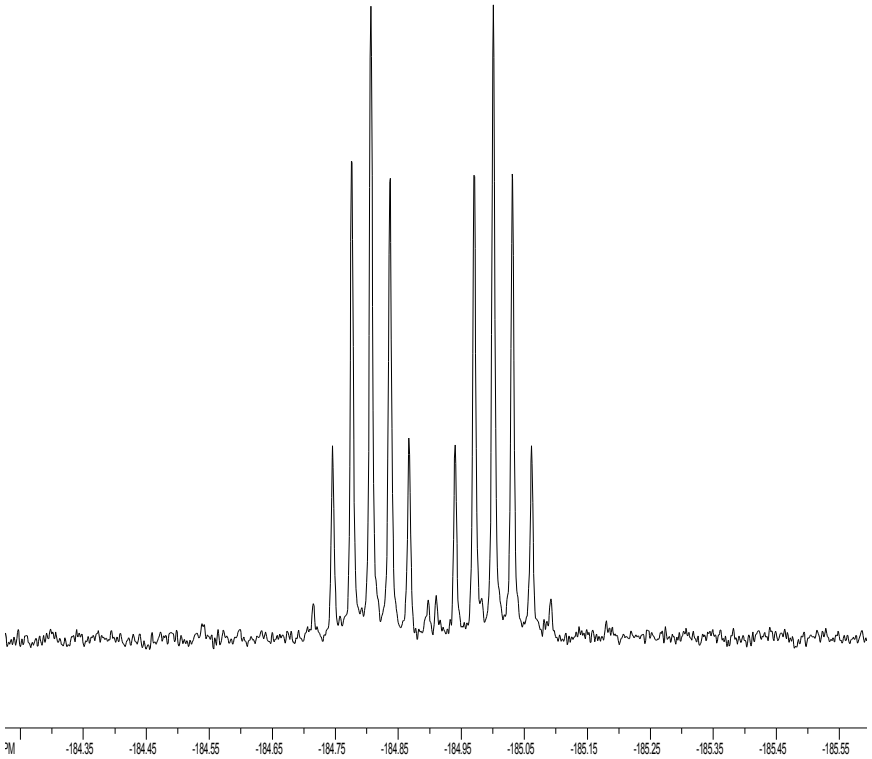
^{19}F NMR spectrum of $Ph_2PCF(CF_3)_2$, **4**



Expansions of signals from the ^{19}F NMR spectrum of $Ph_2PCF(CF_3)_2$, **4**

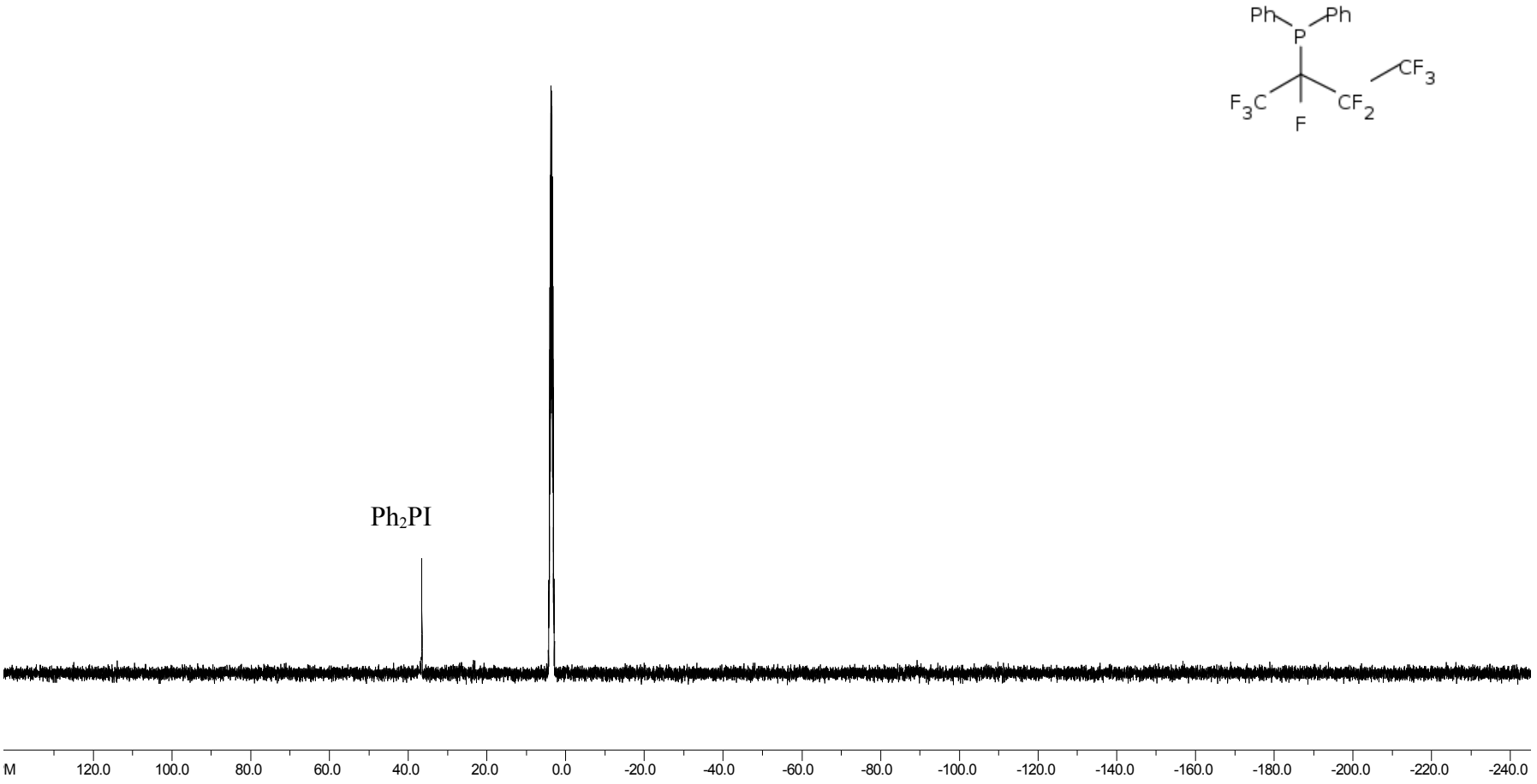


CF_3 signal

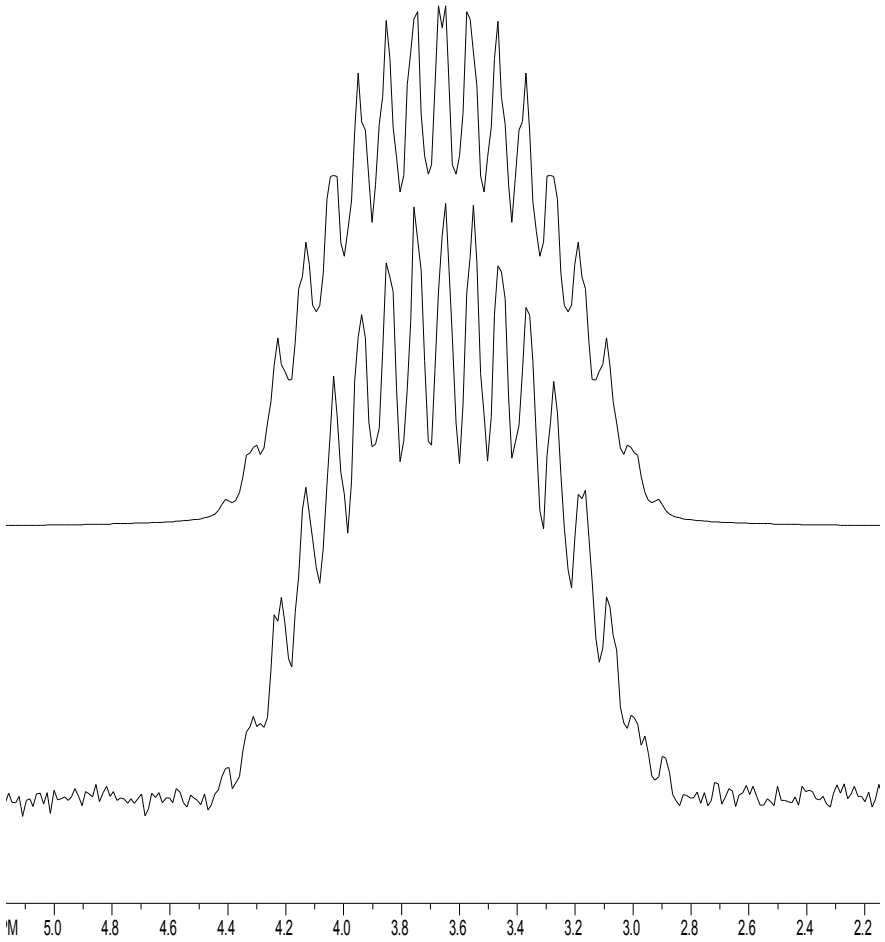


CF signal

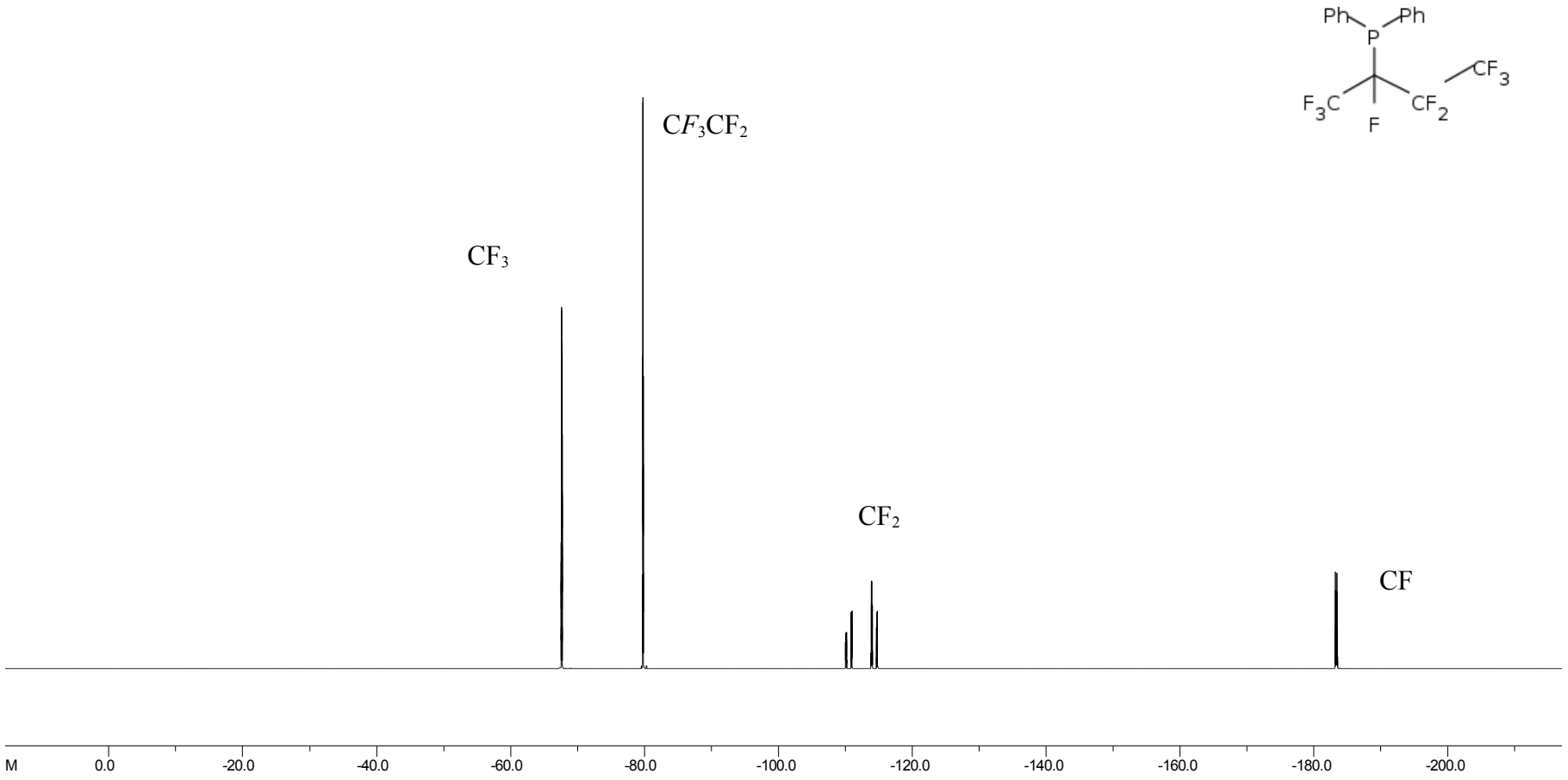
$^{31}P\{^{1}H\}$ NMR spectrum of $Ph_2P(s\text{-}C_4F_9)$ **5**



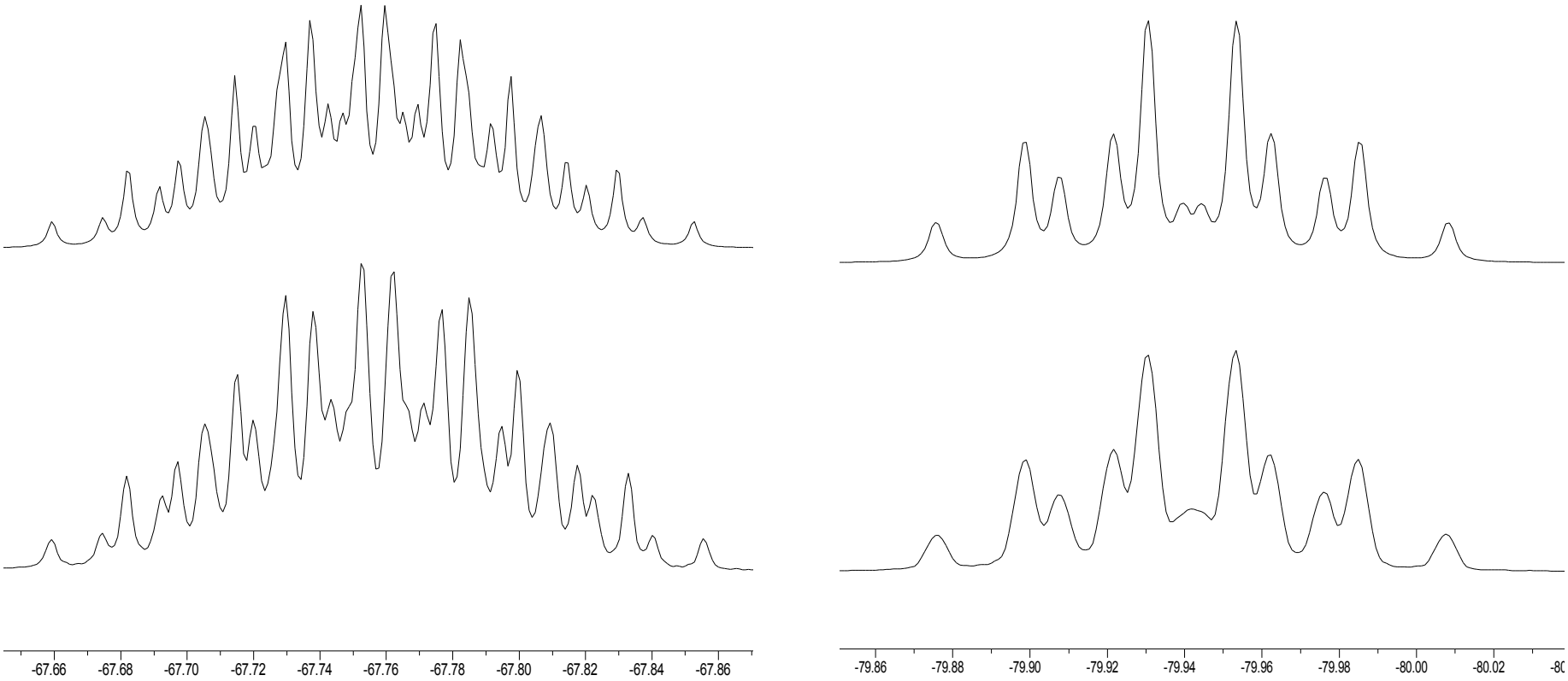
Expansion of the peak at δ + 3.7 (bottom) and simulation (top) in the $^{31}P\{^{1}H\}$ NMR spectrum of $Ph_2P(s\text{-}C_4F_9)$, **5**



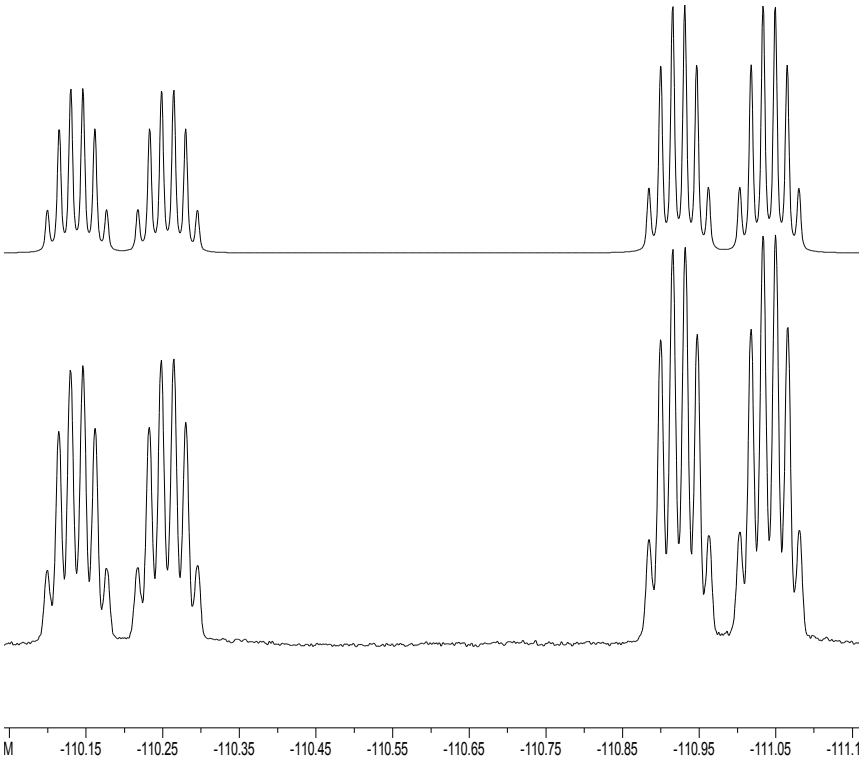
^{19}F NMR spectrum of $Ph_2P(s\text{-}C_4F_9)$, **5**

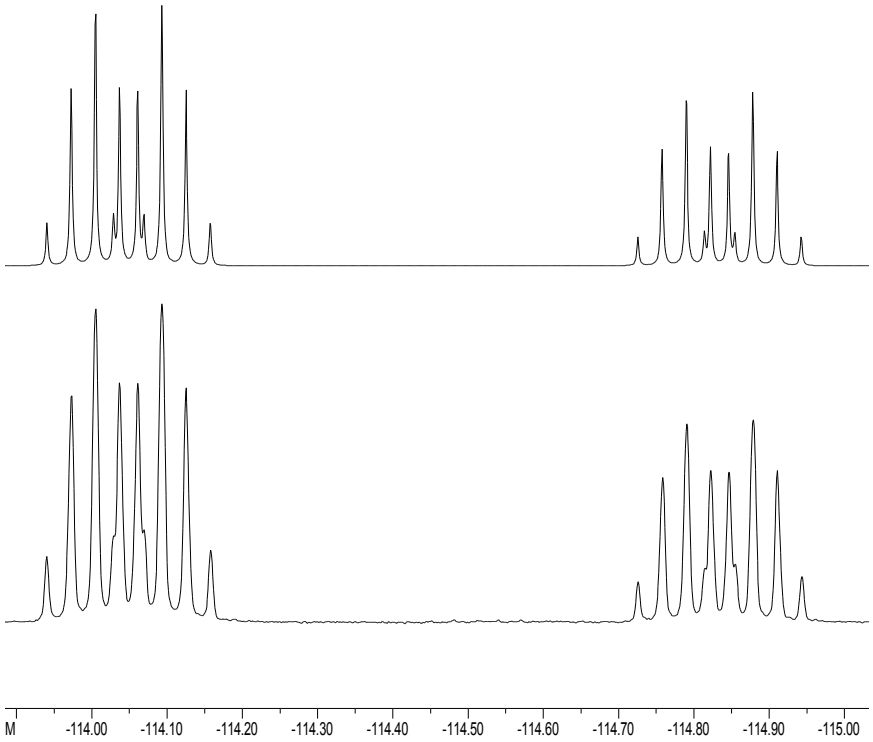


Expansions of CF_3 and CF_3CF_2 signals (simulated (top) and experimental (bottom)) in the ^{19}F NMR spectrum for **5**

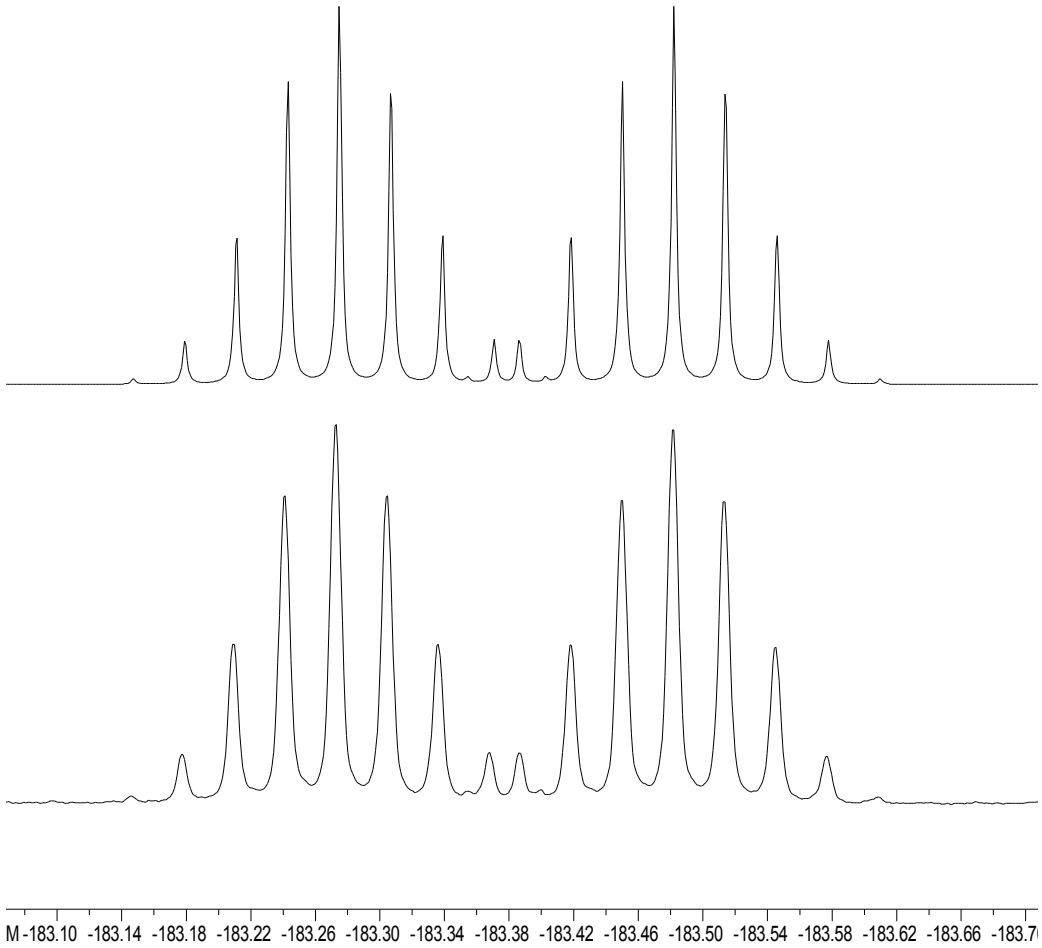


Expansions of diastereotopic fluorine atom signals from the ^{19}F NMR spectrum of $Ph_2P(s\text{-}C_4F_9)$, **5** (simulated = top, expt = bottom)

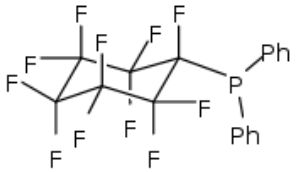


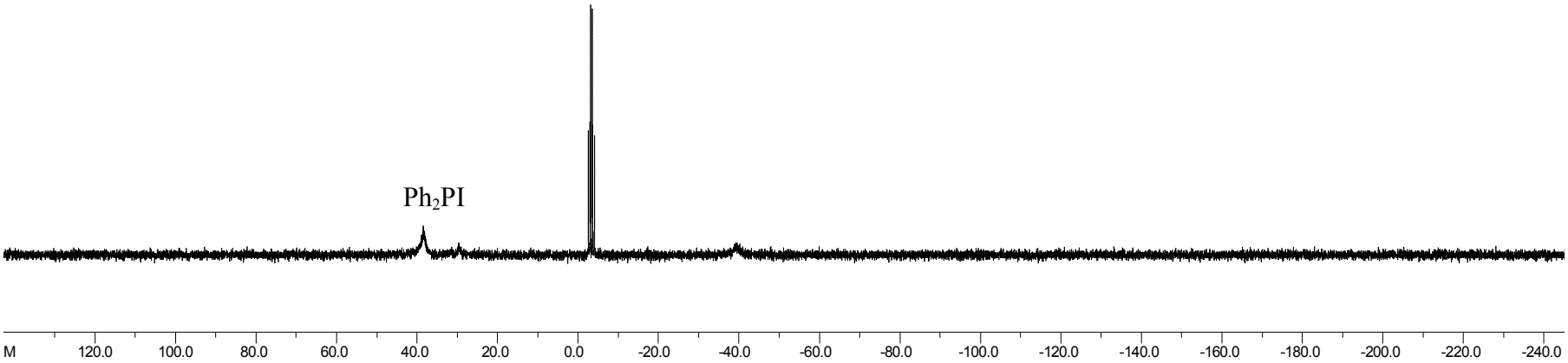


Expansion of the CF signal in the ^{19}F NMR spectrum of $Ph_2P(s\text{-}C_4F_9)$, **5** (simulated = top, expt = bottom)

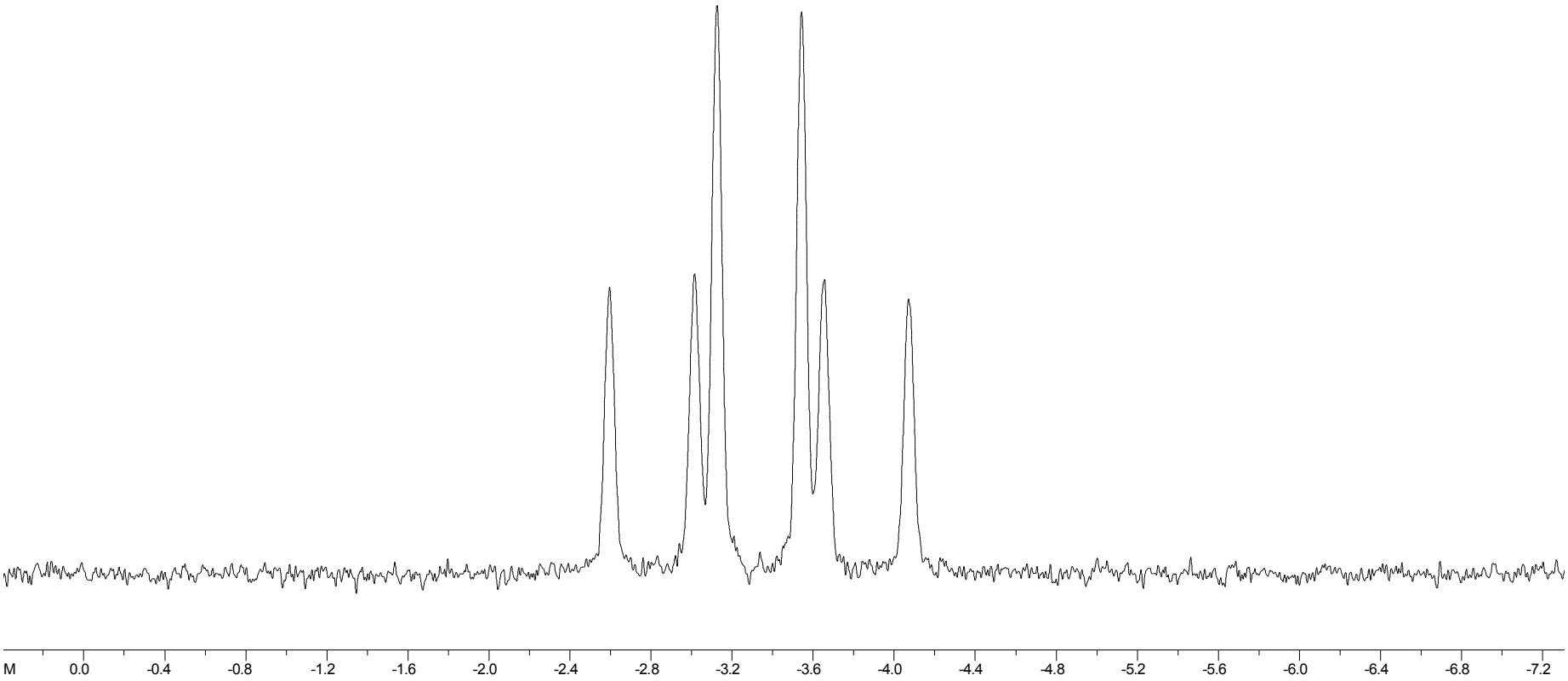


$^{31}P\{^{1}H\}$ NMR spectrum of $Ph_2P(cyc\text{-}C_6F_{11})$, **6**

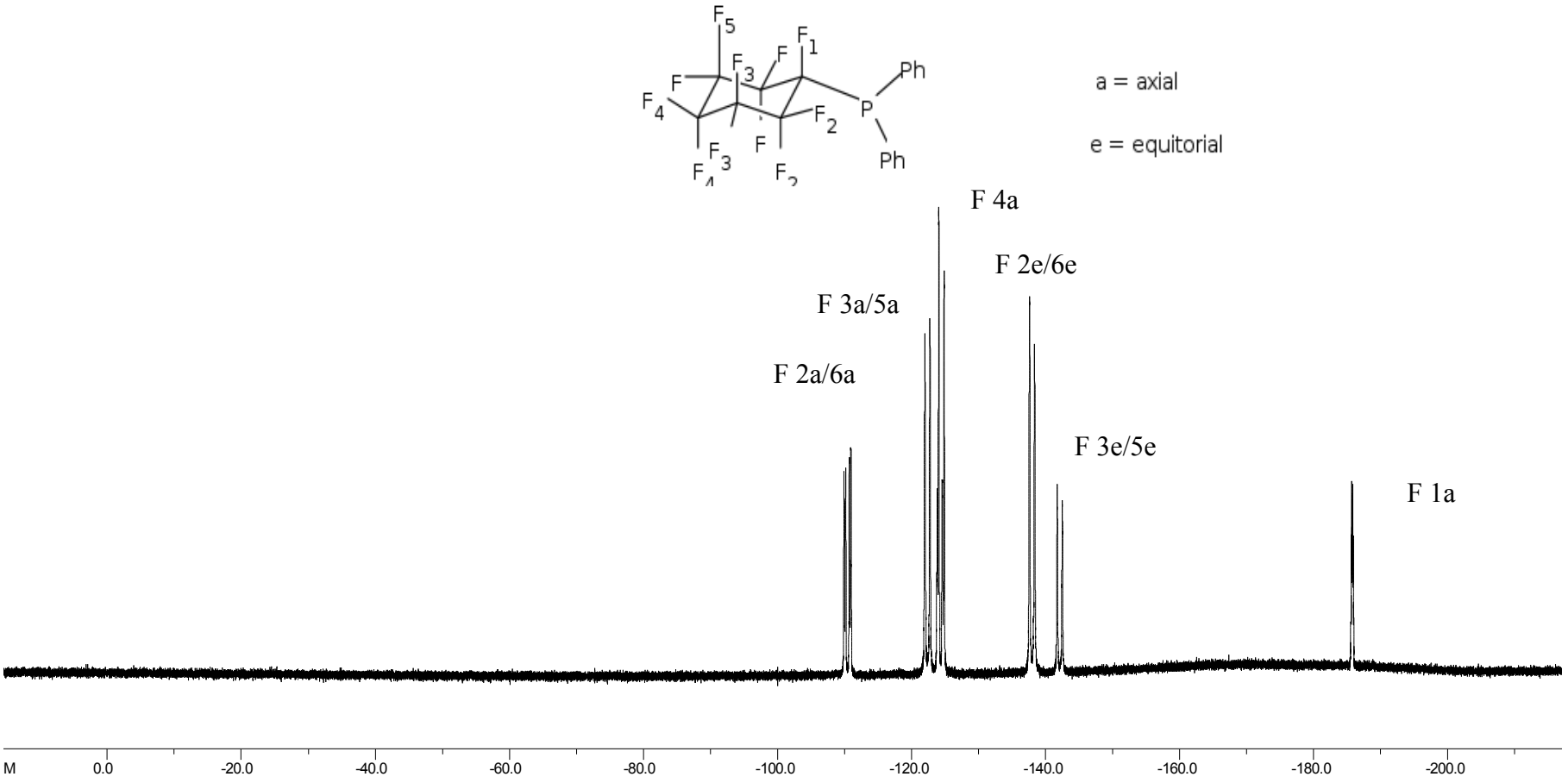




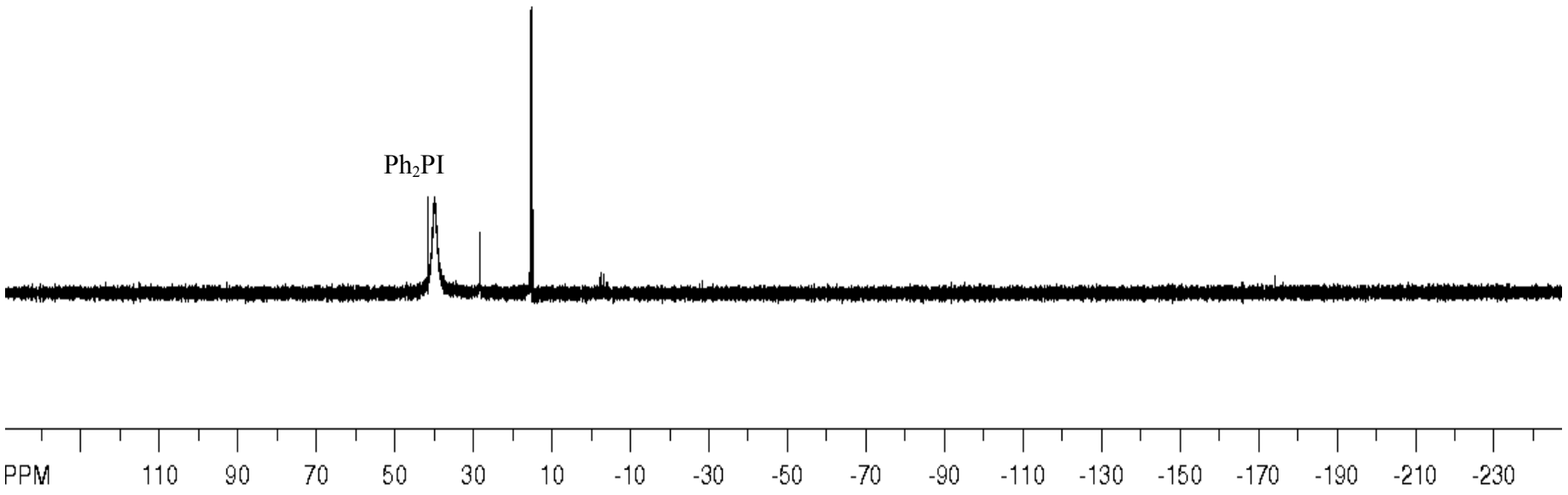
Expansion of signal at δ – 3.4 ppm in the spectrum shown above for **6**



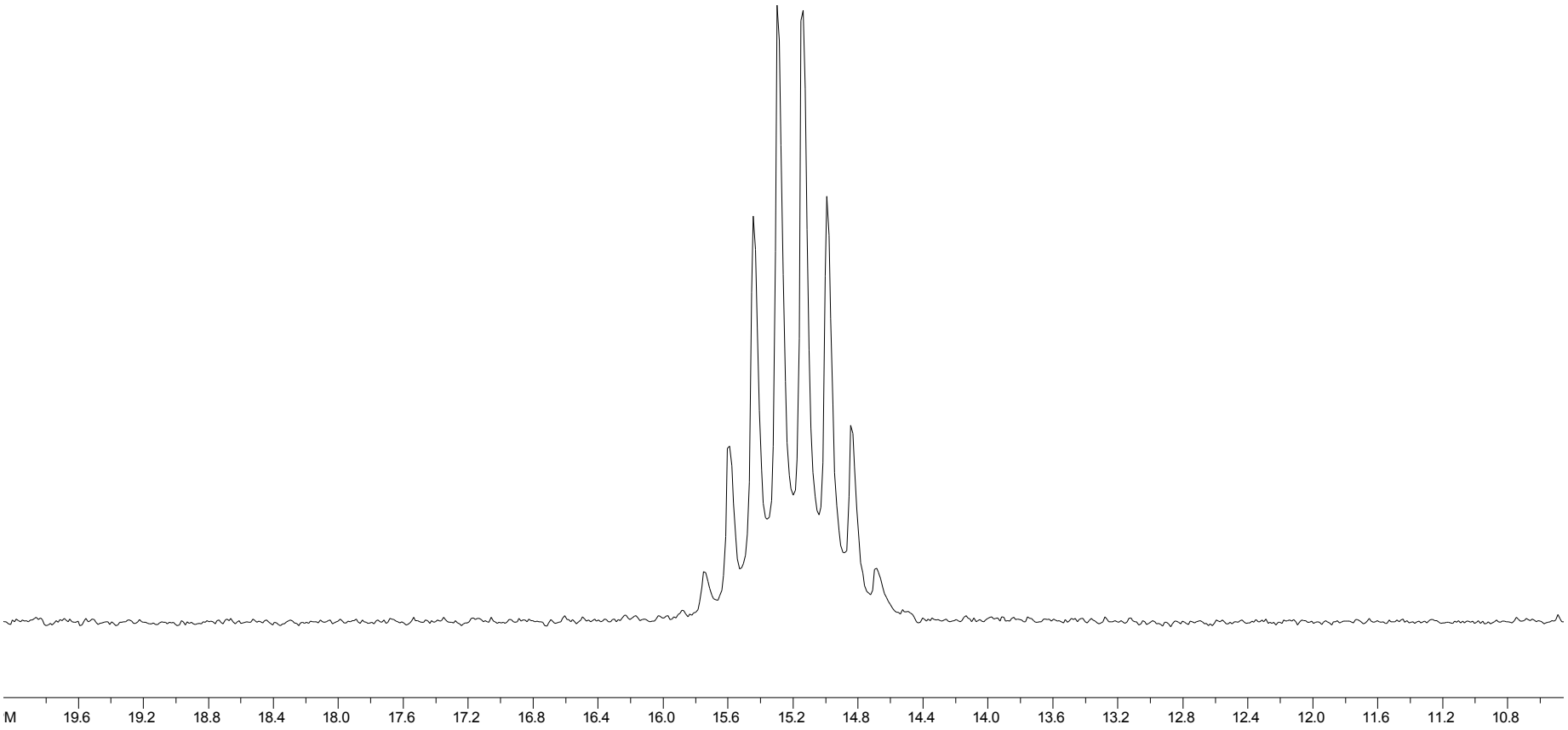
^{19}F NMR spectrum of $Ph_2P(cyc\text{-}C_6F_{11})$, **6**



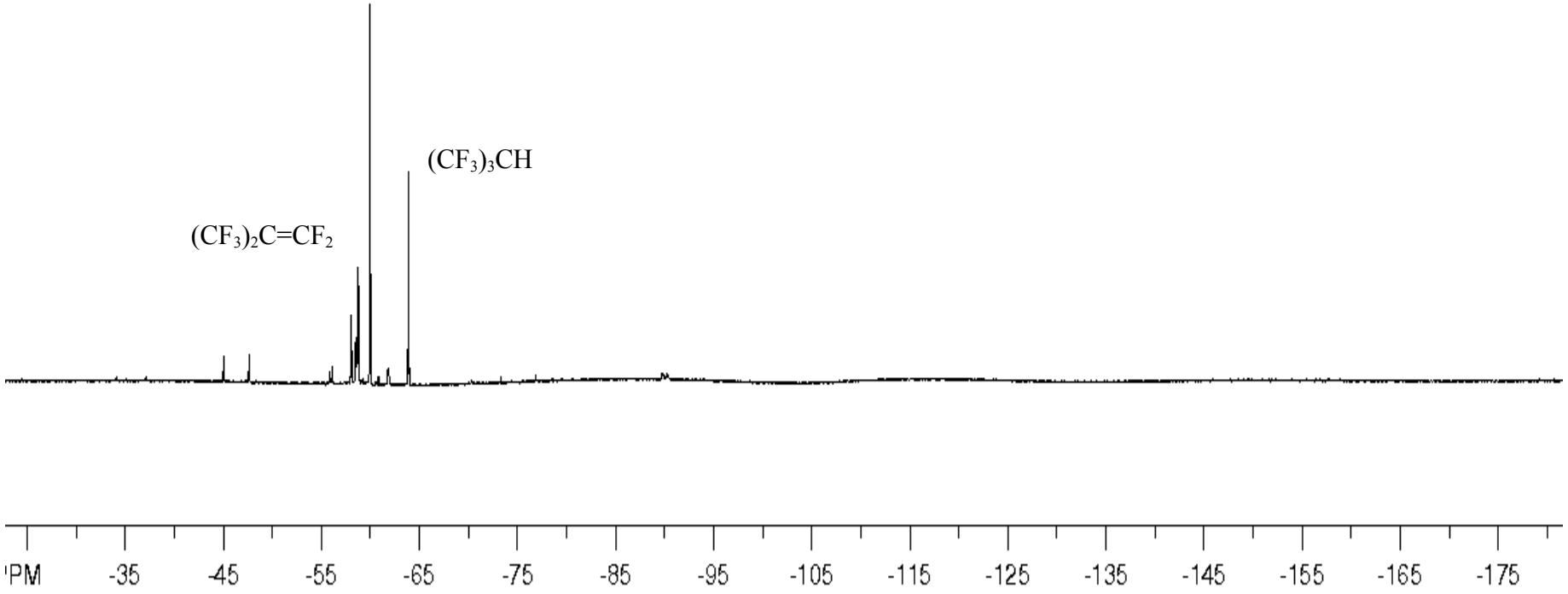
$^{31}P\{^{1}H\}$ NMR spectrum of reaction between Ph_2PSiMe_3 and *tert*-C_4F_9I, **7**



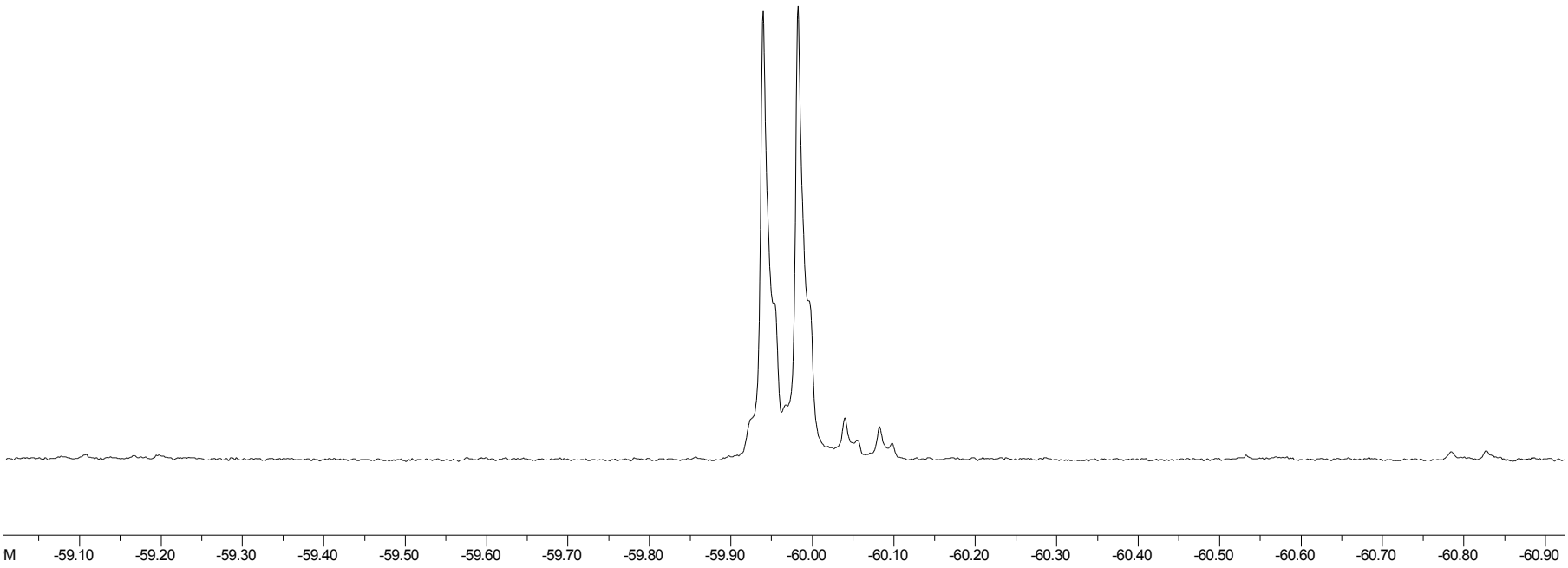
Expansion of signal at δ +15.2 ppm in the spectrum shown above, **7**



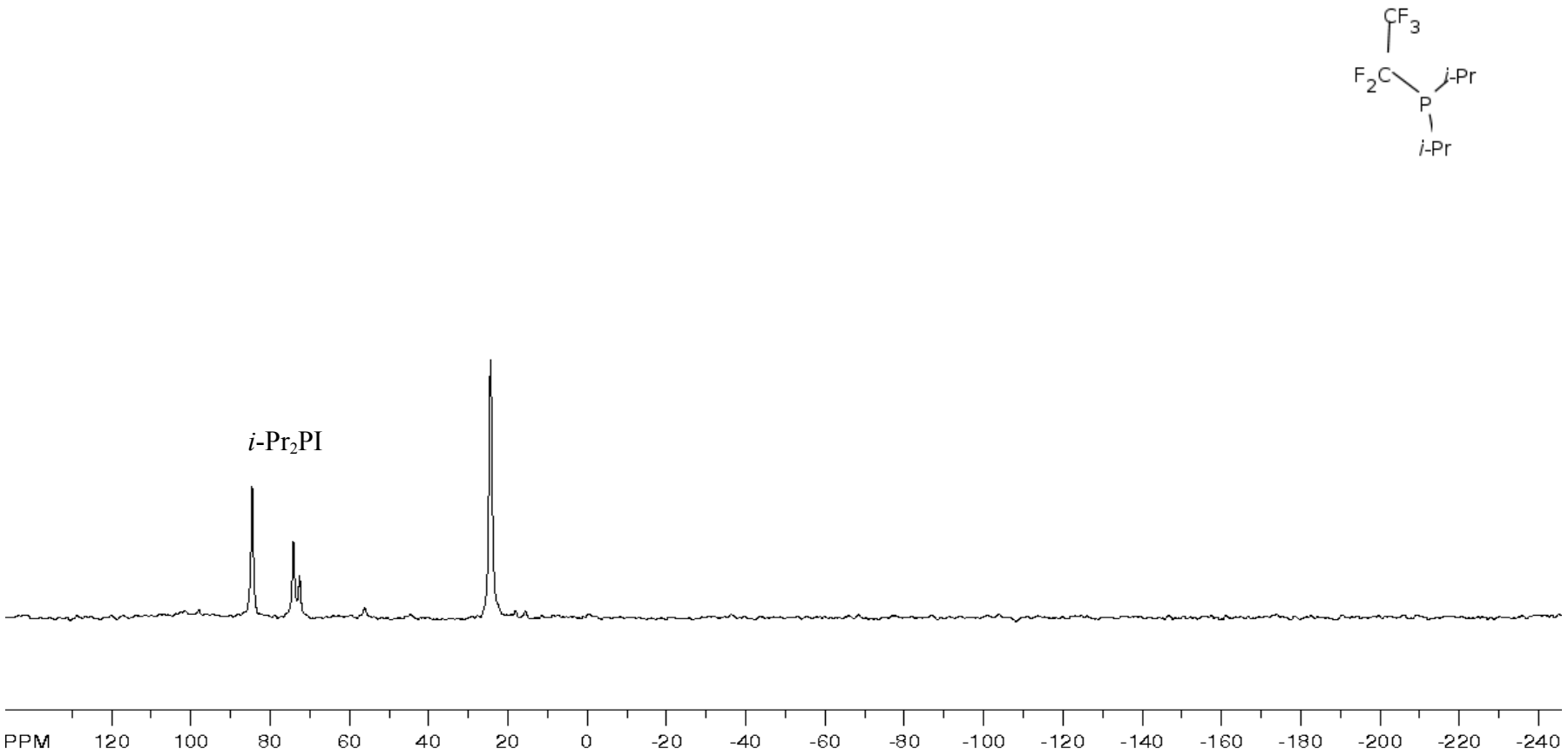
^{19}F NMR spectrum of the $Ph_2P(t\text{-}C_4F_9)$, **7**



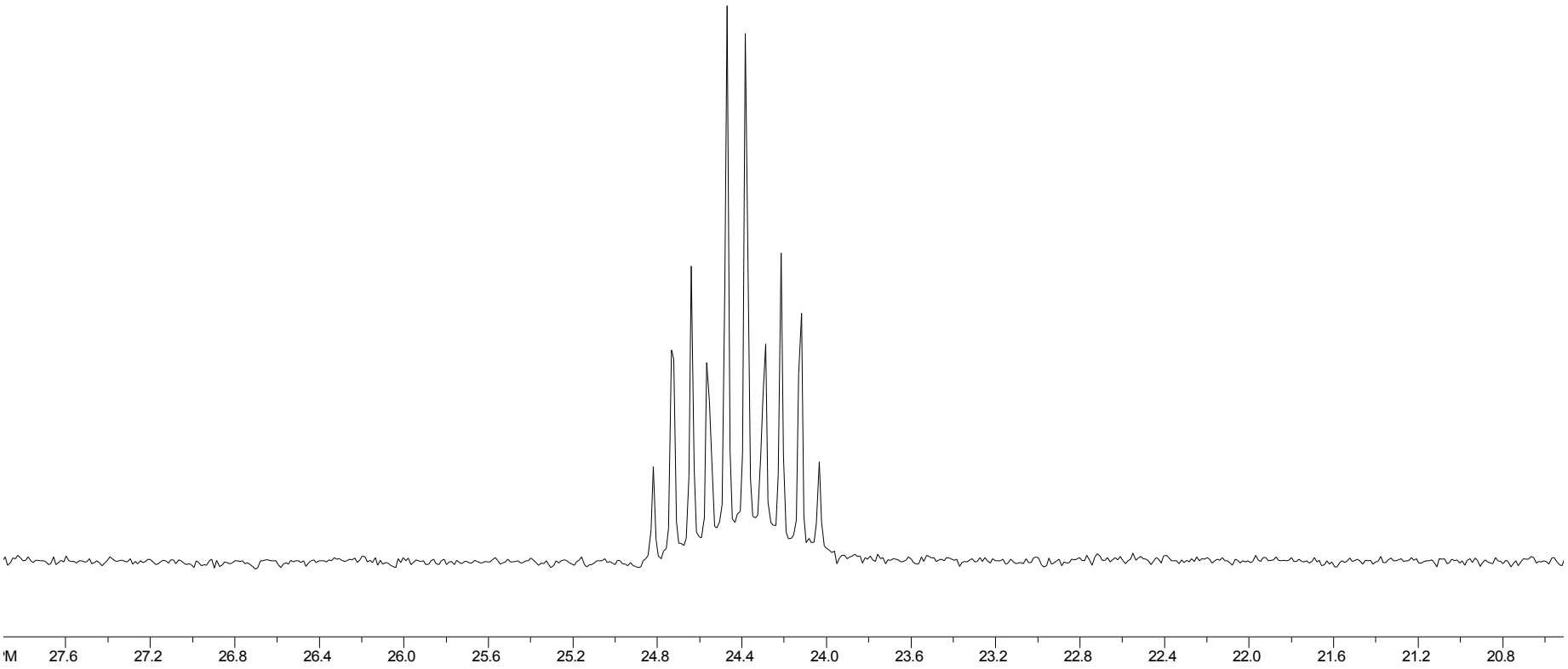
Expansion of peak at δ – 60.0 in the ^{19}F NMR spectrum shown above, **7**



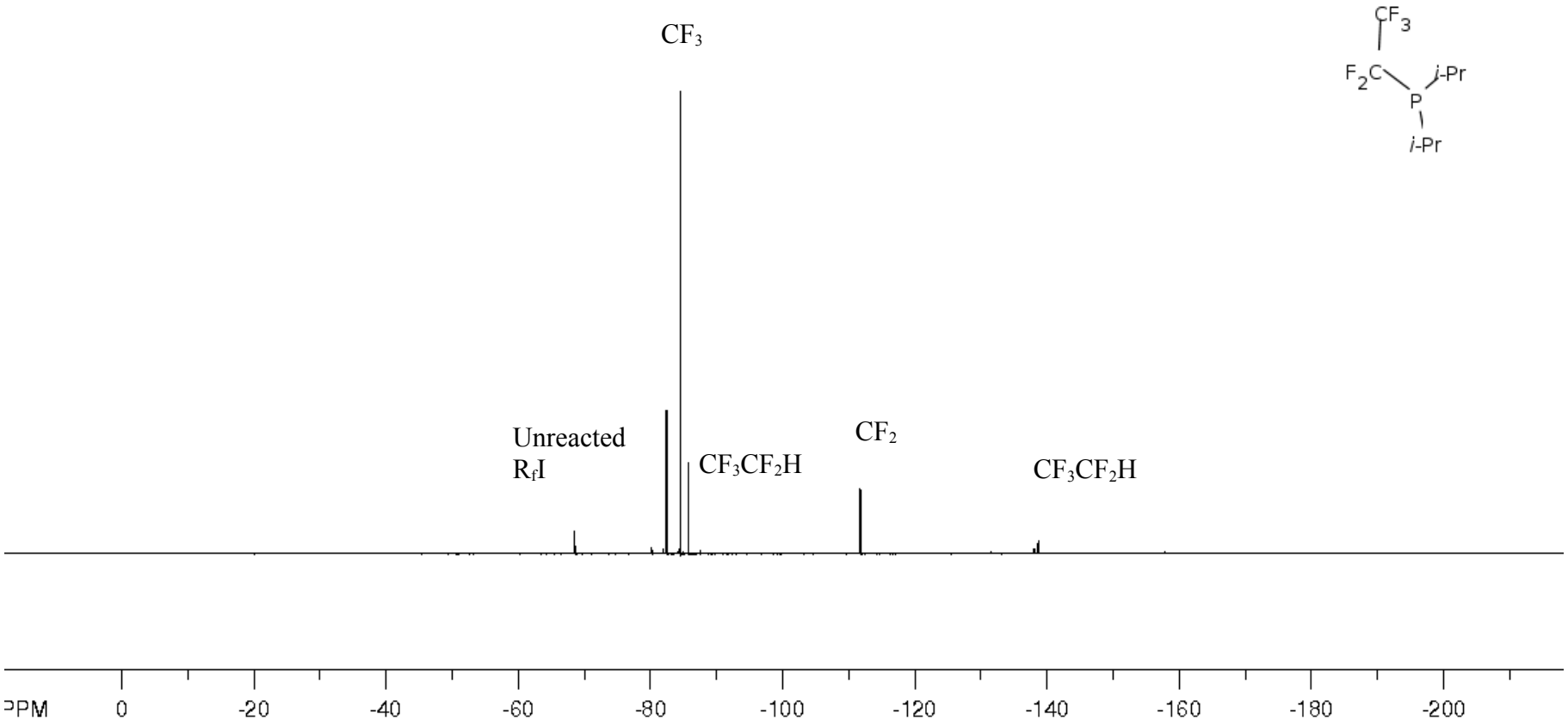
^{31}P $\{^{1}H\}$ NMR spectrum of $^{i}Pr_2PC_2F_5$, **8**



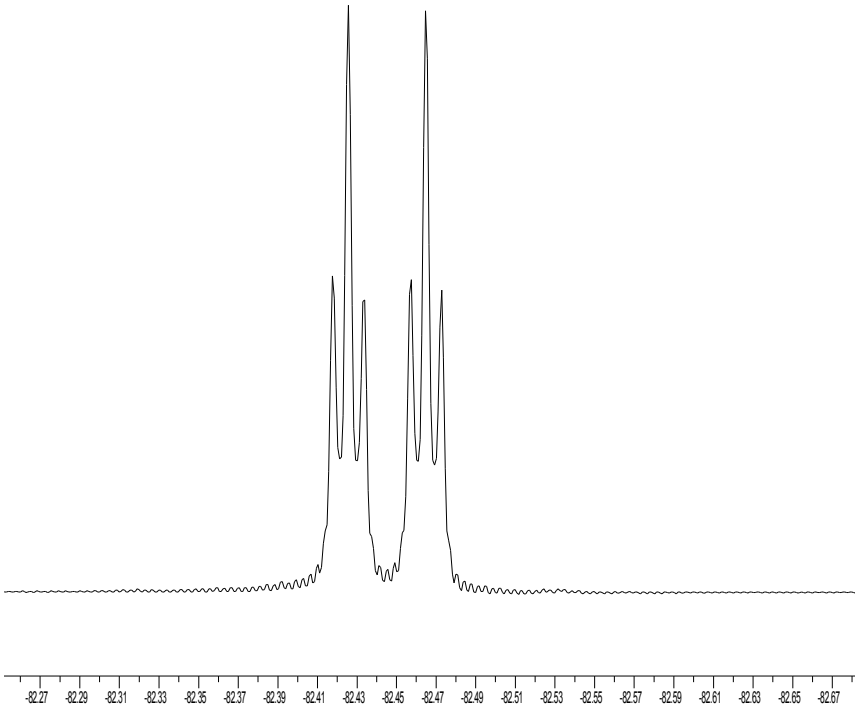
Expansion of signal at δ + 24.4 ppm in the spectrum of **8** (above)



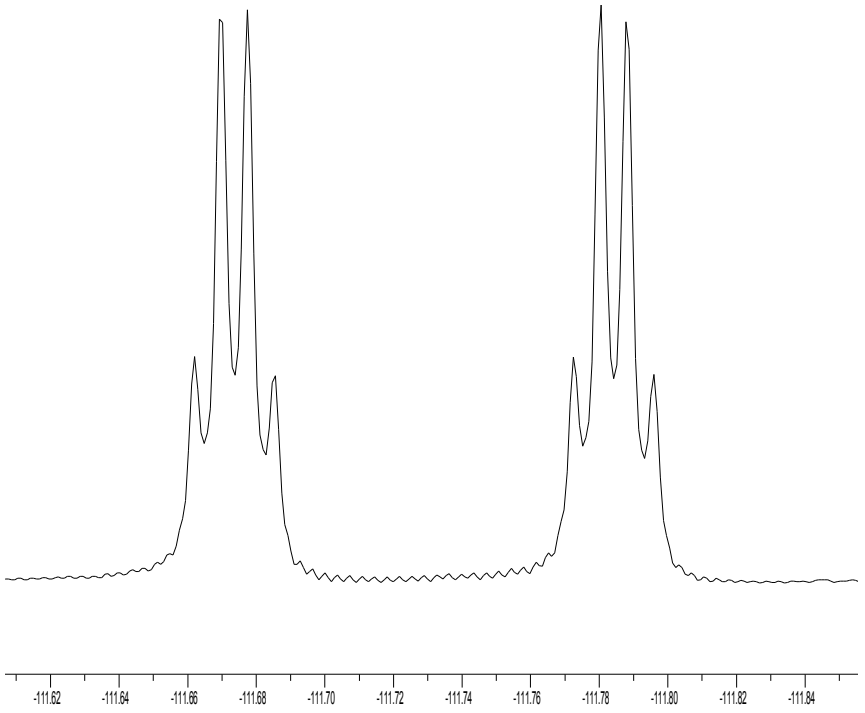
^{19}F NMR spectrum of $^{i}Pr_2PC_2F_5$, **8**



Expansions of the fluorine signals from the spectrum of $^{i}Pr_2PC_2F_5$, **8**

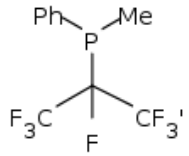


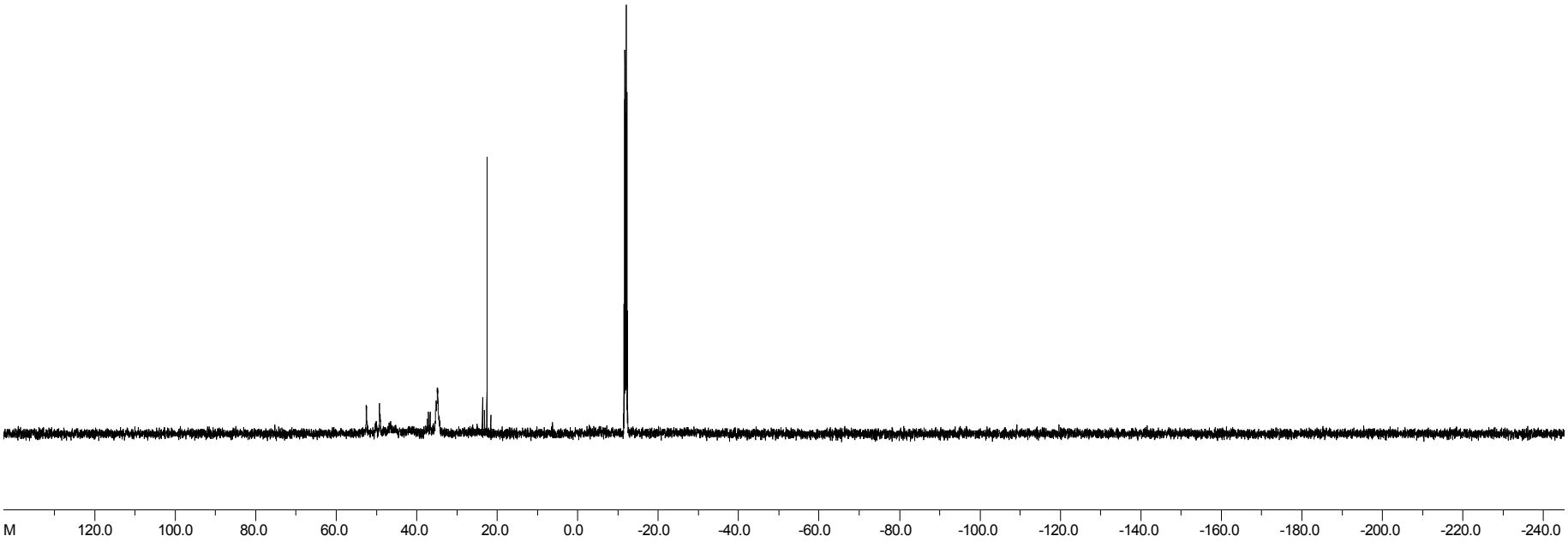
CF_3 signal



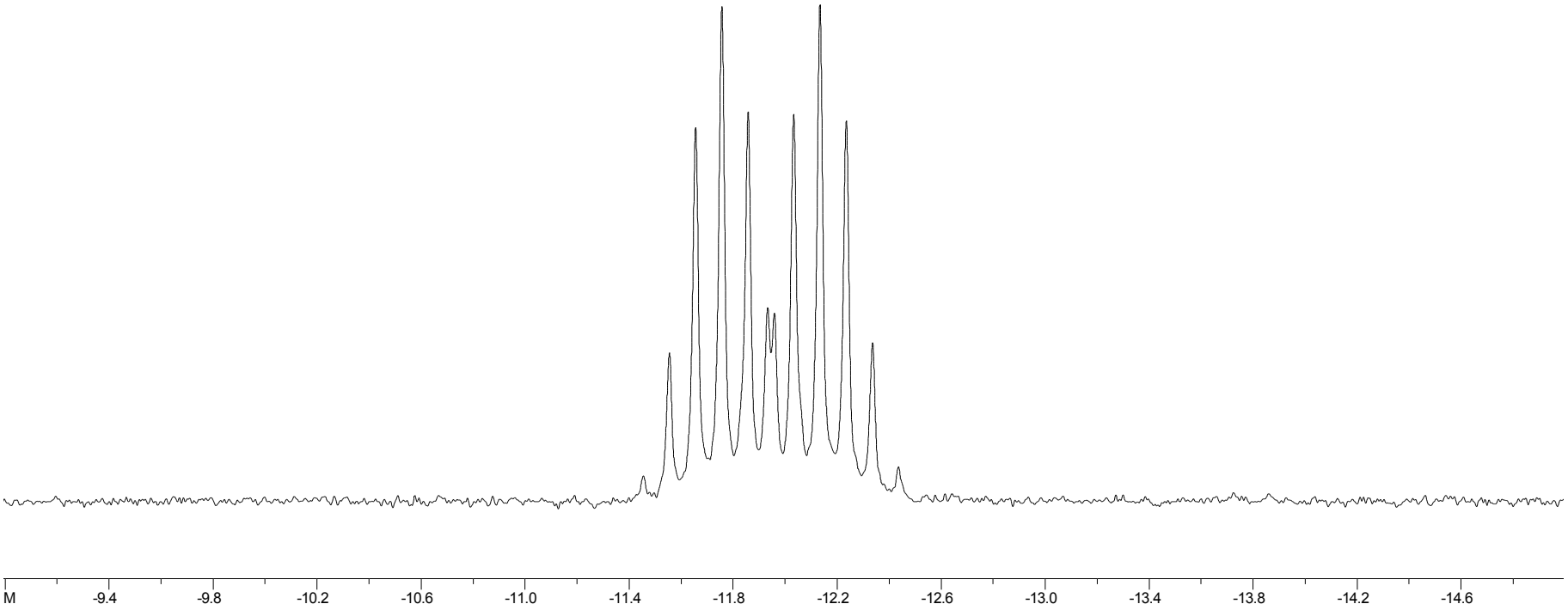
CF_2 signal

$^{31}P\{^{1}H\}$ NMR spectrum of $PhMePCF(CF_3)_2$, **9**

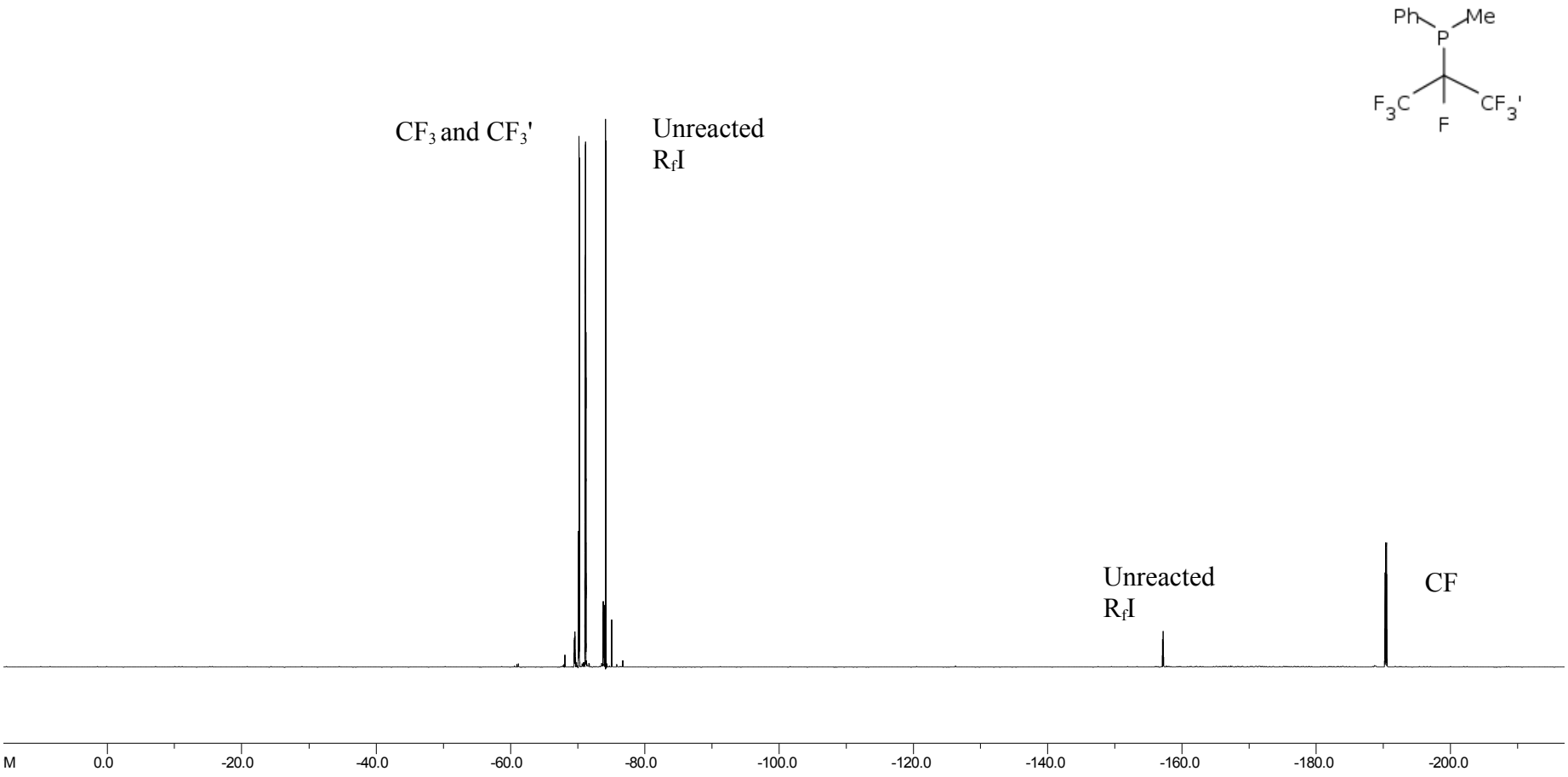




Expansion of the signal at δ -12.0 in the ^{31}P $\{^{1}H\}$ NMR spectrum of $PhMePCF(CF_3)_2$, **9**



^{19}F NMR spectrum of $PhMePCF(CF_3)_2$, **9**



Expansion of the signals for CF_3 and CF_3' in the ^{19}F NMR spectrum of $PhMePCF(CF_3)_2$, **9**