# A new route to α-alkyl-α-fluoromethylenebisphosphonates

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## Supplementary information

**General information**
NMR spectra were recorded at rt in on a Bruker Avance 400 MHz or 600 MHz instrument. Chemical shifts ($\delta$) are reported in ppm and coupling constants ($J$) are given in Hertz. GCMS spectra were recorded on an Agilent 7890A gas chromatograph coupled with a 5975C quadrupole mass-selective electron impact (EI) detector (70 eV). High-resolution mass spectra (HRMS) were recorded on a LTQ Orbitrap XL instrument using electrospray ionization (ESI). Infrared spectra were measured on a FTIR instrument. Reactions were conducted under Ar. DMF was dried under reflux with calcium hydride followed by distillation and kept over molecular sieves (3Å). Andhydrous DMSO was purchased from AlfaAesar in a ChemSeal bottle and was used as received. All other chemicals were used as received. Purification of the products was performed by flash chromatography using silica gel 60.

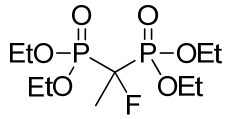
**General procedures**
**Preparation of compounds 2:**
**Method A:** Cesium carbonate (977 mg, 3 mmol, 2 eq) was added to a solution of tetraethyl fluoromethylenebisphosphonate (**1**) (459 mg, 1.5 mmol, 1 eq) and alkyl halide (2.25 mmol, 1.5 eq) in dry DMF (5 mL). The mixture was stirred under argon at rt for appropriate time, then poured into aqueous saturated solution of $NH_4Cl$ (30 mL), extracted with diethyl ether (3 × 30 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (hexane-ethyl acetate) gave pure product **2**.

**Method B:** To a 10-mL round bottom flask containing a suspension of NaH (18 mg, 0.72 mmol, 1.1 eq) in dry DMSO (3 mL) a solution of tetraethyl fluoromethylenebisphosphonate (**1**) (200 mg, 0.65 mmol, 1 eq) in dry DMSO (2 mL) was added at room temperature. The mixture was stirred for 3–4 min, then an alkyl halide (0.72 mmol, 1.1 eq) was added dropwise and the mixture was stirred at room temperature. Reaction completion was monitored by TLC or $^{19}F$ NMR. The reaction mixture was poured into aqueous saturated solution of $NH_4Cl$ (30 mL), extracted with ethyl acetate (3 × 30 mL), dried ($Na_2SO_4$ or $MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (hexane-ethyl acetate) gave pure product **2**.

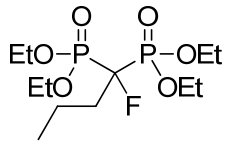
**Preparation of compounds 3:** TMSBr (165 μl, 1.25 mmol, 5 eq) was added dropwise to compound **2** (0.25 mmol, 1 eq). The mixture was stirred in a closed flask for 2 h at rt and

additional 2 h at 50°C, followed by the removal of EtBr and unreacted TMSBr under reduced pressure to give a colorless oil. Water (4 mL) was added and the solution was stirred for 1 h at rt. The resulting solution was extracted with diethyl ether (2 mL). Water from the aqueous phase was removed under reduced pressure and the product **3** was obtained by further drying under high vacuum.

**Preparation of compounds 4:** Compound **2** (0.5 mmol, 1 eq) was added to a solution of $(EtO)_2Mg$ (572 mg, 5 mmol, 10 eq) in dry ethanol (6 mL). The flask was sealed and heated to appropriate temperature for a given time. Then the mixture was cooled to rt and poured into aqueous solution of hydrochloric acid (1M, 25 mL). The product was extracted into diethyl ether (3 × 25 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. Column chromatography (hexane-ethyl acetate) gave pure products **4**.



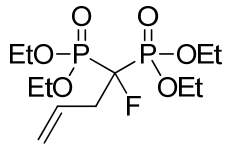
**Tetraethyl (1-fluoroethane-1,1-diyl)bis(phosphonate)**,[1] **2a**: Prepared from $Cs_2CO_3$ (977 mg, 3 mmol, 2 eq), **1** (459 mg, 1.5 mmol, 1 eq) and MeI (319 mg, 2.25 mmol, 1.5 eq) according to the general procedure (Method A, reaction time 22 h) giving **2a** as a colorless liquid (408 mg, 85%). Also prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200mg, 0.65 mmol, 1 eq) and MeI (139 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 1 h) giving **2a** as a colorless liquid (129 mg, 62%). $R_f$ = 0.36 (EtOAc); FTIR (film, $\nu_{max}$ $cm^{-1}$): 2987, 1262, 1021, 978; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.37 (t, 12H, $^3J_{HH}$ = 7.1 Hz, 4 × $CH_2CH_3$), 1.82 (dt, 3H, $^3J_{HF}$ = 25.7 Hz, $^3J_{HP}$ = 15.37 Hz, $CFCH_3$), 4.20–4.39 (m, 8H, 4 × $CH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 16.3–16.5 (m, $CH_2CH_3$), 19.2 (d, $^2J_{CF}$ = 20.6 Hz, $CFCH_3$), 64.0 (dt, $^2J_{CP}$ = 22.2 Hz, $^4J_{CF}$ = 3.1 Hz, $CH_2$), 93.0 (dt, $^1J_{CF}$ = 180.1 Hz, $^1J_{CP}$ = 156.9 Hz, CF); $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –186.5 (tq, $^2J_{FP}$ = 72.7 Hz, $^3J_{FH}$ = 25.7); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 15.2 (d, $^2J_{PF}$ = 72.7 Hz); MS: *m/z* (%) = 265 (31), 237 (30), 208 (100), 191 (32), 182 (30), 128 (38), 99 (67), 65 (40); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{10}H_{23}FNaO_6P_2$: 343.0846; found: 343.0847.



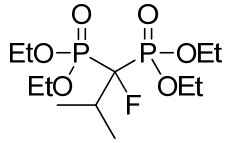
**Tetraethyl (1-fluorobutane-1,1-diyl)bis(phosphonate)**, **2b**: Prepared from $Cs_2CO_3$ (977 mg, 3 mmol, 2 eq), **1** (459 mg, 1.5 mmol, 1 eq) and *n*-PrBr (277 mg, 2.25 mmol, 1.5 eq) according to the general procedure (Method A, reaction time 144 h) giving **2b** as a colorless liquid (298 mg, 57%). $R_f$ = 0.19 (EtOAc); FTIR (film, $\nu_{max}$ $cm^{-1}$): 2982, 2935, 2914, 2876, 1262, 1021, 974; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.89 (t, 3H, $^3J_{HH}$ = 7.4 Hz, $CH_3$), 1.30 (t, 12H, $^3J_{HH}$ = 7.1 Hz, 4 × $OCH_2CH_3$), 1.56–1.66 (m, 2H, $CH_2$), 2.00–2.16 (m, 2H, $CH_2$), 4.15–4.26 (m, 8H, 4 × $OCH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.4, 16.3–16.4 (m), 16.4–16.6 (m), 35.3 (d, $^2J_{CF}$ = 20.0 Hz, $CFCH_2$), 63.7 (dt, $^2J_{CP}$ = 21.6 Hz, $^4J_{CF}$ = 3.2 Hz, $OCH_2$), 95.8 (dt, $^1J_{CF}$ = 187.5 Hz, $^1J_{CP}$ = 156.4 Hz, CF); $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –192.9 (tt, $^2J_{FP}$ = 74.8 Hz, $^3J_{FH}$ = 23.8 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 14.6 (d, $^2J_{PF}$ = 74.8 Hz); MS: *m/z* (%) = 319

(1) Iorga, B.; Eymery, F.; Savignac, P. *Tetrahedron Lett.* **1998**, *39*, 4477.

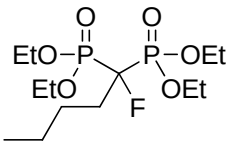
(38), 306 (57), 291 (53), 263 (38), 235 (52), 211 (37), 207 (100), 183 (33), 170 (27), 155 (35), 127 (33); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{27}FNaO_6P_2$: 371.1159; found: 371.1159.



**Tetraethyl (1-fluorobut-3-ene-1,1-diyl)bis(phosphonate)**, **2c**: Prepared from $Cs_2CO_3$ (977 mg, 3 mmol, 2 eq), **1** (459 mg, 1.5 mmol, 1 eq) and allyl bromide (272 mg, 2.25 mmol, 1.5 eq) according to the general procedure (Method A, reaction time 160 h) giving **2c** as a colorless liquid (519 mg, 78%). Also prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and allyl bromide (119 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 1 h) giving **2a** as a colorless liquid (133 mg, 59%). $R_f$ = 0.28 (hexane:acetone, 2:1); FTIR (film, $\nu_{max}$ $cm^{-1}$): 3082, 2985, 1642, 1263, 1024, 976; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.37 (t, 12H, $^3J_{HH}$ = 7.0 Hz, 4 × $CH_2CH_3$), 2.89–3.04 (m, 2H, $CFCH_2$), 4.21–4.37 (m, 8H, 4 × $CH_2CH_3$), 5.16–5.24 (m, 2H, $=CH_2$), 5.95–6.07 (m, 1H, CH); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 16.4–16.5 (m), 37.7 (d, $^2J_{CF}$ = 20.6 Hz, $CFCH_2$), 63.8–64.2 (m), 94.7 (dt, $^1J_{CF}$ = 189.9 Hz, $^1J_{CP}$ = 156.7 Hz, CF), 119.2, 130.4 (m); $^{19}F$ NMR (376 MHz, $CDCl_3$): $\delta$ = –192.6 (tt, $^2J_{FP}$ = 73.6 Hz, $^3J_{FH}$ = 23.5 Hz); $^{31}P$ $\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 13.9 (d, $^2J_{PF}$ = 73.6 Hz); MS: *m/z* (%) = 209 (100), 181 (29), 153 (68), 81 (28), 65 (25); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{25}FNaO_6P_2$: 369.1003; found: 369.1002.

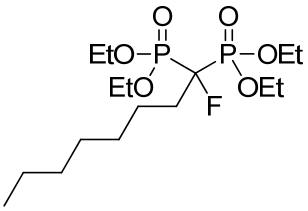


**Tetraethyl (1-fluoro-2-methylpropane- 1,1-diyl)bis(phosphonate)**, **2d**: Prepared from $Cs_2CO_3$ (977 mg, 3 mmol, 2 eq), **1** (459 mg, 1.5 mmol, 1 eq) and *i*-PrI (383 mg, 2.25 mmol, 1.5 eq) according to the general procedure (Method A, reaction time 96 h) giving **2d** as a colorless liquid (298 mg, 57%). $R_f$ = 0.22 (EtOAc); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.24 (d, 6H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 1.37 (t, 12H, $^3J_{HH}$ = 7.1 Hz, 4 × $CH_2CH_3$), 2.50–2.71 (m, 1H, CH), 4.22–4.35 (m, 8H, 4 × $CH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 16.3–16.5 (m, $CH_3$), 17.4–17.5 (m, $CH_3$), 33.5 (d, $^2J_{CF}$ = 19.6 Hz, CH), 63.6–63.7 (m, $CH_2$), 99.0 (dt, $^1J_{CF}$ = 185.0 Hz, $^1J_{CP}$ = 152.9 Hz, CF); $^{19}F$ NMR (376 MHz, $CDCl_3$): $\delta$ = –184.7 (dt, $^2J_{FP}$ = 75.8 Hz, $^3J_{FH}$ = 10.9 Hz); $^{31}P$ $\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ = 14.7 (d, $^2J_{PF}$ = 75.8 Hz); MS: *m/z* (%) = 333 (43), 306 (54), 305 (55), 277 (36), 249 (48), 221 (100), 211 (72), 170 (36), 155 (43), 81 (42), 65 (35); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{27}FNaO_6P_2$: 371.1159; found: 371.1159.

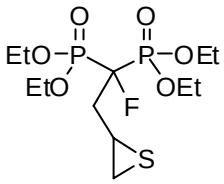


**Tetraethyl (1-fluoropentane-1,1-diyl)bis(phosphonate)**, **2e**: Prepared from $Cs_2CO_3$ (977 mg, 3 mmol, 2 eq), **1** (459 mg, 1.5 mmol, 1 eq) and *n*-BuI (414 mg, 2.25 mmol, 1.5 eq) according to the general procedure (Method A, reaction time 19 h) giving **2e** as a colorless liquid (402 mg, 74%). $R_f$ = 0.40 (hexane:acetone, 2:1); FTIR (film, $\nu_{max}$ $cm^{-1}$): 2983, 2965, 2934, 2913, 2875, 1393, 1369, 1260, 1024, 977; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.93 (t, 3H, $^3J_{HH}$ = 7.3 Hz, $CH_3$), 1.31–1.42 (m, 2H, $CH_2$), 1.37 (t, 12H, $^3J_{HH}$ = 7.0 Hz, 4 × $OCH_2CH_3$), 1.59–1.69 (m, 2H, $CH_2$), 2.05–2.25 (m, 2H, $CH_2$), 4.22–4.33 (m, 8H, 4 × $OCH_2$); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 13.9, 16.4–16.7 (m), 23.3, 25.0–25.2 (m), 33.1 (d, $^2J_{CF}$ = 19.5 Hz,

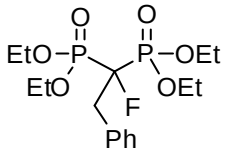
CF*C*H$_2$), 63.6–64.0 (m, OCH$_2$), 95.9 (dt, $^1J_{CF}$ = 187.5 Hz, $^1J_{CP}$ = 157.4 Hz, CF); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = –192.8 (tt, $^2J_{FP}$ = 74.9 Hz, $^3J_{FH}$ = 23.8 Hz); $^{31}$P {$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ = 14.7 (d, $^2J_{PF}$ = 74.9 Hz); MS: *m/z* (%) = 319 (42), 306 (95), 291 (54), 279 (30), 263 (41), 235 (45), 225 (45), 207 (100), 183 (35), 170 (37), 127 (51); HRMS: *m/z* [M + H]$^+$ calcd for $C_{13}H_{30}FO_6P_2$: 363.1496; found: 363.1496.



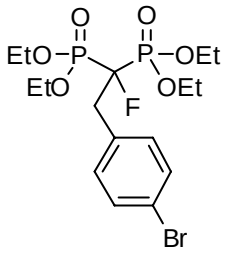
**Tetraethyl (1-fluorooctane-1,1-diyl)bis(phosphonate)**, **2f**: Prepared from $Cs_2CO_3$ (977 mg, 3 mmol, 2 eq), **1** (459 mg, 1.5 mmol, 1 eq) and *n*-$C_7H_{15}I$ (509 mg, 2.25 mmol, 1.5 eq) according to the general procedure (Method A, reaction time 120 h) giving **2f** as a colorless liquid (497 mg, 82%). $R_f$ = 0.27 (EtOAc); FTIR (film, $\nu_{max}$ cm$^{-1}$): 2983, 2960, 2930, 2872, 2857, 1262, 1024, 976; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.86–0.90 (m, 3H, CH$_3$), 1.27–1.32 (m, 8H, 4 × CH$_2$), 1.37 (t, 12H, $^3J_{HH}$ = 7.1 Hz, 4 × OCH$_2$C*H*$_3$), 1.61–1.68 (m, 2H, CH$_2$), 2.05–2.45 (m, 2H, CH$_2$), 4.22–4.33 (m, 8H, 4 × OCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.0, 16.4–16.5 (m), 22.6, 22.9–23.0 (m), 28.9, 29.9, 31.7, 33.3 (d, $^2J_{CF}$ = 20.1 Hz, CF*C*H$_2$), 63.8 (dt, $^2J_{CP}$ = 22.0 Hz, $^4J_{CF}$ = 3.3 Hz, OCH$_2$), 95.9 (dt, $^1J_{CF}$ = 187.7 Hz, $^1J_{CP}$ = 156.4 Hz, CF); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = –192.8 (tt, $^2J_{FP}$ = 75.1 Hz, $^3J_{FH}$ = 23.8 Hz); $^{31}$P {$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ = 14.7 (d, $^2J_{PF}$ = 75.1 Hz); MS: *m/z* (%) = 319 (21), 306 (100), 291 (26), 279 (30), 274 (39), 267 (48), 247 (23), 235 (25), 207 (39), 183 (23), 170 (29), 127 (36), 109 (22); HRMS: *m/z* [M + H]$^+$ calcd for $C_{16}H_{36}FO_6P_2$: 405.1966; found: 405.1965.



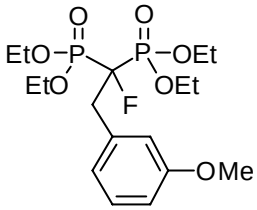
**Tetraethyl (1-fluoro-2-(thiiran-2-yl)ethane-1,1-diyl)bis(phosphonate)**, **2h**: Prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and 2-(chloromethyl)thiirane (106 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 12 h) giving **2h** as a colorless oil (162 mg, 59%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.32 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 x CH$_3$), 1.34 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 x CH$_3$), 2.13 (m, 1H), 2.26 (d, 1H, $^3J_{HH}$ = 5.8 Hz), 2.52 (d, 1H, $^3J_{HH}$ = 5.8 Hz), 2.87 (dt, 1H, $^3J_{HF}$ = 26.2 Hz, $^3J_{HP}$ = 13.7 Hz, C*H*$^a$H$^b$), 3.22 (dt, 1H, $^3J_{HF}$ = 26.2 Hz, $^3J_{HP}$ = 13.7 Hz, CH$^a$*H*$^b$), 4.19–4.31 (m, 8H, 4 × CH$_2$); $^{13}$C (100 MHz, CDCl$_3$): $\delta$ = 16.4 (m), 26.4, 28.6 (m), 40.1, 40.3, 64.0 (m), 64.3 (m), 94.7 (dt, $^1J_{CF}$ = 189.8 Hz, $^1J_{CP}$ = 155.1 Hz, CF); $^{19}$F NMR (372 MHz, CDCl$_3$): $\delta$ = –194.1 (tt, $^2J_{FP}$ = 73.8 Hz, $^3J_{FH}$ = 26.2 Hz); $^{31}$P {$^1$H} NMR (162 MHz, CDCl$_3$): $\delta$ = 13.9 (d, $^2J_{PF}$ = 73.8 Hz); HRMS: *m/z* [M + H]$^+$ calcd for $C_{12}H_{26}FO_6P_2S$: 379.0909; found: 379.0904.



**Tetraethyl (1-fluoro-2-phenylethane-1,1-diyl)bis(phosphonate)**, **2i**: Prepared from $Cs_2CO_3$ (977 mg, 3 mmol, 2 eq), **1** (459 mg, 1.5 mmol, 1 eq) and BnBr (385 mg, 2.25 mmol, 1.5 eq) according to the general procedure (Method A, reaction time 20 h) giving **2i** as a colorless liquid (440 mg, 74%). Also prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and BnBr (168 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 1 h) giving **2i** as a colorless liquid (214 mg, 83%). $R_f$ = 0.18 (EtOAc); FTIR (film, $\nu_{max}$ $cm^{-1}$): 3089, 3064, 3034, 2984, 1605, 1497, 1262, 1025, 978, 701, 653; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.25 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 1.26 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 3.45–3.58 (m, 2H, $PhCH_2$), 4.03–4.33 (m, 8H, 4 × $CH_2$), 7.24–7.30 (m, 3H, $C_{Ar}H$), 7.34–7.36 (m, 2H, $C_{Ar}H$); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 16.3, 28.5 (d, $^2J_{CF}$ = 19.0 Hz, $PhCH_2$), 63.8 (dt, $^2J_{CP}$ = 37.0 Hz, $^4J_{CF}$ = 3.2 Hz, $OCH_2$), 95.8 (dt, $^1J_{CF}$ = 192.7 Hz, $^1J_{CP}$ = 155.0 Hz, CF), 126.9, 127.7, 131.2, 134.1–134.2 (m); $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –193.6 (tt, $^2J_{FP}$ = 72.6 Hz, $^3J_{FH}$ = 28.2 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 13.4 (d, $^2J_{PF}$ = 72.6 Hz); MS: *m/z* (%) = 260 (14), 259 (100), 231 (16), 203 (45), 91 (16); HRMS: *m/z* $[M + H]^+$ calcd for $C_{16}H_{28}FO_6P_2$: 397.1340; found: 397.1340.

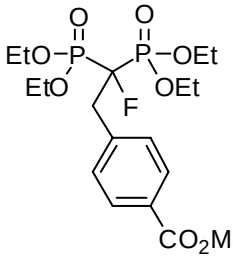



**Tetraethyl (2-(4-bromophenyl)-1-fluoroethane-1,1-diyl)bis(phosphonate)**, **2j**: Prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and 1-bromo-4-(bromomethyl)benzene (245 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 2 h) giving **2j** as a colorless oil (133 mg, 43%). $^1$H NMR (400MHz, $CDCl_3$): $\delta$ = 1.25 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 1.26 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 3.43 (dt, 2H, $^3J_{HF}$ = 27.8 Hz, $^3J_{HP}$ = 12.5 Hz, $CH_2$), 4.04–4.26 (m, 8H, 4 × $CH_2$), 7.17–7.22 (m, 2H, $C_{Ar}H$), 7.37–7.41 (m, 2H, $C_{Ar}H$); $^{13}$C NMR (100MHz, $CDCl_3$): $\delta$ = 16.3 (m), 37.8 (d, $J$ = 20.1 Hz), 63.8 (m), 64.1 (m), 95.0 (dt, $^1J_{CF}$ = 191.5 Hz, $^1J_{CP}$ = 154.3 Hz, CF), 121.01, 130.8, 132.8, 133.1 (m); $^{19}$F NMR (376MHz, $CDCl_3$): $\delta$ = –193.8 (dt, $^2J_{FP}$ = 72.6 Hz, $^3J_{FH}$ = 27.8 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 13.6 (d, $^2J_{PF}$ = 72.6 Hz); HRMS: *m/z* $[M + H]^+$ calcd for $C_{16}H_{26}BrFO_6P_2$: 475.0450; found: 405.0445.

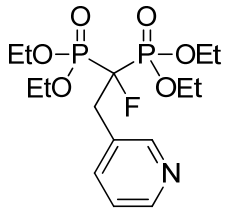



**Tetraethyl (1-fluoro-2-(3-methoxyphenyl)ethane-1,1-diyl)bis(phosphonate)**, **2k**: Prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and 1-(bromomethyl)-3-methoxybenzene (197 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 2 h) giving **2k** as a colorless oil (125 mg, 45%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.25 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 1.26 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 3.48 (dt, 2H, $^3J_{HF}$ = 28.2 Hz, $^3J_{HP}$ = 12.4 Hz, $CH_2$), 3.78 (s, 3H, $OCH_3$), 4.03–4.27 (m, 8H, 4 × $CH_2$), 6.73–6.80 (m, 1H, $C_{Ar}H$), 6.90 (s, 1H, $C_{Ar}H$), 6.86–6.94 (m, 1H, $J$ = 7.8 Hz, $C_{Ar}H$), 7.12–7.19 (m,

1H, $J$ = 7.8Hz, $C_{Ar}H$); $^{13}C$ (100 MHz, $CDCl_3$): $\delta$ = 16.3 (m), 38.4, 38.6, 55.2, 63.7 (m), 64.1 (m), 94.8 (dt, $^1J_{CF}$ = 192.9 Hz, $^1J_{CP}$ = 155.0 Hz, CF), 112.7, 116.6, 123.7, 128.6, 135.5 (m), 159.1; $^{19}F$ NMR (372 MHz, $CDCl_3$): $\delta$ = –193.4 (tt, $^2J_{FP}$ = 72.7 Hz, $^3J_{FH}$ = 28.2 Hz); $^{31}P$ {$^1H$} NMR (162 MHz, $CDCl_3$): $\delta$ = 13.0 (d, $^2J_{PF}$ = 72.7 Hz); HRMS: *m/z* [M + H]$^+$ calcd for $C_{17}H_{30}FO_7P_2$: 427.1451; found: 427.1445.

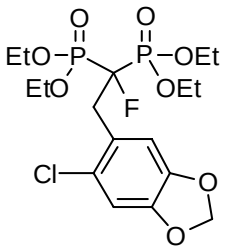



**Methyl 4-(2,2-bis(diethoxyphosphoryl)-2-fluoroethyl)benzoate**, **2l**: Prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and methyl 4-(bromomethyl)benzoate (225 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 1 h) giving **2l** as a colorless oil (148 mg, 50%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.24 (t, 6H, $^3J_{HH}$ = 6.8 Hz, 2 × $CH_3$), 1.26 (t, 6 H, $^3J_{HH}$ = 6.8 Hz, 2 × $CH_3$), 3.54 (dt, 2H, $^3J_{HF}$ = 27.8 Hz, $^3J_{HP}$ = 12.4 Hz, $CH_2$), 3.90 (s, 3H, $OCH_3$), 4.06–4.30 (m, 8H, 4 × $CH_2$), 7.39–7.44 (m, 2H, $C_{Ar}H$), 7.92–7.97 (m, 2H, $C_{Ar}H$); $^{13}C$ (100 MHz, $CDCl_3$): $\delta$ = 16.4 (m), 38.3, 38.5, 52.0, 63.8 (m), 64.2 (m), 95.8 (dt, $^1J_{CF}$ = 193.3 Hz, $^1J_{CP}$ = 155.6 Hz, CF), 128.8, 129.0, 131.2, 139.6 (m), 167.0; $^{19}F$ NMR (372 MHz, $CDCl_3$): $\delta$ = –193.7 (tt, $^2J_{FP}$ = 72.5 Hz, $^3J_{FH}$ = 27.8 Hz); $^{31}P$ {$^1H$} NMR (162 MHz, $CDCl_3$) 13.6 (d, $^2J_{PF}$ = 72.5 Hz); HRMS: *m/z* [M + H]$^+$ calcd for $C_{18}H_{30}FO_8P_2$: 455.1400; found: 455.1395.

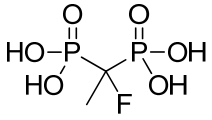



**Tetraethyl (1-fluoro-2-(pyridine-3-yl)ethane-1,1-diyl)bis(phosphonate)**,[2] **2m**: Prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and 3-(bromomethyl)pyridine (169 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 3 h) giving **2m** as a colorless oil (109 mg, 46%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.22 (t, 6H, $^3J_{HH}$ = 7.0 Hz, 2 × $CH_3$), 1.24 (t, 6H, $^3J_{HH}$ = 7.0 Hz, 2 × $CH_3$), 3.47 (dt, 2H, $^3J_{HF}$ = 27.6 Hz, $^3J_{HP}$ = 13.7 Hz, $CH_2$), 4.11–4.20 (m, 8H, 4 × $CH_2$), 7.16–7.22 ( m, 1H, $C_{Ar}H$), 7.61–7.66 (m, 1H, $C_{Ar}H$), 8.44–8.55 (m, 1H, $C_{Ar}H$), 8.52 (s, 1H, $C_{Ar}H$); $^{13}C$ (100 MHz, $CDCl_3$): $\delta$ = 16.2 (m), 35.7, 35.9, 63.8 (m), 64.2 (m), 95.0 (dt, $^1J_{CF}$ = 192.3 Hz, $^1J_{CP}$ = 156.0 Hz, CF), 122.7, 138.5, 148.2, 151.7 (m); $^{19}F$ NMR (372 MHz, $CDCl_3$): $\delta$ = –193.8 (tt, $^2J_{FP}$ = 72.6 Hz, $^3J_{FH}$ = 27.6 Hz); $^{31}P$ {$^1H$} NMR (162 MHz, $CDCl_3$): $\delta$ = 13.5 (d, $^2J_{PF}$ = 72.6 Hz); HRMS: *m/z* [M + H]$^+$ calcd for $C_{15}H_{27}FNO_6P_2$: 398.1298; found: 398.1292.

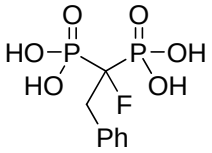
2 Inoue, S; Okauchi, T.; Minami, T. *Synthesis* **2003**, 1971.



**Tetraethyl (2-(6-chlorobenzo[*d*][1,3]dioxol-5-yl)-1-fluoroethane-1,1-diyl)bis(phosphonate)**, **2n**: Prepared from NaH (17.3 mg, 0.72 mmol, 1.1 eq), **1** (200 mg, 0.65 mmol, 1 eq) and 5-(bromomethyl)-6-chlorobenzo[*d*][1,3]dioxole (245 mg, 0.98 mmol, 1.5 eq) according to the general procedure (Method B, reaction time 12 h) giving **2n** as a colorless oil (133 mg, 43%). $^{1}$H NMR (400MHz, $CDCl_3$): $\delta$ = 1.26 (t, 6H, $^{3}J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 1.28 (t, 6H, $^{3}J_{HH}$ = 7.1 Hz, 2 × $CH_3$), 3.60 (dt, 2H, $^{3}J_{HF}$ = 27.0 Hz, $^{3}J_{HP}$ = 12.2 Hz, $CH_2$), 4.13–4.28 (m, 8H, 4 × $CH_2$), 5.91 (s, 2H, $CH_2$), 6.79 (s, 1H, $C_{Ar}H$), 6.94 (s, 1H, $C_{Ar}H$); $^{13}$C NMR (100 MHz, $CDCl_3$): 16.2 (m), 34.6 (d, $^{2}J_{CF}$ = 19.0 Hz), 63.8 (m), 64.1 (m), 95.6 (dt, $^{1}J_{CF}$ = 192.3 Hz, $^{1}J_{CP}$ = 156.0 Hz, CF), 101.5, 109.3, 112.3 (d, $J$ = 3.4 Hz), 125.1 (m), 126.9, 145.9, 147.1; $^{19}$F NMR (372 MHz, $CDCl_3$): $\delta$ = –194.2 (dt, $^{2}J_{FP}$ = 74.0 Hz, $^{3}J_{FH}$ = 27.0 Hz); $^{31}$P {$^{1}$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 13.6 (d, $^{2}J_{PF}$ = 74.0 Hz); HRMS: *m/z* $[M + H]^+$ calcd for $C_{17}H_{27}ClFO_8P_2$: 475.0854; found: 475.0848.



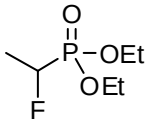
**(1-Fluoroethane-1,1-diyl)diphosphonic acid**,[3] **3a**: Prepared from TMSBr (165 µl, 1.25 mmol, 5 eq) and **2a** (80 mg, 0.25 mmol, 1 eq) according to the general procedure giving **3a** as a colorless liquid (50.4 mg, 97%). FTIR (film, $\nu_{max}$ $cm^{-1}$): 2850, 2290, 1680, 1442, 1383, 1140, 1019, 934, 824; $^{1}$H NMR (400 MHz, $D_2O$): $\delta$ = 1.70 (dt, 3H, $^{3}J_{HF}$ = 26.1 Hz, $^{3}J_{HP}$ = 15.0 Hz, $CH_3$); $^{13}$C NMR (100 MHz, $D_2O$): $\delta$ = 21.0 (d, $^{2}J_{CF}$ = 20.8 Hz, $CH_3$), 95.0 (dt, $^{1}J_{CF}$ = 178.2 Hz, $^{1}J_{CP}$ = 151.5, CF); $^{19}$F NMR (376 MHz, $D_2O$): $\delta$ = –183.5 (tq, $^{2}J_{PF}$ = 73.0 Hz, $^{3}J_{HF}$ = 26.0 Hz); $^{31}$P {$^{1}$H} NMR (162 MHz, $D_2O$): $\delta$ = 14.0 (d, $^{2}J_{PF}$ = 73.0 Hz); HRMS: *m/z* $[M - H]^-$ calcd for $C_2H_6FO_6P_2$: 206.9629; found: 206.9631.



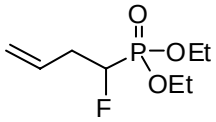
**(1-Fluoro-2-phenylethane-1,1-diyl)diphosphonic acid**, **3i**: Prepared from TMSBr (165 µl, 1.25 mmol, 5 eq) and **2i** (99 mg, 0.25 mmol, 1 eq) according to the general procedure giving **3i** as a white solid (65 mg, 92%). m.p. = 208.2–209.1 °C; FTIR (film, $\nu_{max}$ $cm^{-1}$): 3088, 3063, 3033, 3765, 3370, 1630, 1622, 1606, 1496, 1152, 990, 920, 757, 699; $^{1}$H NMR (400 MHz, $D_2O$): $\delta$ = 3.46 (dt, 2H, $^{3}J_{HF}$ = 25.7 Hz, $^{3}J_{HP}$ = 12.3 Hz, $PhCH_2$), 4.81 (br s, 4H, 4 × OH), 7.25–7.34 (m, 3H, $C_{Ar}H$), 7.34–7.40 (m, 2H, $C_{Ar}H$); $^{13}$C NMR (100 MHz, $D_2O$): $\delta$ = 40.2 (d, $^{2}J_{CF}$ = 18.6 Hz, $CH_2$), 97.7 (dt, $^{1}J_{CF}$ = 186.5 Hz, $^{1}J_{CP}$ = 148.3, CF), 129.8, 130.8, 133.7, 137.7; $^{19}$F NMR (376 MHz, $D_2O$): $\delta$ = –192.3 (tt, $^{2}J_{PF}$ = 73.7 Hz, $^{3}J_{HF}$ = 26.0 Hz); $^{31}$P {$^{1}$H} NMR

3 Martynov, B. I.; Sokolov, V. B.; Aksinenko, A. Yu.; Goreva, T. V.; Epishina, T. A.; Pushin, A. N. *Russian Chem. Bull.* **1998** , *47*, 1983.

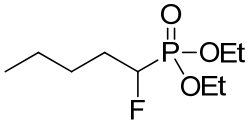
(162 MHz, $D_2O$): $\delta$ = 12.9 (d, $^2J_{PF}$ = 73.7 Hz); HRMS: *m/z* $[M - H]^-$ calcd for $C_8H_{10}FO_6P_2$: 282.9942; found: 282.9948.



**Diethyl (1-fluoroethyl)phosphonate,**[4] **4a:** Prepared from **2a** (160 mg, 0.5 mmol, 1 eq) and $(EtO)_2Mg$ (572 mg, 5 mmol, 10 eq) according to the general procedure (145°C, 22 h) giving an inseparable mixture of **4a** and triethylphosphate as a colorless liquid (corresponding to 24 mg, 26% of pure **4a**). $R_f$ = 0.32 ($CH_2Cl_2$: EtOAc, 4:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.38 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_2CH_3$), 1.60 (ddd, 3H, $^3J_{HF}$ = 25.6 Hz, $^3J_{HP}$ = 16.7 Hz, $^3J_{HH}$ = 7.1 Hz, $CH_3$), 4.22 (dq, 4H, $^3J_{HP}$ = 15.1 Hz, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_2CH_3$), 4.87 (ddq, 1H, $^2J_{HF}$ = 46.3 Hz, $^2J_{HP}$ = 7.1 Hz, $^3J_{HH}$ = 2.4 Hz, CFH); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 15.9–16.1 (m), 16.3–16.5 (m), 62.9 (dd, $^2J_{CP}$ = 32.7 Hz, $^4J_{CF}$ = 6.9 Hz, $OCH_2CH_3$), 85.1 (dd, $^1J_{CF}$ = 177.7 Hz, $^1J_{CP}$ = 172.2 Hz, CHF); $^{19}$F {$^1$H} NMR (376 MHz, $CDCl_3$): $\delta$ = –202.3 (d, $^2J_{FP}$ = 75.1 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 18.7 (d, $^2J_{PF}$ = 75.1 Hz); MS: *m/z* (%) = 157 (31), 137 (26), 129 (24), 109 (100), 101 (20), 91 (26), 81 (46); HRMS: *m/z* $[M + H]^+$ calcd for $C_6H_{15}FO_3P$: 185.07374; found: 185.07352.



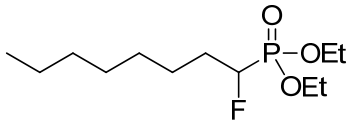
**Diethyl (1-fluorobut-3-en-1-yl)phosphonate,**[5] **4c:** Prepared from **2c** (346 mg, 1 mmol, 1 eq) and $(EtO)_2Mg$ (1.14 g, 10 mmol, 10 eq) according to the general procedure (90°C, 18 h) giving **4c** as a colorless liquid (10.5 mg, 5%). $R_f$ = 0.53 (hexane:EtOAc, 1:2); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.36 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_2CH_3$), 2.57–2.74 (m, 2H, $CH_2$), 4.21 (dq, 4H, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 7.2 Hz, 2 × $CH_2CH_3$), 4.64–4.84 (m, 1H, CFH), 5.14–5.26 (m, 2H, $CHCH_2$), 5.81–5.93 (m, 1H, $CHCH_2$); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 16.4–16.5 (m), 34.6 (d, $^2J_{CF}$ = 20.5 Hz, $CFCH_2$), 63.0 (dd, $^2J_{CP}$ = 35.9 Hz, $^4J_{CF}$ = 6.9 Hz, $OCH_2CH_3$), 88.0 (dd, $^1J_{CF}$ = 182.3 Hz, $^1J_{CP}$ = 170.0 Hz, CHF), 118.6, 131.9–132.1 (m); $^{19}$F {$^1$H} NMR (376 MHz, $CDCl_3$): $\delta$ = –208.8 (d, $^2J_{FP}$ = 75.4 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 17.6 (d, $^2J_{PF}$ = 75.4 Hz); MS: *m/z* (%) = 183 (25), 166 (29), 138 (81), 121 (25), 111 (100), 109 (74), 91 (24), 81 (85); HRMS: *m/z* $[M + H]^+$ calcd for $C_8H_{17}FO_3P$: 211.08939; found: 211.08934.



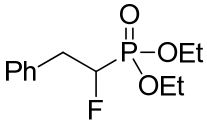
**Diethyl (1-fluoropentyl)phosphonate,**[6] **4e:** Prepared from **2e** (181 mg, 0.5 mmol, 1 eq) and $(EtO)_2Mg$ (572 mg, 5 mmol, 10 eq) according to the general procedure (150°C, 20 h) giving **4e** as a colorless liquid (69 mg, 61%). $R_f$ = 0.57 (hexane:EtOAc, 1:2); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.94 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $(CH_2)_3CH_3$), 1.37 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_2CH_3$), 1.30–1.66 (m, 4H, 2 × $CH_2$), 1.77–1.98 (m, 2H, $CH_2$), 4.21 (dq, 4H, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_2CH_3$), 4.71 (ddt, 1H, $^2J_{HF}$ = 47.0 Hz, $^2J_{HP}$ = 10.1 Hz, $^3J_{HH}$ = 3.2 Hz, CFH); $^{13}$C

4 Wnuk, S. F.; Bergolla, L. A.; Garcia, P. I. *J. Org. Chem.* **2002**, *67*, 3065.
5 Zhang, X.; Qiu, W.; Burton, D. J. *Tetrahedron Lett.* **1999**, *40*, 2681.
6 Waschbuesch, R.; Carran, J.; Savignac, P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1135.

NMR (100 MHz, $CDCl_3$): $\delta$ = 13.7, 16.3–16.5 (m), 22.1, 27.3–27.5 (m), 29.7 (d, $^2J_{CF}$ = 20.2 Hz, CF*C*$H_2$), 62.8 (dd, $^2J_{CP}$ = 38.7 Hz, $^4J_{CF}$ = 6.9 Hz, O*C*$H_2$CH$_3$), 89.0 (dd, $^1J_{CF}$ = 179.9 Hz, $^1J_{CP}$ = 169.9 Hz, CHF); $^{19}$F {$^1$H} NMR (376 MHz, $CDCl_3$): $\delta$ = –209.4 (d, $^2J_{FP}$ = 75.7 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 18.5 (d, $^2J_{PF}$ = 75.7 Hz); MS: *m/z* (%) = 183 (20), 170 (100), 143 (68), 138 (51), 114 (29), 109 (65), 101 (42), 81 (40); HRMS: *m/z* [M + H]$^+$ calcd for $C_9H_{21}FO_3P$: 227.12069; found: 227.12033.

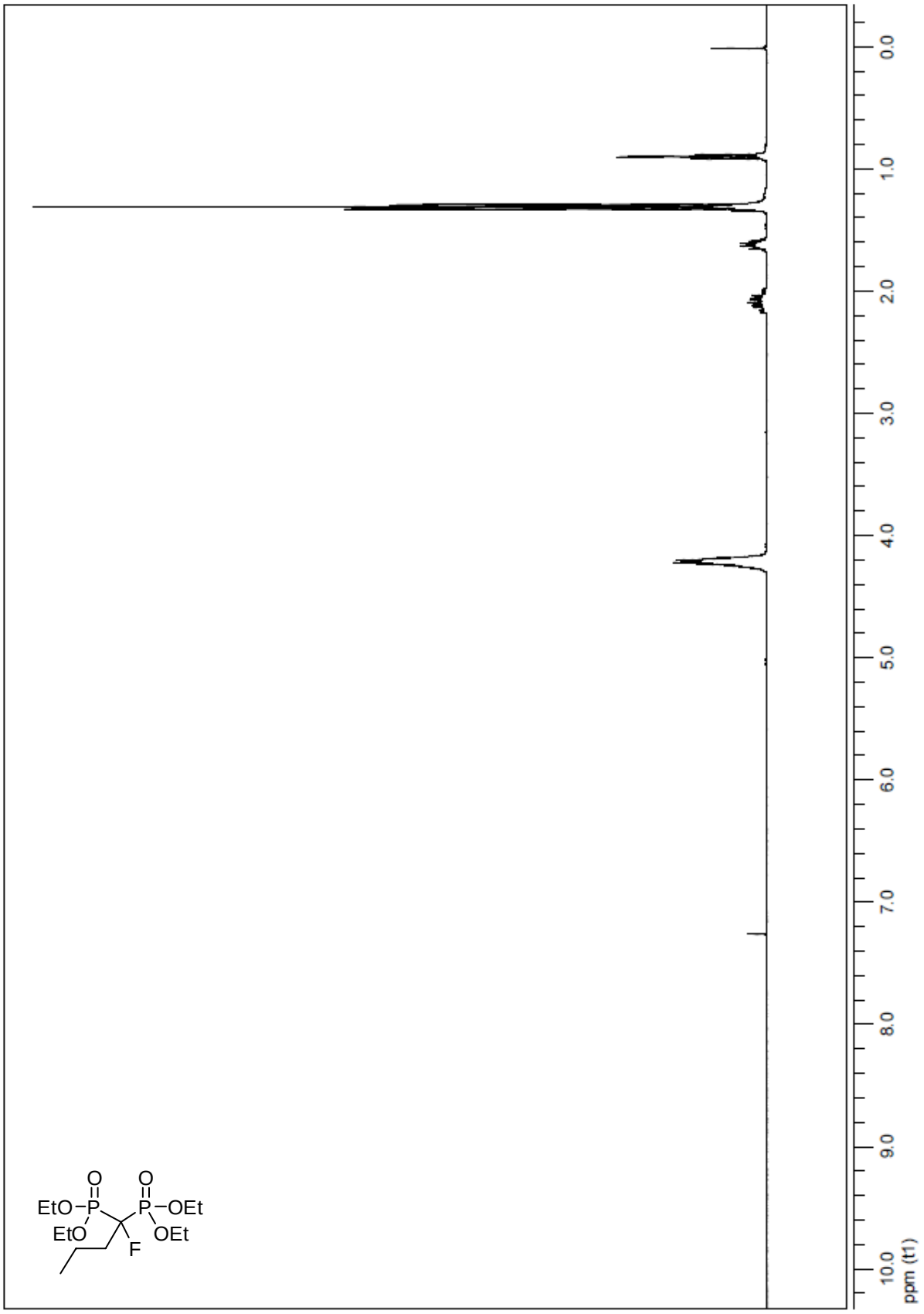



**Diethyl (1-fluorooctyl)phosphonate, 4f:** Prepared from **2f** (202 mg, 0.5 mmol, 1 eq) and $(EtO)_2Mg$ (572 mg, 5 mmol, 10 eq) according to the general procedure (155°C, 44 h) giving **4f** as a colorless liquid (83 mg, 62%). $R_f$ = 0.31 (hexane:EtOAc, 2:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.88 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $(CH_2)_6CH_3$), 1.36 (t, 6H, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_2CH_3$), 1.21–1.62 (m, 10H, 5 × $CH_2$), 1.76–1.97 (m, 2H, $CH_2$), 4.21 (dq, 4H, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 7.1 Hz, 2 × $CH_2CH_3$), 4.71 (ddt, 1H, $^2J_{HF}$ = 47.0 Hz, $^2J_{HP}$ = 10.2 Hz, $^3J_{HH}$ = 3.2 Hz, CFH); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 14.0, 16.3–16.5 (m), 22.6, 25.2–25.4 (m), 28.9, 29.0, 30.1 (d, $^2J_{CF}$ = 20.1 Hz, CF*C*$H_2$), 31.7, 62.9 (dd, $^2J_{CP}$ = 38.7 Hz, $^4J_{CF}$ = 7.0 Hz, O*C*$H_2$CH$_3$), 88.9 (dd, $^1J_{CF}$ = 179.8 Hz, $^1J_{CP}$ = 169.8 Hz, CHF); $^{19}$F NMR (376 MHz, $CDCl_3$): $\delta$ = –209.7 to –209.2 (m); $^{19}$F {$^1$H} NMR (376 MHz, $CDCl_3$): $\delta$ = –209.4 (d, $^2J_{FP}$ = 75.7 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 18.5 (d, $^2J_{PF}$ = 75.7 Hz); MS: *m/z* (%) = 211 (20), 183 (25), 170 (72), 143 (52), 138 (100), 109 (46), 81 (28); HRMS: *m/z* [M + H]$^+$ calcd for $C_{12}H_{27}FO_3P$: 269.16764; found: 269.16761.

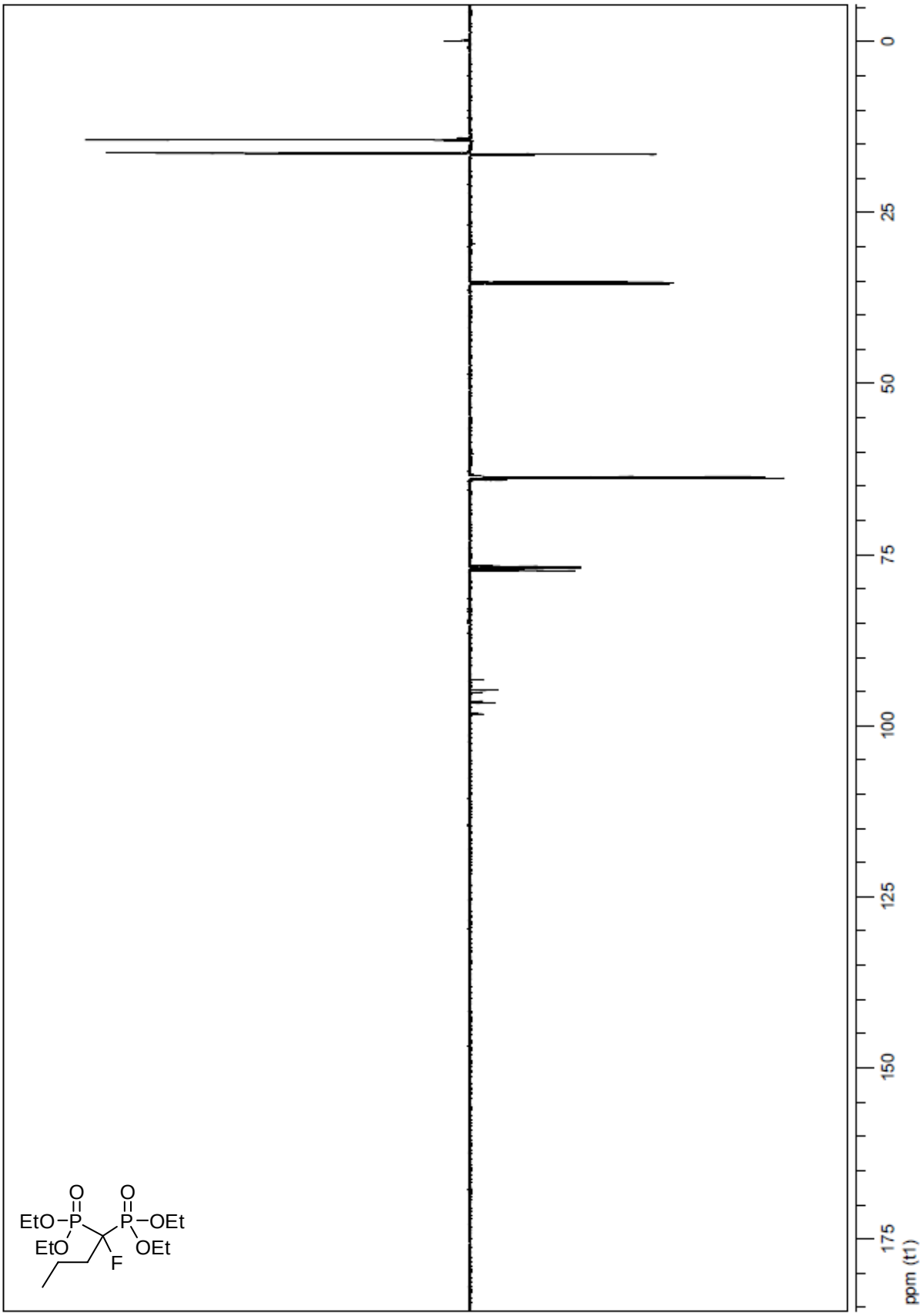



**Diethyl (1-fluoro-2-phenylethyl)phosphonate,**[7] **4i:** Prepared from **2i** (198 mg, 0.5 mmol, 1 eq) and $(EtO)_2Mg$ (572 mg, 5 mmol, 10 eq) according to the general procedure (100°C, 20 h) giving **4i** as a colorless liquid (65 mg, 50%). $R_f$ = 0.46 (EtOAc); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.35 (dt, 6H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 3.9 Hz, 2 × $CH_2CH_3$), 3.14–3.26 (m, 2H, $PhCH_2$), 4.15–4.26 (m, 4H, 2 × $CH_2CH_3$), 4.81–4.98 (m, 1H, CFH), 7.25–7.29 (m, 3H, $C_{Ar}H$), 7.30–7.35 (m, 2H, $C_{Ar}H$); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 16.3–16.5 (m), 36.5 (d, $^2J_{CF}$ = 20.3 Hz, CF*C*$H_2$), 63.1 (dd, $^2J_{CP}$ = 41.7 Hz, $^4J_{CF}$ = 6.9 Hz, O*C*$H_2$CH$_3$), 89.1 (dd, $^1J_{CF}$ = 183.3 Hz, $^1J_{CP}$ = 168.8 Hz, CHF), 127.0, 128.5, 129.1, 136.1–136.3 (m); $^{19}$F {$^1$H} NMR (376 MHz, $CDCl_3$): $\delta$ = –207.4 (d, $^2J_{FP}$ = 75.2 Hz); $^{31}$P {$^1$H} NMR (162 MHz, $CDCl_3$): $\delta$ = 17.4 (d, $^2J_{PF}$ = 75.2 Hz); MS: *m/z* (%) 240 (26), 187 (18), 148 (24), 138 (30), 131 (100), 122 (26), 111 (81), 103 (35), 91 (36), 82 (37); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{12}H_{18}NaFO_3P$: 283.0870; found: 283.0870.

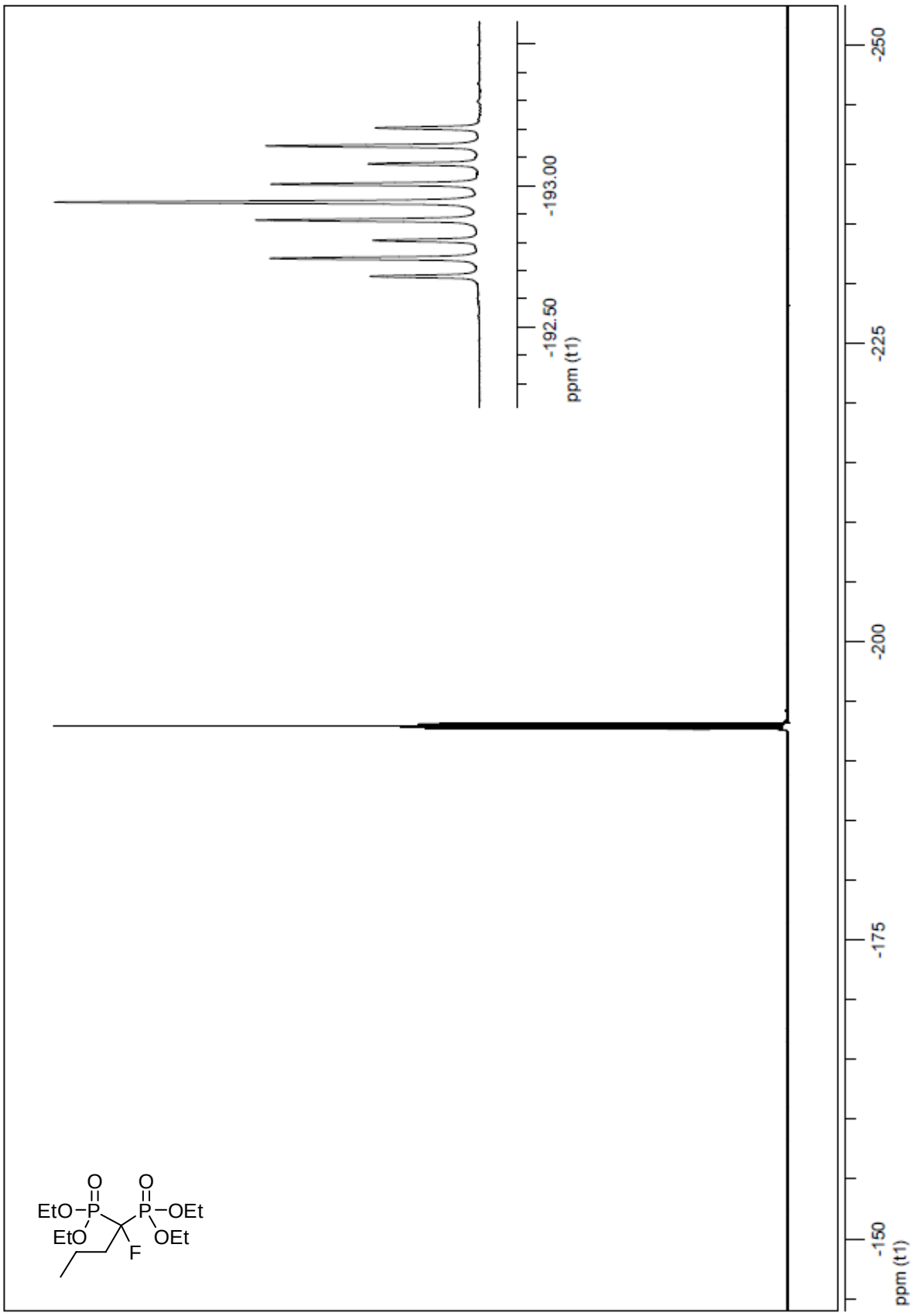
7 Blackburn, G. M.; Parratt, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1270.



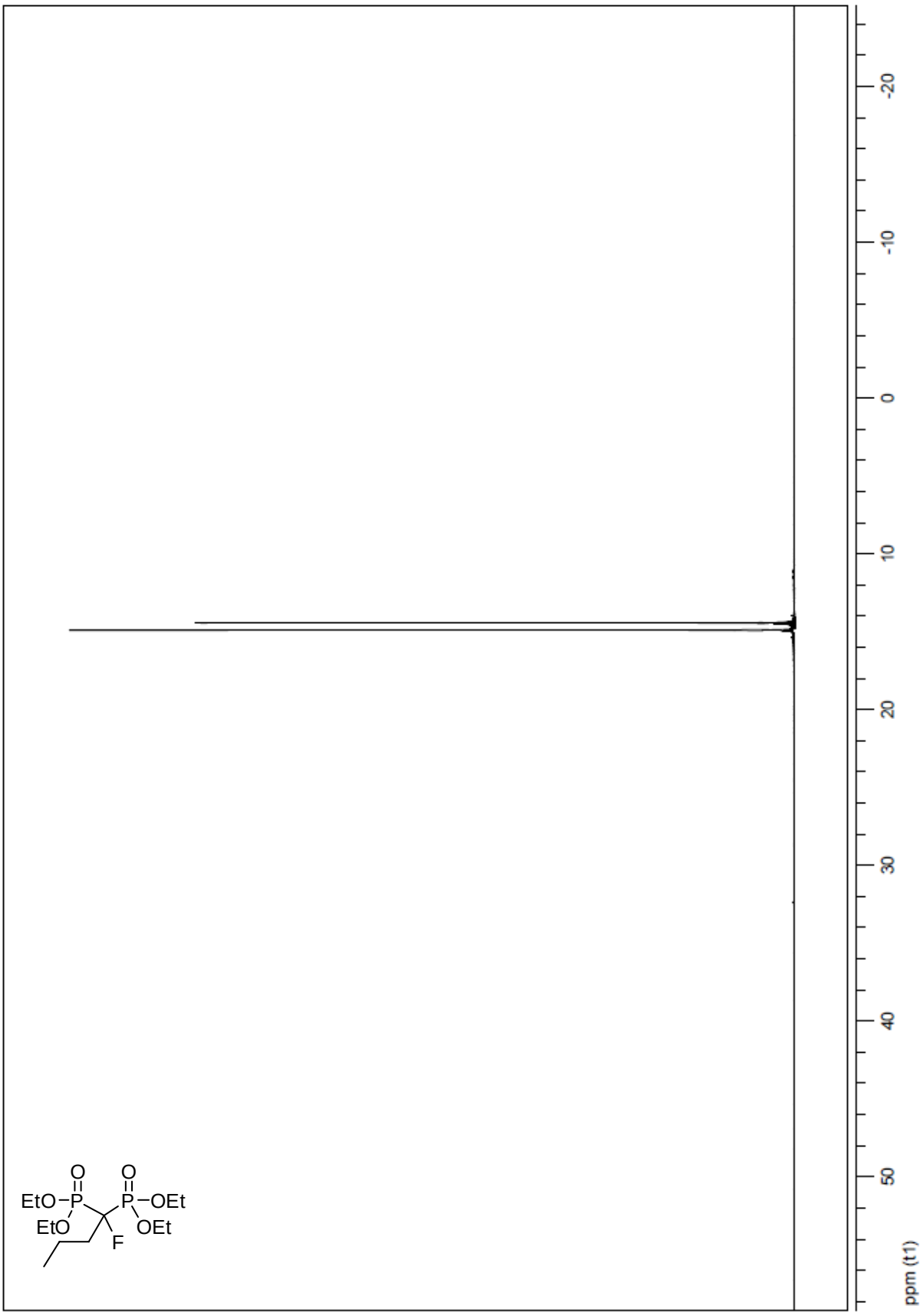

$^{1}$H NMR spectrum of **2b**.



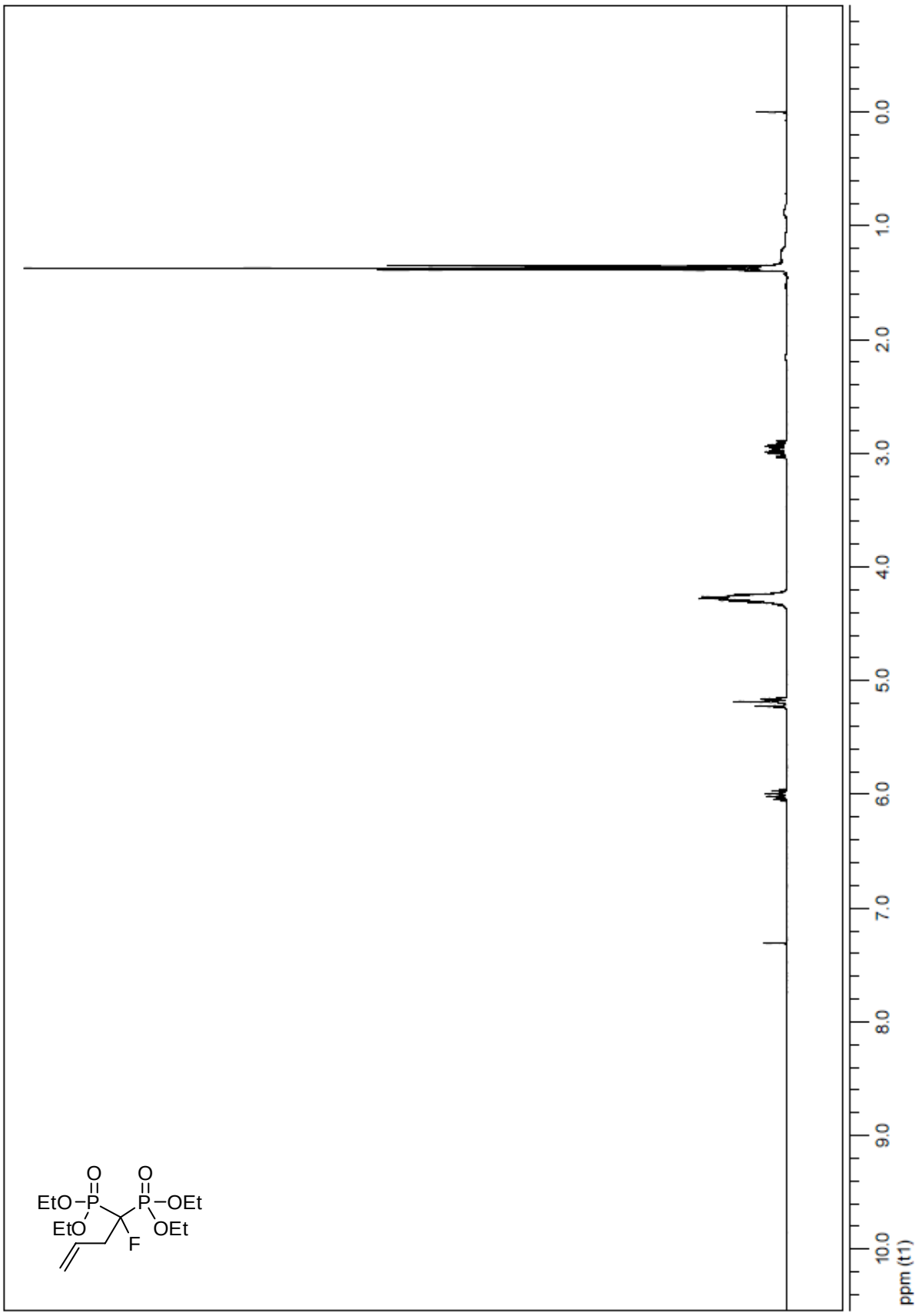

$^{13}$C NMR spectrum of **2b**.



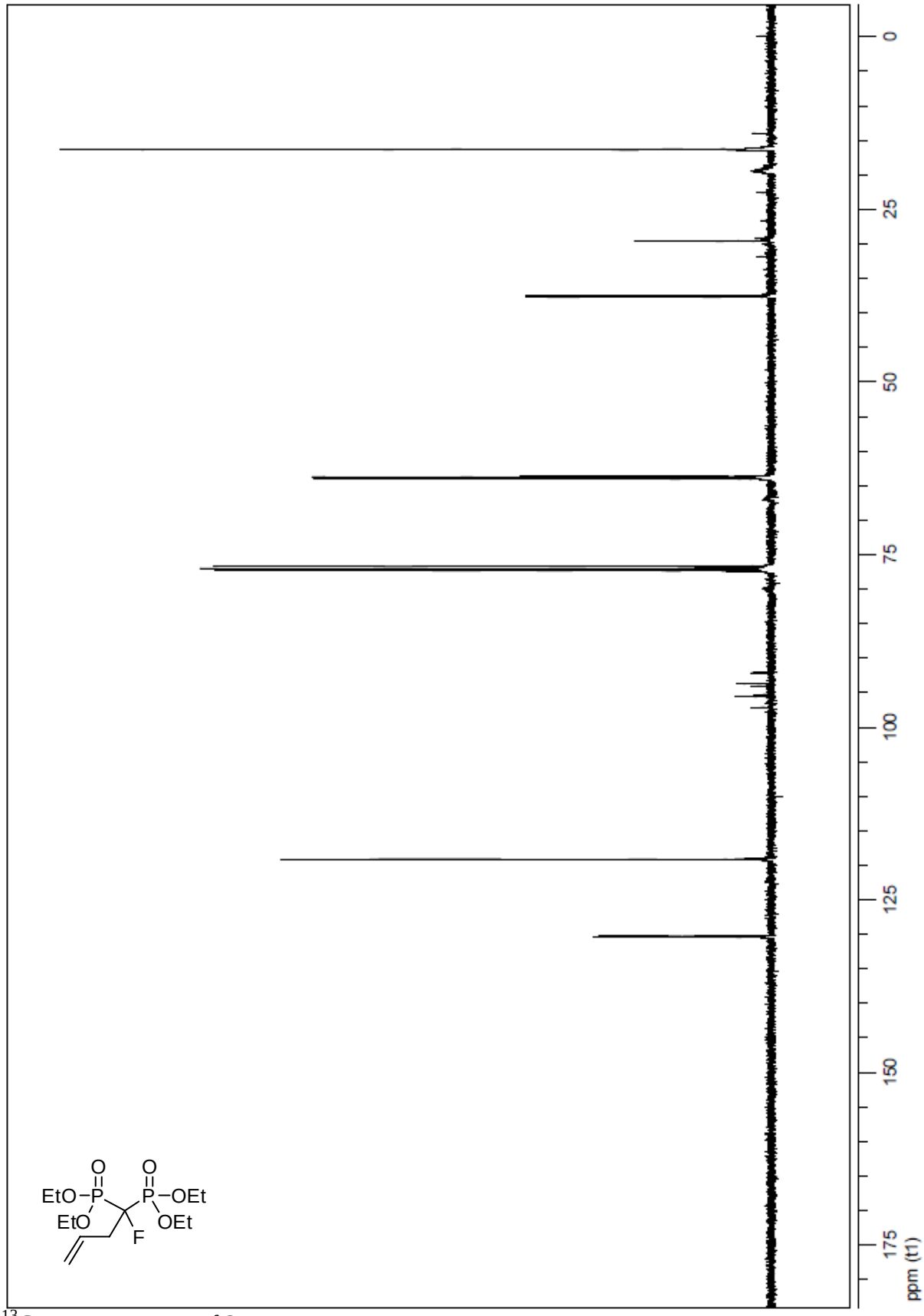

$^{19}$F NMR spectrum of **2b**.



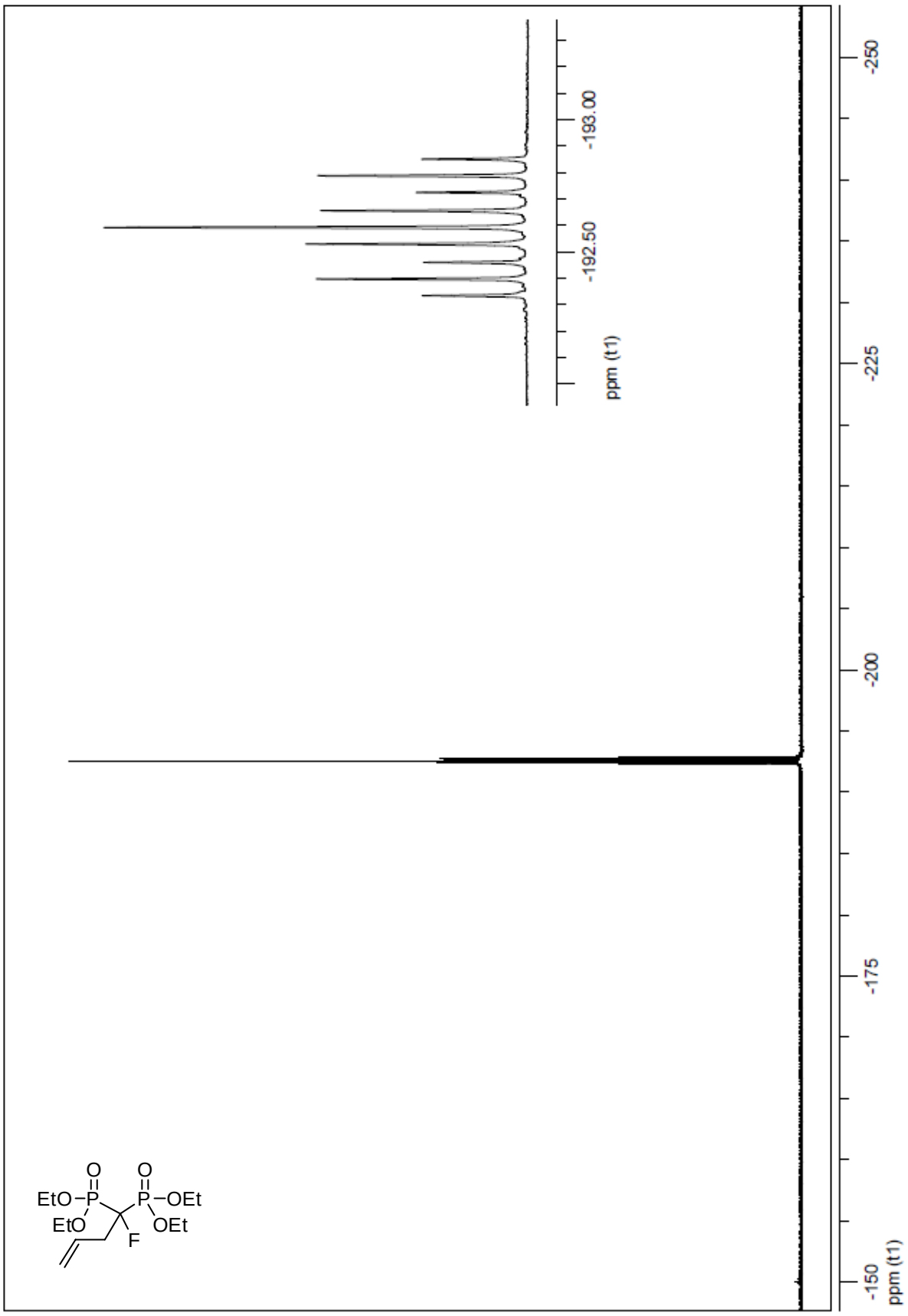

$^{31}$P NMR spectrum of **2b**.



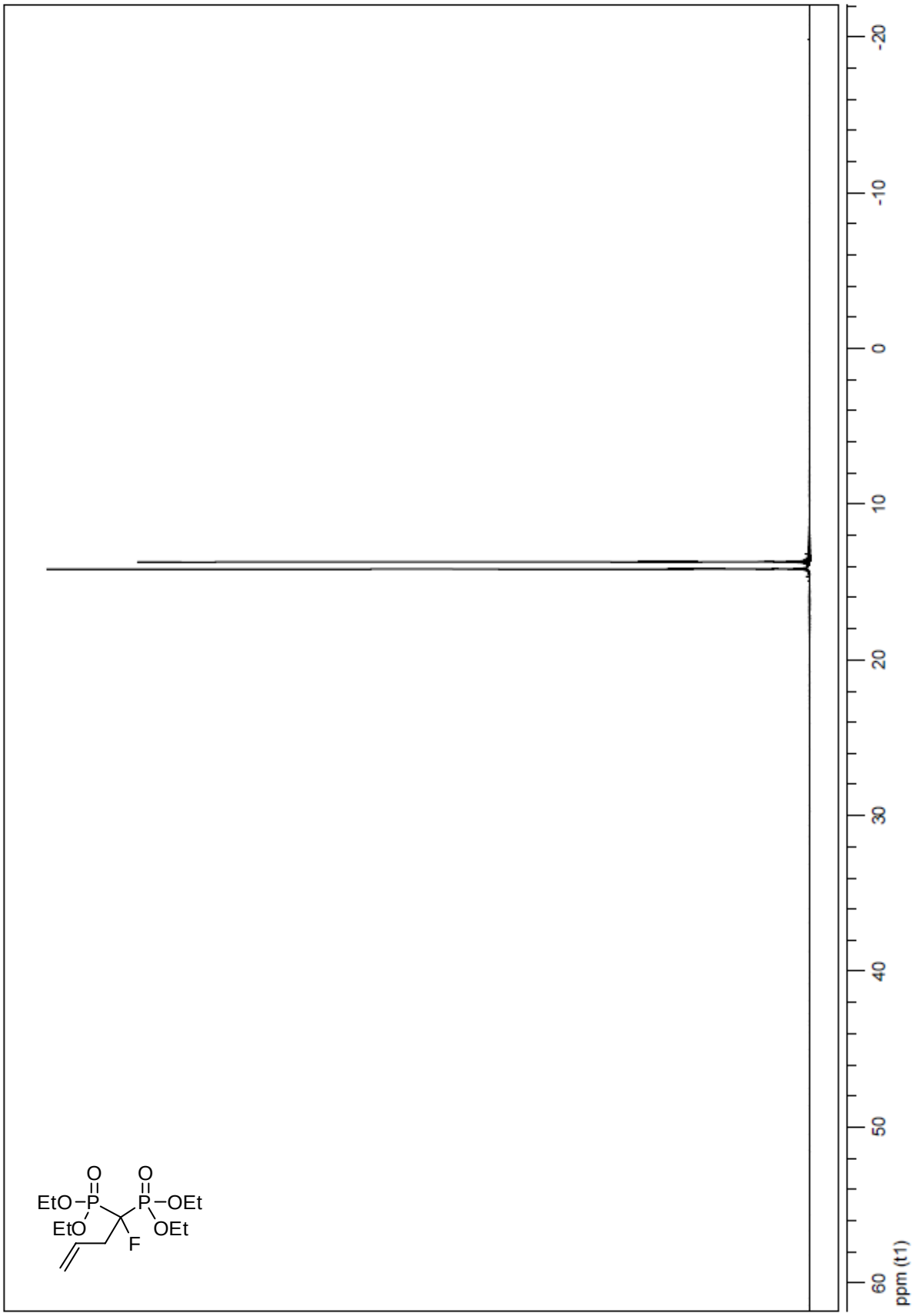

$^{1}$H NMR spectrum of **2c**.



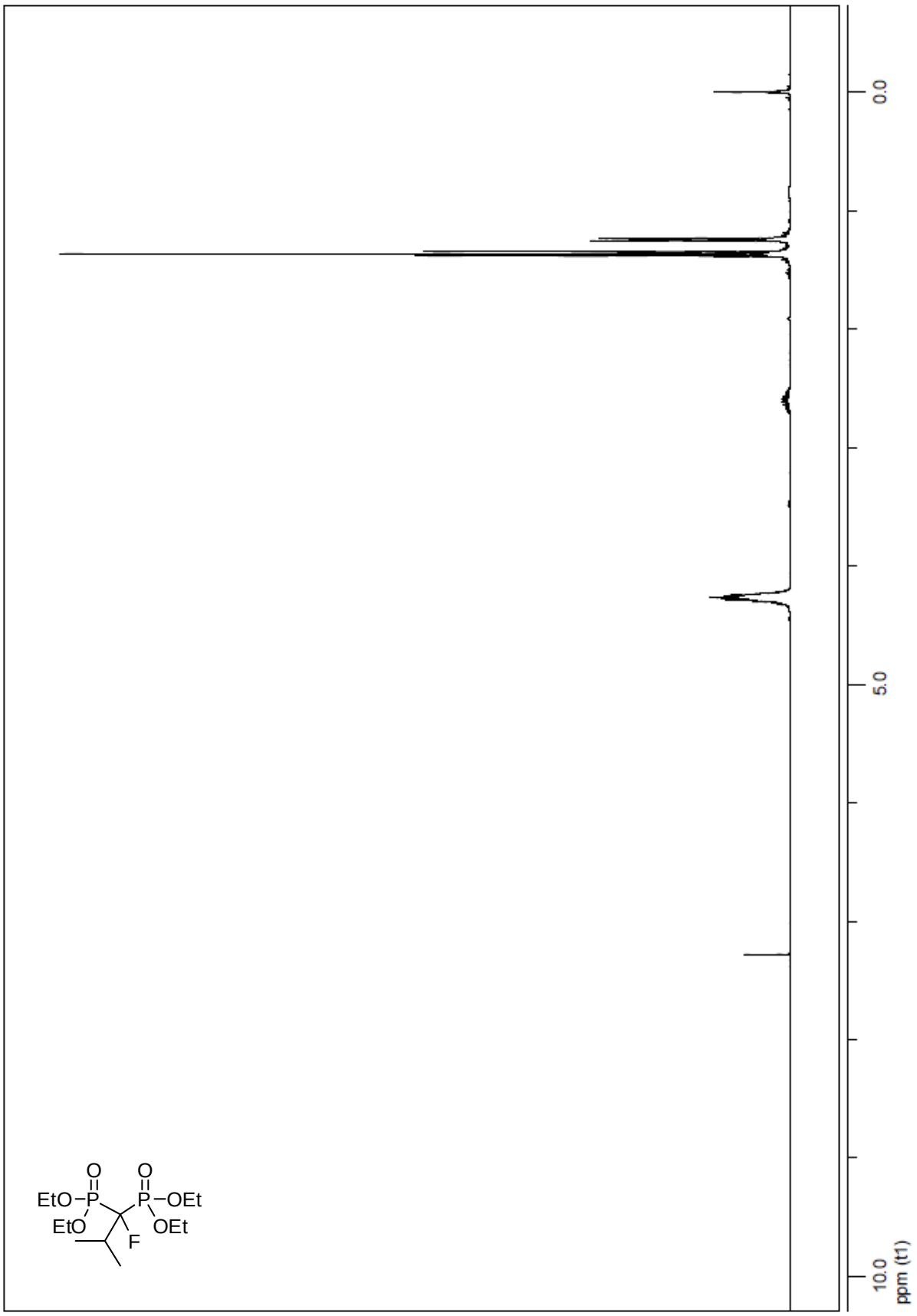

$^{13}$C NMR spectrum of **2c**.



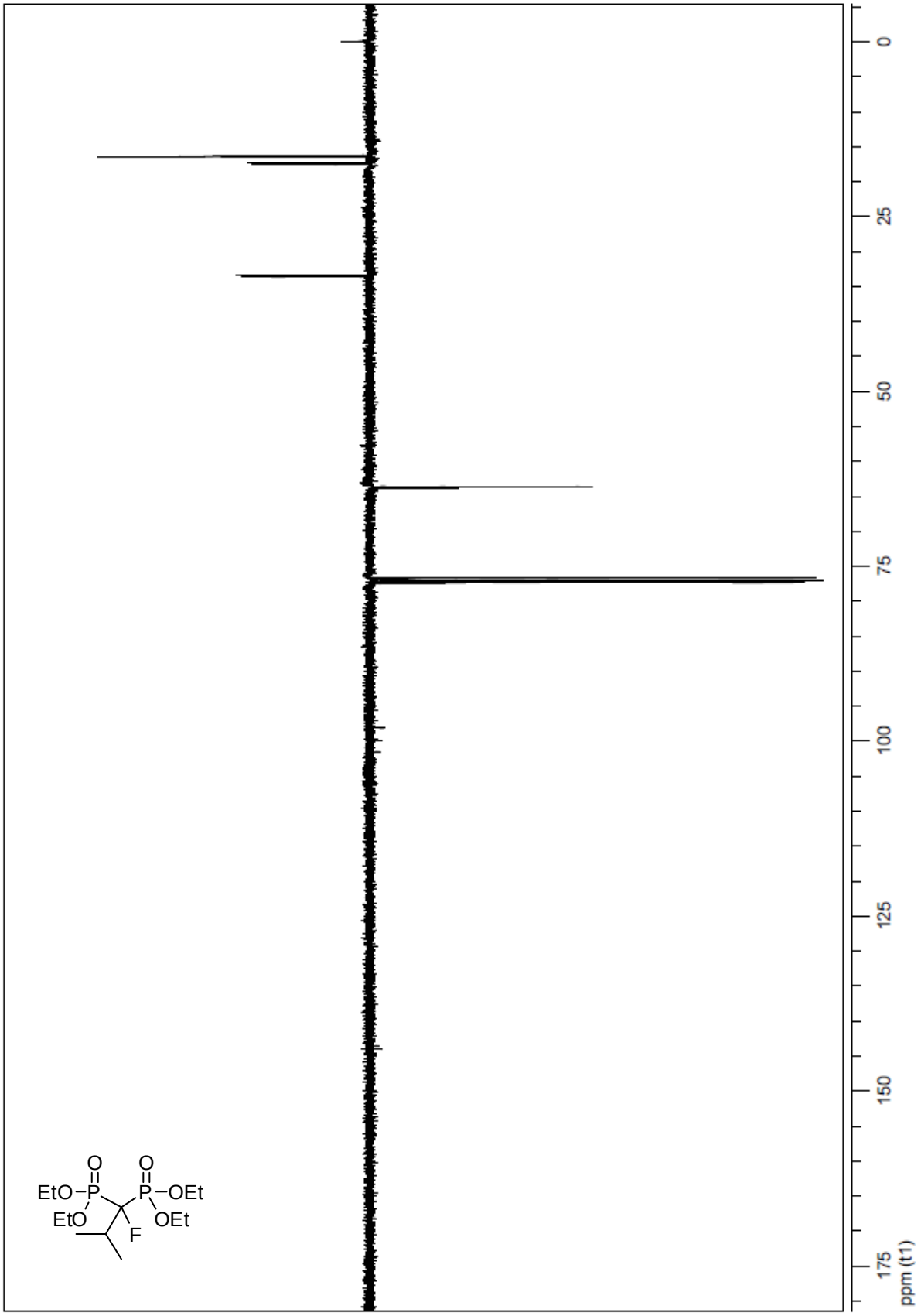

$^{19}$F NMR spectrum of **2c**.



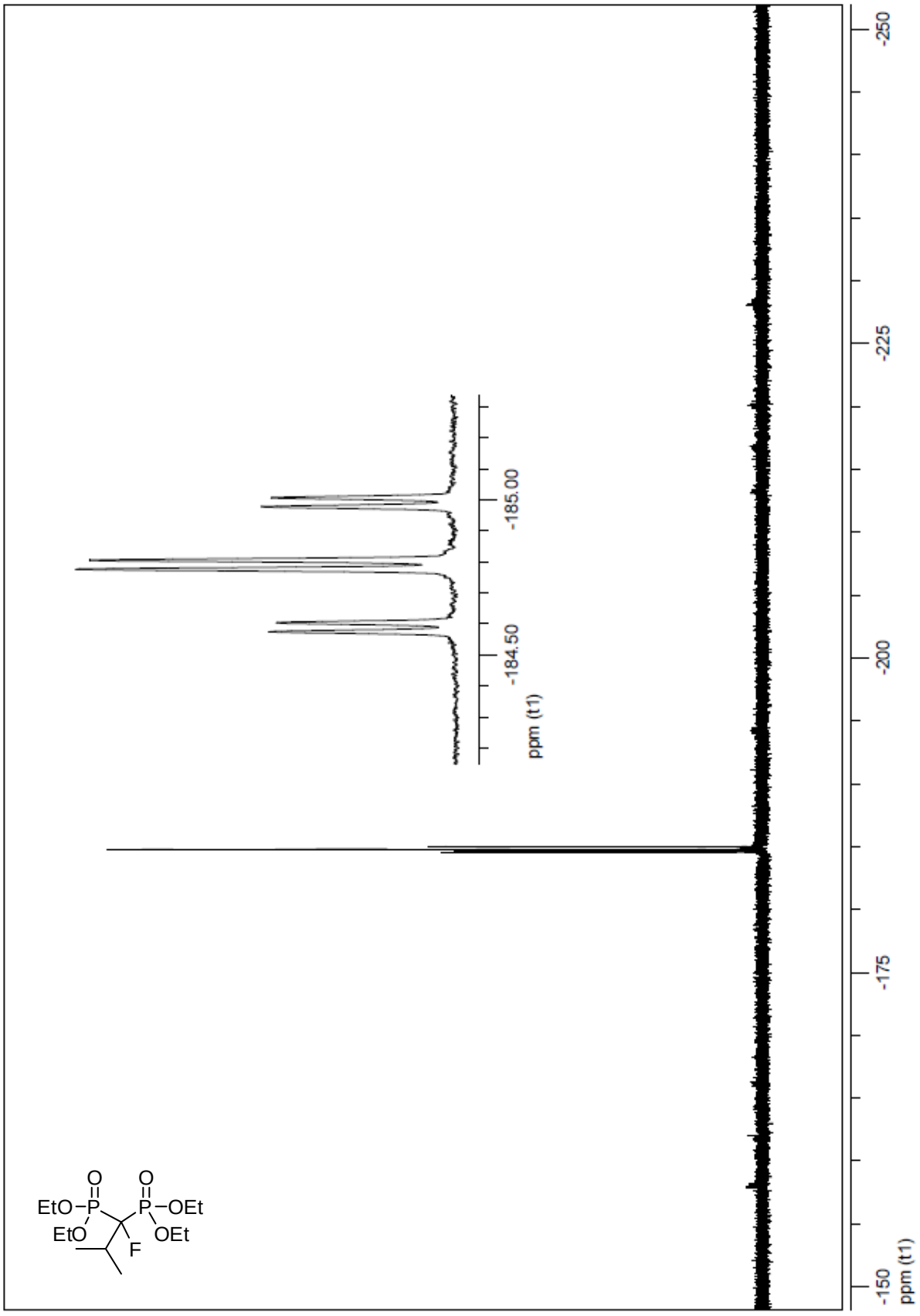

$^{31}$P NMR spectrum of **2c**.



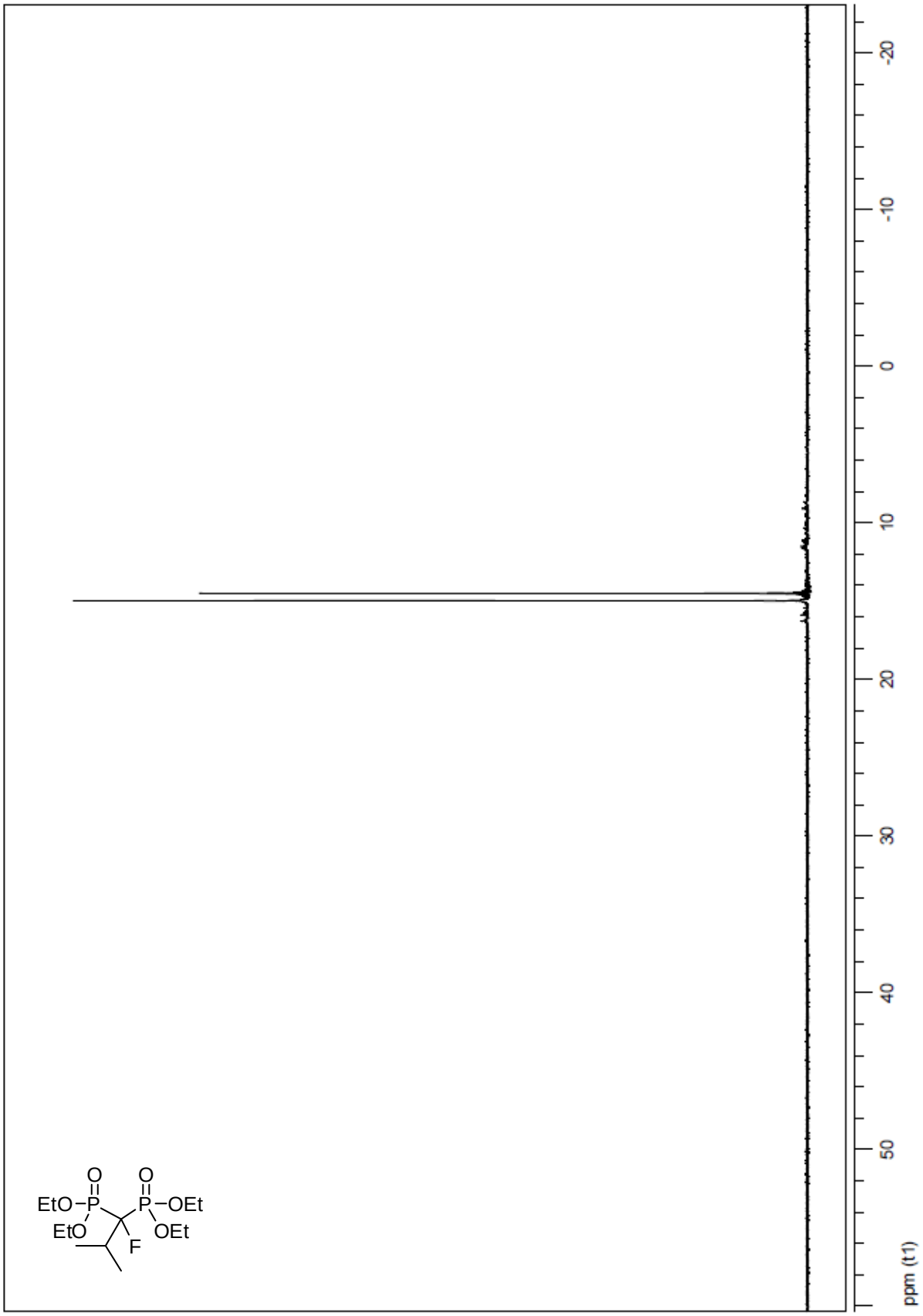

$^{1}$H NMR spectrum of **2d**.



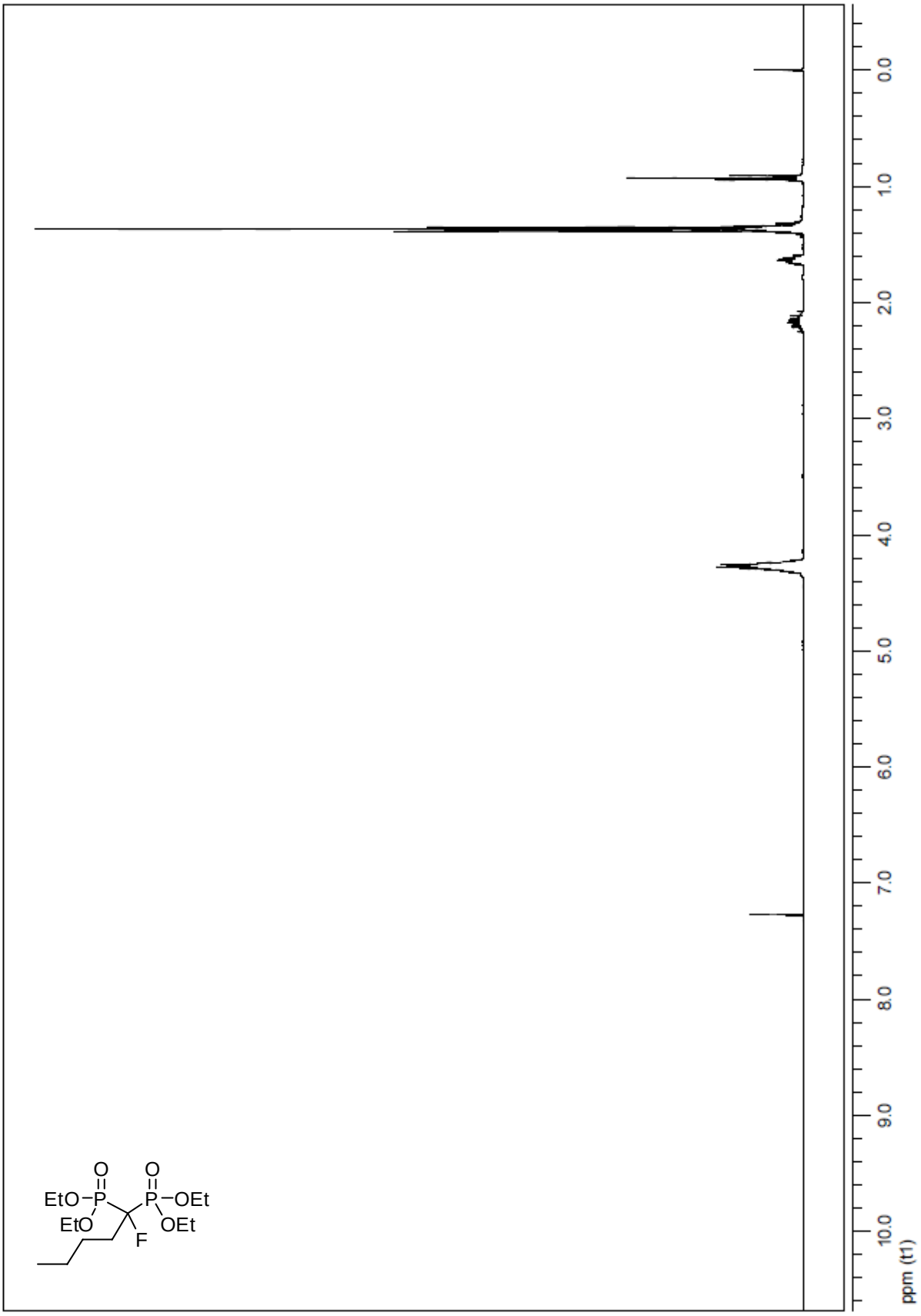

$^{13}$C NMR spectrum of **2d**.



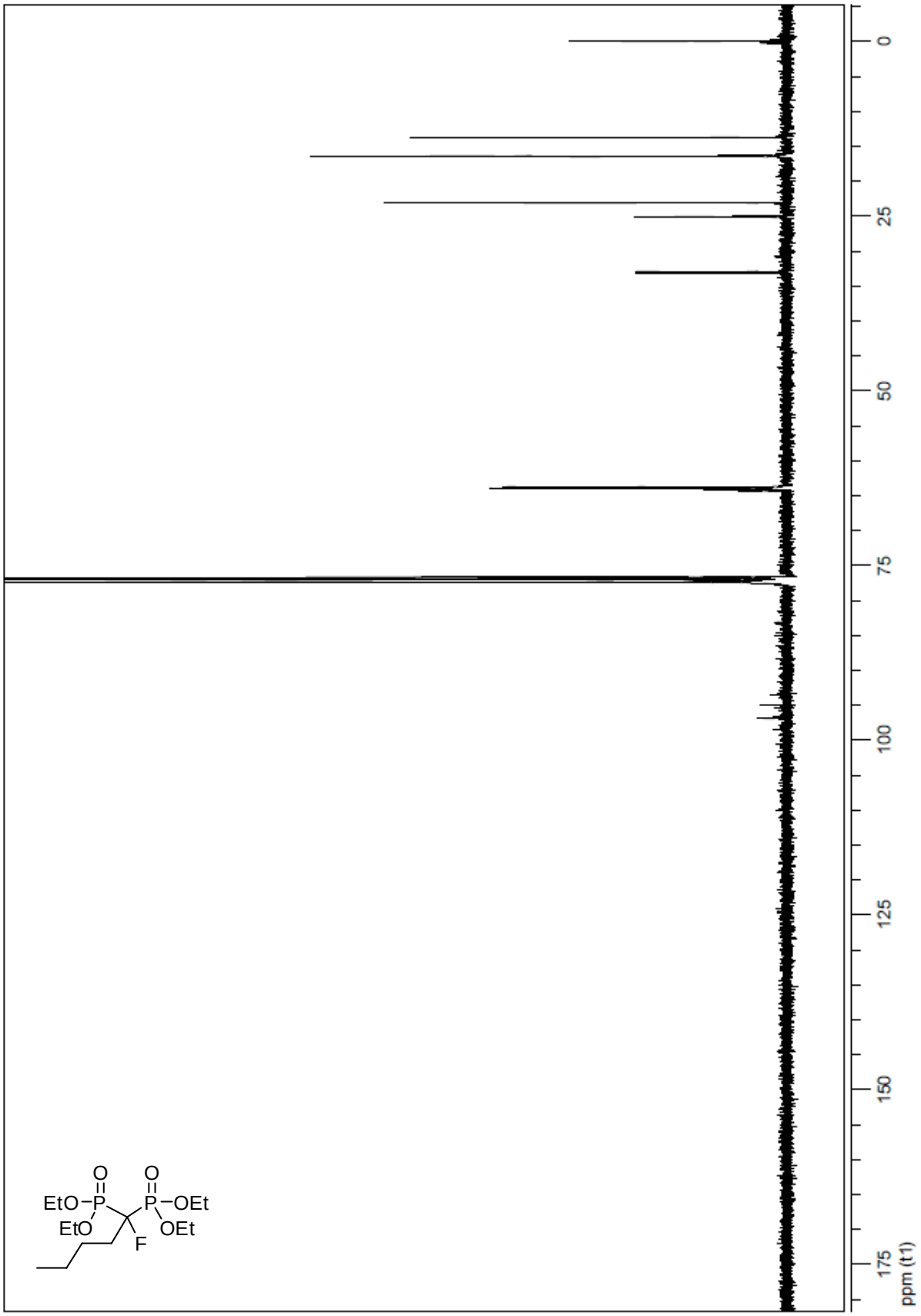

$^{19}$F NMR spectrum of **2d**.



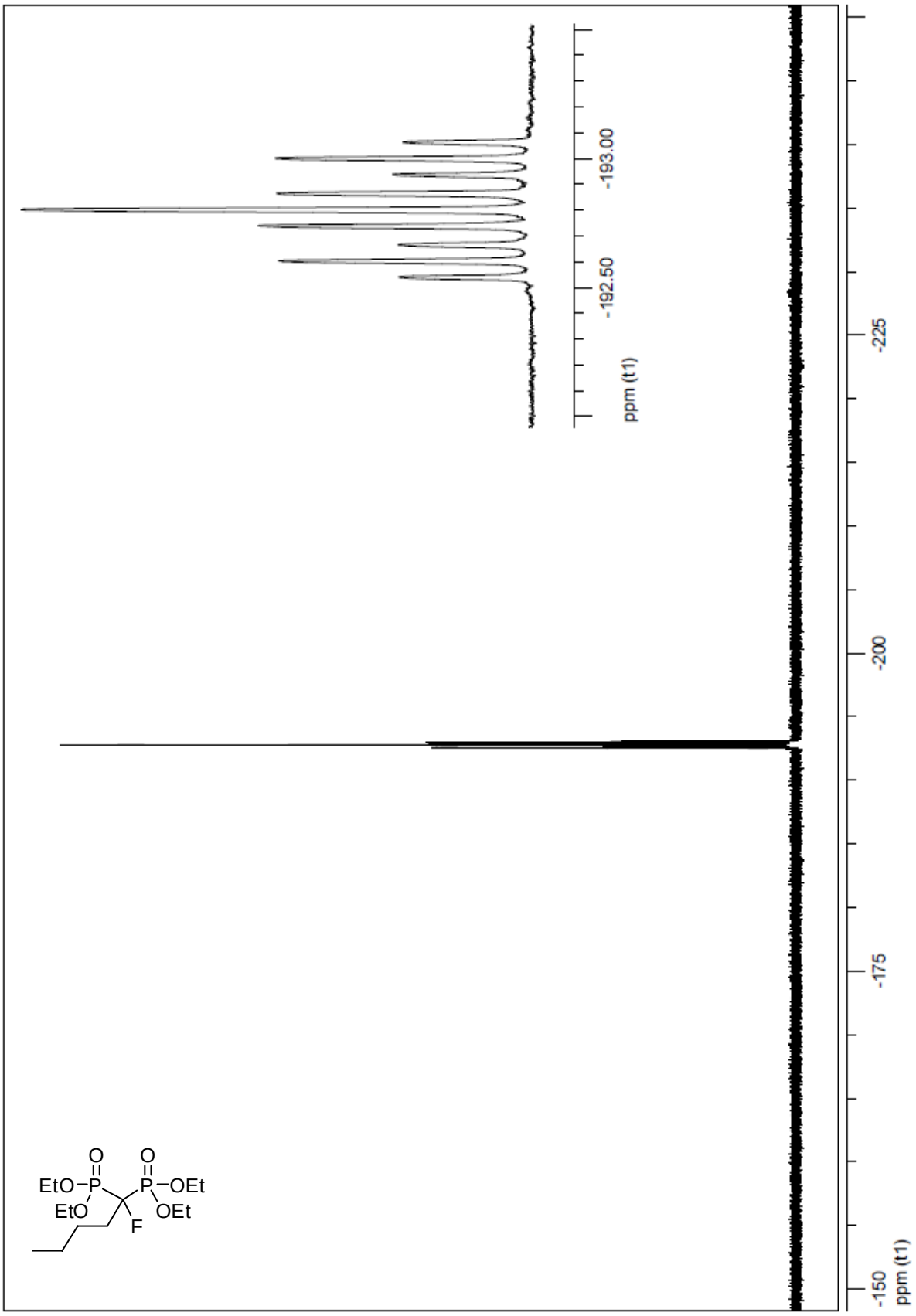

$^{31}$P NMR spectrum of **2d**.



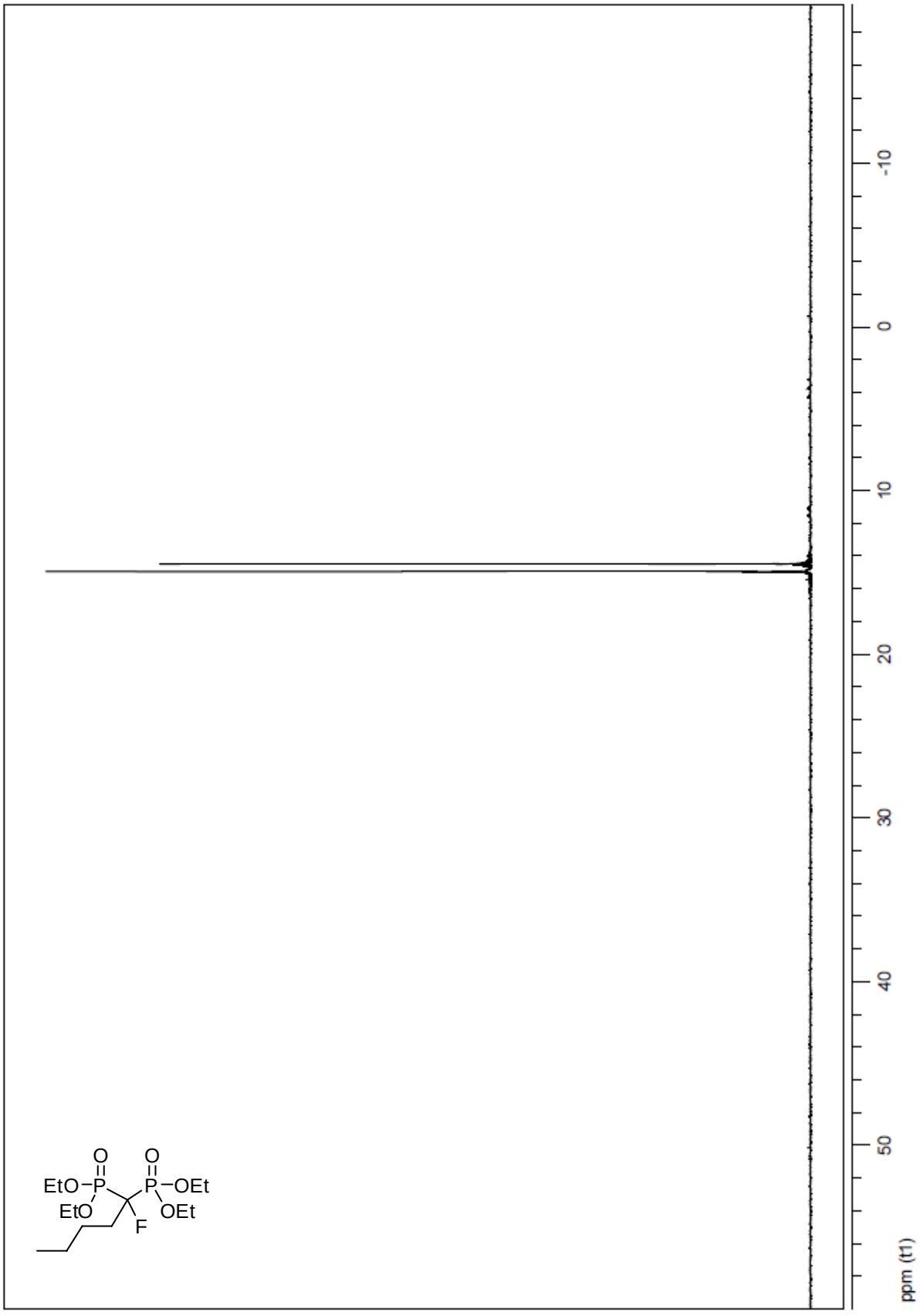

$^{1}$H NMR spectrum of **2e**.



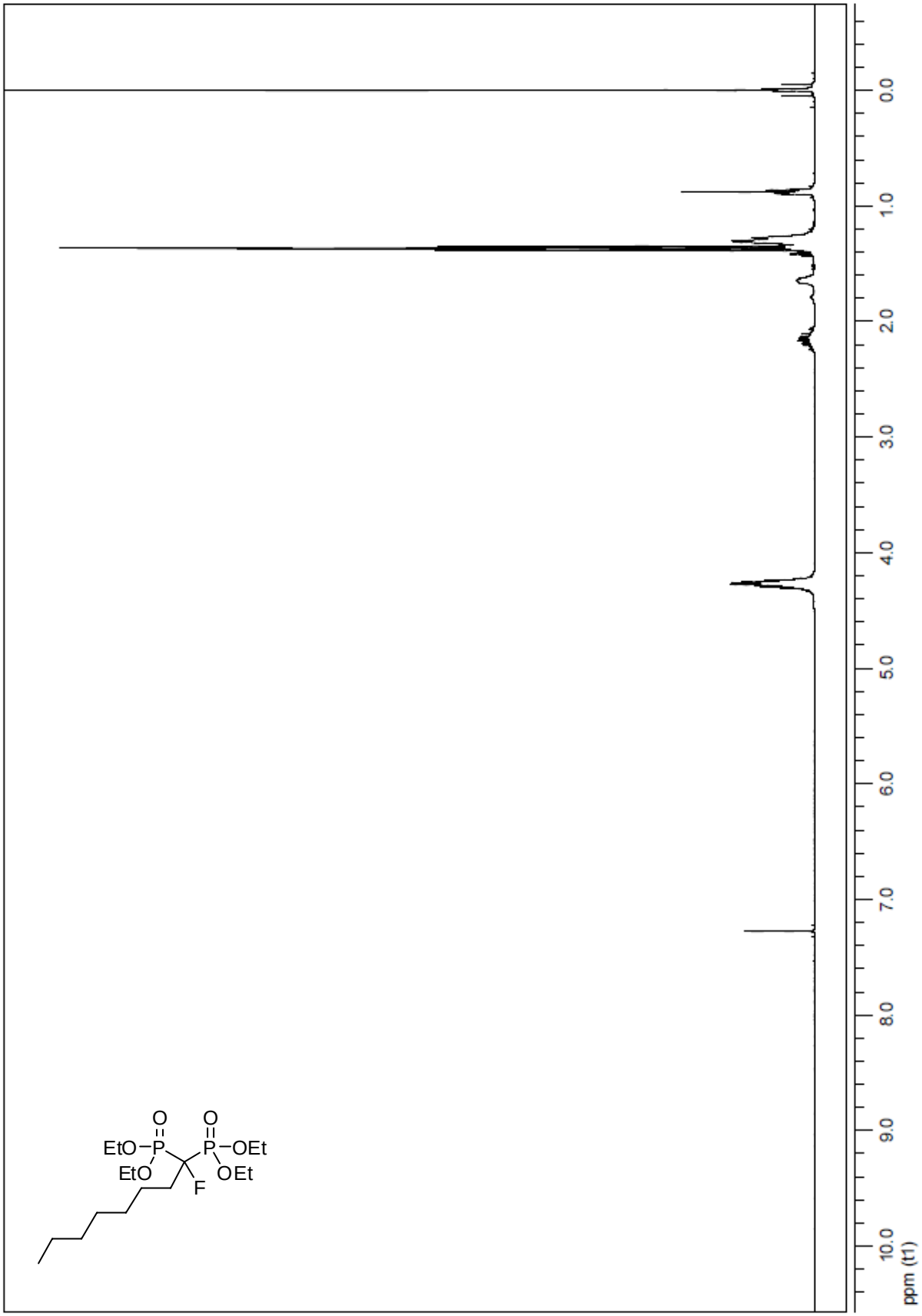

$^{13}$C NMR spectrum of **2e**.



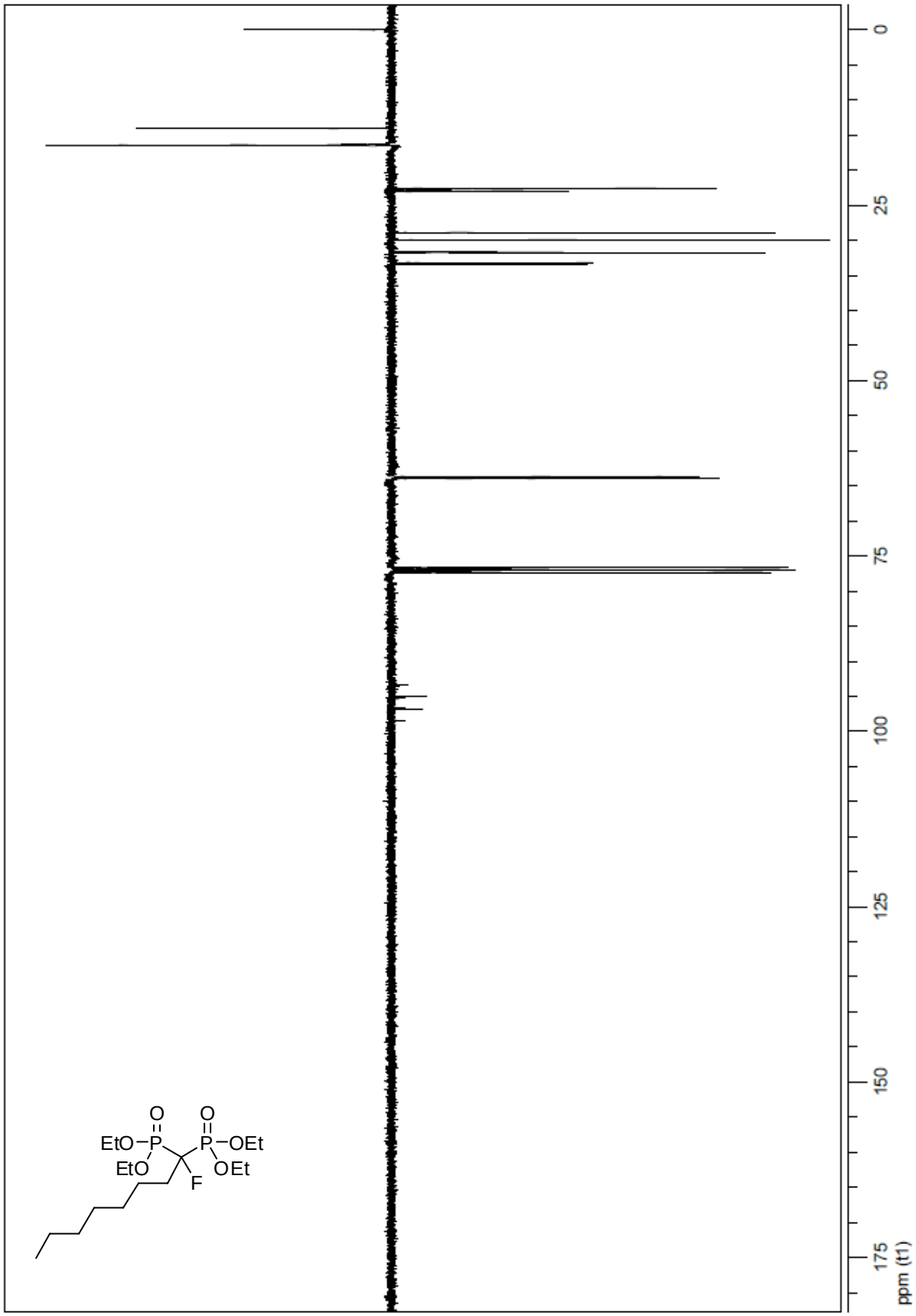

$^{19}$F NMR spectrum of **2e**.



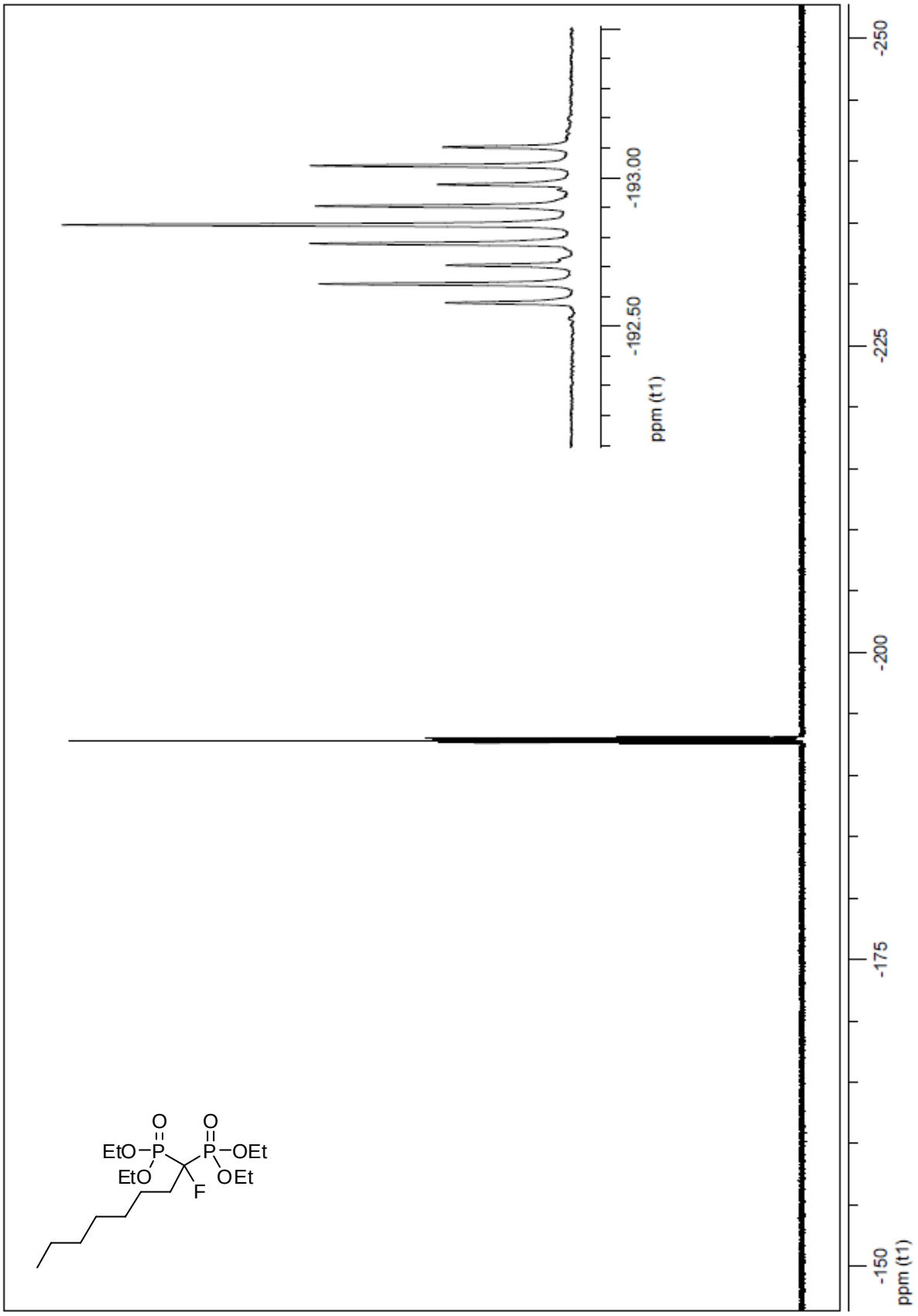

$^{31}$P NMR spectrum of **2e**.



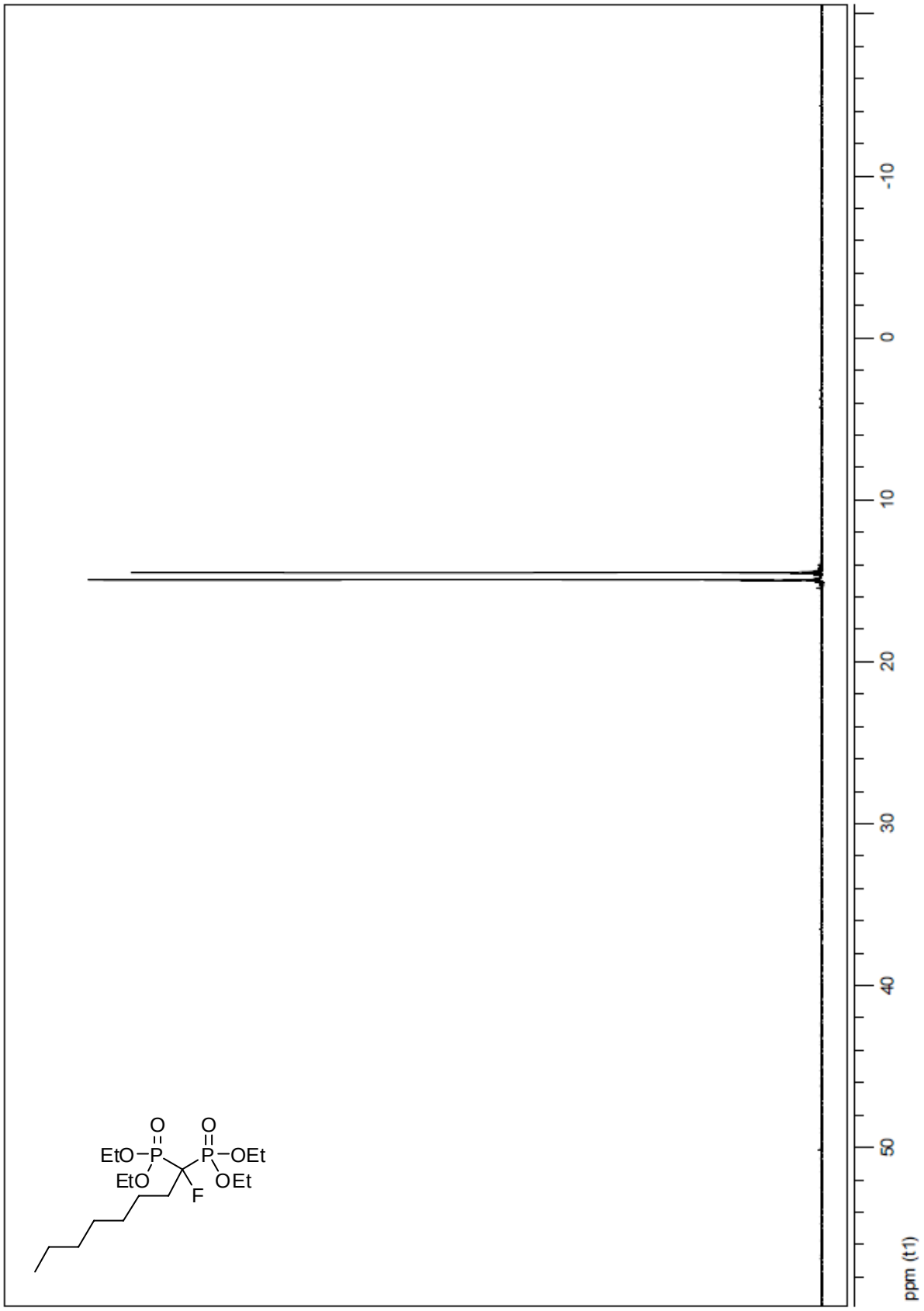

$^{1}$H NMR spectrum of **2f**.



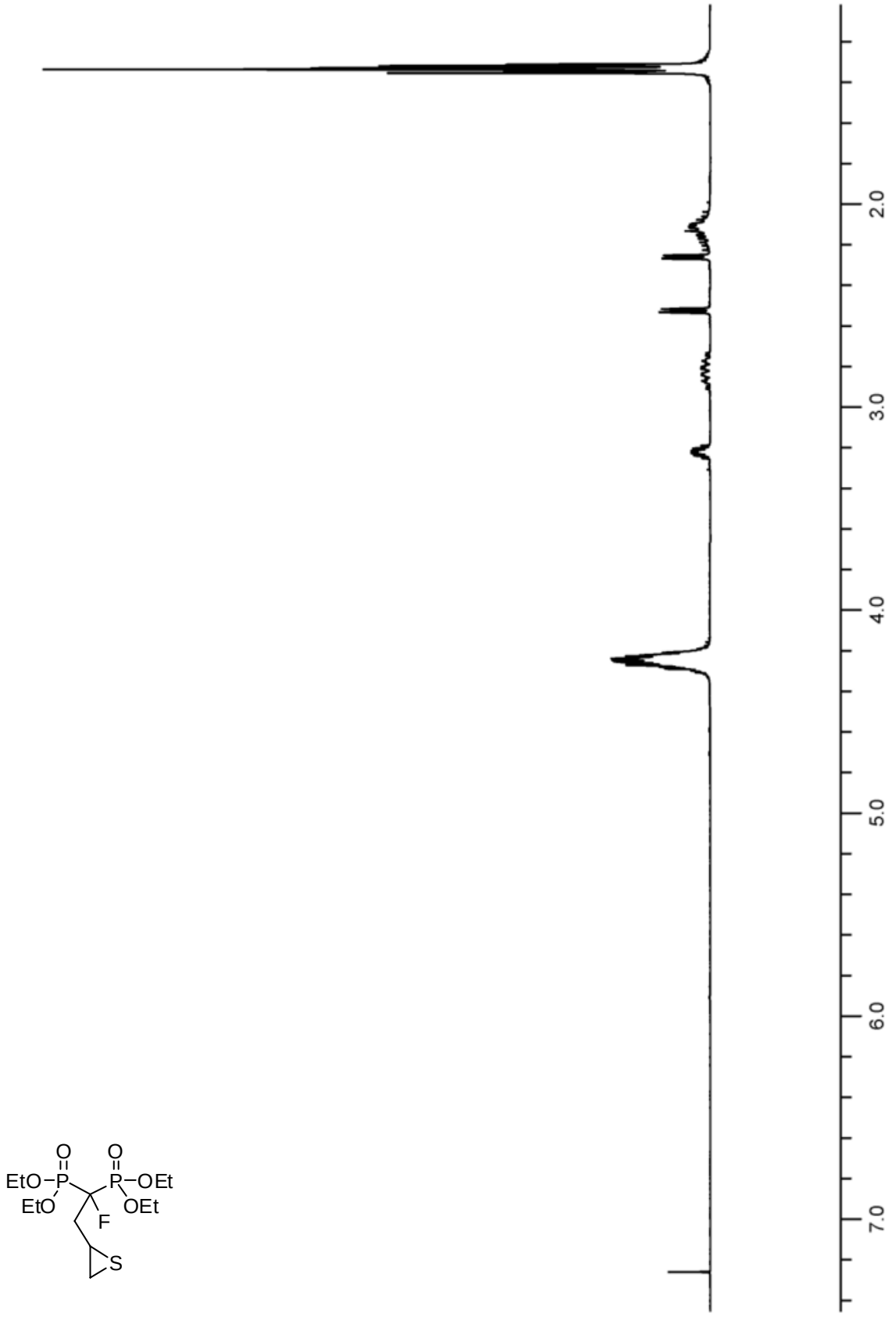

$^{13}$C NMR spectrum of **2f**.



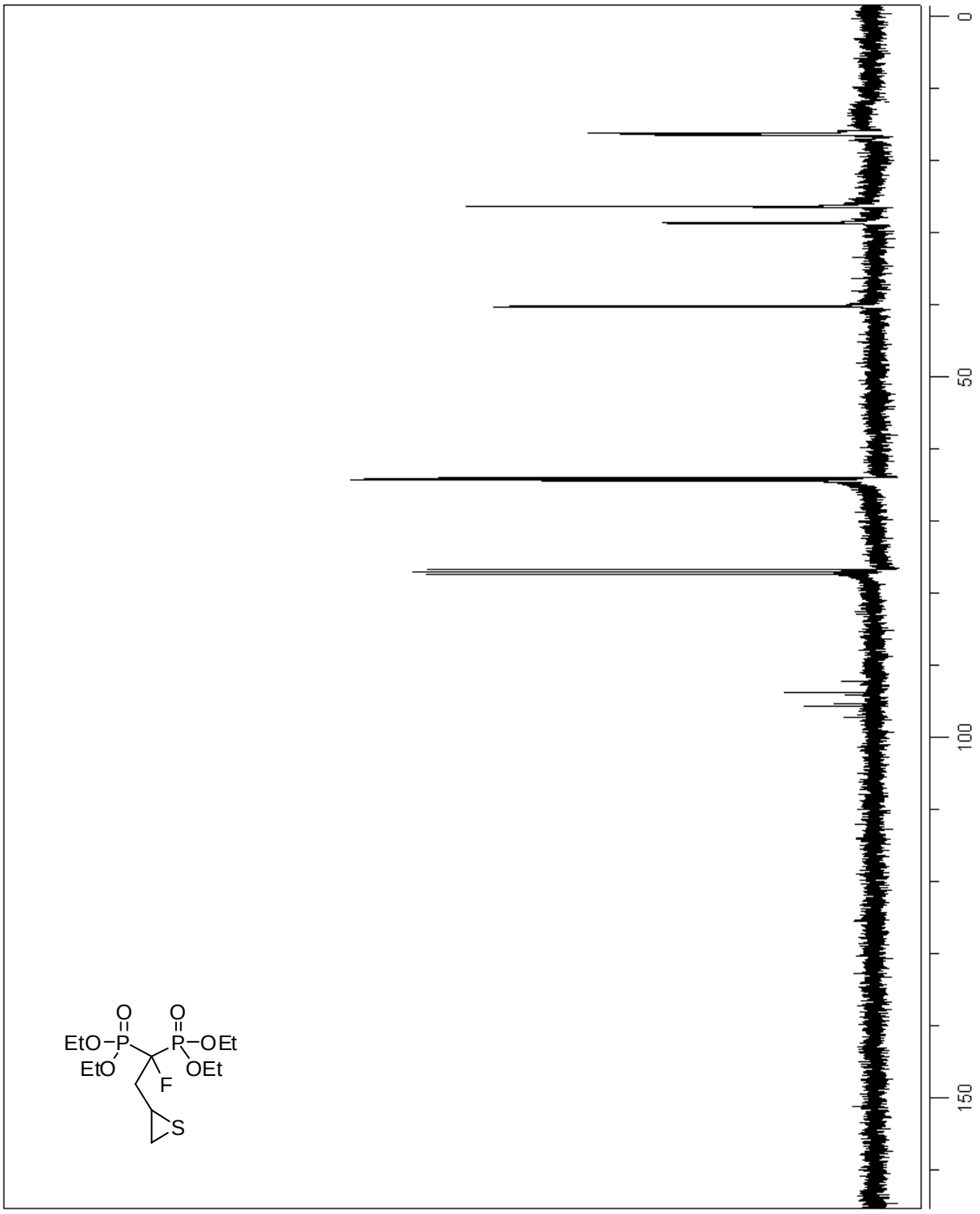

$^{19}$F NMR spectrum of **2f**.



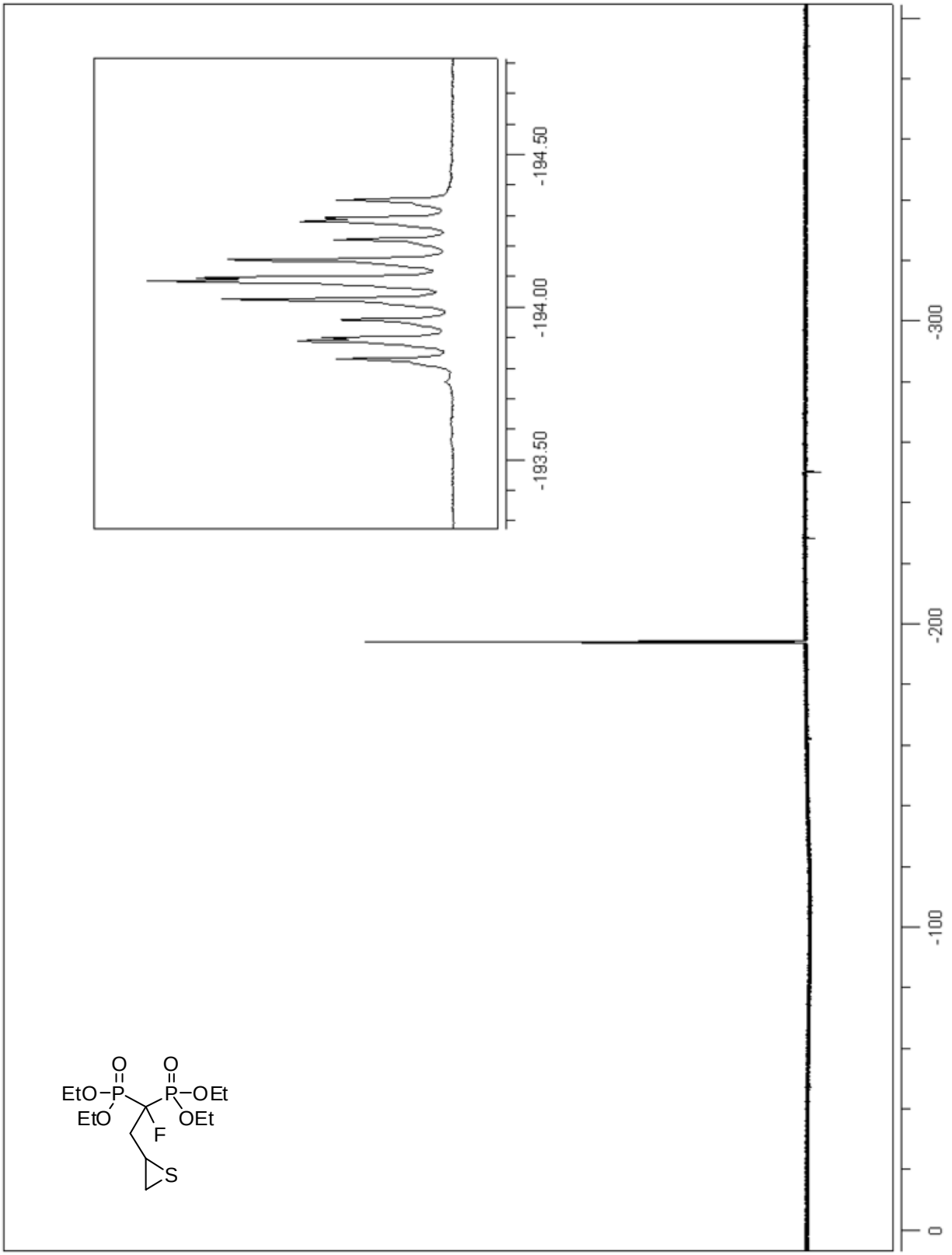

$^{31}$P NMR spectrum of **2f**.



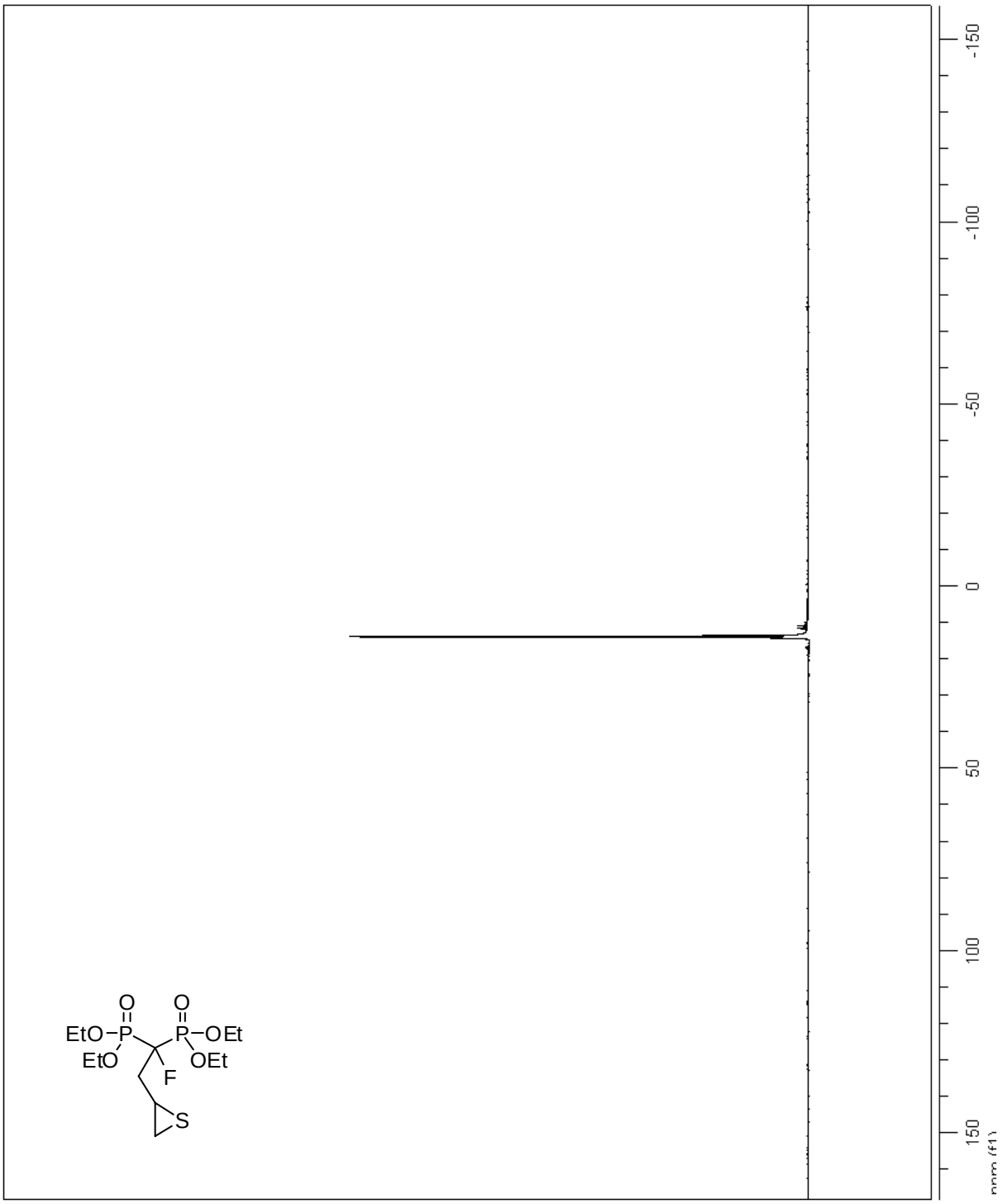

$^{1}$H NMR spectrum of **2h**



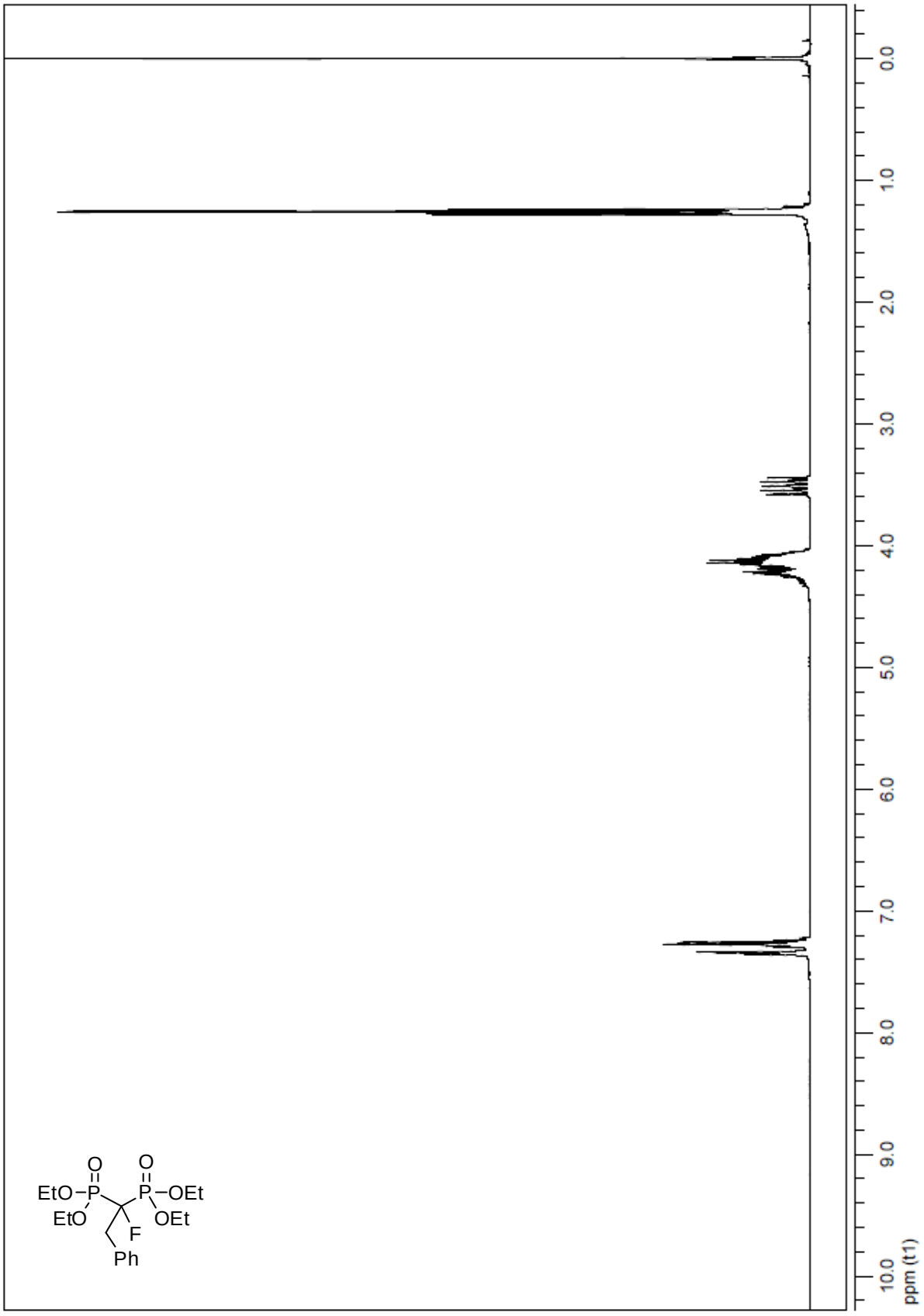

$^{13}$C NMR spectrum of **2h**



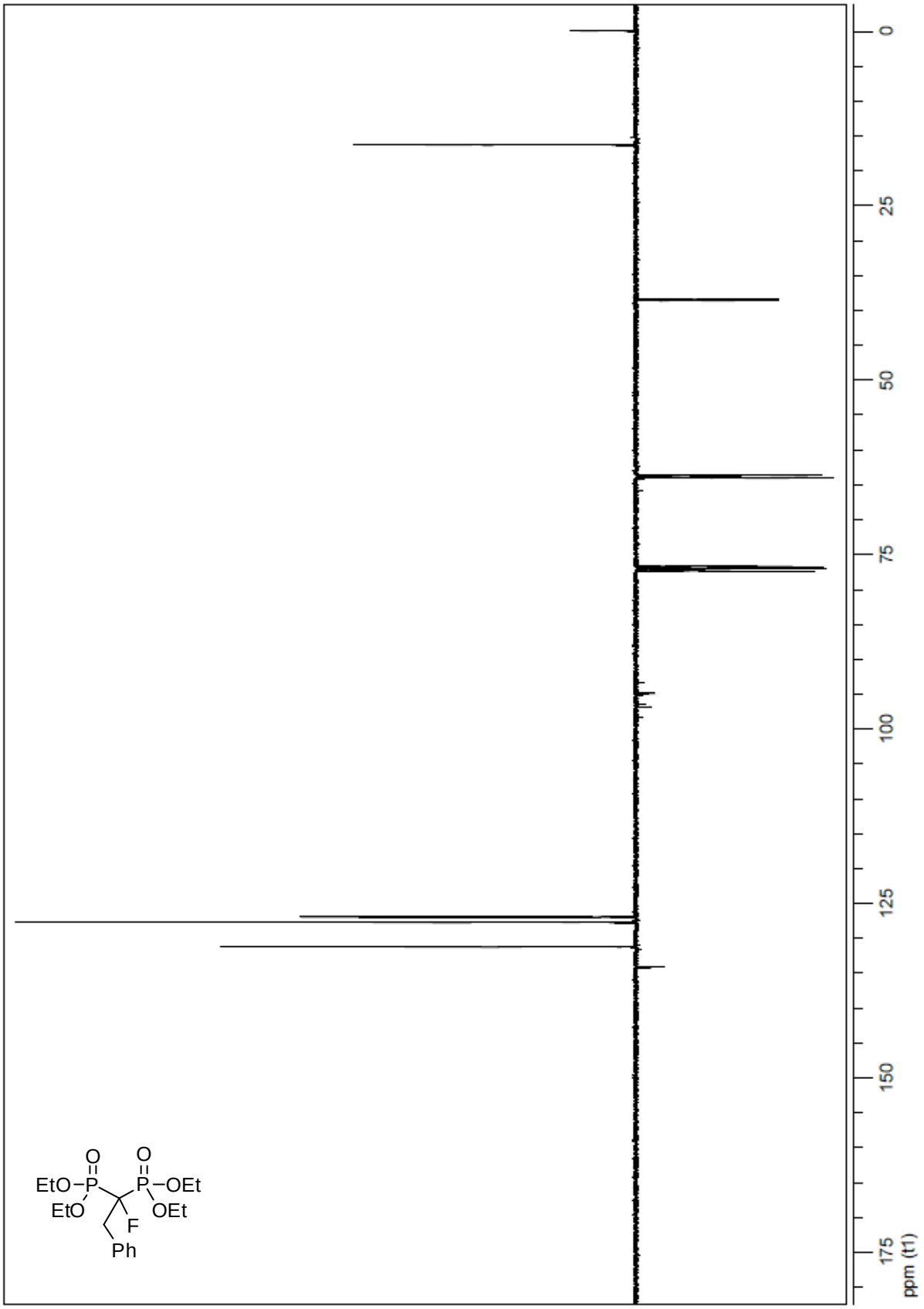

$^{19}$F NMR spectrum of **2h**



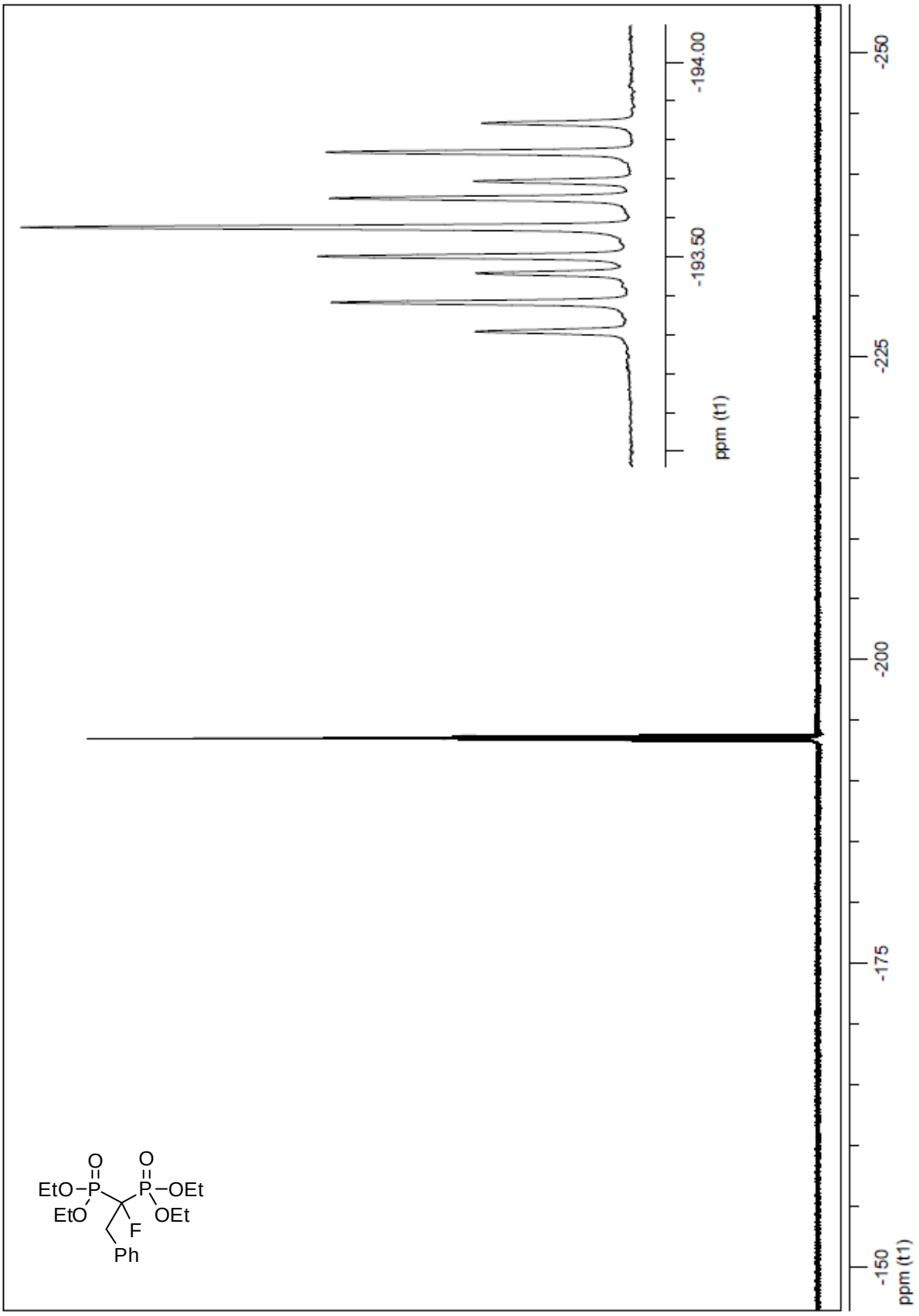

$^{31}$P NMR spectrum of **2h**



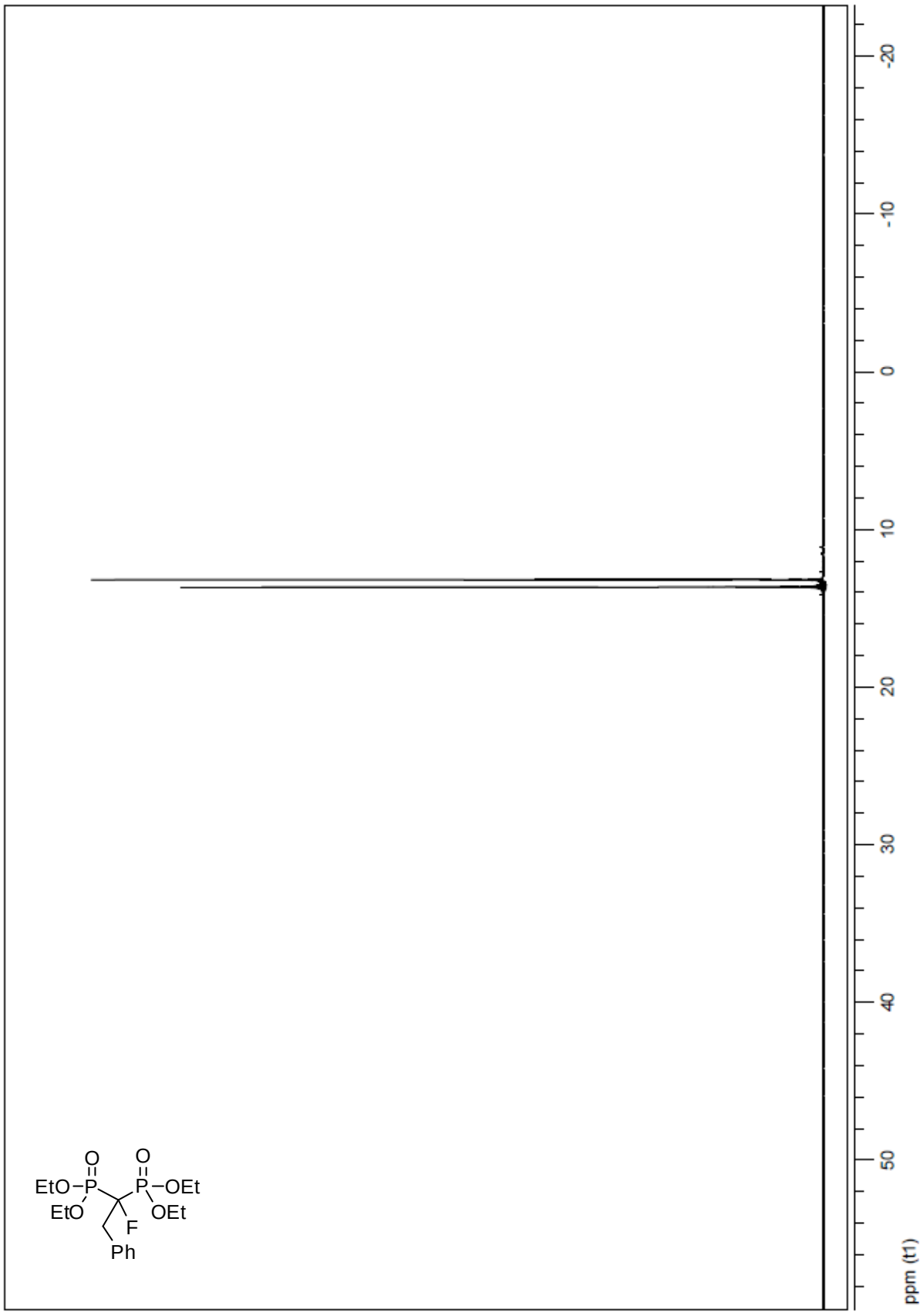

$^{1}$H NMR spectrum of **2i**.



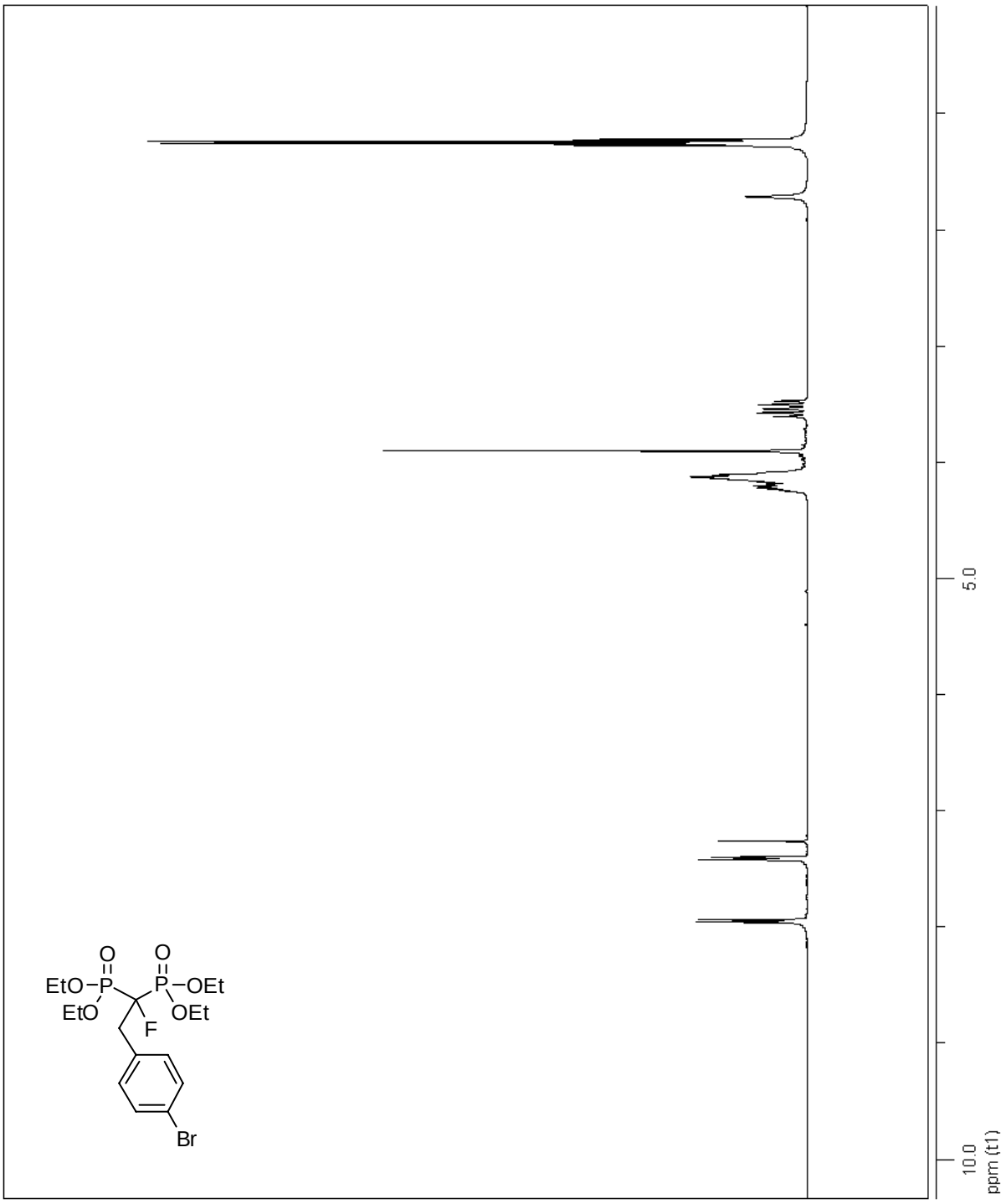

$^{13}$C NMR spectrum of **2i**.



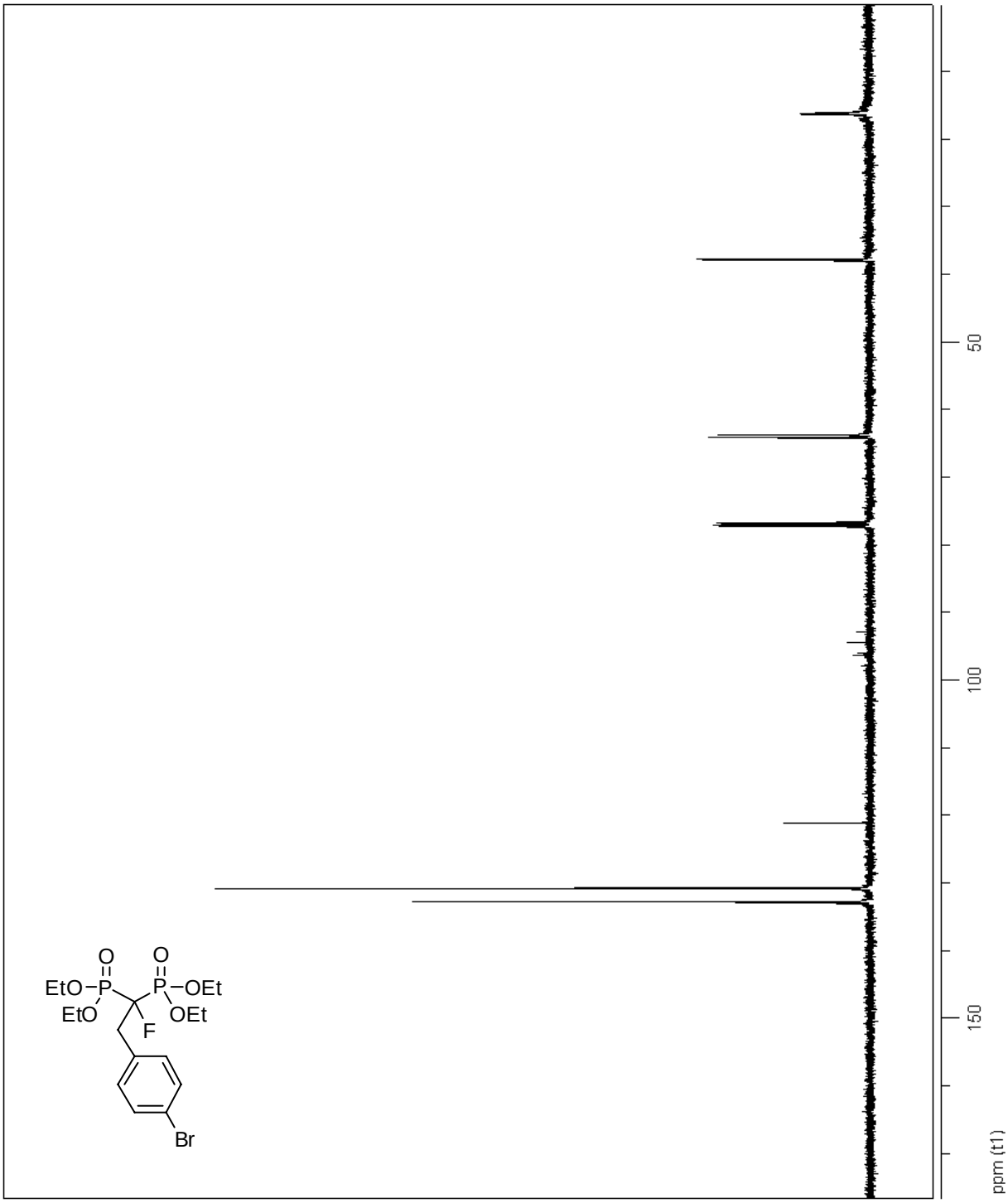

$^{19}$F NMR spectrum of **2i**.



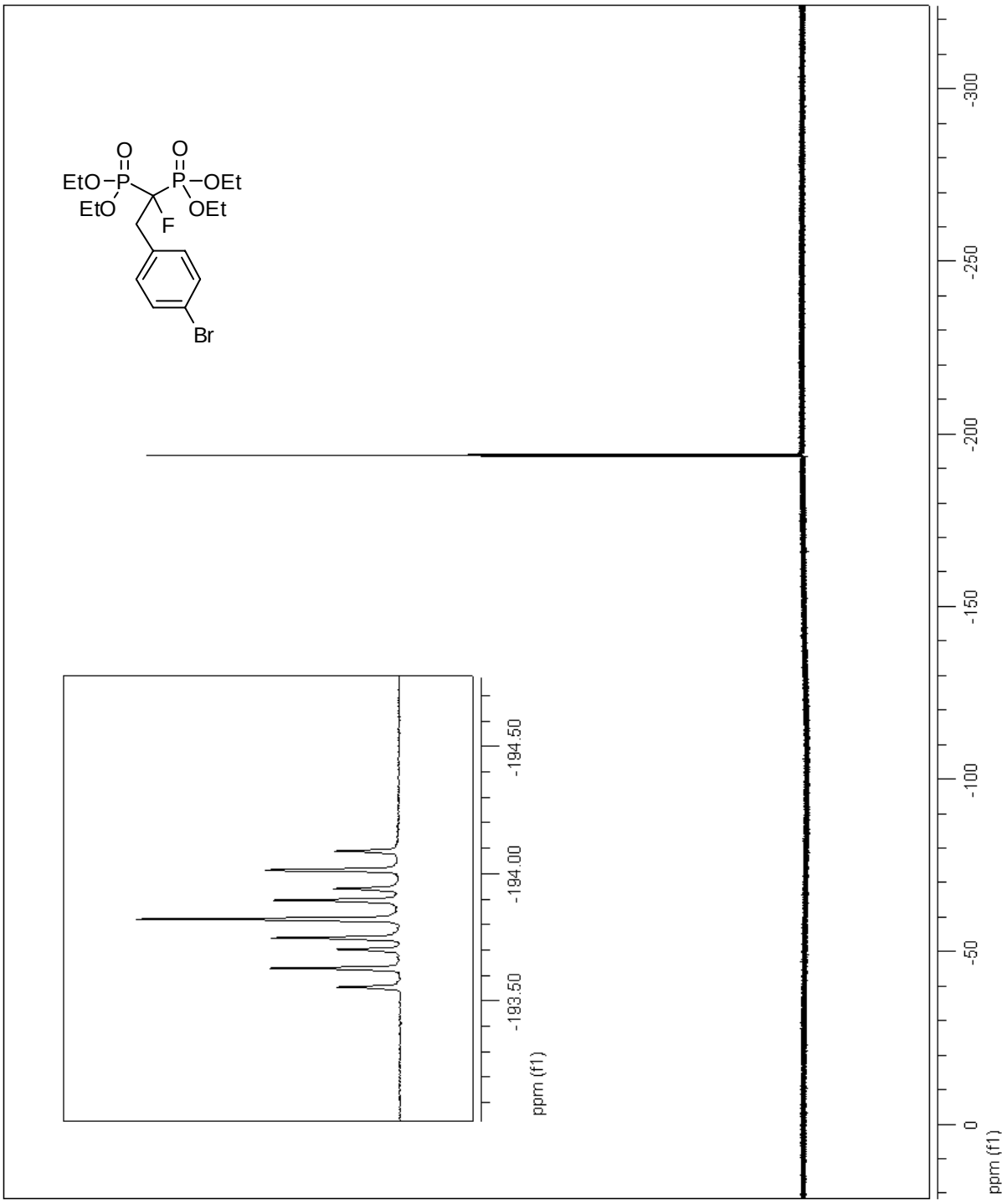

$^{31}$P NMR spectrum of **2i**.



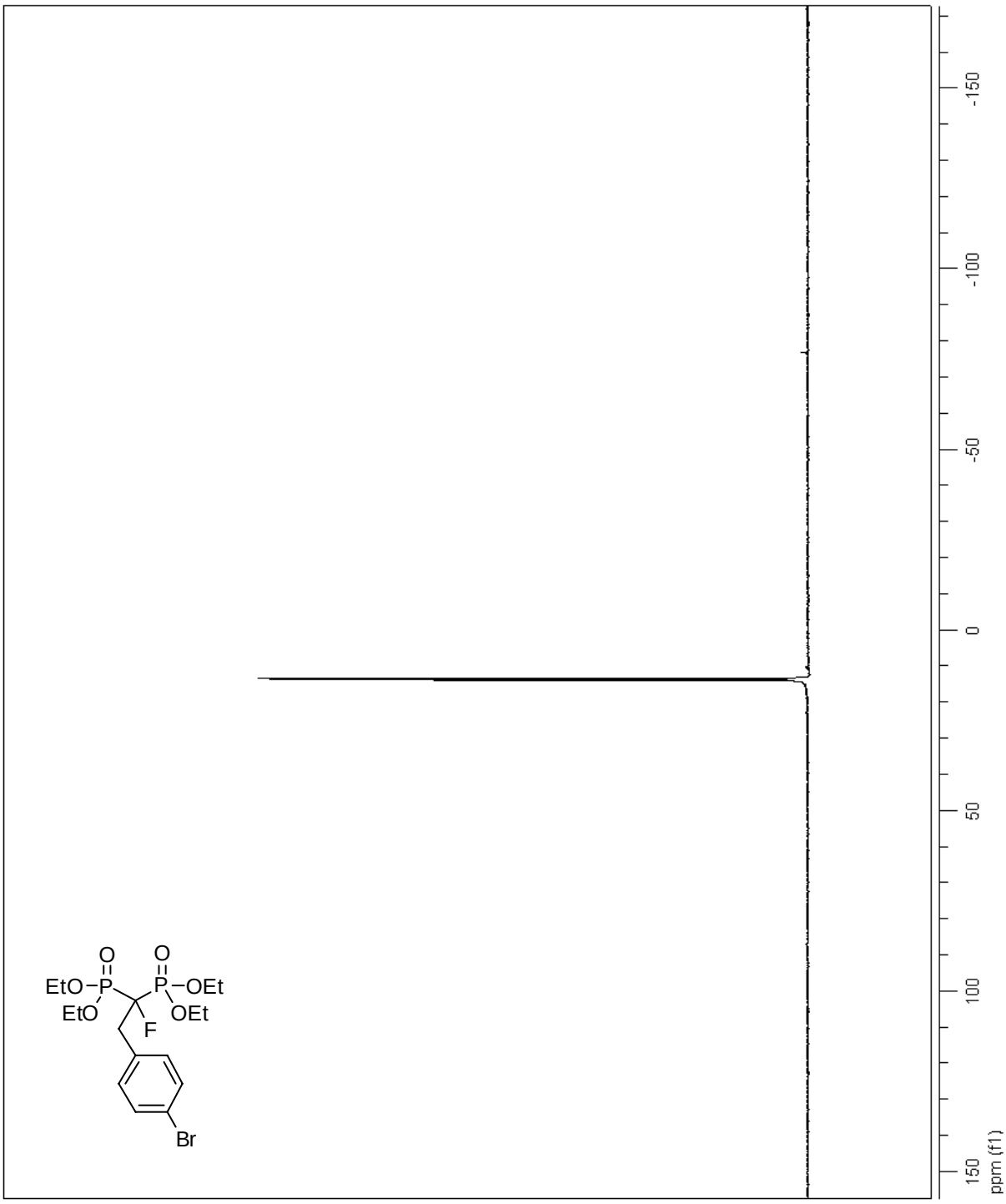

$^{1}$H NMR spectra of **2j**



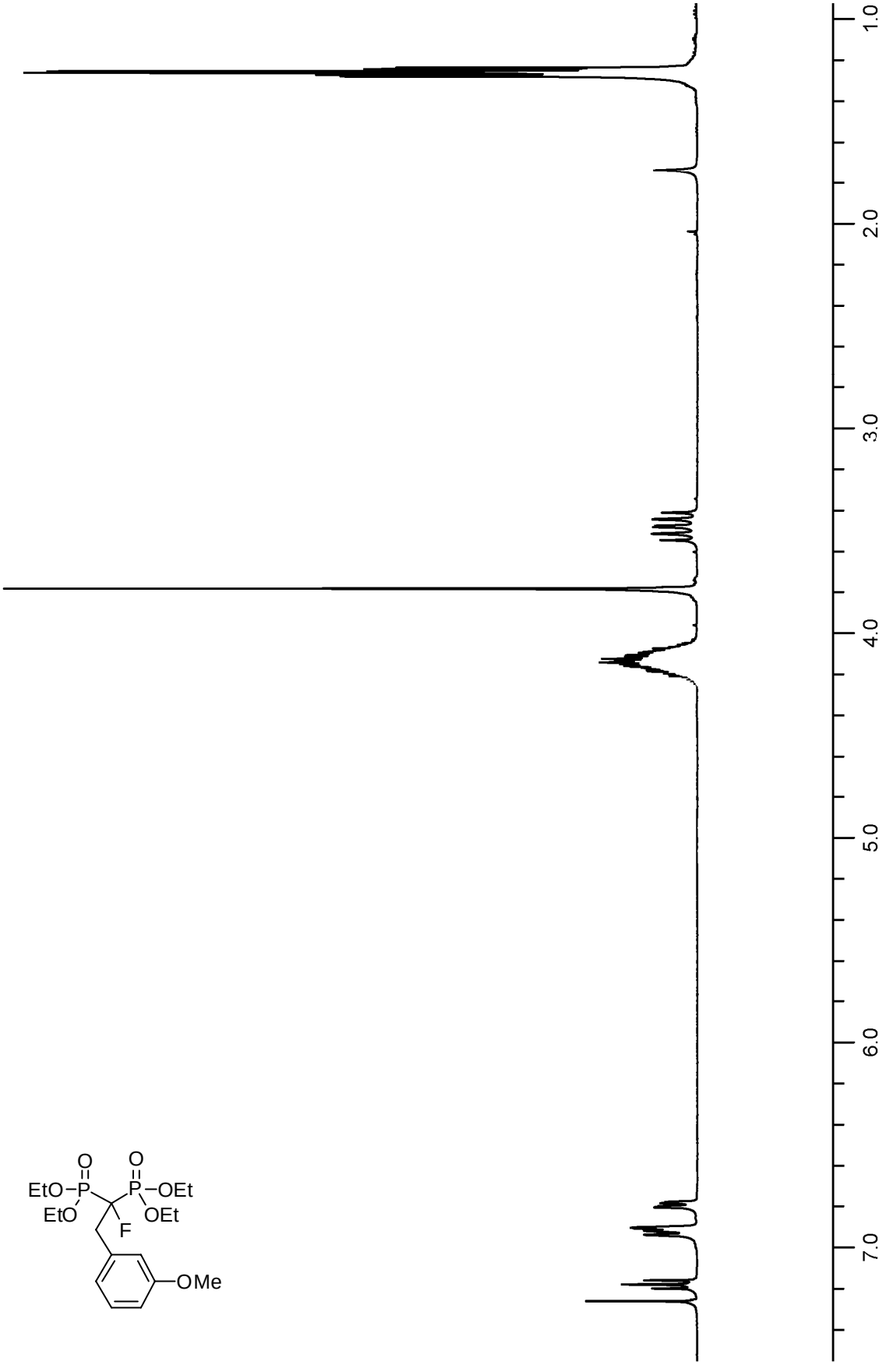

$^{13}$C NMR spectrum of **2j**



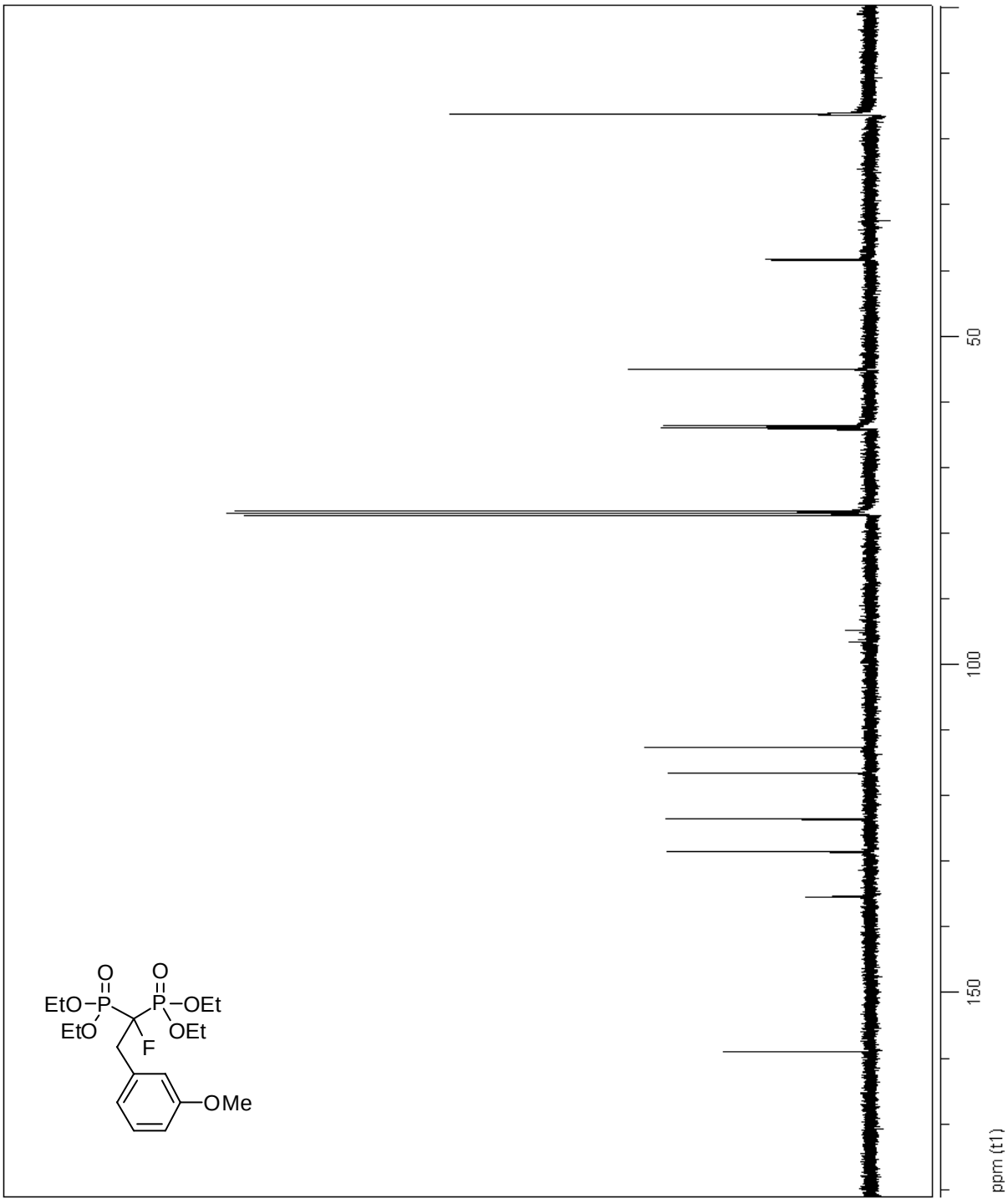

$^{19}$F spectrum of **2j**



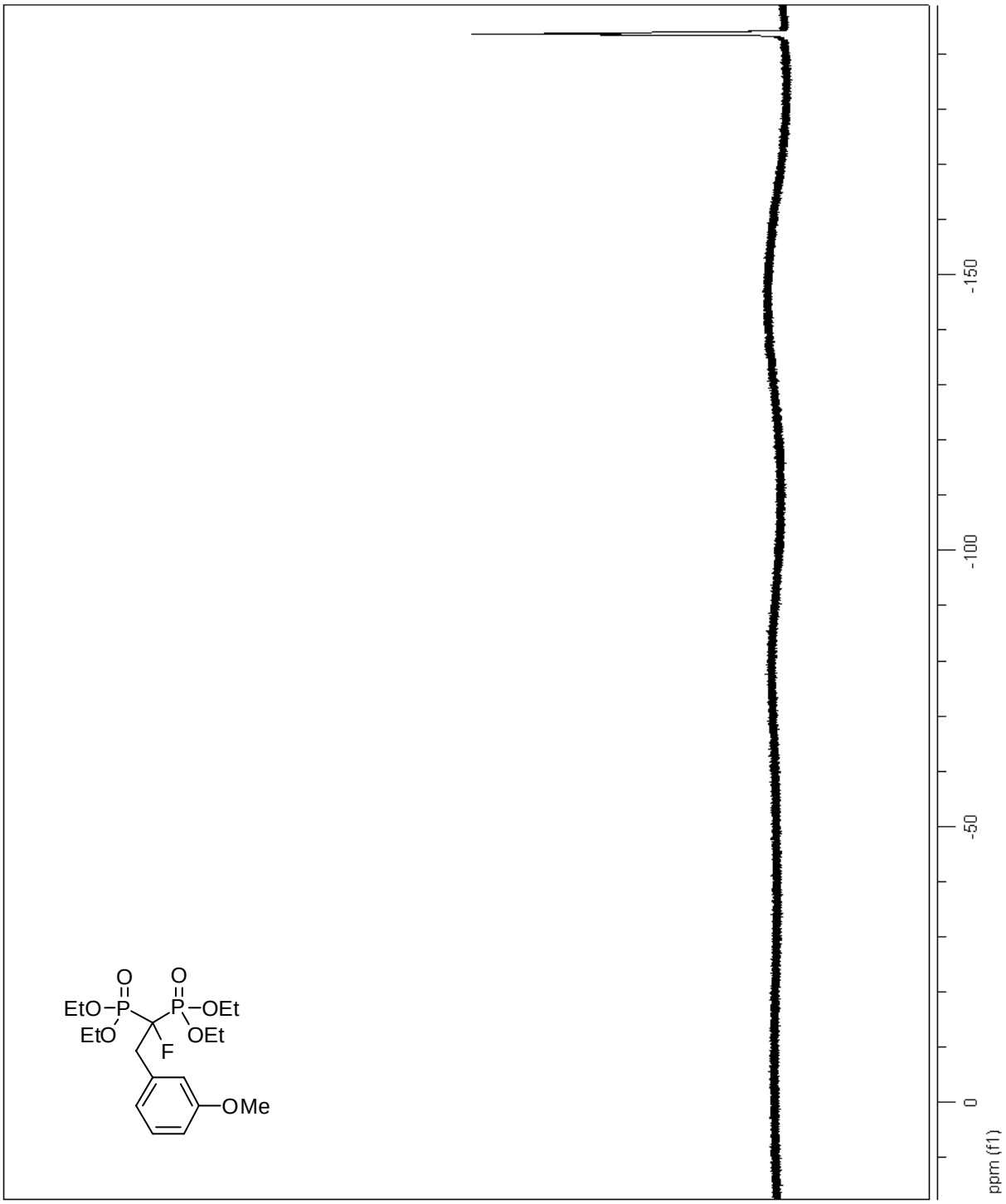

$^{31}$P NMR spectrum of **2j**



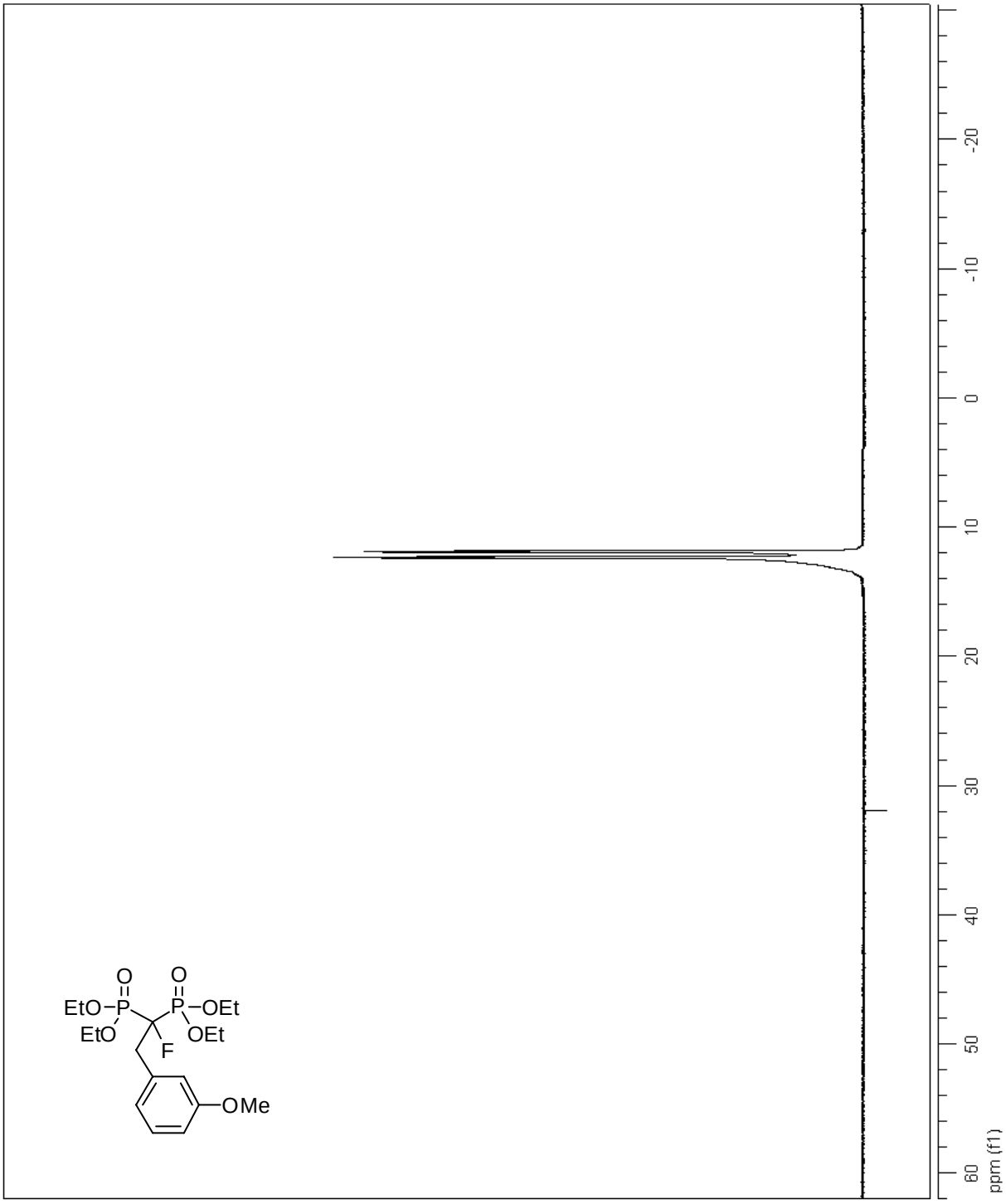

$^{1}$H NMR spectrum of **2k**



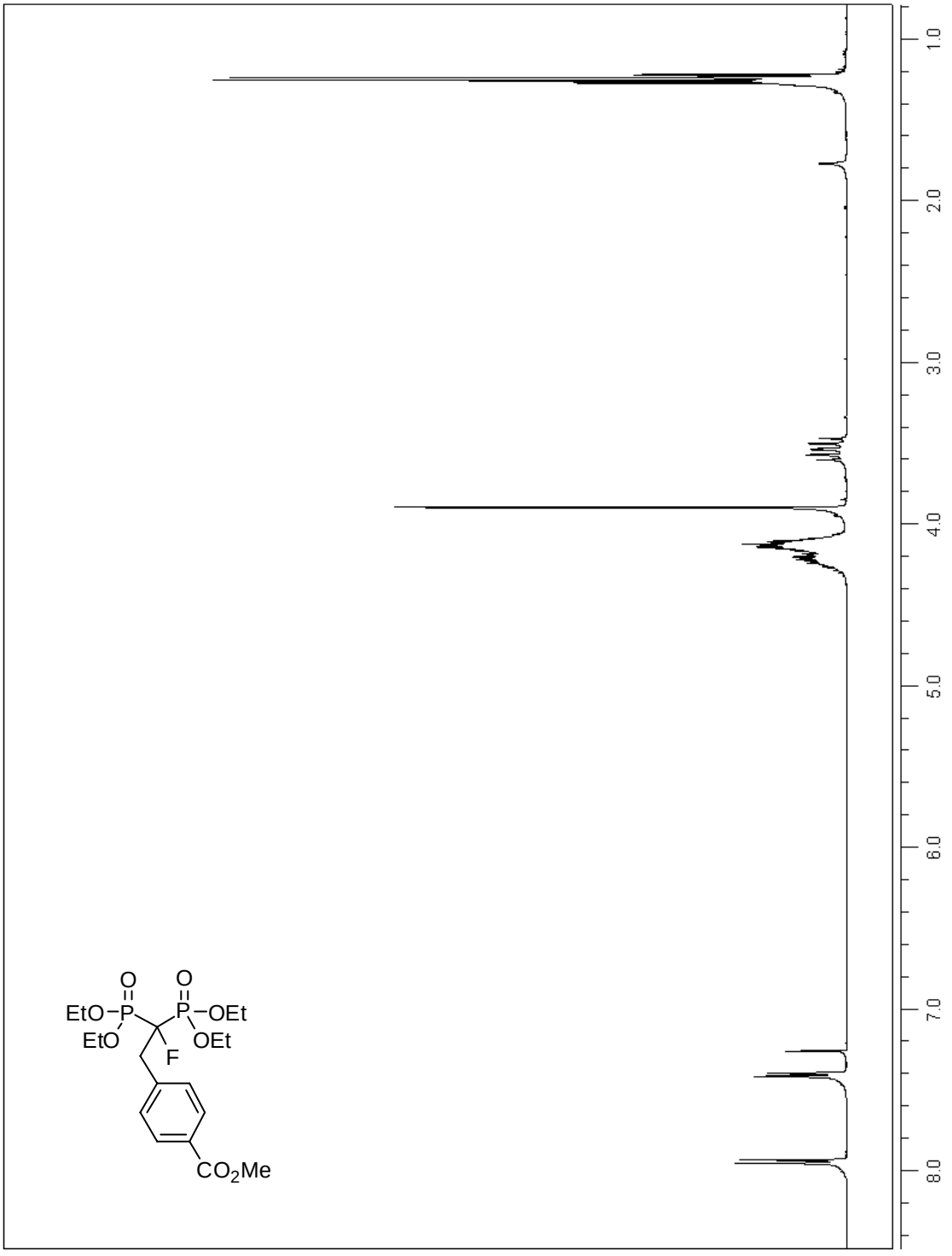

$^{13}$C NMR spectrum of **2k**



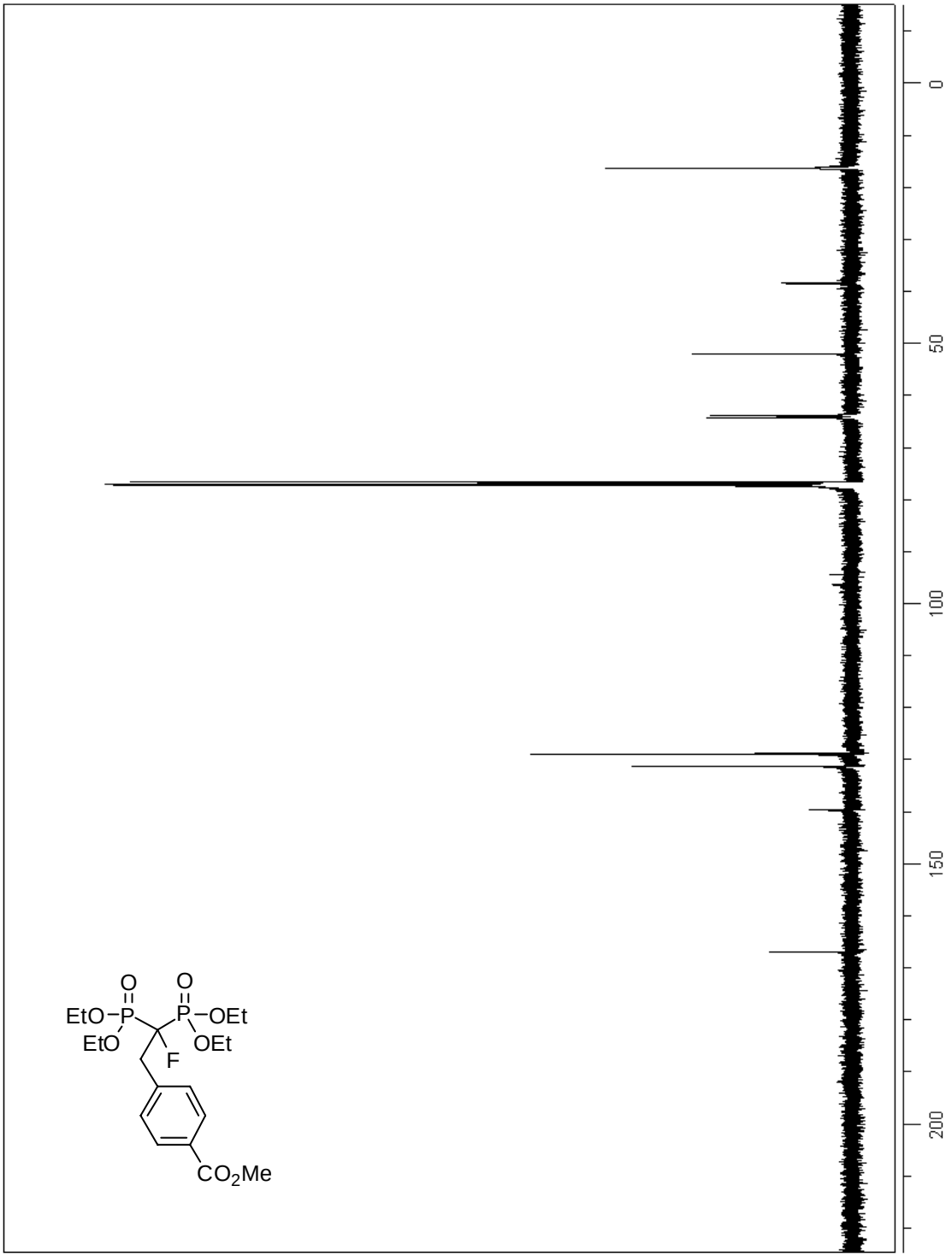

$^{19}$F NMR spectrum of **2k**



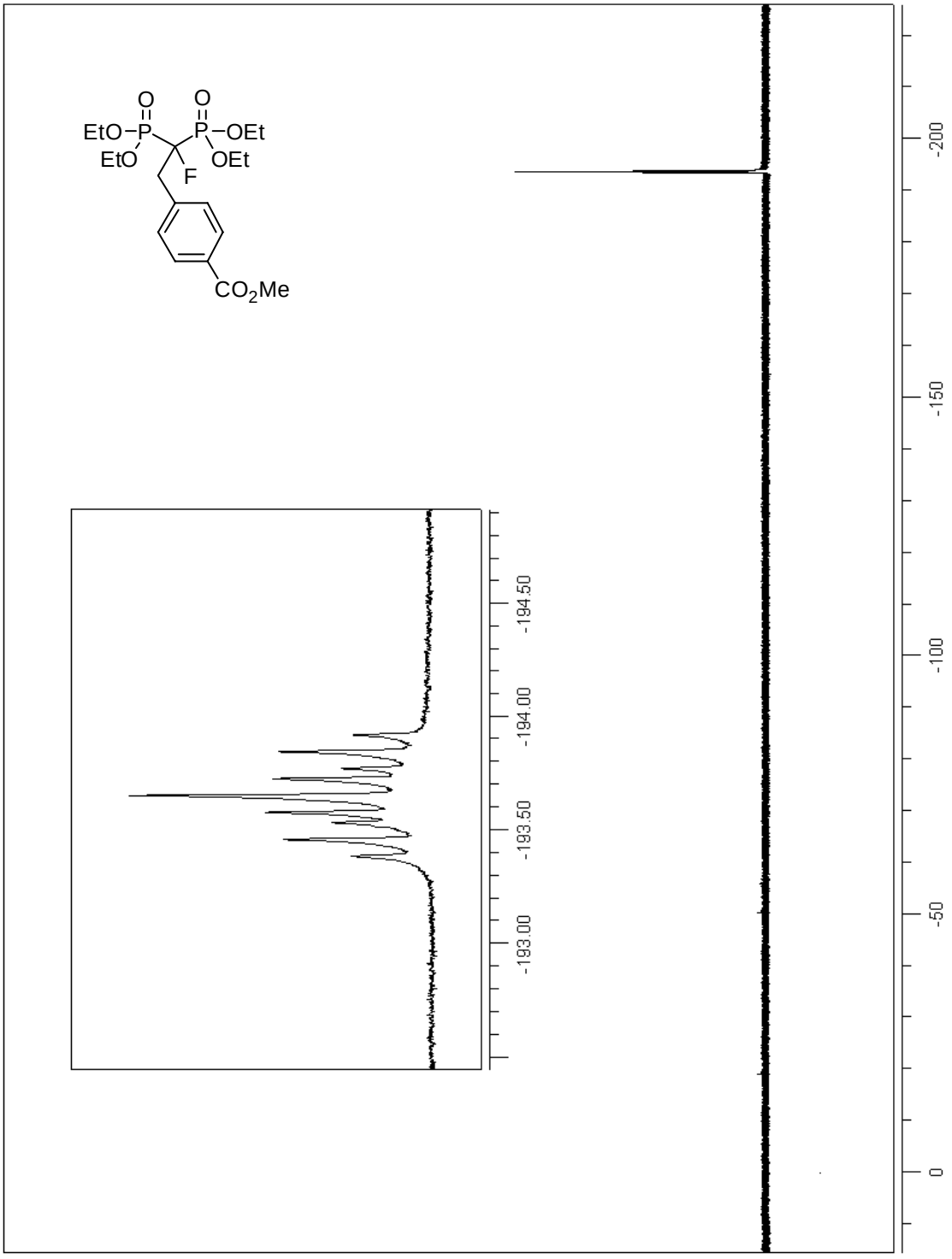

$^{31}$P NMR spectrum of **2k**



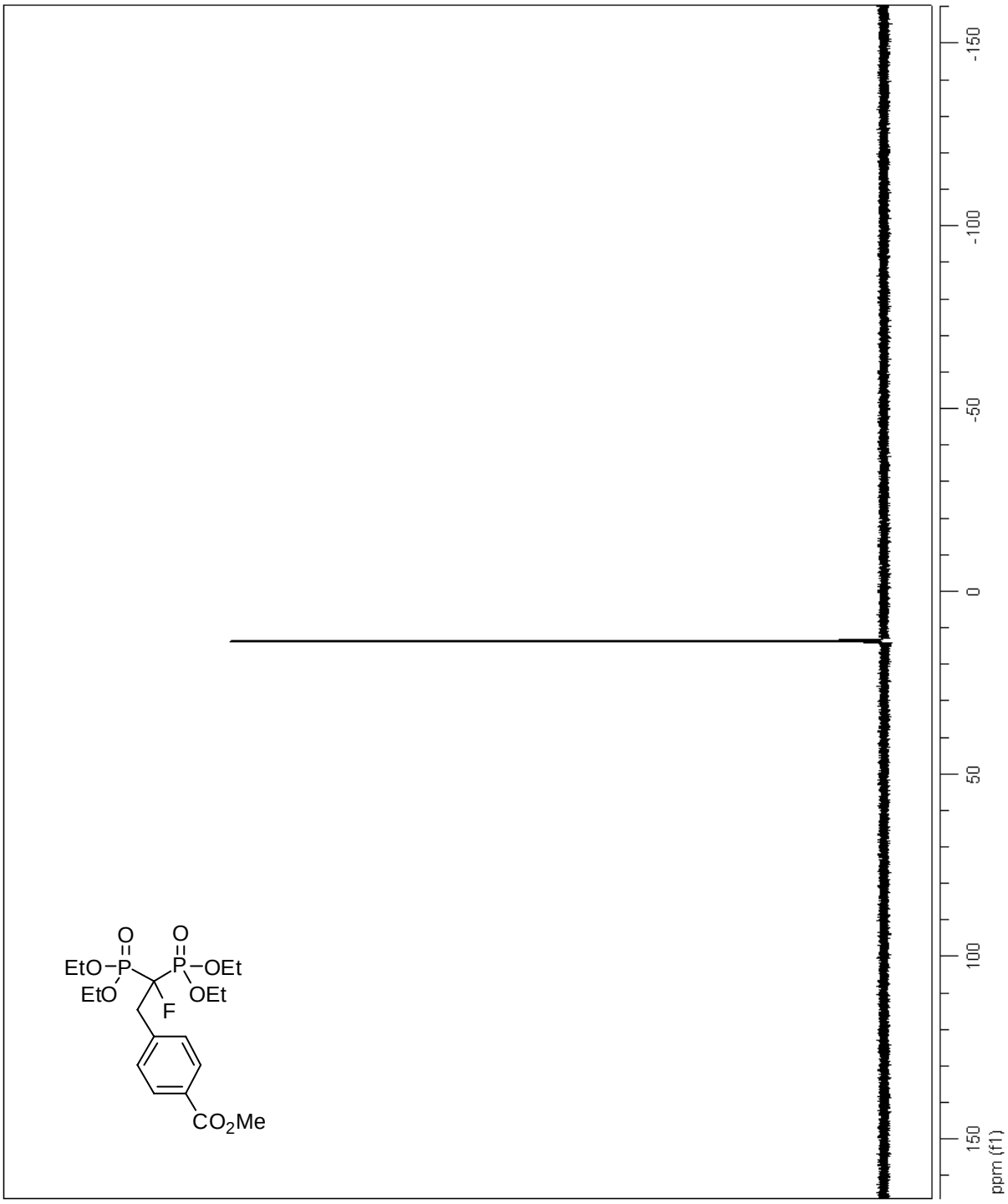

$^{1}$H NMR spectrum of **2l**



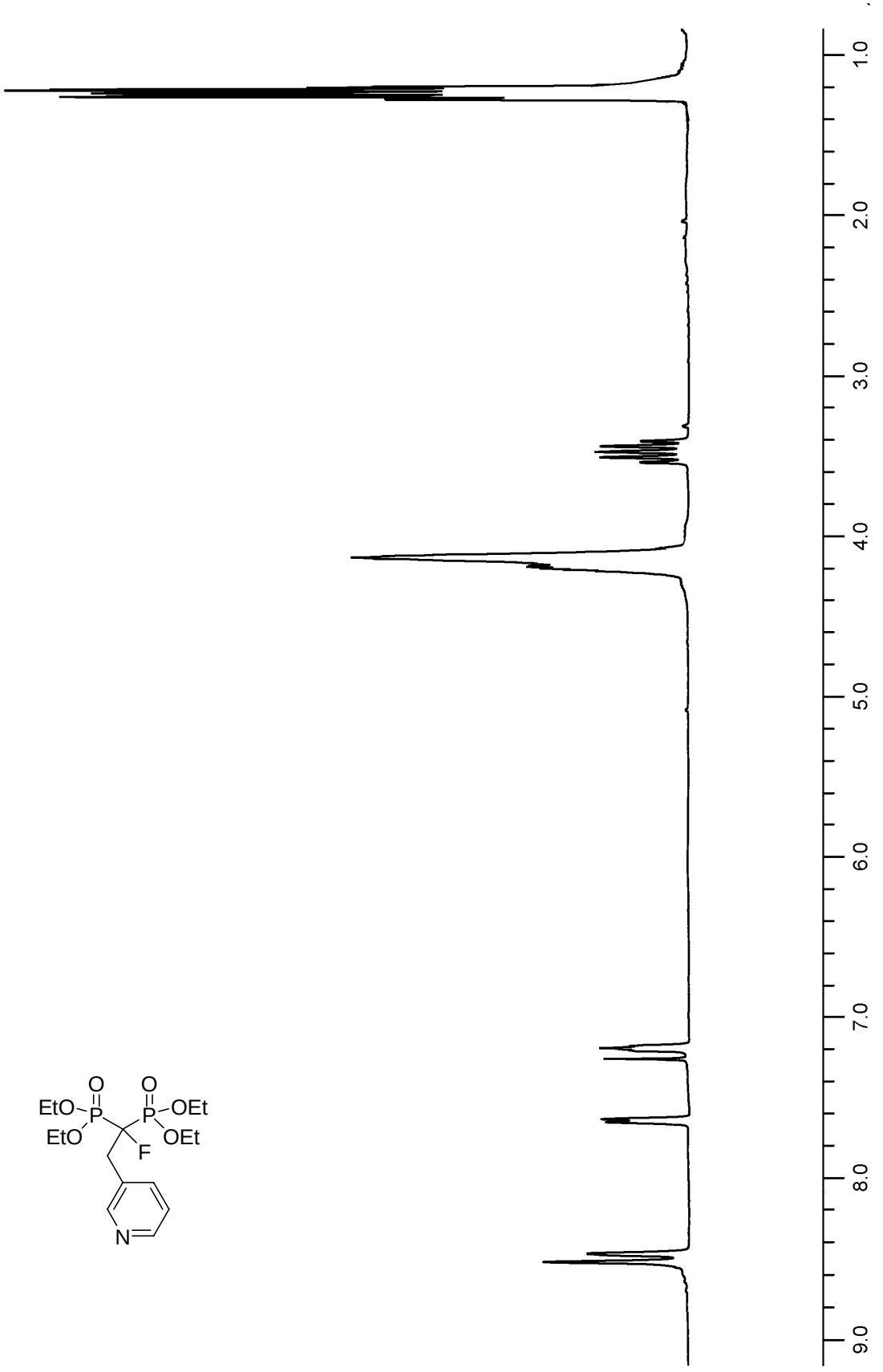

$^{13}$C NMR spectrum of **2l**



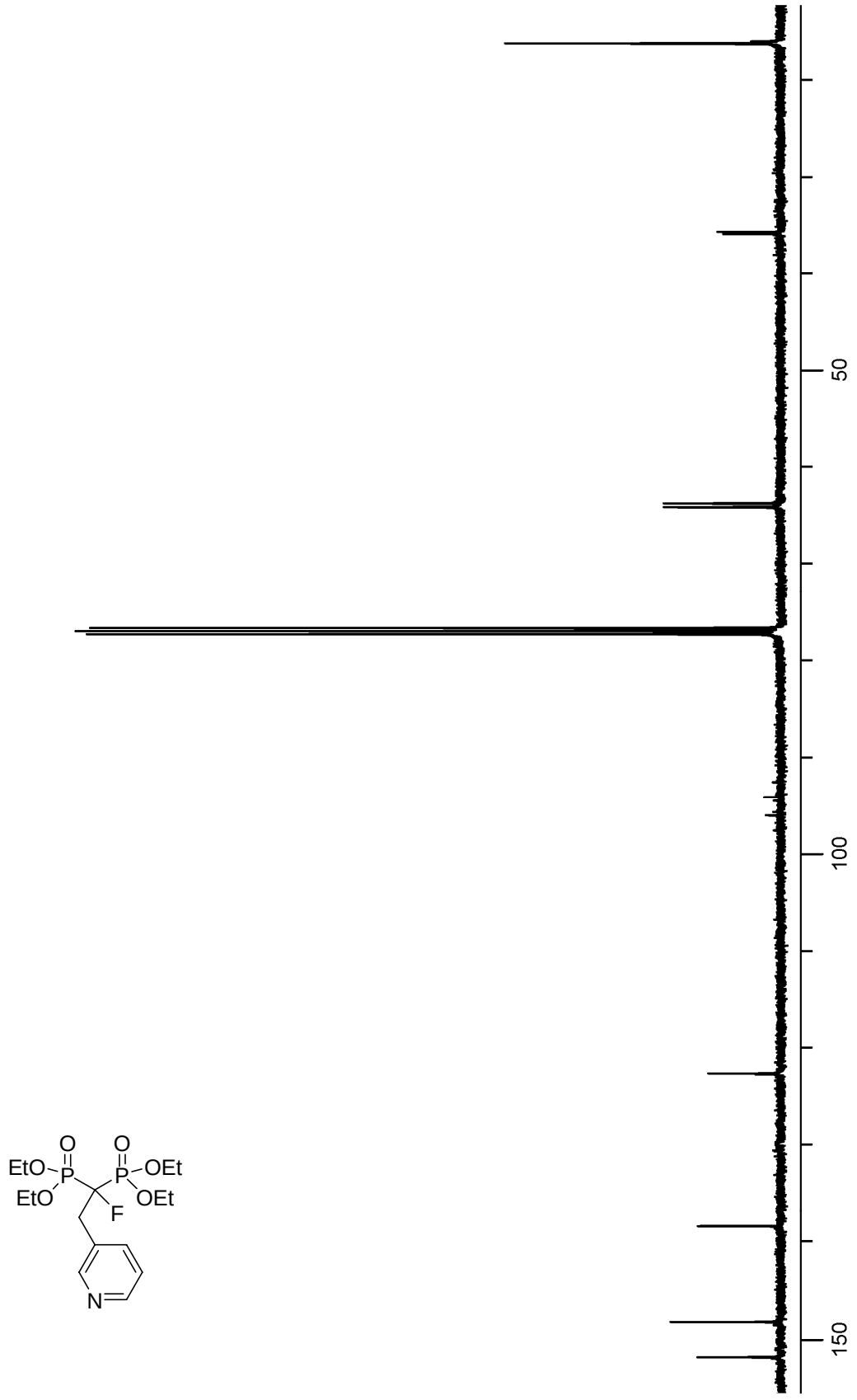

$^{19}$F NMR spectrum of **2l**



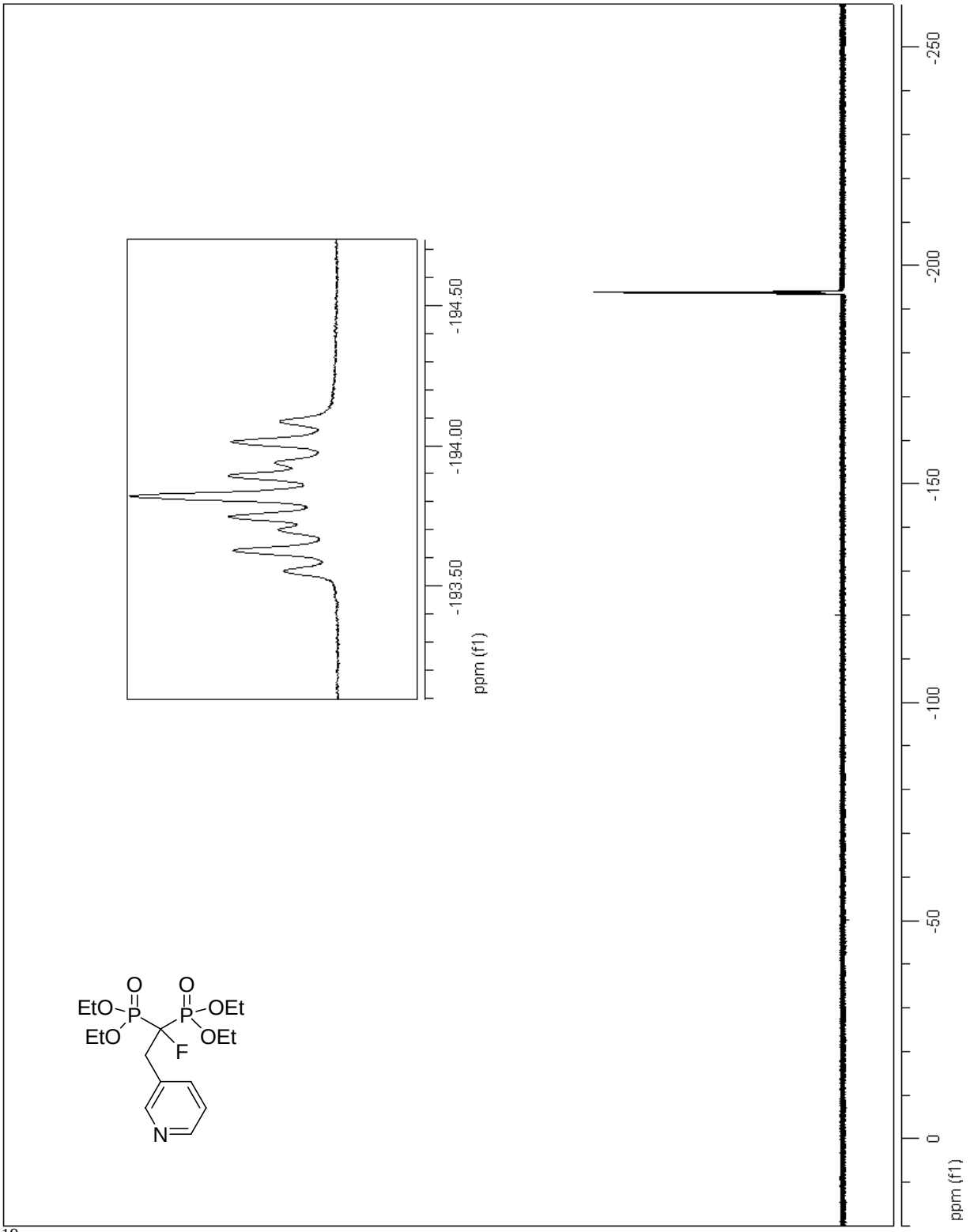

$^{31}$P NMR spectrum of **2l**



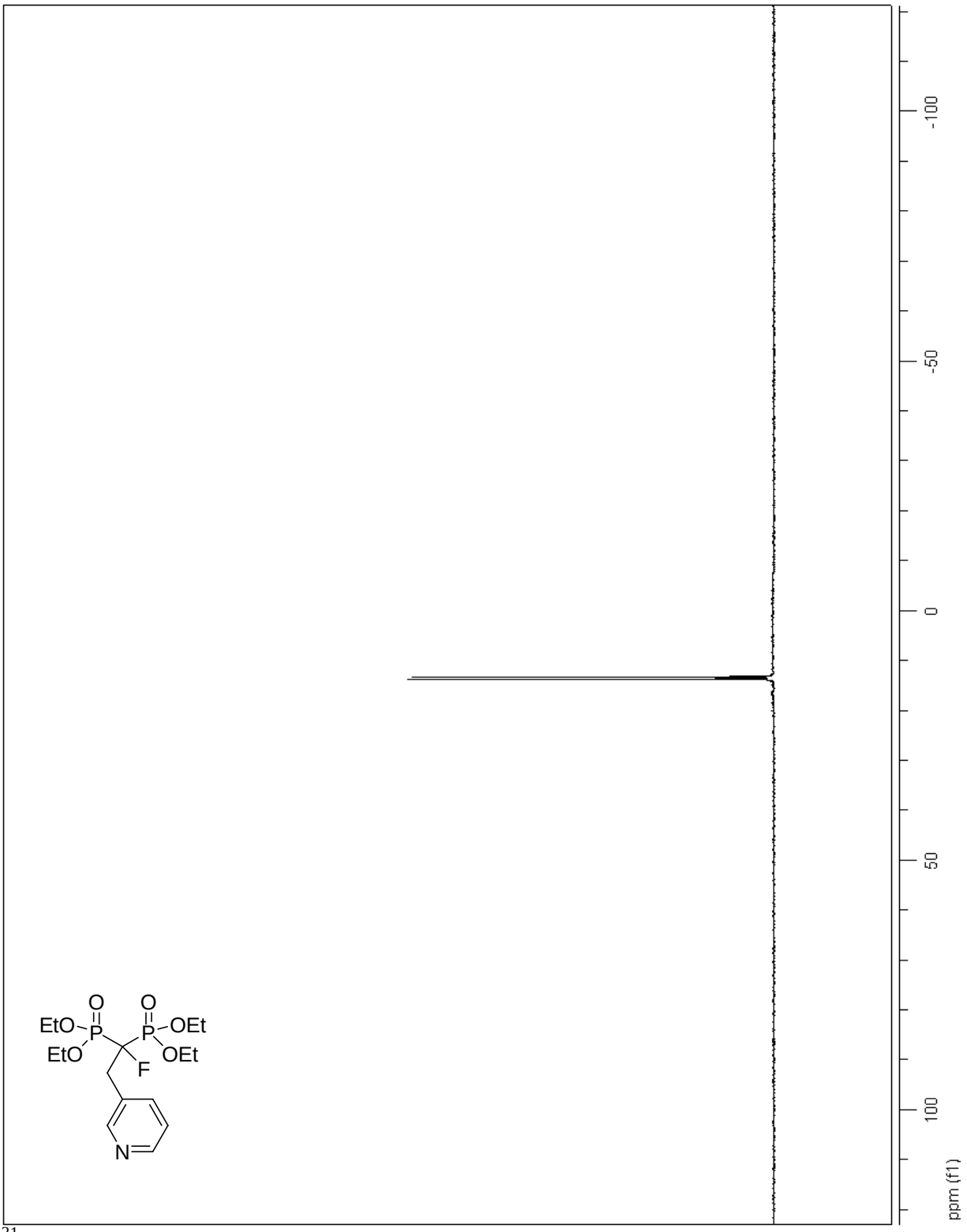

$^{1}$H NMR spectrum of **2m**



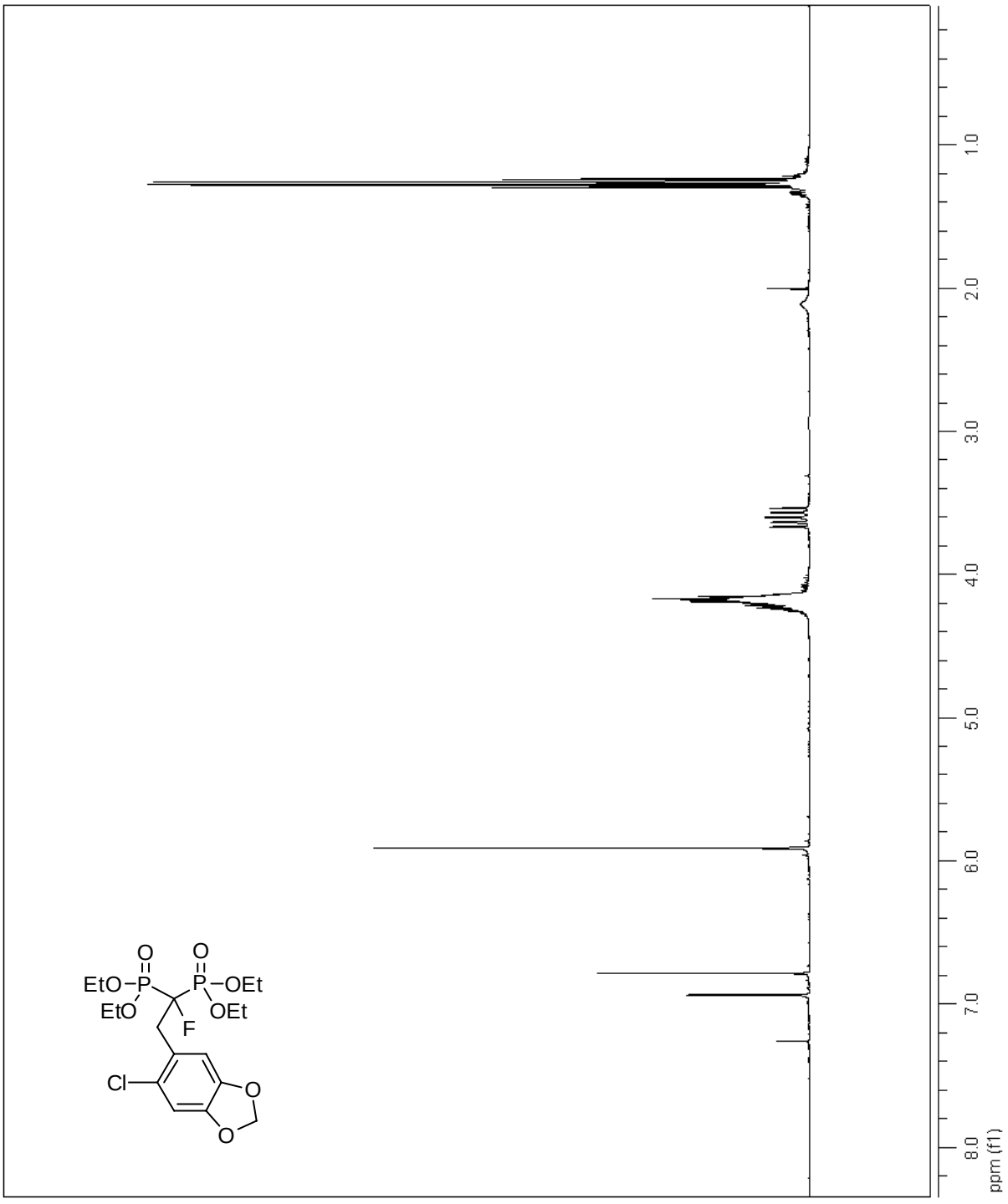

$^{13}$C NMR spectrum of **2m**



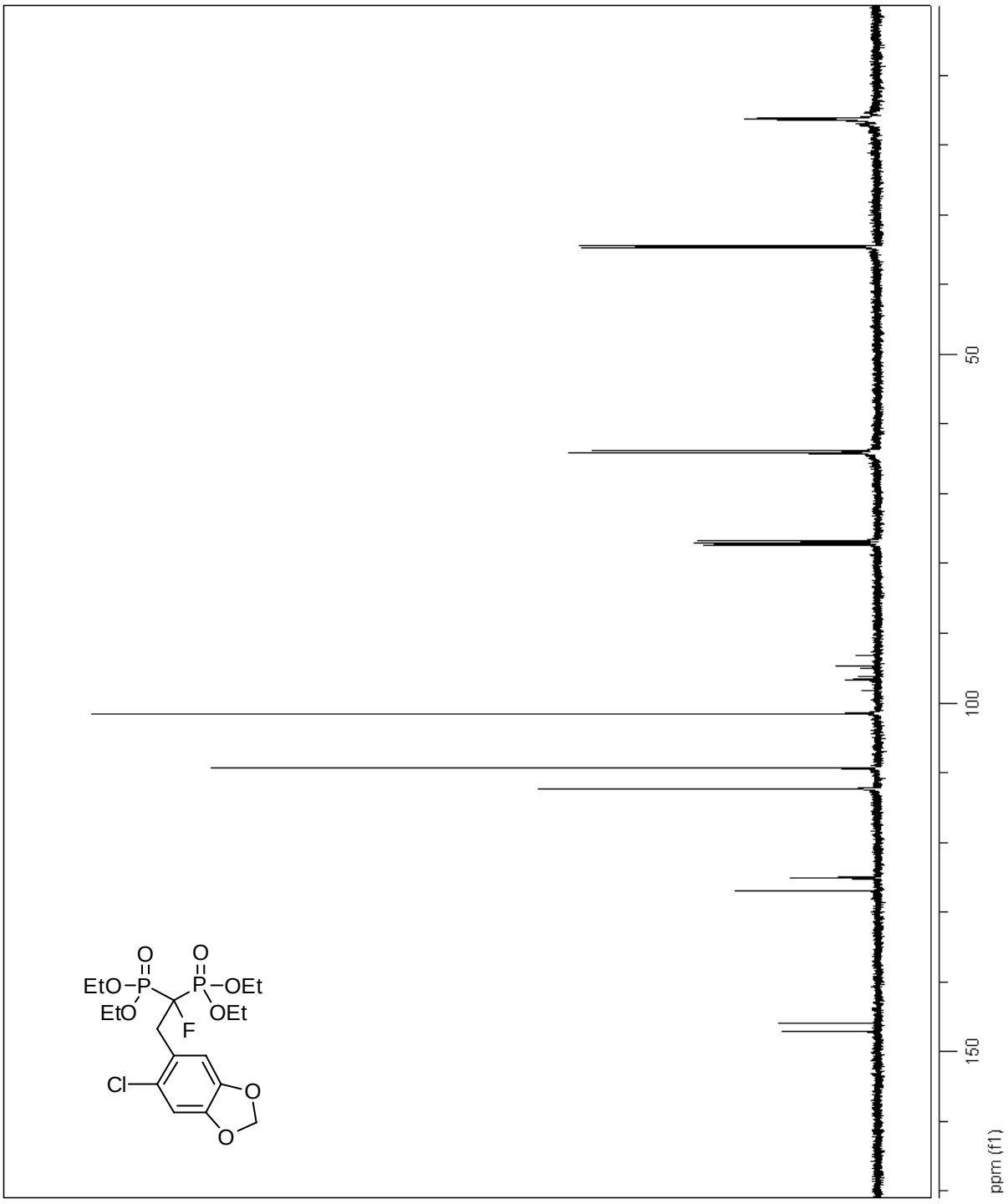

$^{19}$F NMR spectrum of **2m**



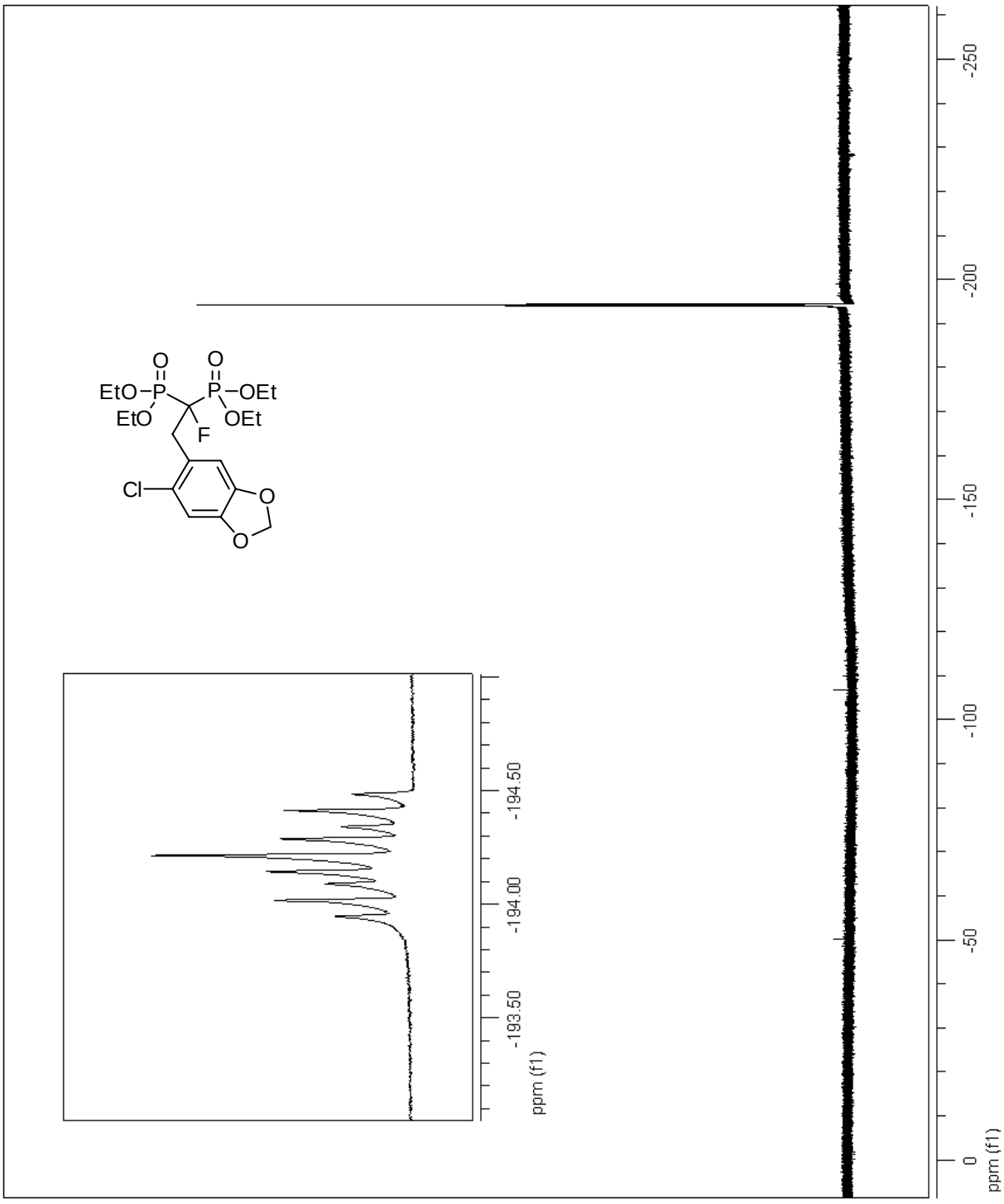

$^{31}$P NMR spectrum of **2m**



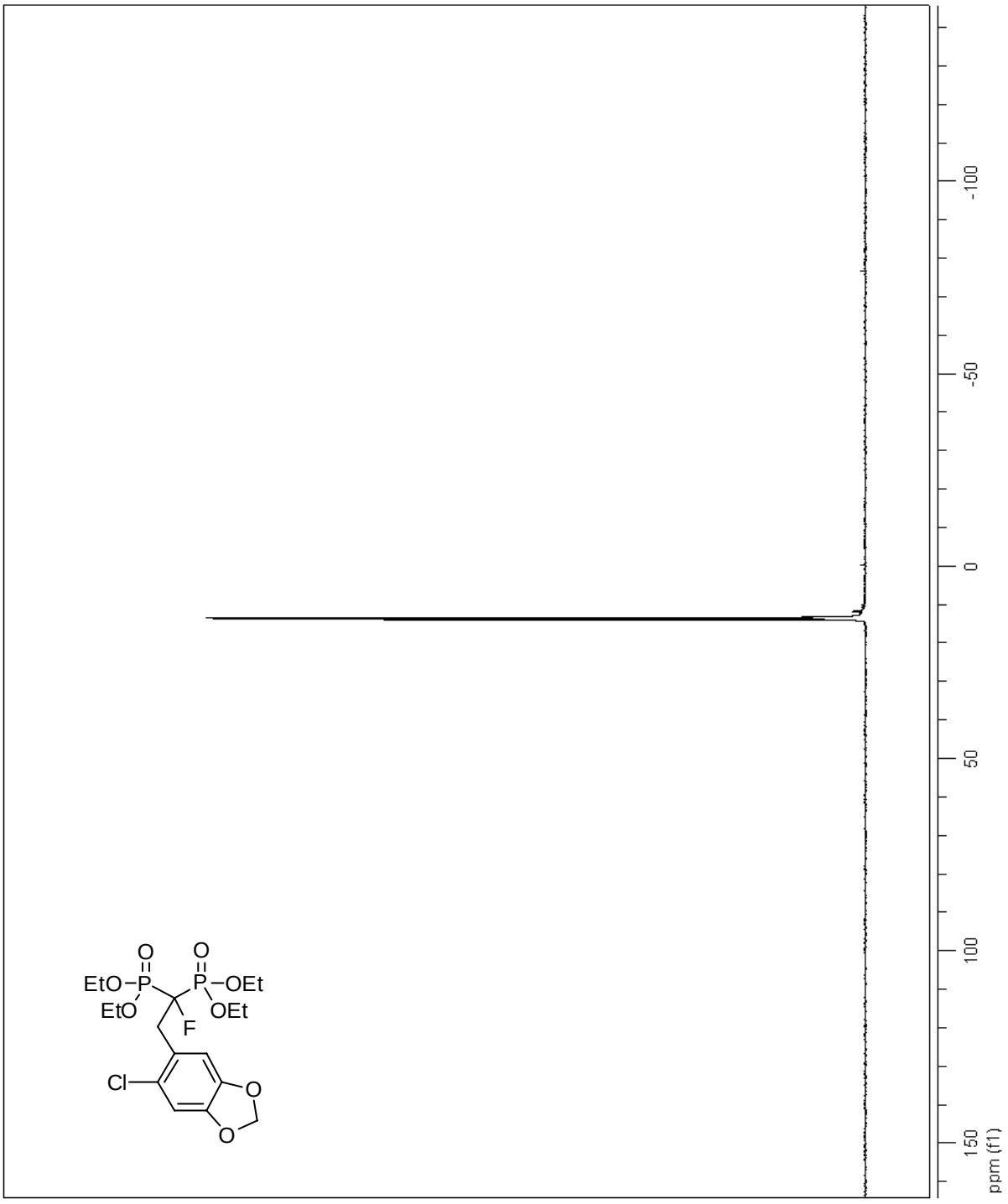

$^{1}$H NMR spectrum of **2n**



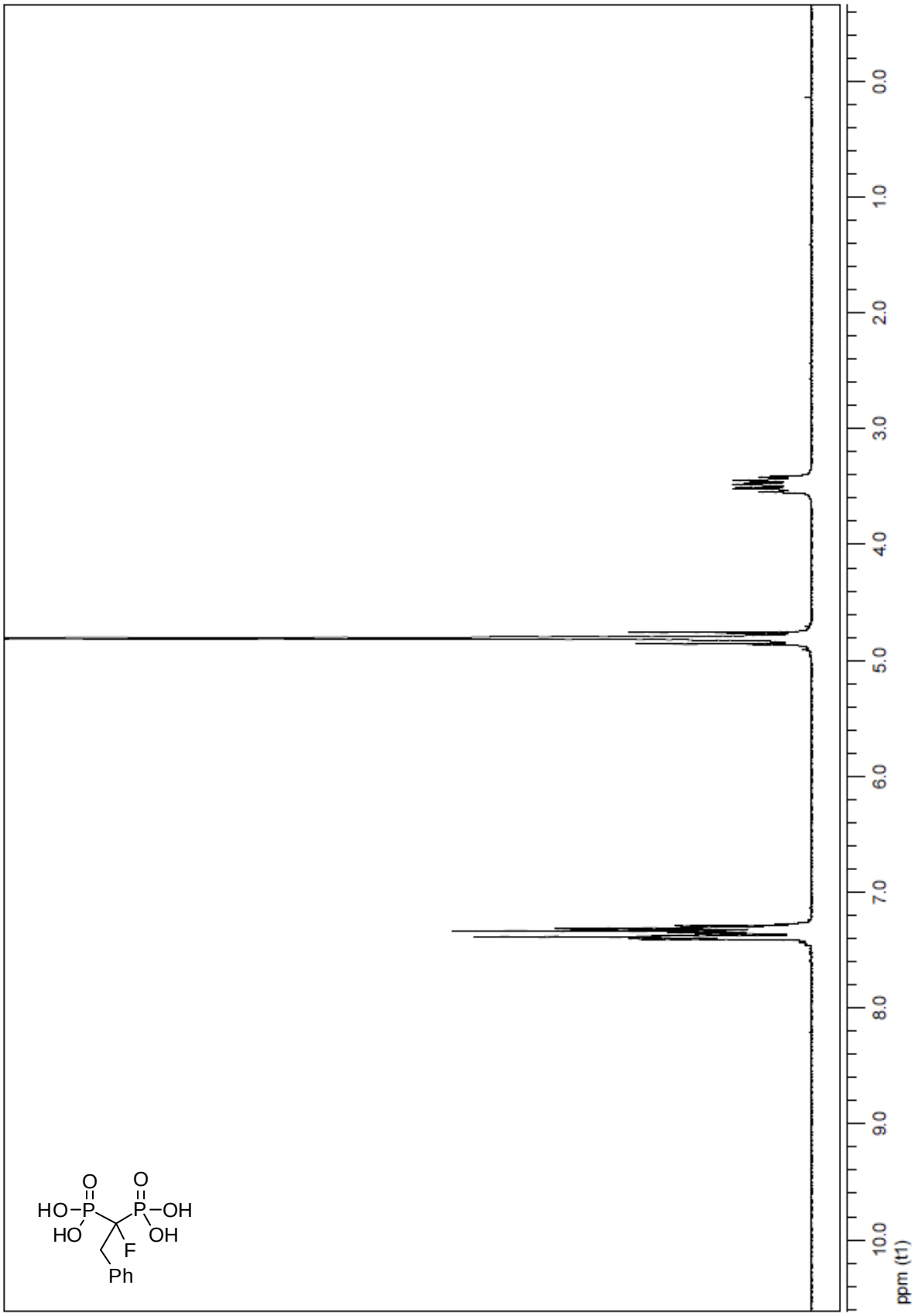

$^{13}$C NMR spectrum of **2n**



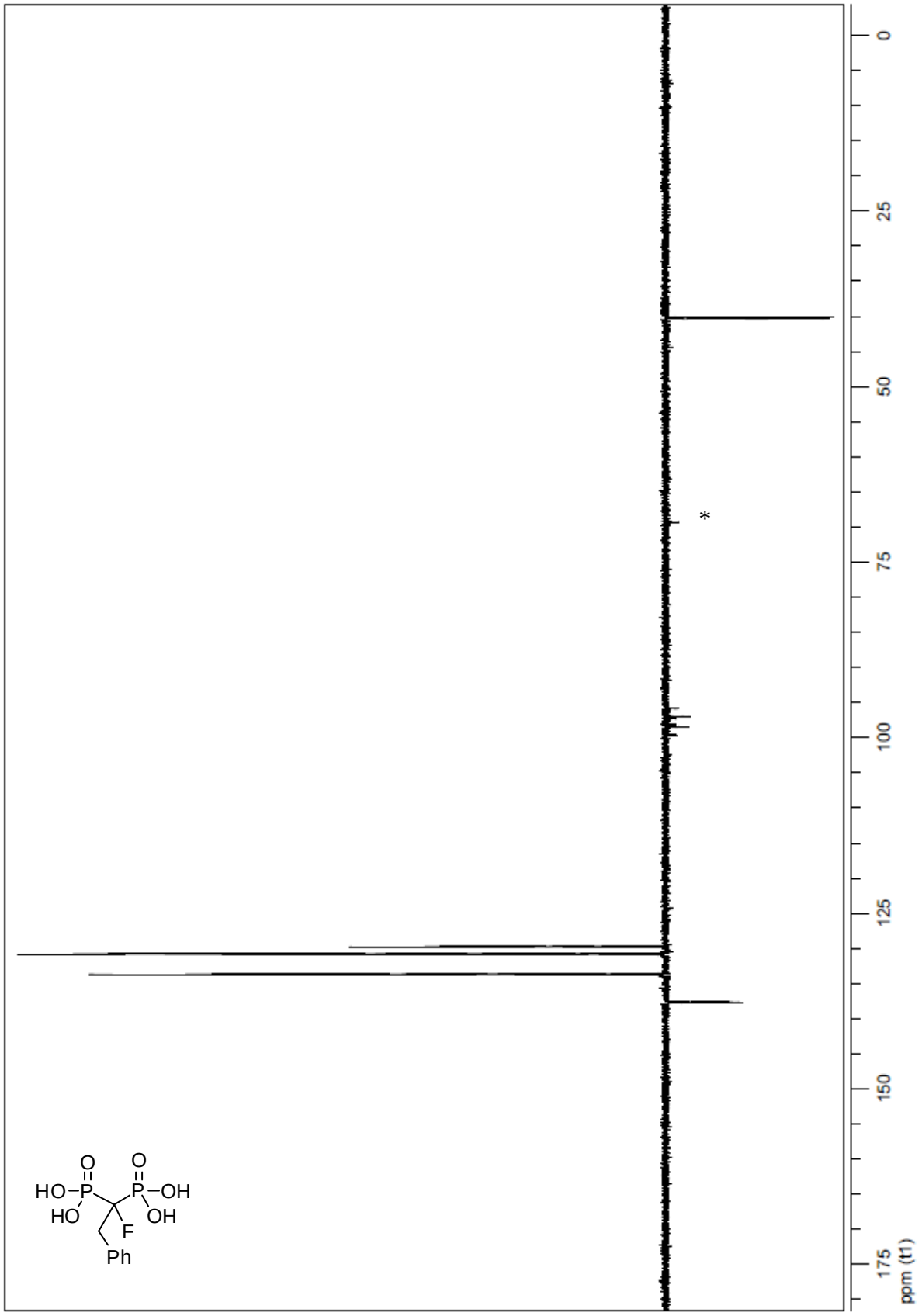

$^{19}$F NMR spectrum of **2n**



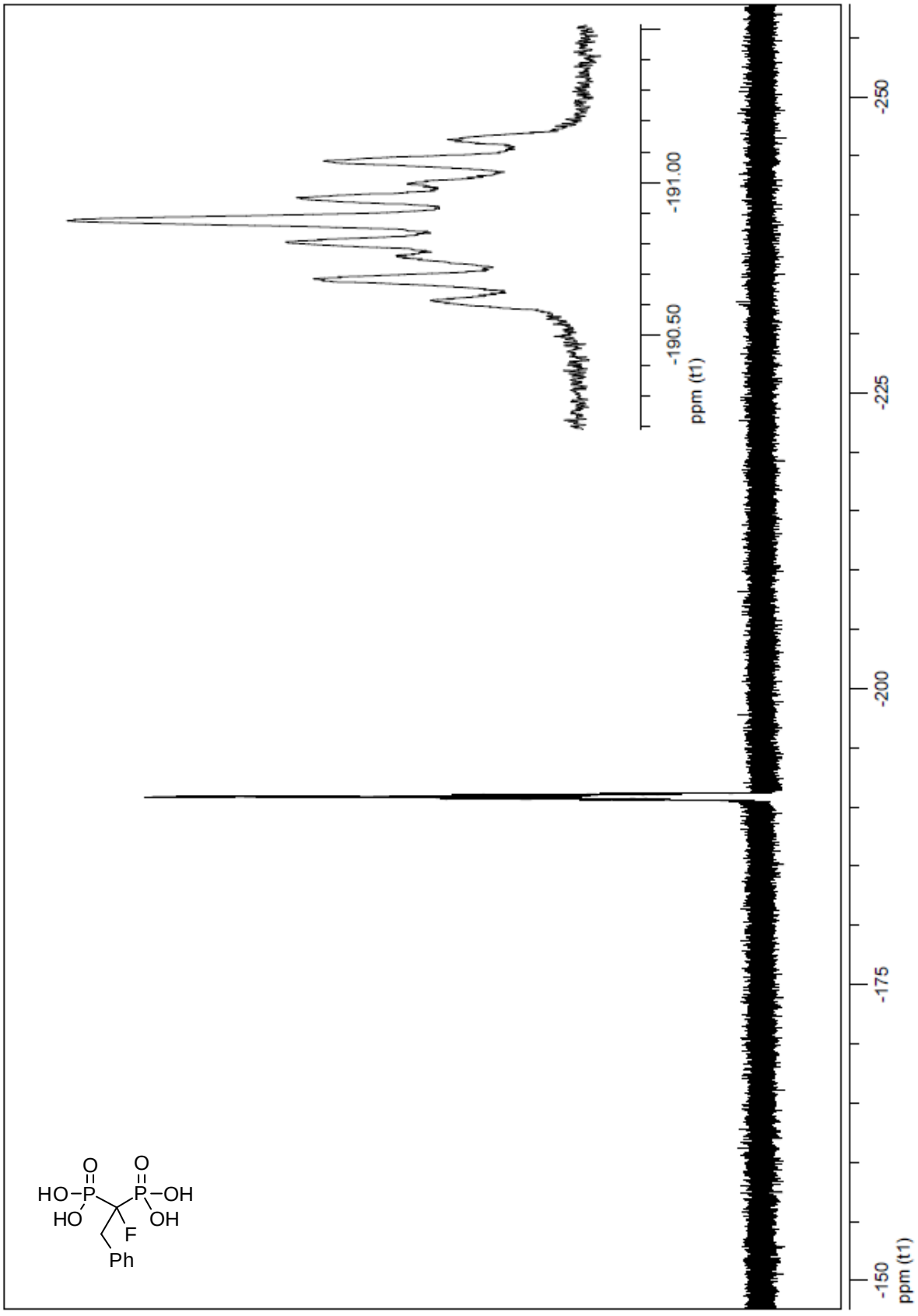

$^{31}$P NMR spectrum **2n**



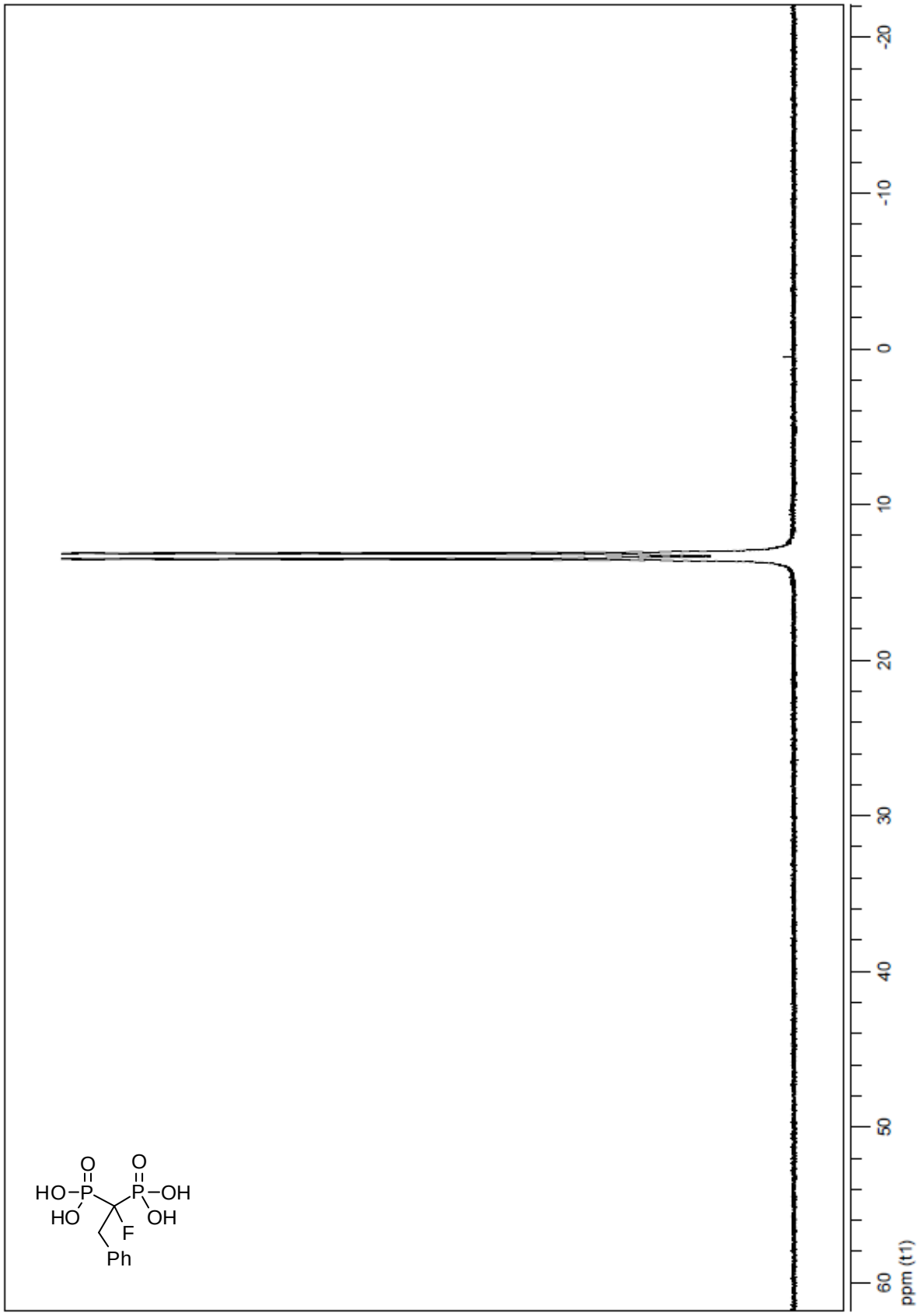

$^{1}$H NMR spectrum of **3i**.



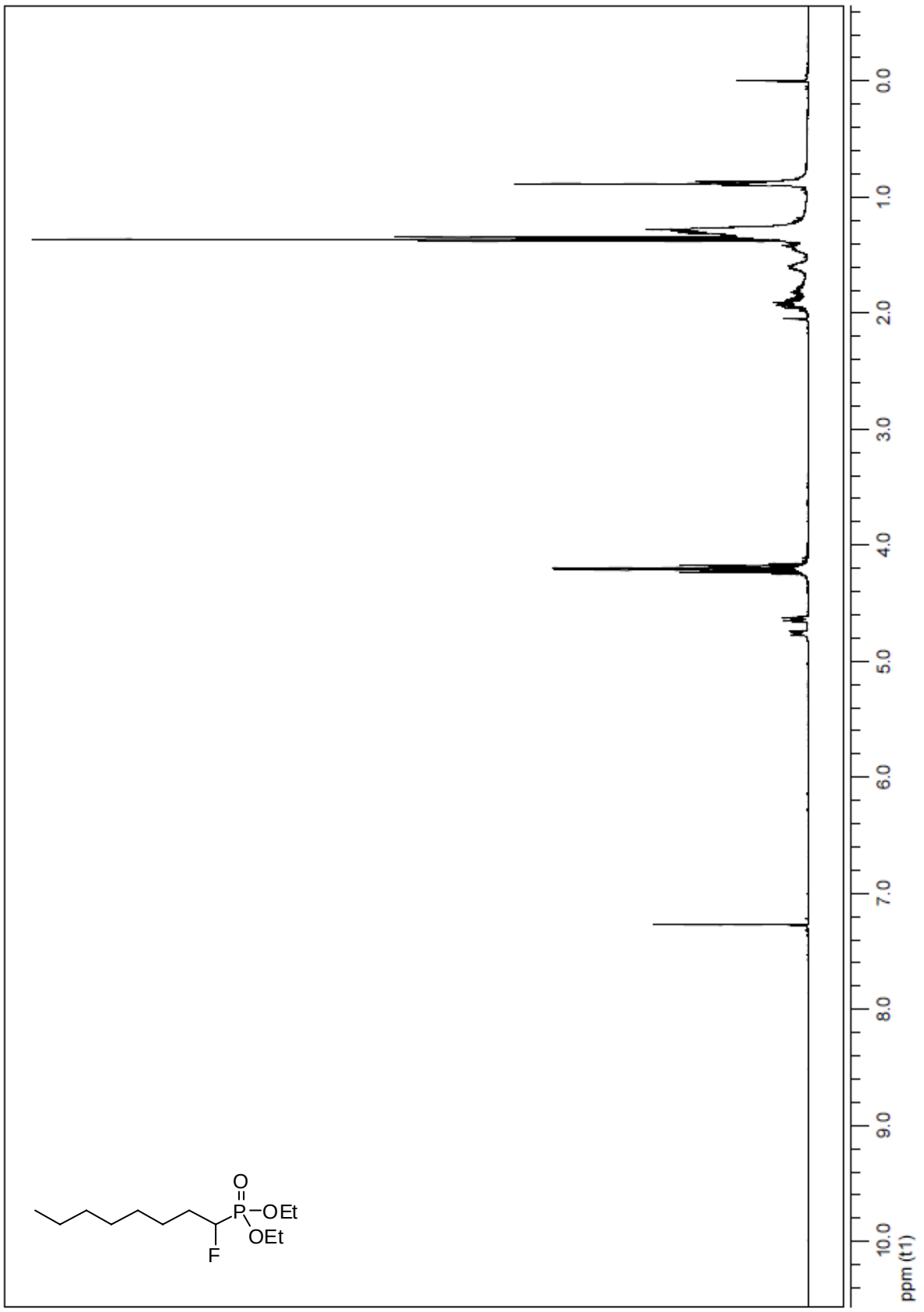

$^{13}$C NMR spectrum of **3i**.



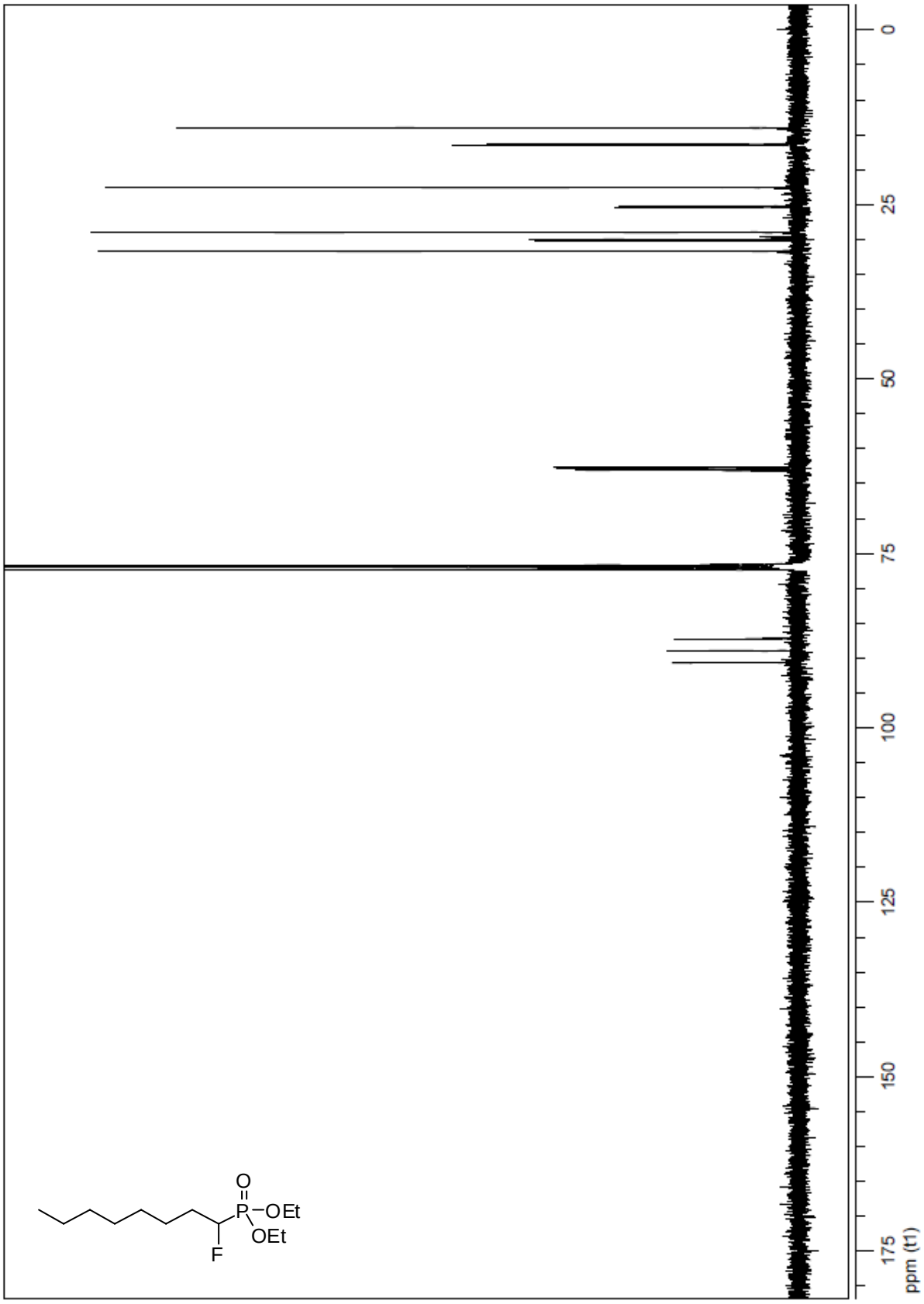

$^{19}$F NMR spectrum of **3i**.



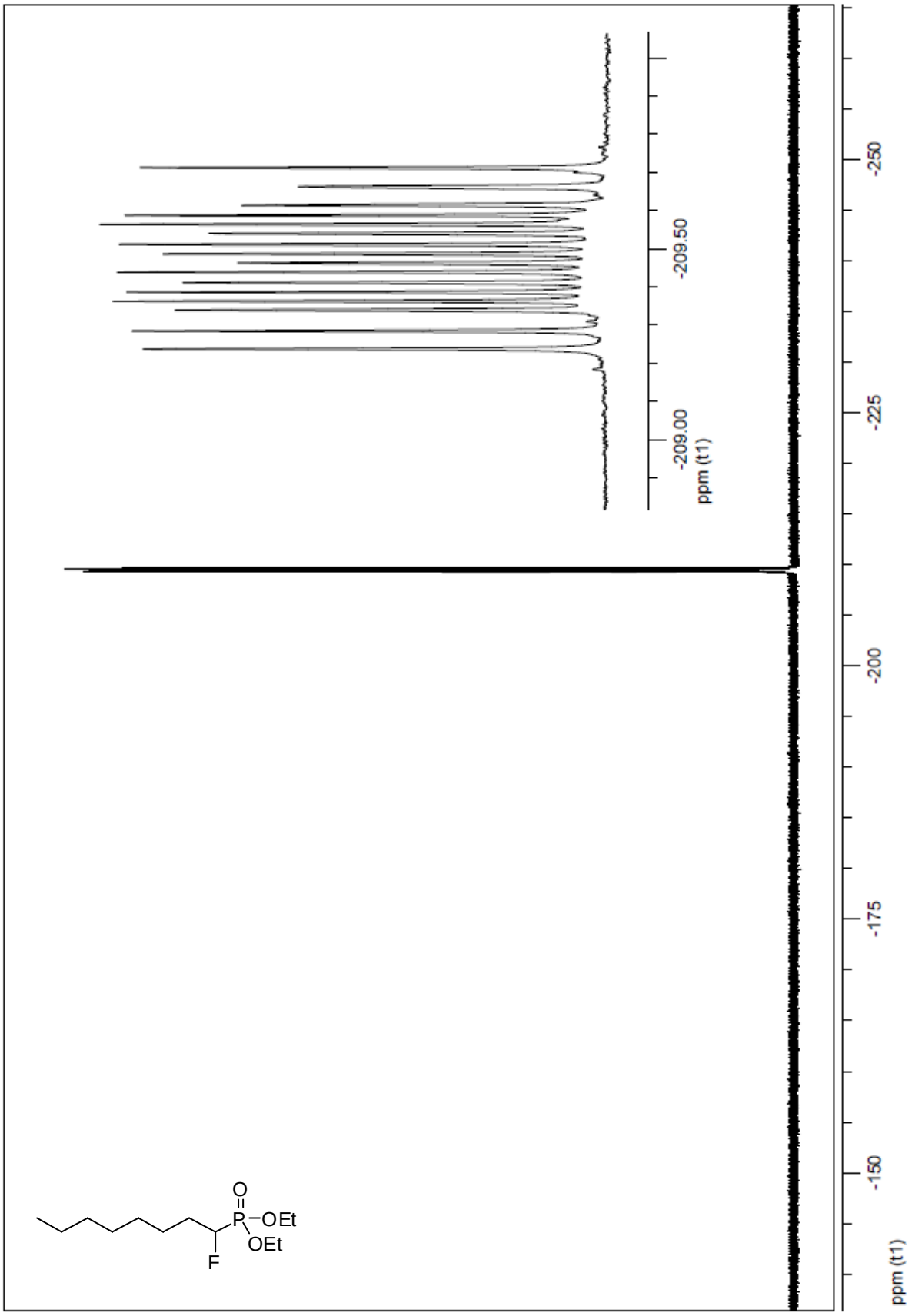

$^{31}$P NMR spectrum of **3i**.



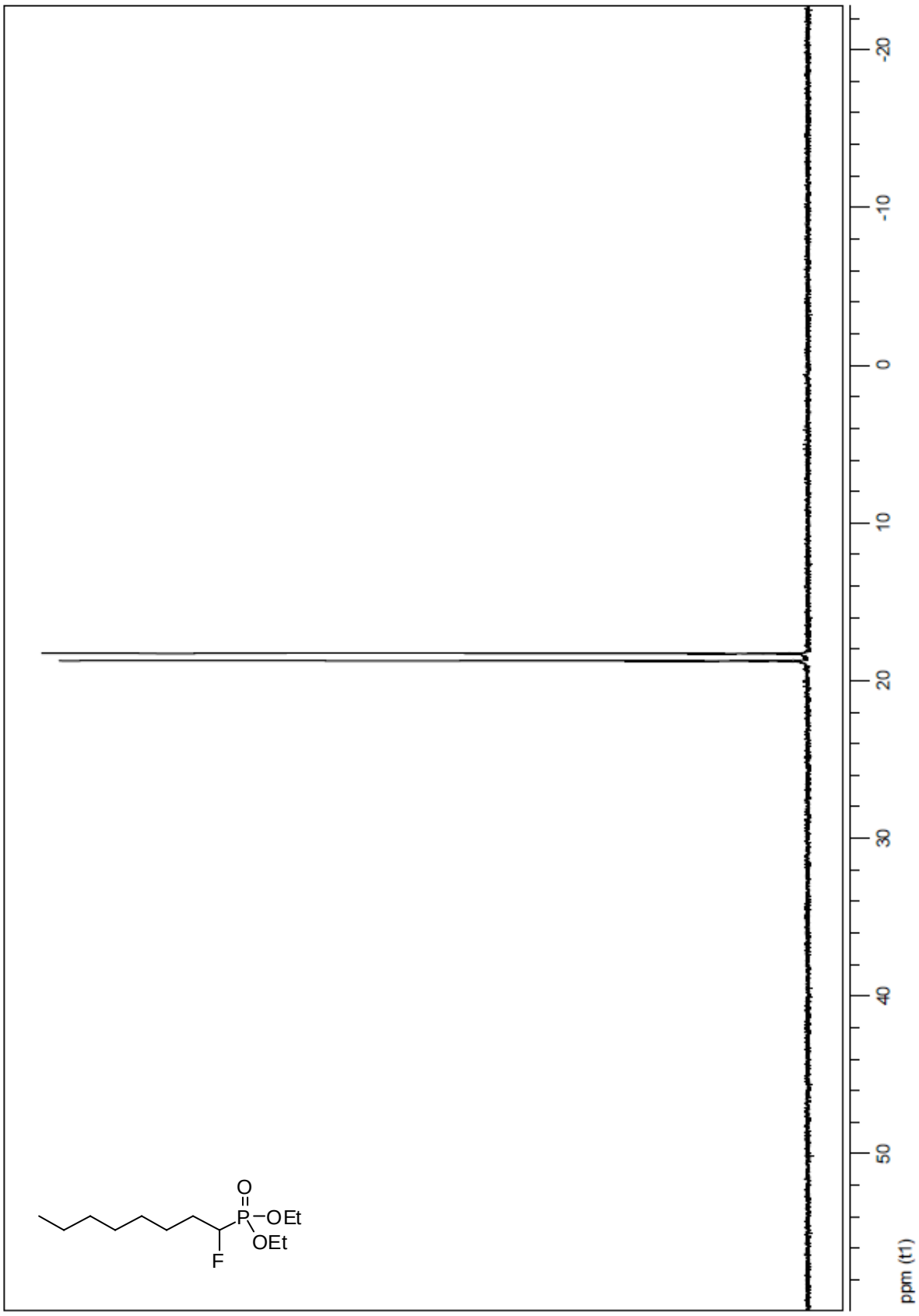

$^{1}$H NMR spectrum of **4f**.




$^{13}$C NMR spectrum of **4f**.




$^{19}$F NMR spectrum of **4f**.




$^{31}$P NMR spectrum of **4f**.