

Supplementary Materials: Organocatalytic Enantioselective Epoxidation of Aryl Substituted Vinylidenebisphosphonate Esters: On the Way to Chiral Anti-Osteoporosis Drugs

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General.

^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were run on:

BrukerAvance 300 spectrometer operating at 300 and 122 MHz, respectively, at 298 K.

BrukerAvance 400 spectrometer operating at 400 and 162 MHz, respectively, at 298 K.

δ values in ppm are relative to $\text{Si}(\text{CH}_3)_4$ and 85% H_3PO_4 .

GC-MS analyses were performed on a GC Trace GC 2000 coupled with a quadrupole MS Thermo Finnigan Trace MS with *Full Scan* method. Experimental conditions are reported in the following table.

Table S1. Experimental conditions for GC-MS analyses.

Capillary column:	HP5-MS 30 m, 0.25 mm x 0.25 μm
Initial T, $^{\circ}\text{C}$:	80 $^{\circ}\text{C}$ for 5 min
Rate, $^{\circ}\text{C}/\text{min}$:	30 $^{\circ}\text{C}/\text{min}$
Final T, $^{\circ}\text{C}$:	280 $^{\circ}\text{C}$ for 30 min
Injector T (split), $^{\circ}\text{C}$:	280 $^{\circ}\text{C}$
Gas carrier flow, mL/min.	0.8 mL/min
Injected volume, μL	0.8-1 μL
Solvent delay, min.	4 min.
Mass range, amu:	35-500 amu
Detector voltage, V:	350 V
Interface T, $^{\circ}\text{C}$	280 $^{\circ}\text{C}$
Source T, $^{\circ}\text{C}$:	200 $^{\circ}\text{C}$

Column chromatography was performed on 230-400 mesh silica, thin layer chromatography was carried out on 20 cm x 20 cm ALUGRAM[®]Xtra SIL G/UV₂₅₄ MACHEREY-NAGEL.

HPLC analyses were performed on a Hewlett Packard Series 1100 G1311A QuatPump with 20 μL injection loop and Chiralcel OD-H column with hexane:iPrOH eluent 97:3 to 90:10 (see example on Figure S26).

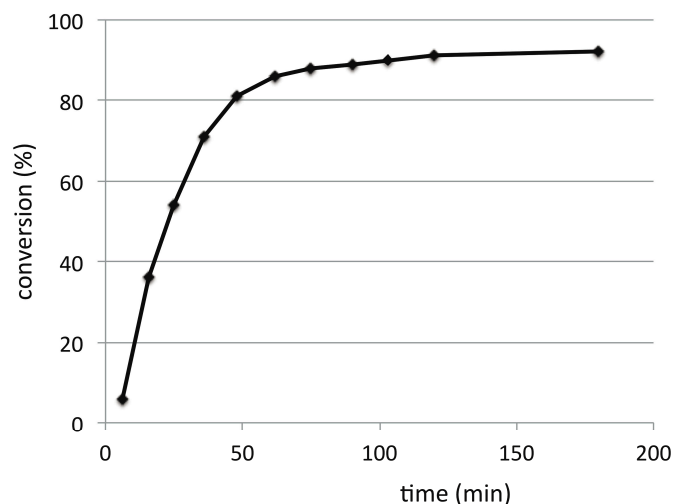
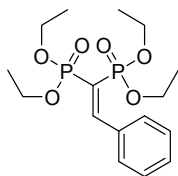


Figure S1. Stereoselective epoxidation of PPh with hydrogen peroxide catalyzed by sparteine.

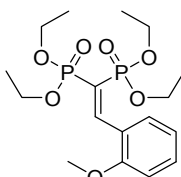
**PPh**Tetraethyl 2-phenylethene-1,1-diyl diphosphonate

^1H NMR (400 MHz, CDCl_3) δ 8.26 (dd, $J = 47.7, 29.1$ Hz, 1H), 7.73 – 7.66 (m, 2H), 7.37 – 7.31 (m, 3H), 4.22 – 4.10 (m, 4H), 4.04 – 3.92 (m, 4H), 1.34 (t, $J = 7.1$ Hz, 6H), 1.10 (t, $J = 7.1$ Hz, 6H).

^{31}P {1H}-NMR (162 MHz, CDCl_3) δ 17.15 (d, $J = 50.6$ Hz, 1P), 11.94 (d, $J = 50.5$ Hz, 1P).

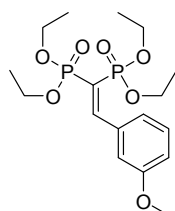
^{13}C {1H}-NMR (101 MHz, CDCl_3) δ 161.36 (d, $J = 2.0$ Hz), 134.59 (dd, $J = 21.7, 8.6$ Hz), 130.45 (s), 130.27 (t, $J = 1.4$ Hz), 128.00 (s), 120.96 (dd, $J = 170.2, 165.2$ Hz), 62.62 (s), 62.39 (d, $J = 6.3$ Hz), 16.28 (d, $J = 6.6$ Hz), 15.97 (d, $J = 6.7$ Hz).

GC-MS (70 eV) m/z : 376 [M^+], 331 [$\text{M}^+ - \text{OCH}_2\text{CH}_3$], 239 [$\text{M}^+ - \text{PO}(\text{OEt})_2$].

**PoMe**Tetraethyl 2-(2-methoxyphenyl)ethene-1,1-diyl diphosphonate

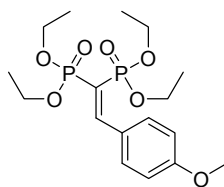
^1H NMR (300 MHz, CDCl_3) δ 8.48 (dd, $J = 48.2, 28.8$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.41 – 7.34 (m, 1H), 6.96 (t, $J = 7.4$ Hz, 1H), 6.86 (d, $J = 8.3$ Hz, 1H), 4.27 – 4.13 (m, 4H), 4.11 – 3.94 (m, 4H), 3.84 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 6H), 1.14 (t, $J = 7.1$ Hz, 6H) ppm.

^{31}P {1H}-NMR (122 MHz, CDCl_3) δ 16.06 (d, $J = 53.2$ Hz, 1P), 11.32 (d, $J = 53.1$ Hz, 1P) ppm.

**PmMe**Tetraethyl 2-(3-methoxyphenyl)ethene-1,1-diyl diphosphonate

^1H NMR (300 MHz, CDCl_3) δ 8.29 (dd, $J = 47.6, 29.1$ Hz, 1H), 7.46 (s, 1H), 7.31 – 7.26 (m, 2H), 6.98 – 6.93 (m, 1H), 4.27 – 4.15 (m, 4H), 4.11 – 3.97 (m, 4H), 3.84 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 6H), 1.17 (t, $J = 7.1$ Hz, 6H) ppm.

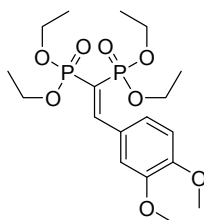
^{31}P {1H}-NMR (122 MHz, CDCl_3) δ 18.53 (d, $J = 50.0$ Hz, 1P), 13.35 (d, $J = 50.0$ Hz, 1P) ppm.

**PpMe**Tetraethyl 2-(4-methoxyphenyl)ethene-1,1-diyl diphosphonate

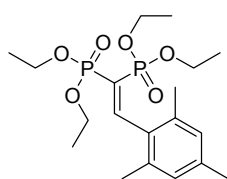
^1H NMR (300 MHz, CDCl_3) δ 8.23 (dd, $J = 48.0, 29.5$ Hz, 1H), 7.85 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.25 – 4.12 (m, 4H), 4.12 – 4.01 (m, 4H), 3.85 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 6H), 1.21 (t, $J = 7.1$ Hz, 6H) ppm.

^{31}P {1H}-NMR (122 MHz, CDCl_3) δ 19.86 (d, $J = 49.8$ Hz, 1P), 14.40 (d, $J = 49.8$ Hz, 1P) ppm.

GC-MS, (70 eV) m/z : 406 [M^+], 391 [$\text{M}^+ - \text{Me}$], 361 [$\text{M}^+ - \text{OEt}$], 269 [$\text{M}^+ - \text{PO}(\text{OEt})_2$].

**PVVeR**Tetraethyl 2-(3,4-dimethoxyphenyl)ethene-1,1-diyl diphosphonate

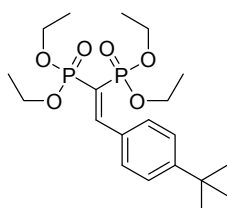
^1H NMR (300 MHz, CDCl_3) δ 8.22 (dd, $J = 47.9, 29.6$ Hz, 1H), 7.84 (d, $J = 2.1$ Hz, 1H), 7.33 (dd, $J = 8.4, 2.1$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 4H), 4.25 – 4.12 (m, 4H), 4.11 – 3.99 (m, 4H), 3.93 (d, $J = 1.3$ Hz, 6H), 1.37 (t, $J = 7.1$ Hz, 6H), 1.21 (t, $J = 7.1$ Hz, 6H) ppm. ^{31}P {1H}-NMR (122 MHz, CDCl_3) δ 17.43 (d, $J = 49.1$ Hz, 1P), 12.06 (d, $J = 49.1$ Hz, 1P) ppm.

Tetraethyl 2-mesitylethene-1,1-diylidiphosphonate**PMES**

^1H NMR (300 MHz, CDCl_3) δ 8.29 (dd, $J = 48.7, 27.7$ Hz, 1H), 6.84 (s, 2H), 4.31 – 4.14 (m, 2H), 4.00 – 3.85 (m, 2H), 3.81 – 3.64 (m, 2H), 2.26 (s, 3H), 2.19 (s, 6H), 1.40 (t, $J = 7.1$ Hz, 6H), 1.12 (t, $J = 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 14.32 (d, $J = 55.0$ Hz, 1P), 9.98 (d, $J = 55.0$ Hz, 1P) ppm.

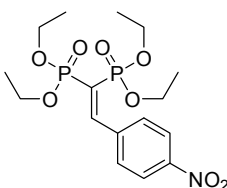
GC-MS, (70 eV) m/z : 418 [M^+], 403 [$\text{M}^+ - \text{Me}$], 373 [$\text{M}^+ - \text{OEt}$], 281 [$\text{M}^+ - \text{PO}(\text{OEt})_2$].

Tetraethyl 2-(4-tert-butylphenyl)ethene-1,1-diylidiphosphonate**PptBut**

^1H NMR (300 MHz, CDCl_3) δ 8.28 (dd, $J = 47.9, 29.2$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 4.28 – 4.11 (m, 4H), 4.11 – 3.96 (m, 4H), 1.37 (t, $J = 7.1$ Hz, 6H), 1.31 (s, 9H), 1.15 (t, $J = 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.58 (d, $J = 50.8$ Hz, 1P), 11.19 (d, $J = 50.8$ Hz, 1P) ppm.

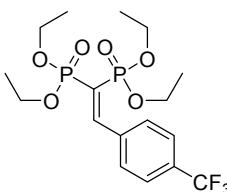
GC-MS, (70 eV) m/z : 432 [M^+], 295 [$\text{M}^+ - \text{PO}(\text{OEt})_2$], 239 [$\text{M}^+ - \text{PO}(\text{OEt})_2 - \text{tBut} + \text{H}$].

Tetraethyl 2-(4-nitrophenyl)ethene-1,1-diylidiphosphonate**PpNO₂**

^1H NMR (300 MHz, CDCl_3) δ 8.31 (dd, $J = 46.7, 28.5$ Hz, 1H), 8.24 (d, $J = 8.8$ Hz, 2H), 7.84 (d, $J = 8.8$ Hz, 2H), 4.31 – 4.15 (m, 4H), 4.14 – 3.99 (m, 4H), 1.40 (t, $J = 7.1$ Hz, 6H), 1.19 (t, $J = 7.1$ Hz, 6H) ppm.

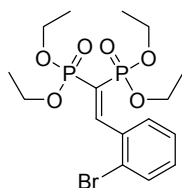
^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.61 (d, $J = 46.8$ Hz, 1P), 11.83 (d, $J = 46.8$ Hz, 1P) ppm.

GC-MS, (70 eV) m/z : 421 [M^+], 376 [$\text{M}^+ - \text{OEt}$], 284 [$\text{M}^+ - \text{PO}(\text{OEt})_2$].

Tetraethyl 2-(4-(trifluoromethyl)phenyl)ethene-1,1-diylidiphosphonate**PpCF₃**

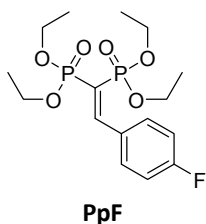
^1H NMR (300 MHz, CDCl_3) δ 8.31 (dd, $J = 47.1, 28.9$ Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 2H), 7.64 (d, $J = 8.3$ Hz, 2H), 4.30 – 4.13 (m, 4H), 4.13 – 3.93 (m, 4H), 1.39 (t, $J = 7.1$ Hz, 6H), 1.16 (t, $J = 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 17.26 (d, $J = 48.4$ Hz, 1P), 12.28 (d, $J = 48.3$ Hz, 1P) ppm.

Tetraethyl 2-(2-bromophenyl)ethene-1,1-diylidiphosphonate**PoBr**

^1H NMR (300 MHz, CDCl_3) δ 8.25 (dd, $J = 46.7, 27.7$ Hz, 1H), 7.70 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.56 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.32 (td, $J = 7.6, 1.1$ Hz, 1H), 7.22 (td, $J = 7.7, 1.6$ Hz, 1H), 4.29 – 4.15 (m, 4H), 4.03 – 3.86 (m, 4H), 1.38 (t, $J = 7.1$ Hz, 6H), 1.10 (t, $J = 7.1$ Hz, 6H) ppm.

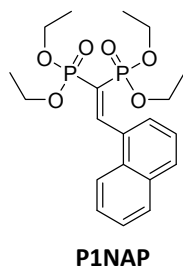
^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 14.15 (d, $J = 50.3$ Hz, 1P), 9.53 (d, $J = 50.3$ Hz, 1P) ppm. GC-MS, (70 eV) m/z : 454 [M^+ , Cluster Br], 375 [$\text{M}^+ - \text{Br}$], 317 [$\text{M}^+ - \text{PO}(\text{OEt})_2$].

Tetraethyl 2-(4-fluorophenyl)ethene-1,1-diyl diphosphonate

^1H NMR (300 MHz, CDCl_3) δ 8.21 (dd, $J = 47.6, 29.1$ Hz, 1H), 7.77 (dd, $J = 8.7, 5.4$ Hz, 2H), 7.03 (t, $J = 8.7$ Hz, 2H), 4.24 – 4.09 (m, 4H), 4.10 – 3.92 (m, 4H), 1.33 (t, $J = 7.1$ Hz, 6H), 1.14 (t, $J = 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 15.96 (d, $J = 48.7$ Hz, 1P), 10.72 (d, $J = 48.7$ Hz, 1P) ppm.

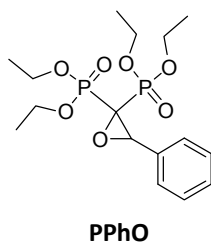
GC-MS, (70 eV) m/z : 394 [M^+], 349 [$\text{M}^+ - \text{OEt}$], 257 [$\text{M}^+ - \text{PO}(\text{OEt})_2$].

Tetraethyl 2-(naphthalen-1-yl)ethene-1,1-diyl diphosphonate

^1H NMR (300 MHz, CDCl_3) δ 8.47 (dd, $J = 47.7, 29.2$ Hz, 1H), 8.28 (s, 1H), 7.86 (dd, $J = 18.1, 8.3$ Hz, 4H), 7.57 – 7.47 (m, 2H), 4.32 – 4.15 (m, 4H), 4.12 – 3.97 (m, 4H), 1.41 (t, $J = 7.1$ Hz, 6H), 1.13 (t, $J = 7.1$ Hz, 6H) ppm.

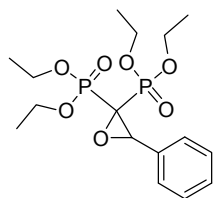
^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.16 (d, $J = 50.1$ Hz, 1P), 11.00 (d, $J = 50.1$ Hz, 1P) ppm.

GC-MS, (70 eV) m/z : 426 [M^+], 411 [$\text{M}^+ - \text{Me}$], 381 [$\text{M}^+ - \text{OEt}$], 289 [$\text{M}^+ - \text{PO}(\text{OEt})_2$].

Tetraethyl 3-phenyloxirane-2,2-diyl diphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.48 – 7.41 (m, 2H), 7.38 – 7.30 (m, 3H), 4.69 (t, $J = 5.0$ Hz, 1H), 4.38 – 4.24 (m, 3H), 4.02 – 3.85 (m, 3H), 3.83 – 3.71 (m, 1H), 1.41 (td, $J = 7.1, 2.0$ Hz, 6H), 1.13 (q, $J = 7.0$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.51 (d, $J = 72.6$ Hz, 1P), 14.65 (d, $J = 72.6$ Hz, 1P) ppm.

**PPhO**Tetraethyl 3-phenyloxirane-2,2-diylidiphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.48 – 7.41 (m, 2H), 7.38 – 7.30 (m, 3H), 4.69 (t, $J = 5.0$ Hz, 1H), 4.38 – 4.24 (m, 3H), 4.02 – 3.85 (m, 3H), 3.83 – 3.71 (m, 1H), 1.41 (td, $J = 7.1, 2.0$ Hz, 6H), 1.13 (q, $J = 7.0$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.51 (d, $J = 72.6$ Hz, 1P), 14.65 (d, $J = 72.6$ Hz, 1P) ppm.

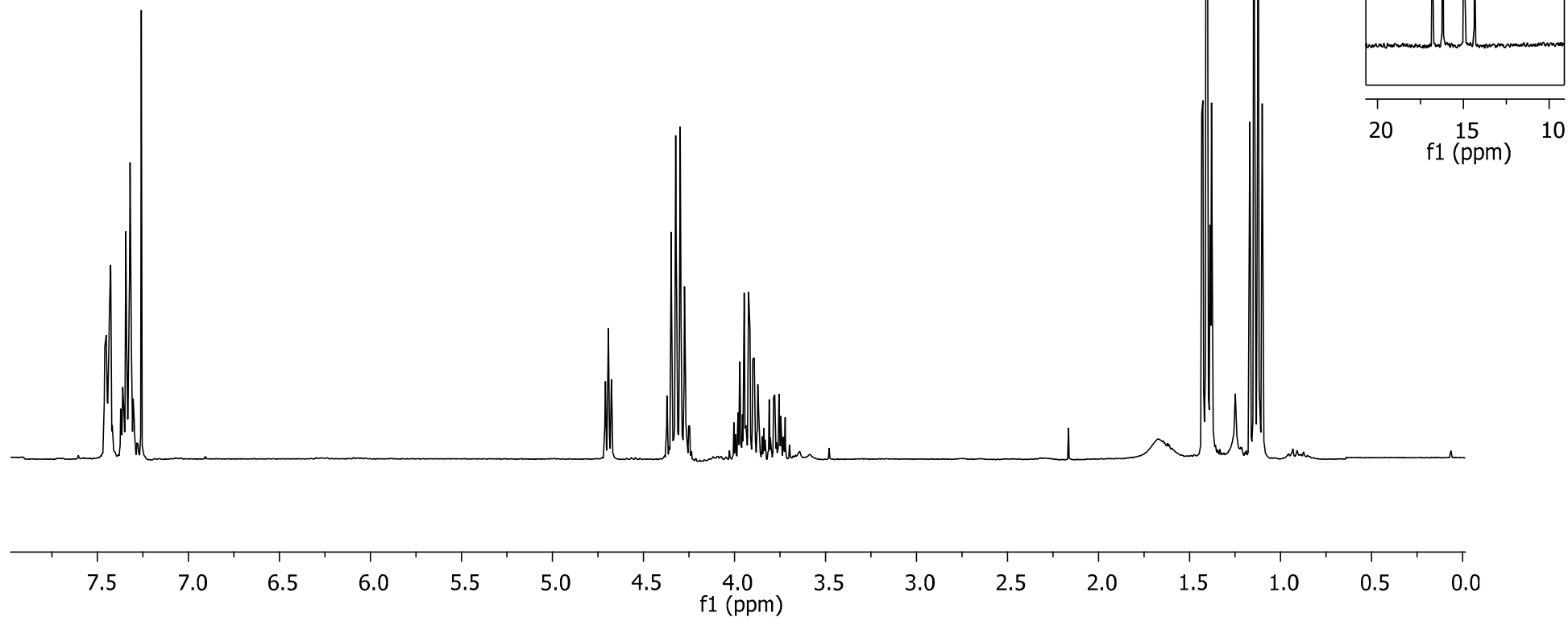


Figure S2. ^1H NMR (300 MHz, CDCl_3) spectrum of **PPhO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PPhO**.

GC-MS, (70 eV) m/z: 392 [M⁺], 377 [M⁺ - Me]; 347 [M⁺ - OEt]; 255 [M⁺ - PO(OEt)₂];

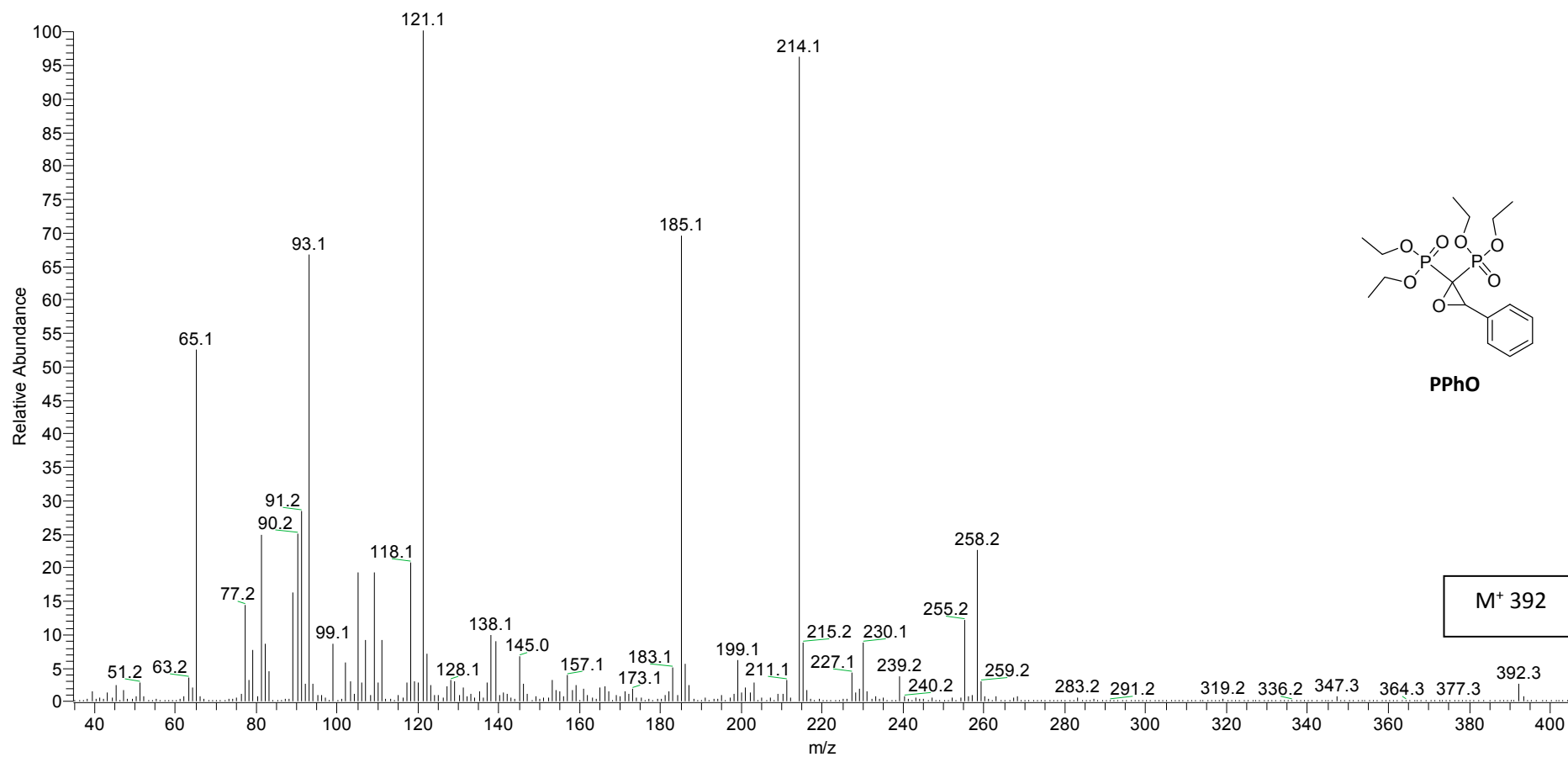
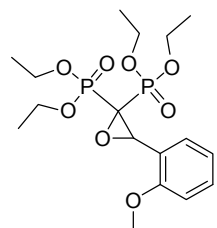


Figure S3. GC-MS spectrum of PPhO.

**PoOMeO**Tetraethyl 3-(2-methoxyphenyl)oxirane-2,2-diylldiphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.37 (d, $J = 7.5$ Hz, 1H), 7.30 (dd, $J = 7.8, 1.6$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 4.71 (t, $J = 5.1$ Hz, 1H), 4.39 – 4.25 (m, 4H), 4.01 – 3.85 (m, 3H), 3.84 (s, 3H), 3.82 – 3.75 (m, 1H), 1.40 (td, $J = 7.1, 2.4$ Hz, 6H), 1.14 (q, $J = 7.2$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 17.24 (d, $J = 72.4$ Hz, 1P), 15.03 (d, $J = 72.3$ Hz, 1P) ppm.

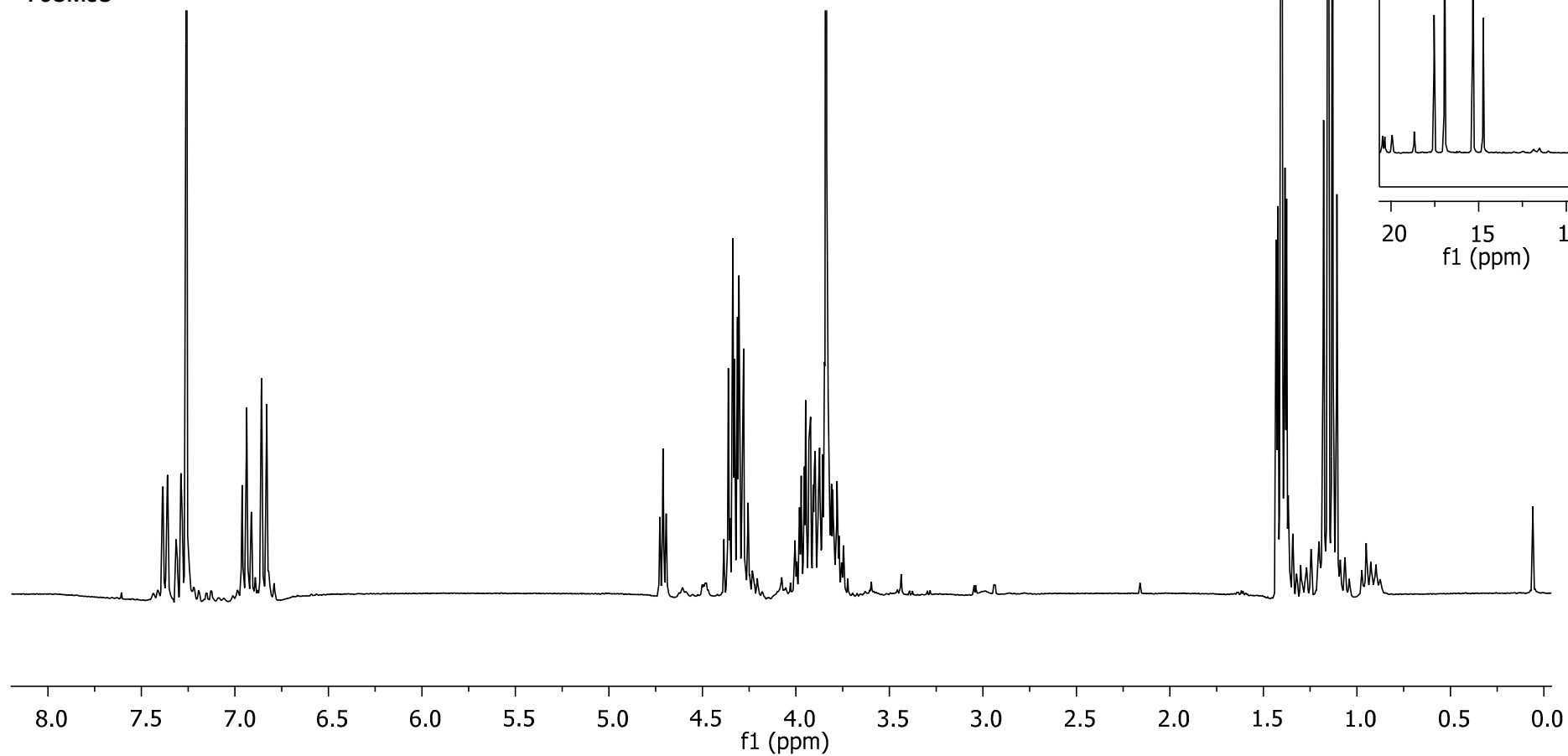


Figure S4. ^1H NMR (300 MHz, CDCl_3) spectrum of **PoOMeO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PoOMeO**.

GC-MS, (70 eV) m/z: 422 [M⁺], 377 [M⁺ -OEt], 285 [M⁺ -PO(OEt)₂], 148 [M⁺ -2PO(OEt)₂].

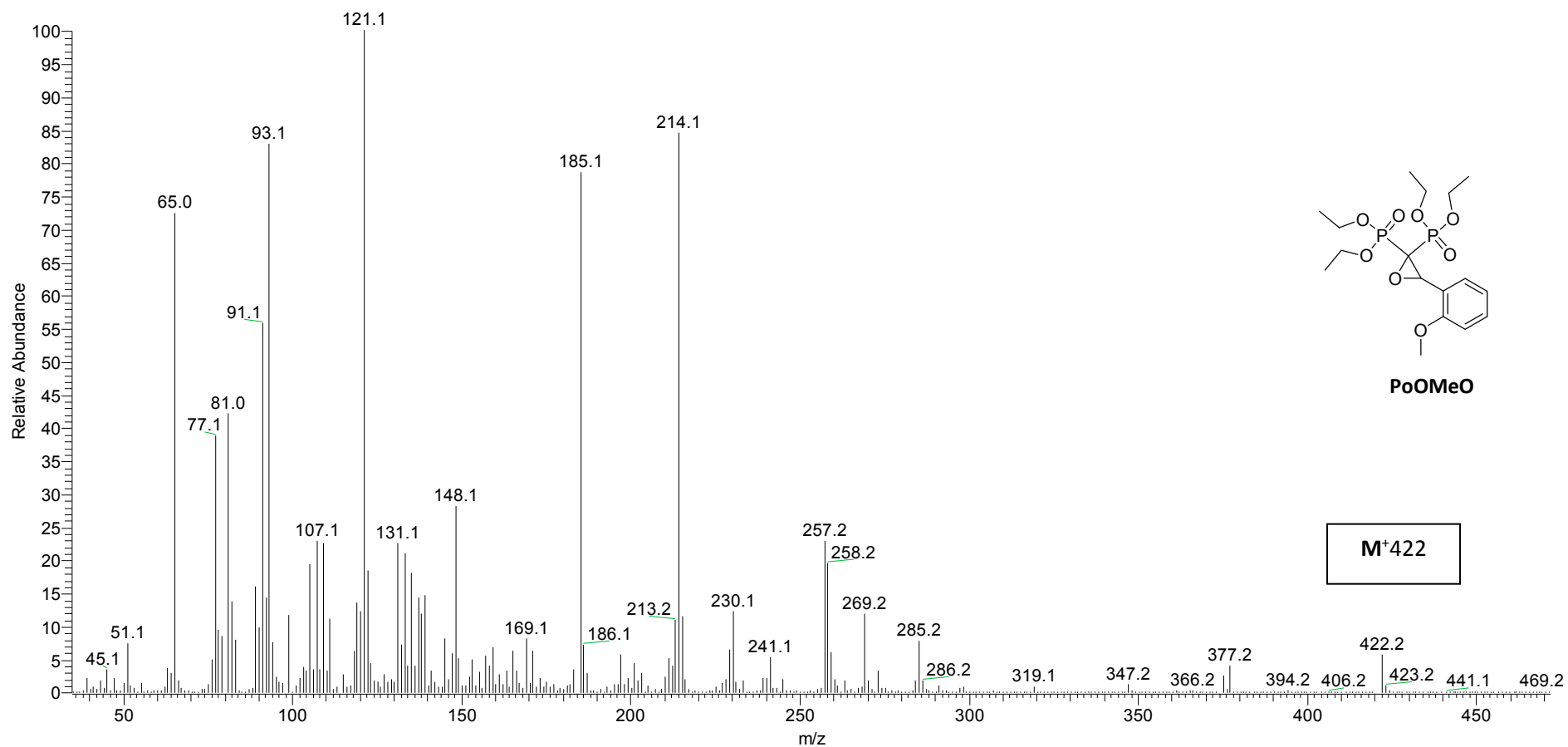
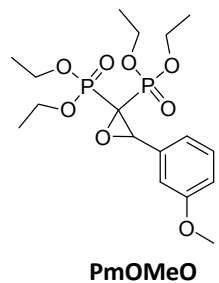


Figure S5.GC-MS spectrum of PoOMeO.



Tetraethyl 3-(3-methoxyphenyl)oxirane-2,2-diyl diphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.23 (d, $J = 7.9$ Hz, 1H), 7.06 – 6.95 (m, 2H), 6.84 (dd, $J = 8.2, 2.4$ Hz, 1H), 4.66 (t, $J = 5.0$ Hz, 1H), 4.39 – 4.24 (m, 4H), 4.02 – 3.82 (m, 4H), 3.80 (s, 6H), 1.40 (td, $J = 7.1, 2.0$ Hz, 6H), 1.14 (t, $J = 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.42 (d, $J = 72.6$ Hz, 1P), 14.66 (d, $J = 72.6$ Hz, 1P) ppm.

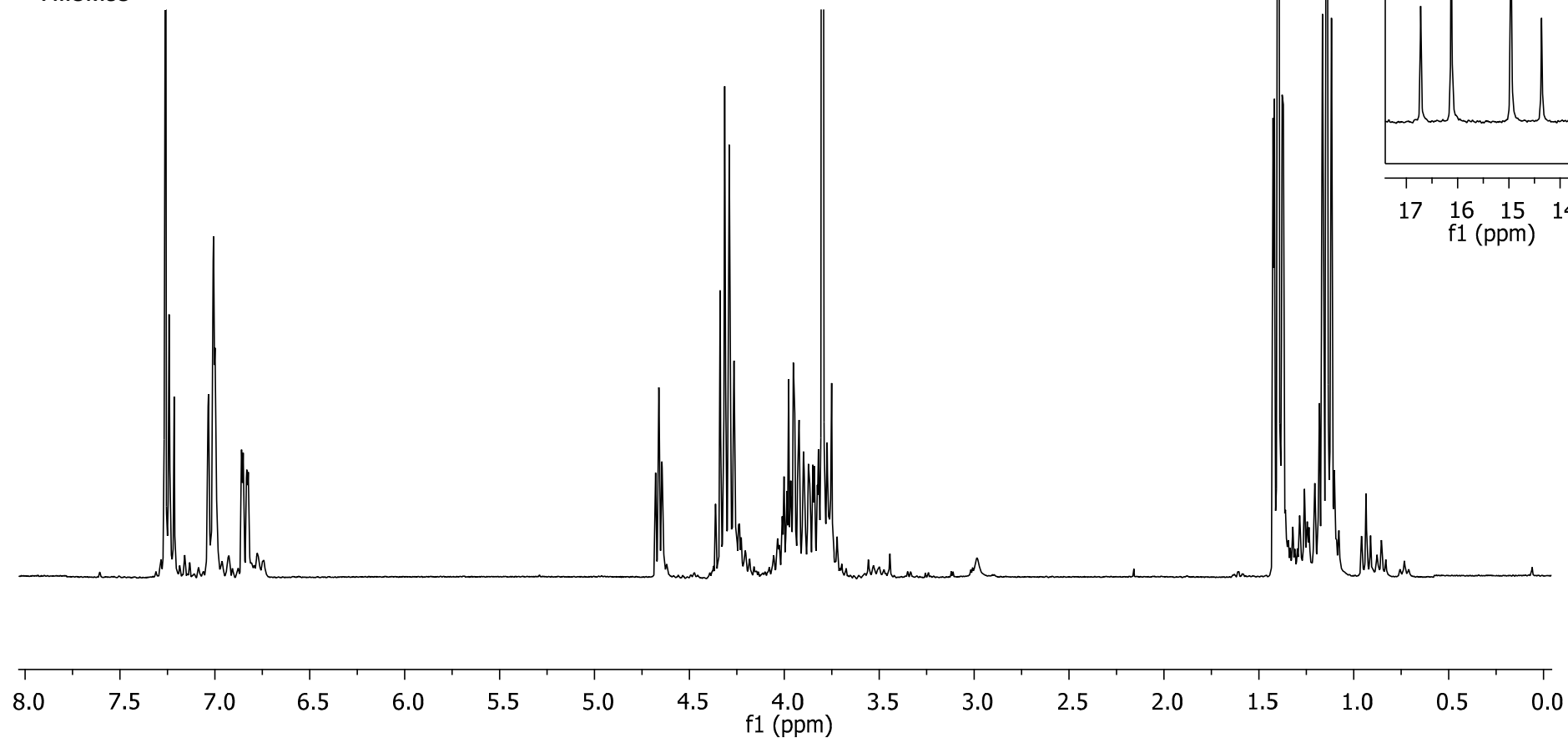


Figure S6: ^1H NMR (300 MHz, CDCl_3) spectrum of **PmOMeO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PmOMeO**.

GC-MS, (70 eV) m/z: 422 [M⁺], 391 [M⁺ -OMe], 377 [M⁺ -OEt], 148 [M⁺ -2PO(OEt)₂].

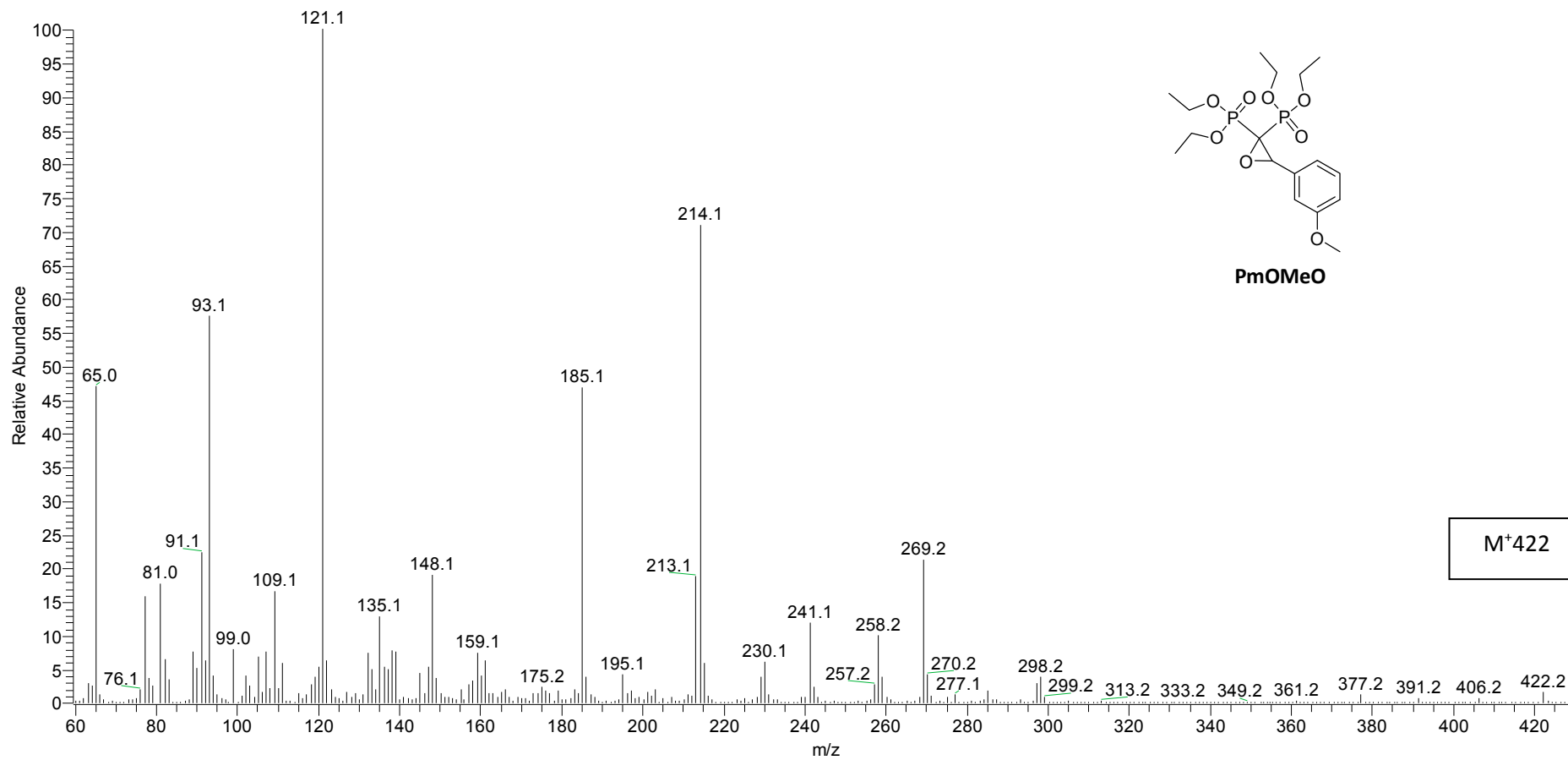
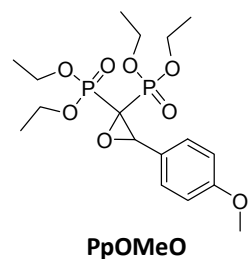


Figure S7. GC-MS spectrum of **PmOMeO**.



Tetraethyl 3-(4-methoxyphenyl)oxirane-2,2-diyl diphosphate

^1H NMR (300 MHz, CDCl_3) δ 7.37 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 4.64 (t, $J = 4.8$ Hz, 1H), 4.38 – 4.23 (m, 4H), 4.05 – 3.83 (m, 4H), 3.80 (s, 3H), 1.40 (td, $J = 7.1, 1.2$ Hz, 6H), 1.17 (td, $J = 7.1, 2.4$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.64 (d, $J = 72.7$ Hz, 1P), 14.98 (d, $J = 72.6$ Hz, 1P) ppm.

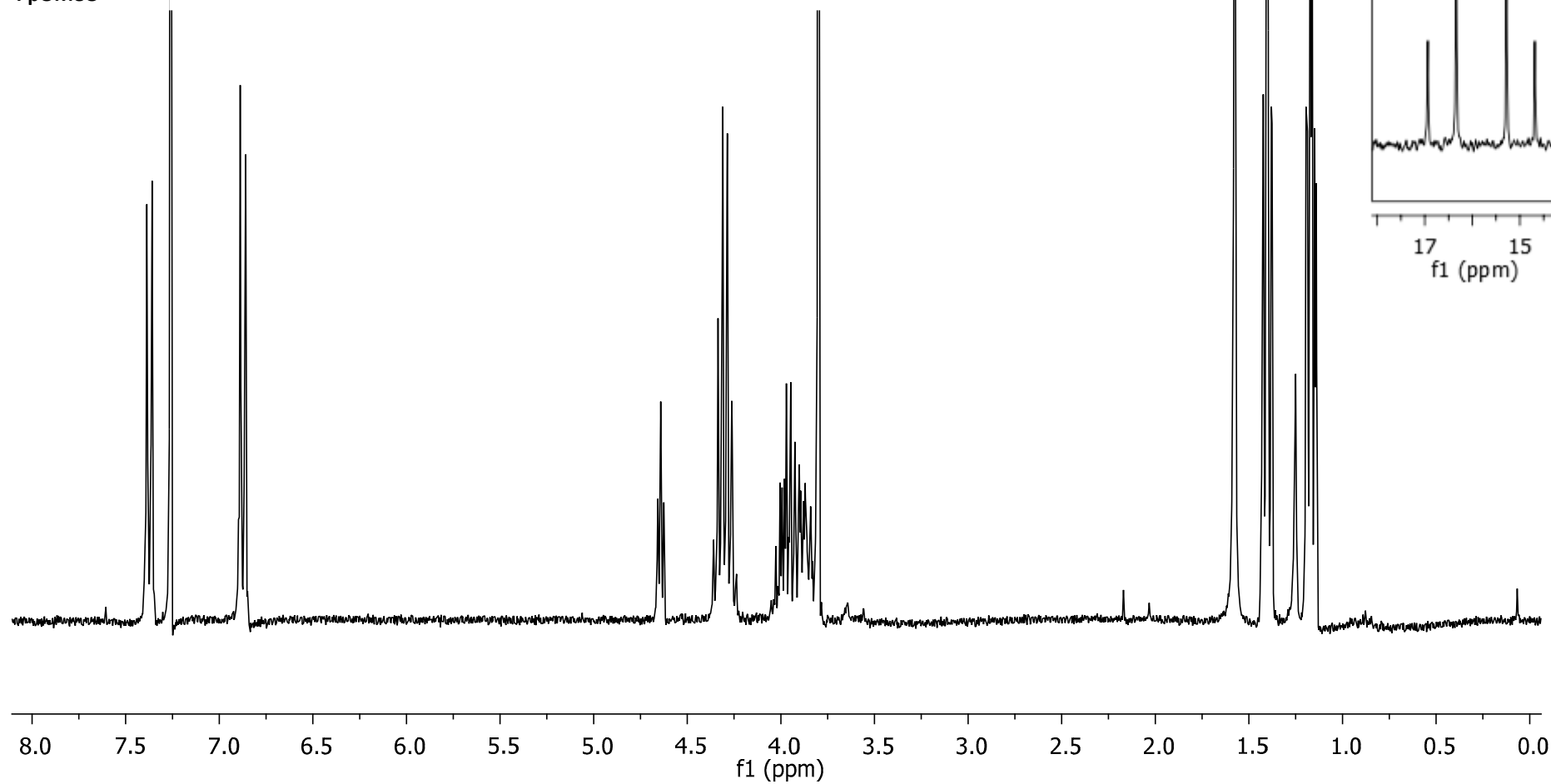


Figure S8. ^1H NMR (300 MHz, CDCl_3) spectrum of **PpOMeO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PpOMeO**.

GC-MS, (70 eV) m/z: 422 [M⁺], 284 [M⁺ - PO(OEt)₂ - H⁺], 148 [M⁺ - 2PO(OEt)₂]

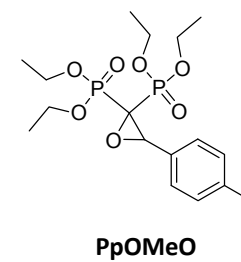
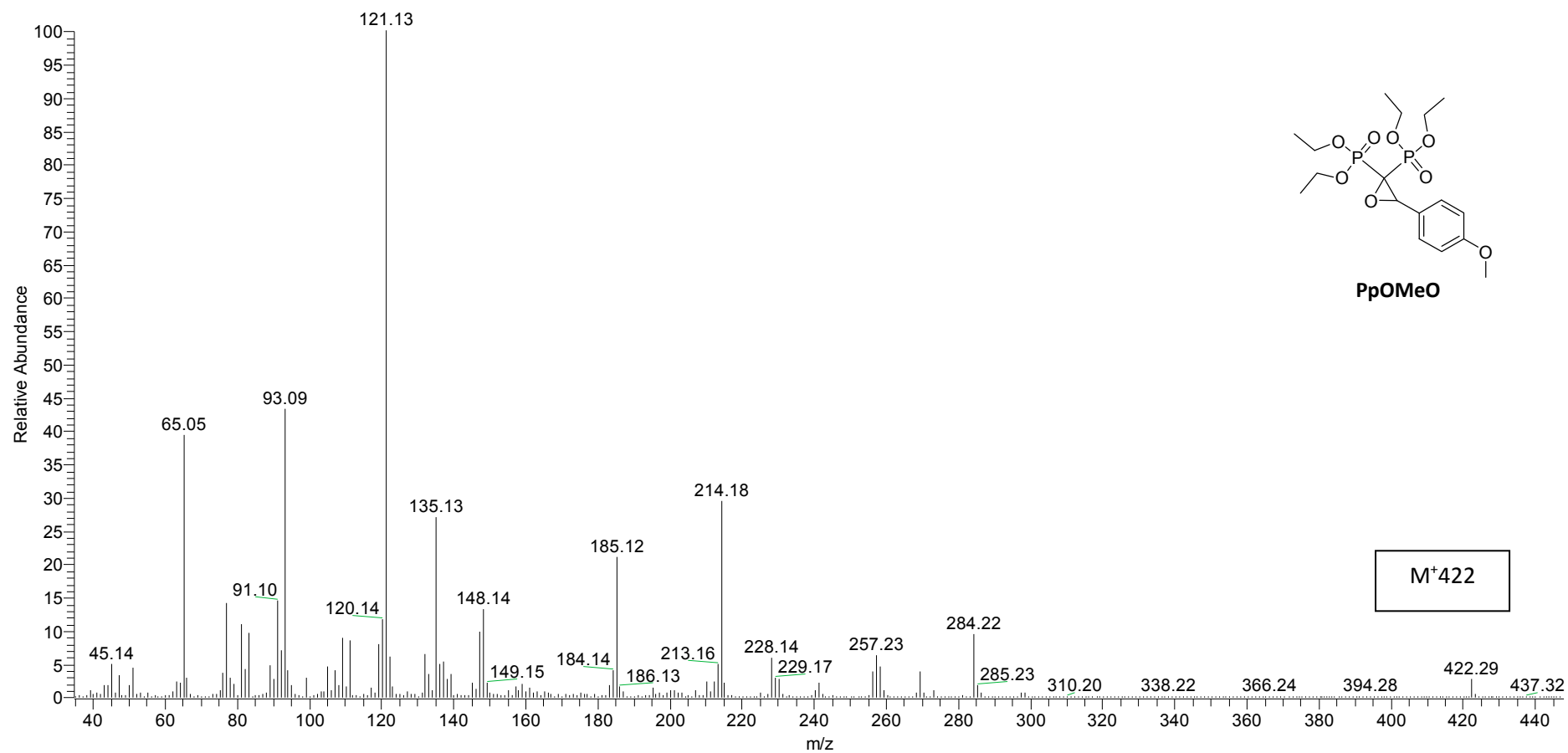
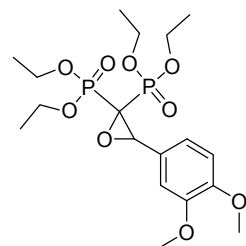


Figure S9. GC-MS spectrum of PpOMeO.

**PVERO**

Tetraethyl 3-(3,4-dimethoxyphenyl)oxirane-2,2-diyl diphosphate

^1H NMR (300 MHz, CDCl_3) δ 7.29 (s, 1H), 7.02 (d, $J = 6.9$ Hz, 1H), 6.86 (s, 1H), 4.64 (t, $J = 4.8$ Hz, 1H), 4.38 – 4.24 (m, 4H), 4.08 – 3.92 (m, 4H), 3.89 (s, 3H), 3.87 (s, 3H), 1.40 (td, $J = 7.1, 1.4$ Hz, 6H), 1.16 (dt, $J = 11.1, 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.47 (d, $J = 72.6$ Hz, 1P), 15.10 (d, $J = 72.6$ Hz, 1P) ppm.

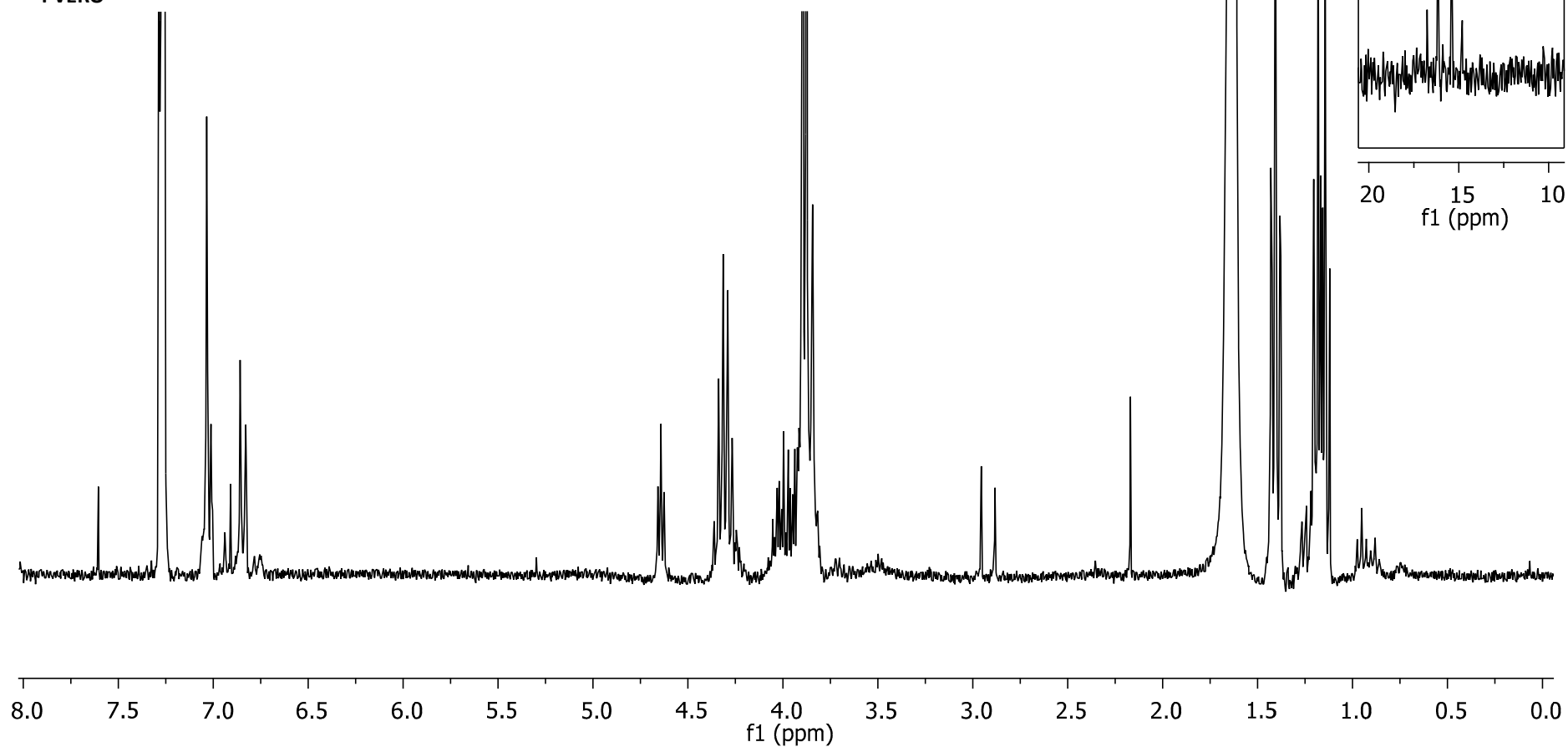
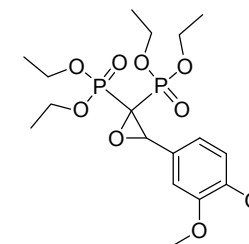
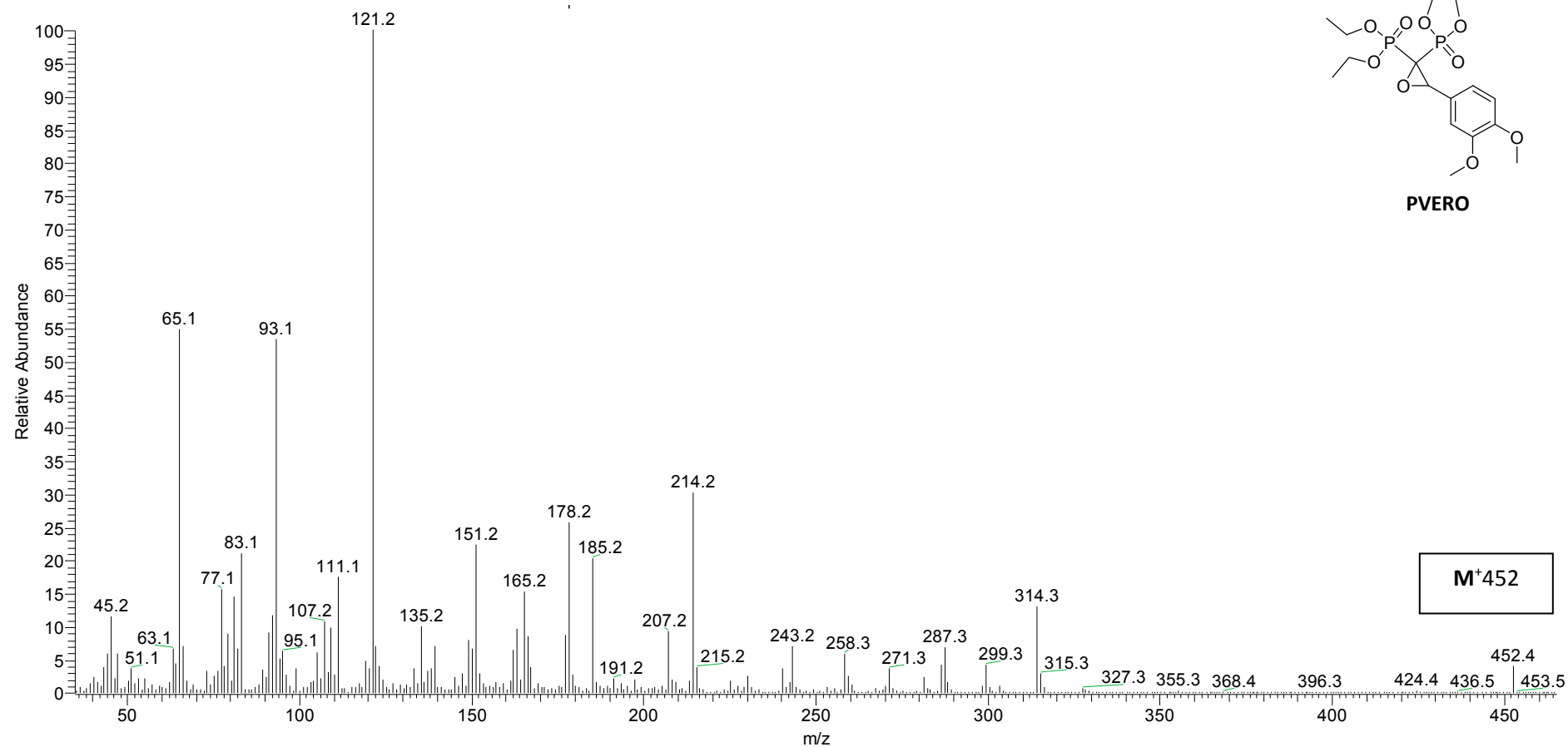


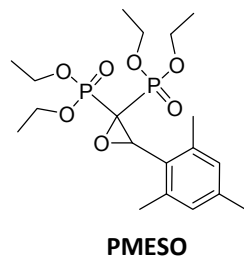
Figure S10. ^1H NMR (300 MHz, CDCl_3) spectrum of **PVERO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PVERO**.

GC-MS, (70 eV) m/z: 452 [M⁺], 315 [M⁺ - PO(OEt)₂], 314 [M⁺ - PO(OEt)₂ - H⁺], 178 [M⁺ - 2PO(OEt)₂].



PVERO

Figure S11. GC-MS spectrum of PVERO



Tetraethyl 3-mesityloxirane-2,2-diylidiphosphonate

^1H NMR (300 MHz, CDCl_3) δ 6.79 (s, 1H), 6.77 (s, 1H), 4.57 (t, $J = 5.1$ Hz, 1H), 4.40 – 4.23 (m, 4H), 4.13 – 3.93 (m, 2H), 3.83 – 3.71 (m, 1H), 3.52 – 3.36 (m, 1H), 2.41 (s, 3H), 2.36 (s, 3H), 2.24 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 6H), 1.21 (t, $J = 7.1$ Hz, 3H), 1.04 (t, $J = 7.1$ Hz, 3H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 17.40 (d, $J = 76.4$ Hz, 1P), 14.82 (d, $J = 76.3$ Hz, 1P) ppm.

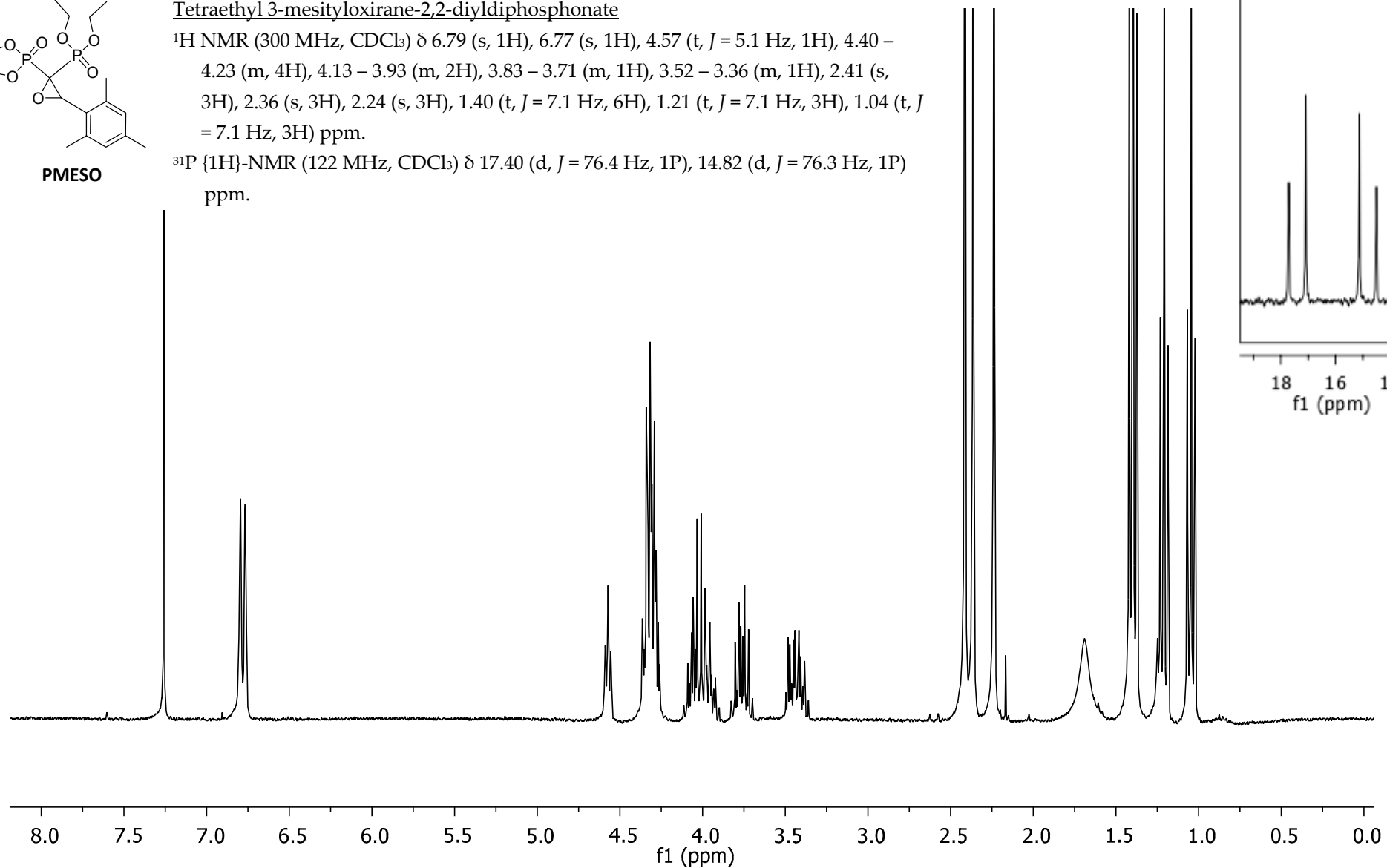


Figure S12. ^1H NMR (300 MHz, CDCl_3) spectrum of **PMESO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PMESO**.

GC-MS, (70 eV) m/z: 434 [M⁺], 419 [M⁺ - Me], 389 [M⁺ - OEt], 297 [M⁺ - PO(OEt)₂] 160 [M⁺ - 2PO(OEt)₂]

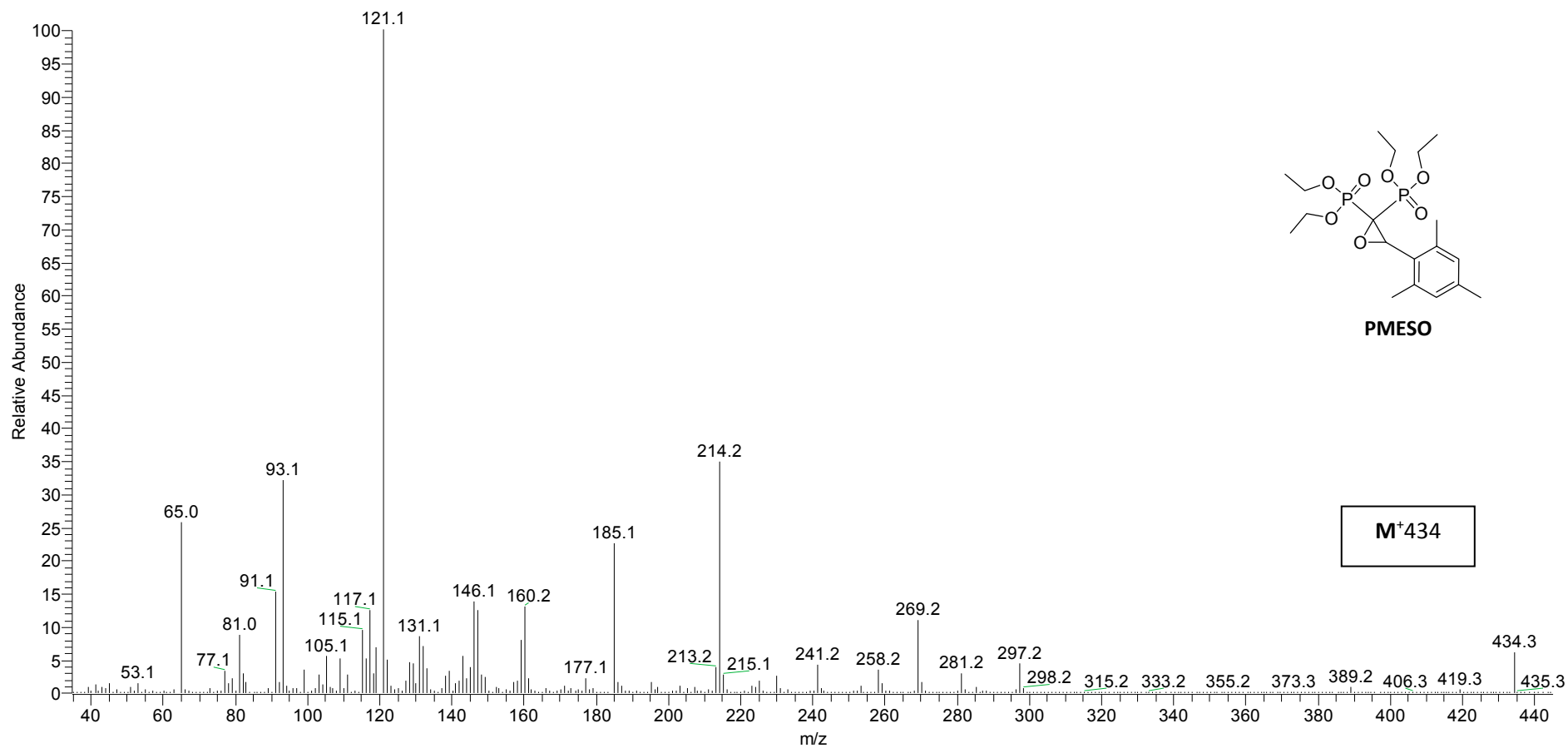
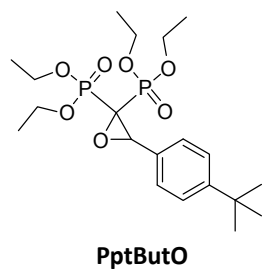


Figure S13. GC-MS spectrum of PMESO.



Tetraethyl 3-(4-tert-butylphenyl)oxirane-2,2-diylldiphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.37 (s, 4H), 4.66 (t, $J = 5.0$ Hz, 1H), 4.38 – 4.22 (m, 4H), 3.99 – 3.82 (m, 3H), 3.75 – 3.61 (m, 1H), 1.40 (td, $J = 7.1, 2.1$ Hz, 6H), 1.29 (s, 9H), 1.10 (dt, $J = 10.1, 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.68 (d, $J = 73.2$ Hz, 1P), 14.82 (d, $J = 73.3$ Hz, 1P) ppm.

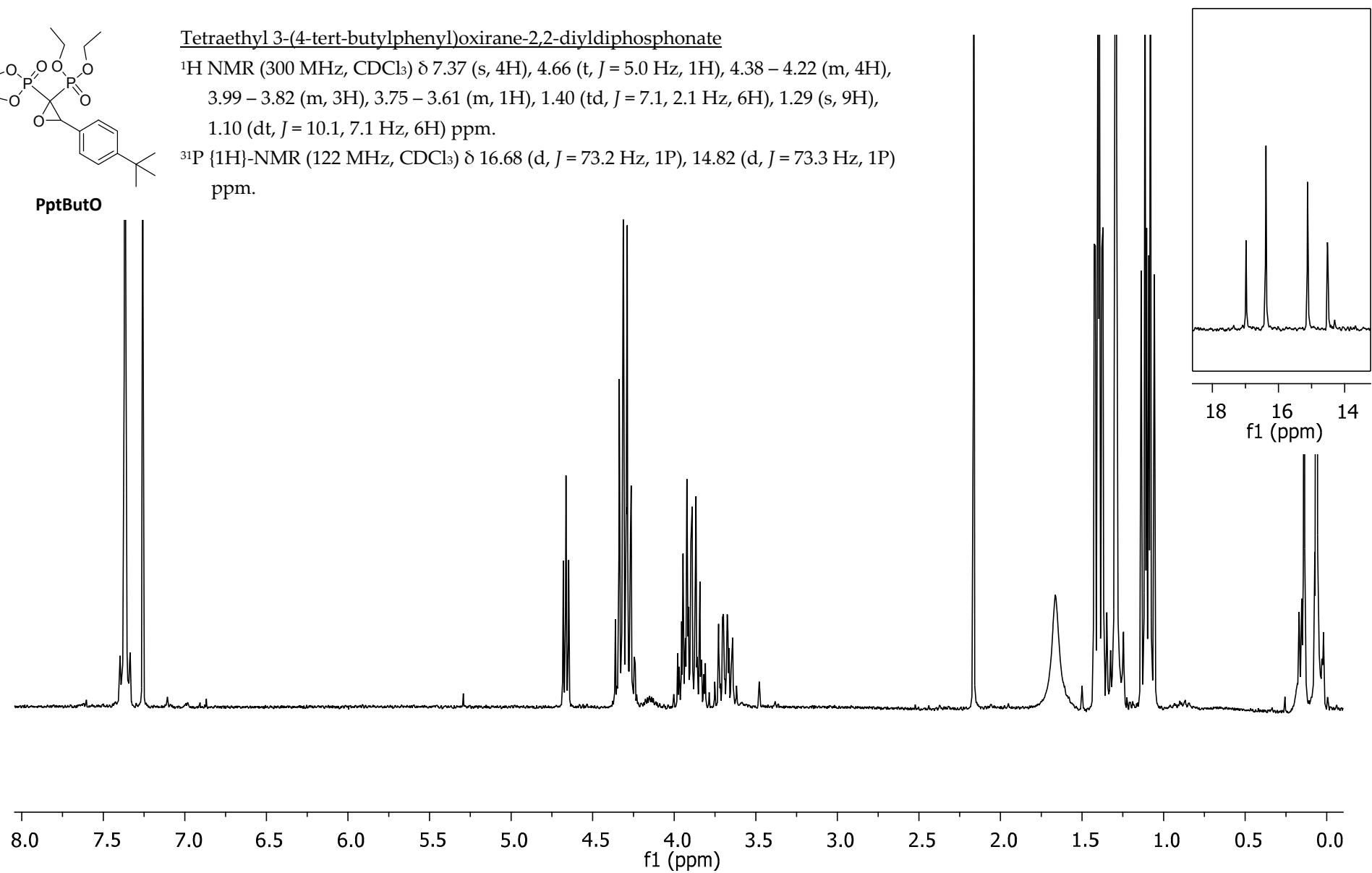


Figure S14. ^1H NMR (300 MHz, CDCl_3) spectrum of **PtButO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PtButO**.

GC-MS, (70 eV) m/z: 448 [M⁺], 433 [M⁺ - Me], 403 [M⁺ - OEt], 311 [M⁺ - PO(OEt)₂]

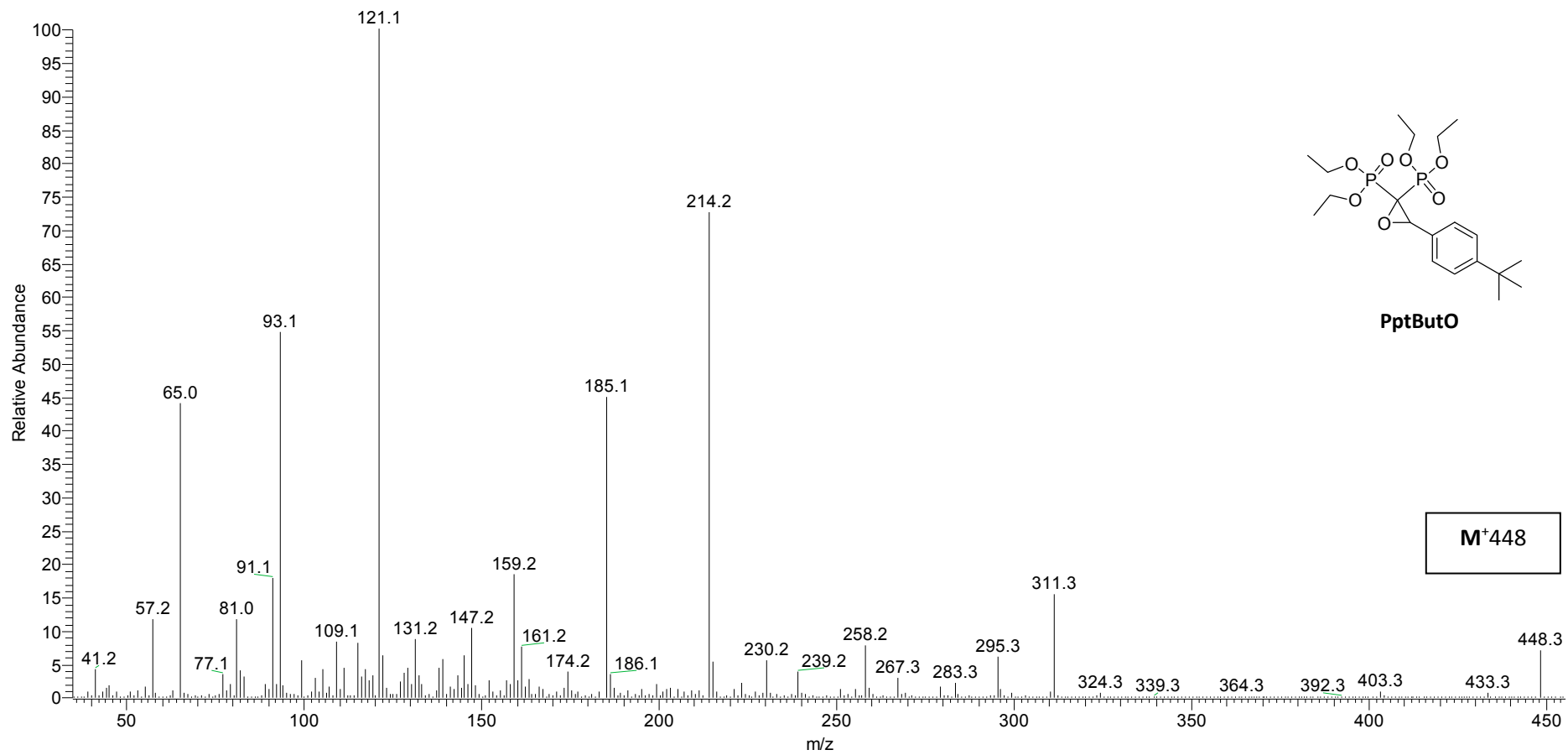
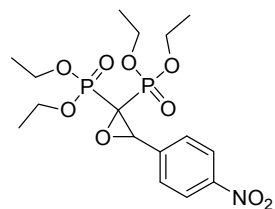


Figure S15.GC-MS spectrum of PtButO.

**PpNO₂O**Tetraethyl 3-(4-nitrophenyl)oxirane-2,2-diylldiphosphonate

¹H NMR (300 MHz, CDCl₃) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 4.73 (t, *J* = 5.0 Hz, 1H), 4.39 – 4.23 (m, 4H), 4.12 – 3.86 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 6H), 1.19 (dt, *J* = 10.8, 7.1 Hz, 6H) ppm.

³¹P {¹H}-NMR (122 MHz, CDCl₃) δ 15.49 (d, *J* = 68.4 Hz, 1P), 13.93 (d, *J* = 68.2 Hz, 1P)

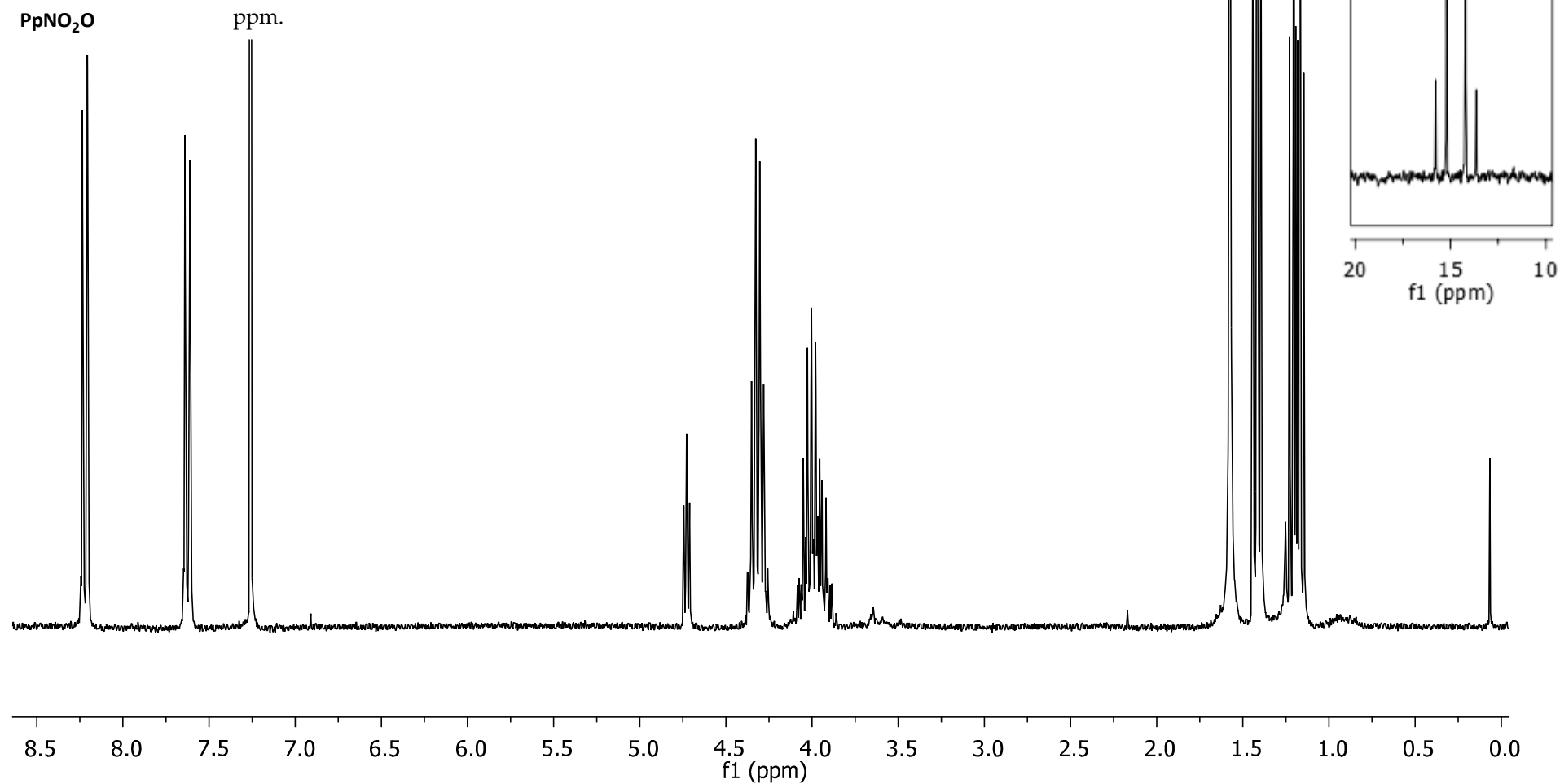
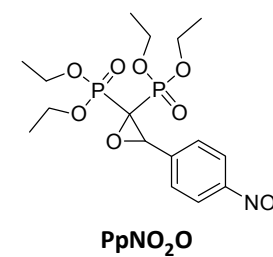
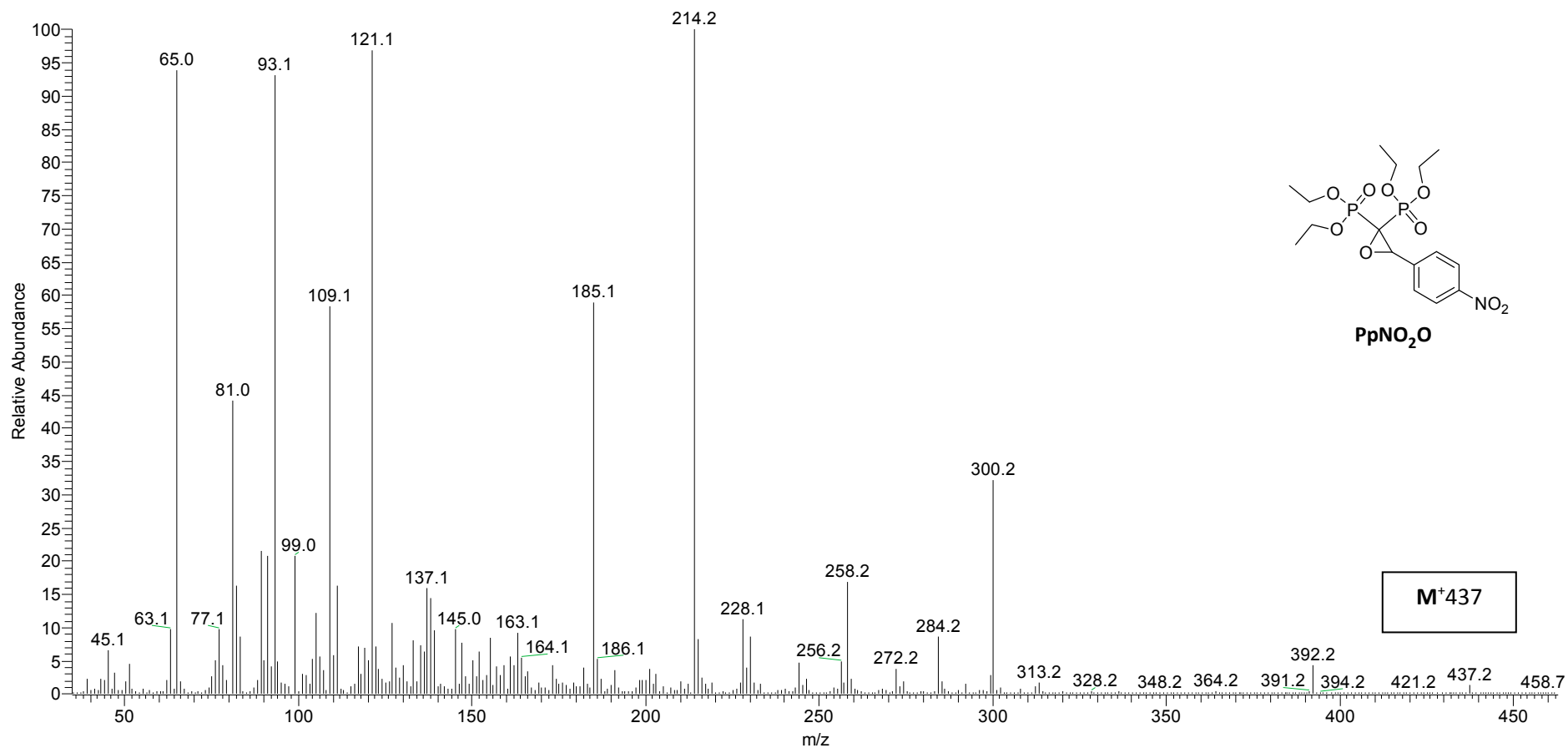
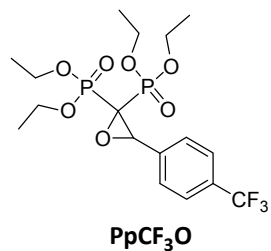


Figure S16. ¹H NMR (300 MHz, CDCl₃) spectrum of **PpNO₂O**; insert: ³¹P {¹H}-NMR (122 MHz, CDCl₃) spectrum of **PpNO₂O**.

GC-MS, (70 eV) m/z: 437 [M⁺], 392 [M⁺ -OEt], 300 [M⁺ -PO(OEt)₂]Figure S17.GC-MS spectrum of PpNO₂O.



Tetraethyl 3-(4-(trifluoromethyl)phenyl)oxirane-2,2-diylldiphosphonate

¹H NMR (300 MHz, D₂O) δ 7.61 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 4.70 (t, *J* = 5.0 Hz, 1H), 4.41 – 4.23 (m, 4H), 4.06 – 3.80 (m, 4H), 1.41 (td, *J* = 7.1, 0.7 Hz, 6H), 1.14 (td, *J* = 7.1, 2.8 Hz, 6H) ppm.

³¹P {¹H}-NMR (122 MHz, CDCl₃) δ 15.90 (d, *J* = 70.5 Hz, 1P), 14.22 (d, *J* = 70.3 Hz, 1P) ppm.

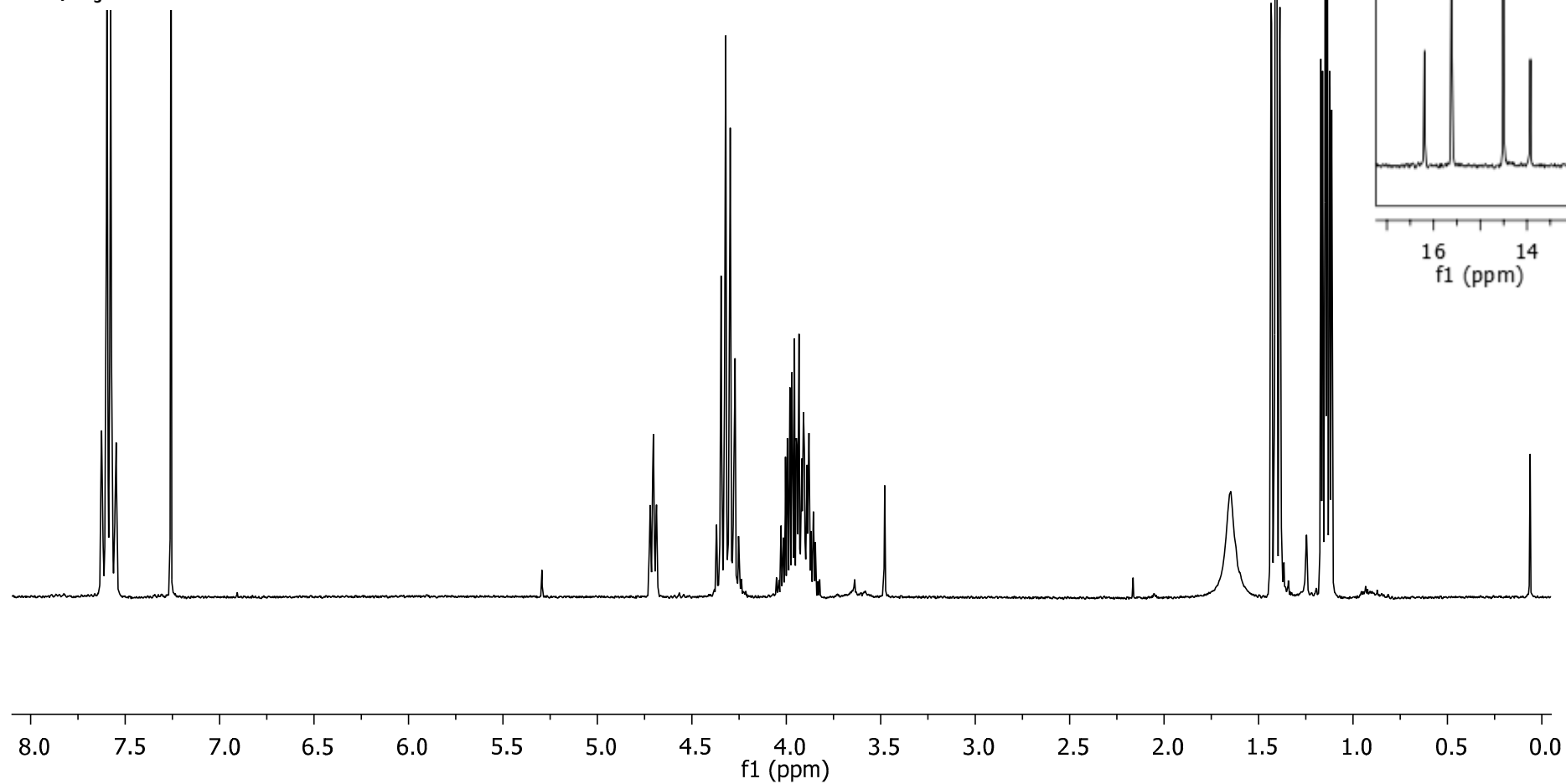


Figure S18. ¹H NMR (300 MHz, CDCl₃) spectrum of **PpCF₃O**; insert: ³¹P {¹H}-NMR (122 MHz, CDCl₃) spectrum of **PpCF₃O**.

GC-MS, (70 eV) m/z: 460 [M⁺], 441 [M⁺ - F], 415 [M⁺ - OEt], 323 [M⁺ - PO(OEt)₂], 185 [M⁺ - 2PO(OEt)₂ - H⁺].

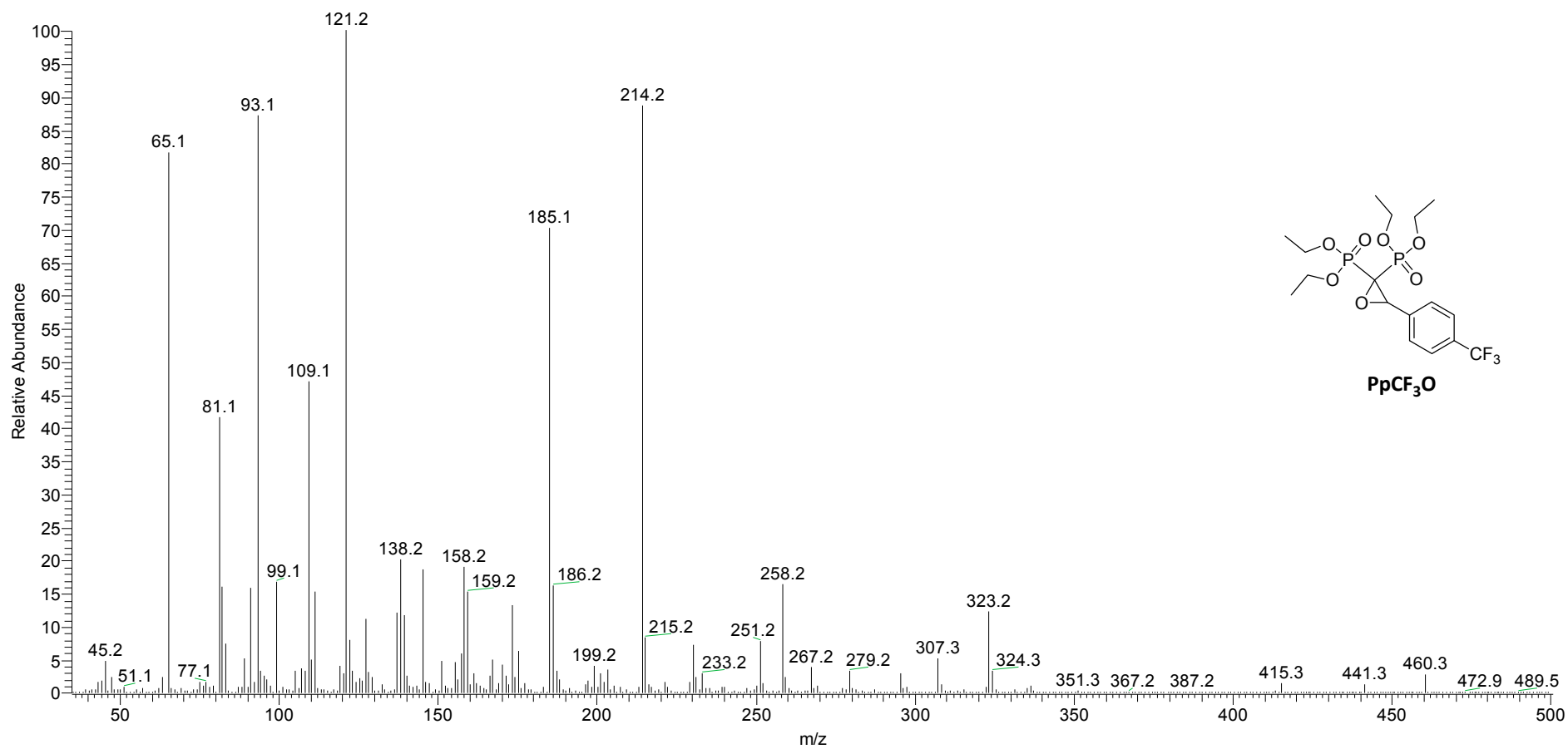
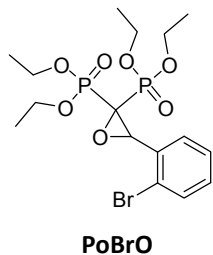


Figure S19.GC-MS spectrum of PpCF₃O.



Tetraethyl 3-(2-bromophenyl)oxirane-2,2-diyl diphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.53 (d, $J = 7.9$ Hz, 1H), 7.47 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.20 (td, $J = 7.7, 1.8$ Hz, 1H), 4.66 (t, $J = 5.0$ Hz, 1H), 4.40 – 4.25 (m, 4H), 4.12 – 3.80 (m, 4H), 1.40 (td, $J = 7.1, 2.3$ Hz, 6H), 1.18 (dt, $J = 10.0, 7.1$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.00 (d, $J = 70.1$ Hz, 1P), 14.49 (d, $J = 70.1$ Hz, 1P) ppm.

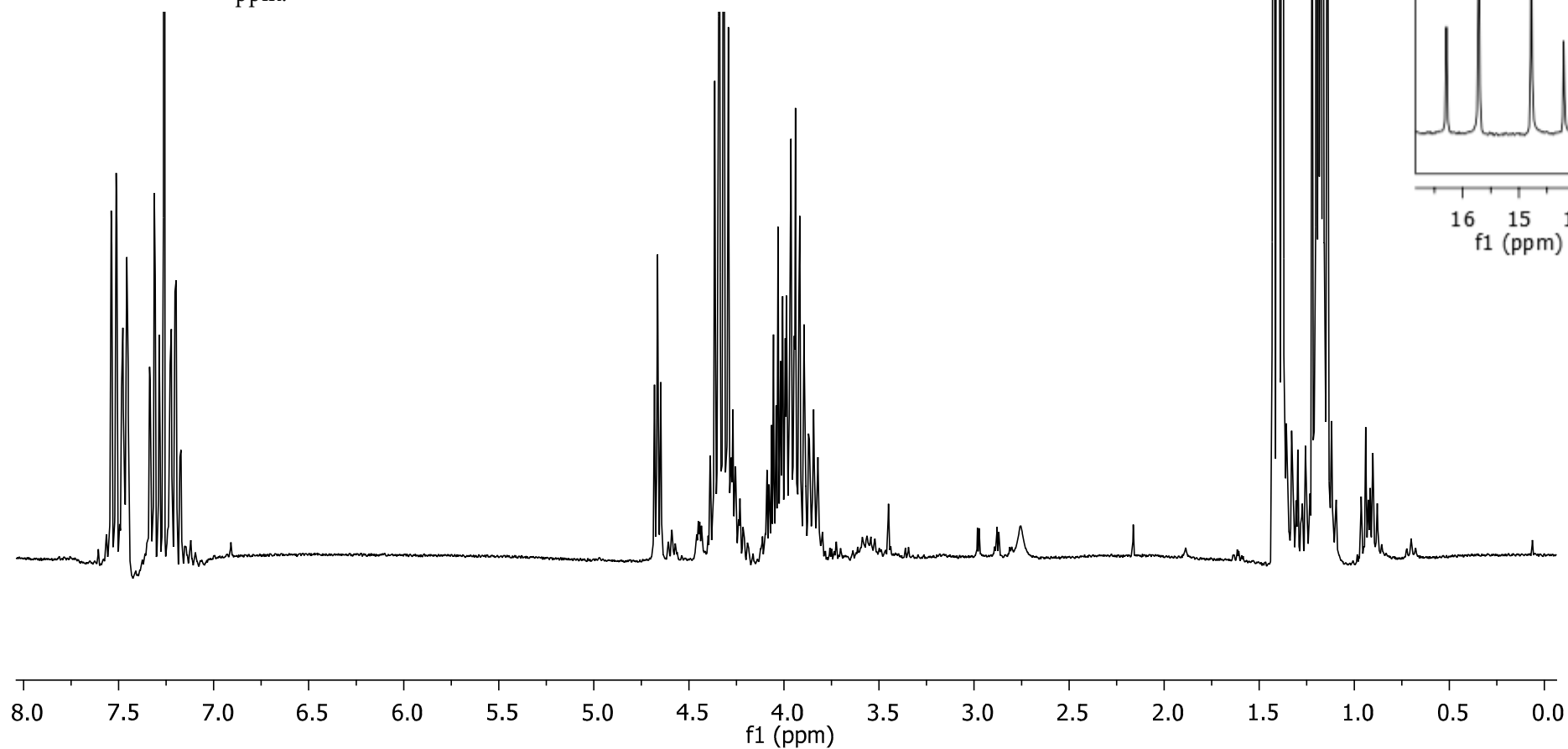


Figure S20. ^1H NMR (300 MHz, CDCl_3) spectrum of **PoBrO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PoBrO**.

GC-MS, (70 eV) m/z: 470 [M⁺, cluster Br], 425 [M⁺ -OEt, cluster Br], 391 [M⁺ - Br].

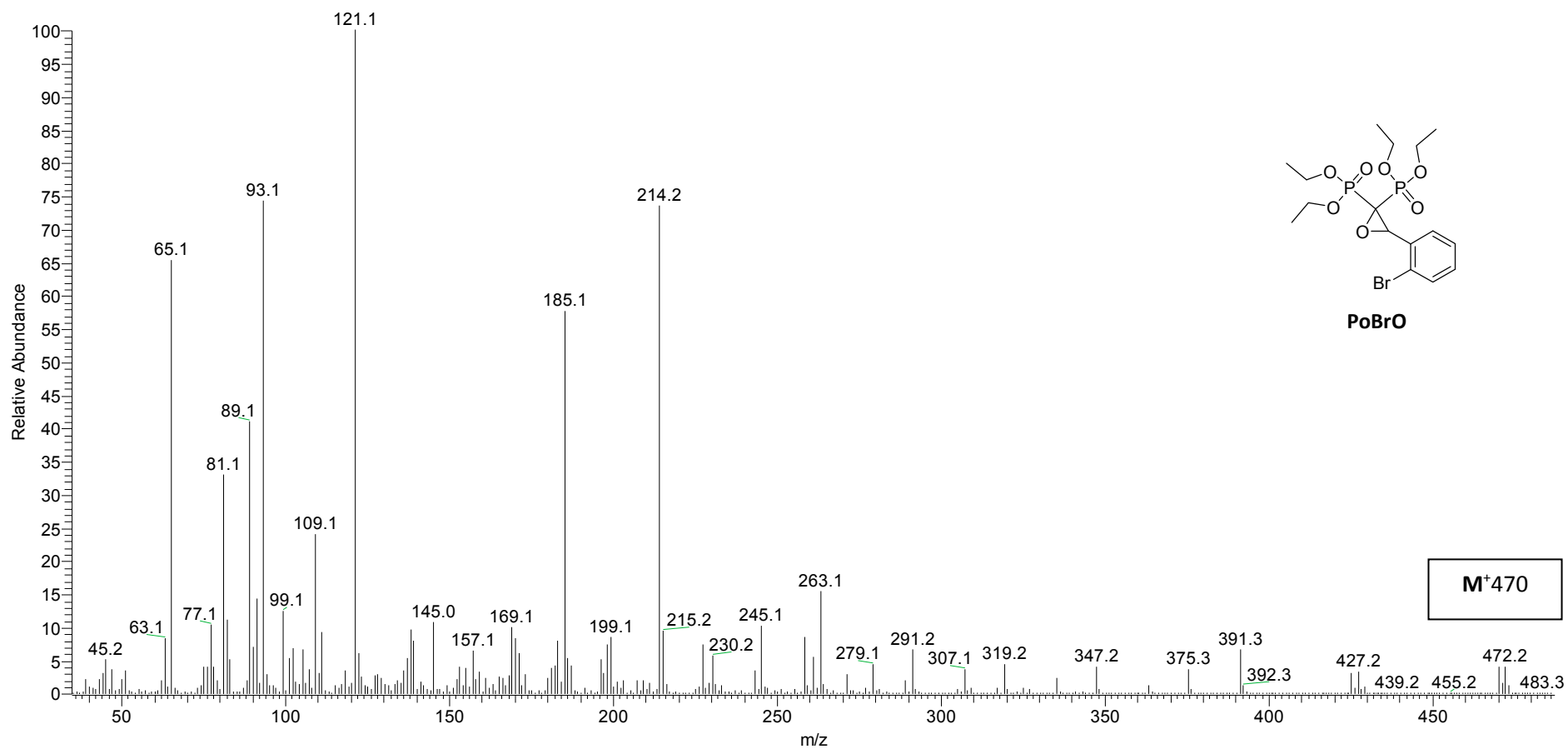
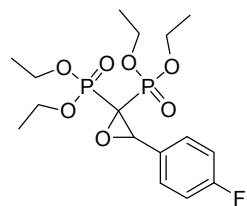


Figure S21.GC-MS spectrum of PoBrO.

**PpFO**

Tetraethyl 3-(4-fluorophenyl)oxirane-2,2-diylldiphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.42 (dd, $J = 8.8, 5.3$ Hz, 2H), 7.03 (t, $J = 8.7$ Hz, 2H), 4.64 (t, $J = 4.9$ Hz, 1H), 4.37 – 4.22 (m, 4H), 4.05 – 3.85 (m, 4H), 1.40 (t, $J = 6.4$ Hz, 6H), 1.16 (td, $J = 7.1, 4.3$ Hz, 6H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.25 (d, $J = 71.4$ Hz, 1P), 14.62 (d, $J = 71.4$ Hz, 1P) ppm.

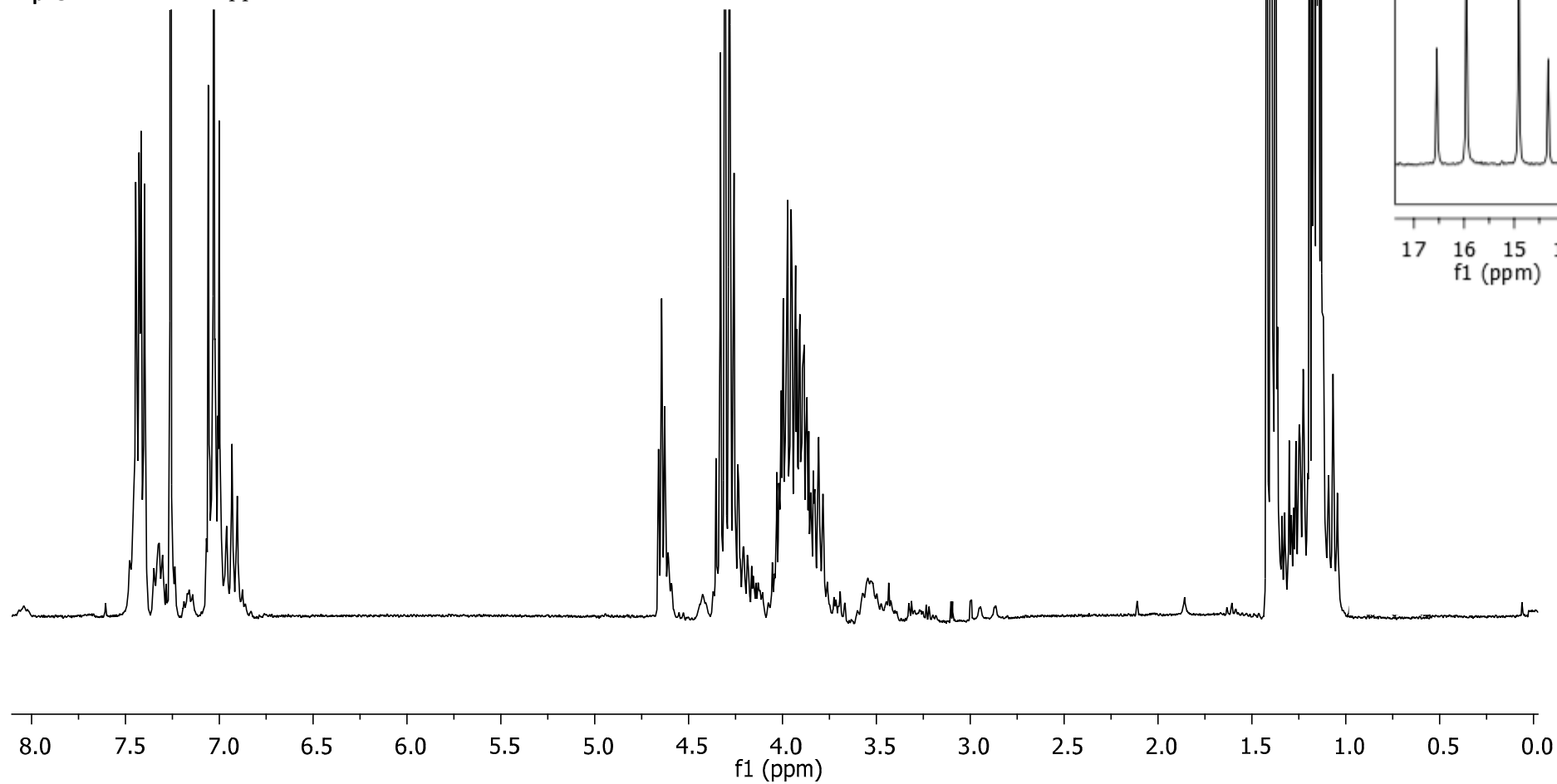


Figure S22. ^1H NMR (300 MHz, CDCl_3) spectrum of **PpFO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **PpFO**.

GC-MS, (70 eV) m/z: 410 [M⁺], 365 [M⁺ -OEt], 273 [M⁺ -PO(OEt)₂], 136 [M⁺ -2PO(OEt)₂].

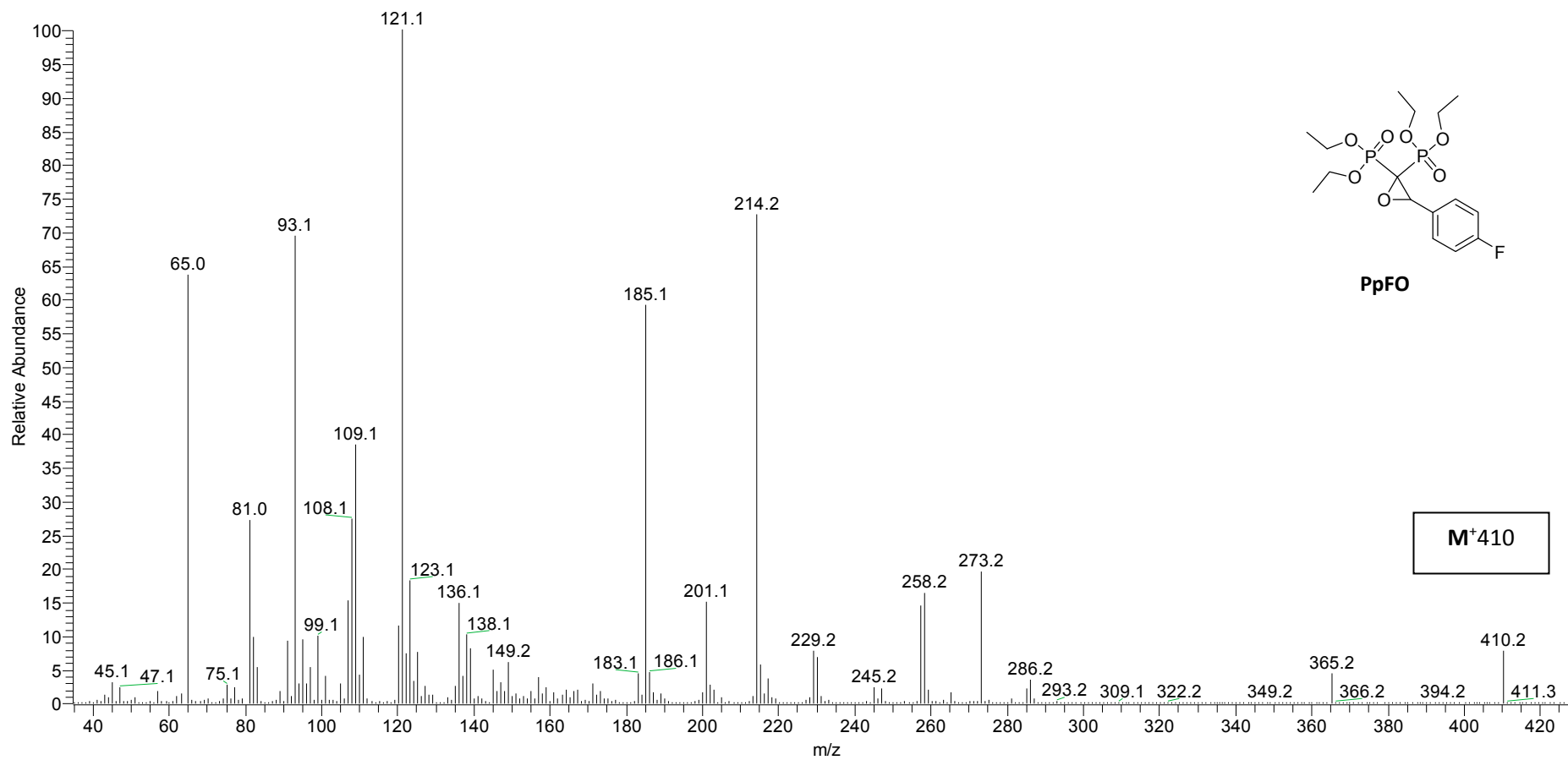
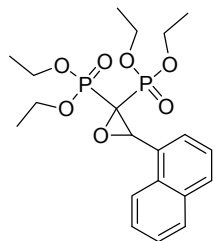


Figure S23. GC-MS spectrum of PpFO.



Tetraethyl 3-(naphthalen-1-yl)oxirane-2,2-diylidiphosphonate

^1H NMR (300 MHz, CDCl_3) δ 7.92 (s, 1H), 7.87 – 7.79 (m, 3H), 7.54 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.51 – 7.44 (m, 2H), 4.85 (t, $J = 4.9$ Hz, 1H), 4.43 – 4.26 (m, 4H), 3.98 – 3.68 (m, 4H), 1.43 (td, $J = 7.1, 2.2$ Hz, 6H), 1.06 (dt, $J = 12.0, 7.1$ Hz, 7H) ppm.

^{31}P { ^1H }-NMR (122 MHz, CDCl_3) δ 16.44 (d, $J = 72.7$ Hz, 1P), 14.69 (d, $J = 72.7$ Hz, 1P) ppm.

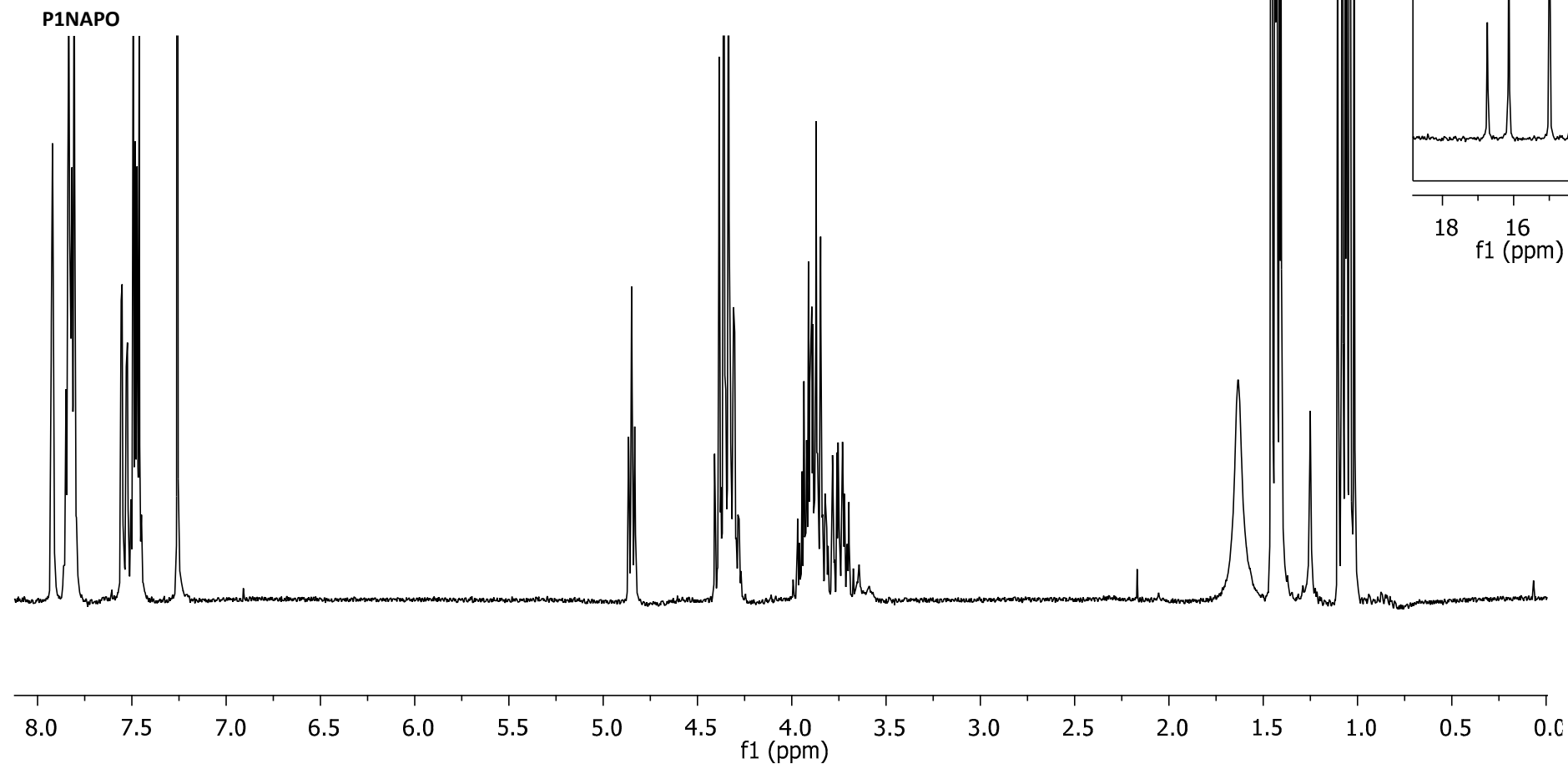


Figure S24. ^1H NMR (300 MHz, CDCl_3) spectrum of **P1NAPO**; insert: ^{31}P { ^1H }-NMR (122 MHz, CDCl_3) spectrum of **P1NAPO**.

GC-MS, (70 eV) m/z: 442 [M⁺], 305 [M⁺ -PO(OEt)₂], 127 [M⁺ -CHOC₂PO(OEt)₂].

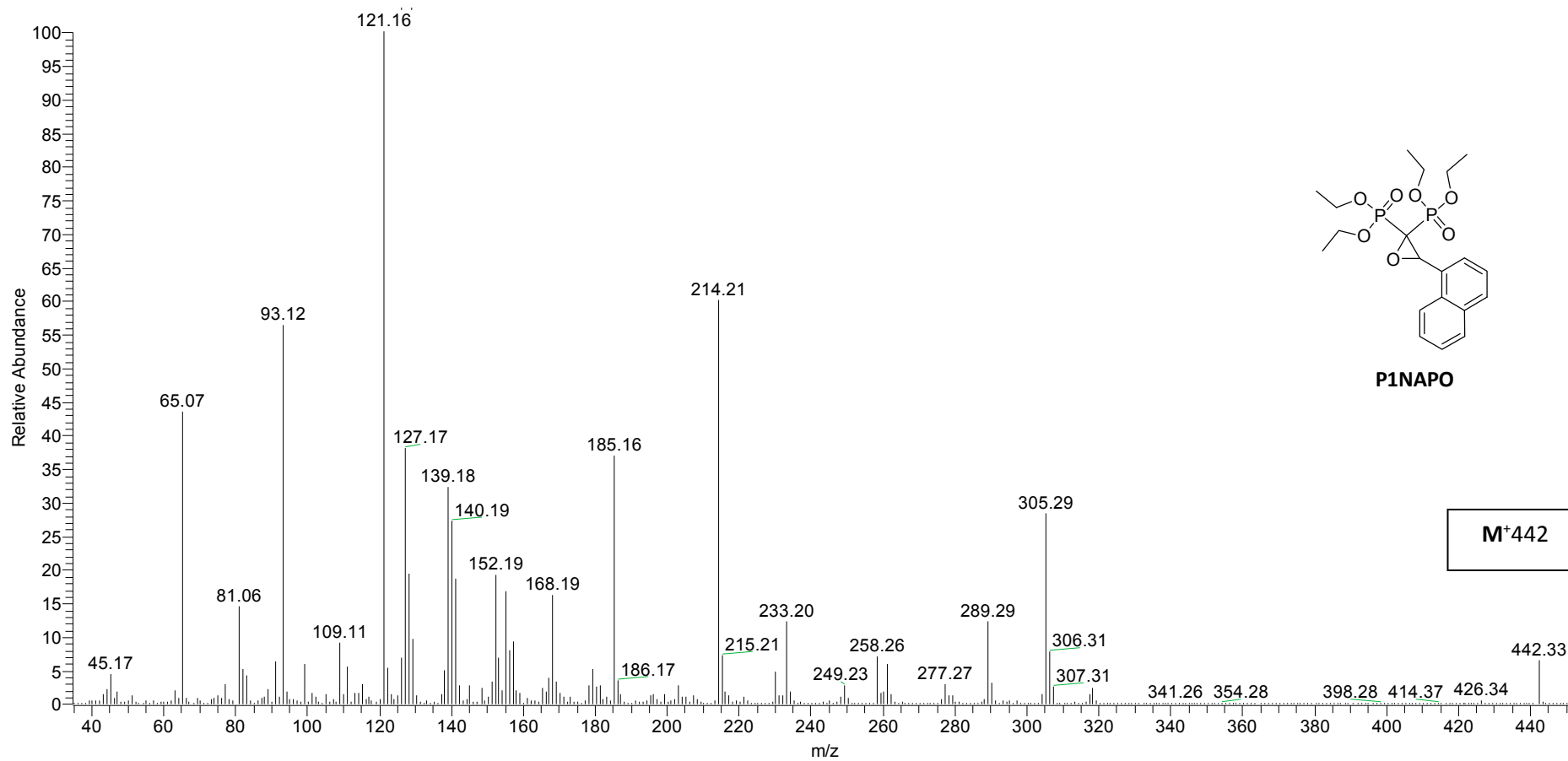


Figure S25. GC-MS spectrum of P1NAPO.

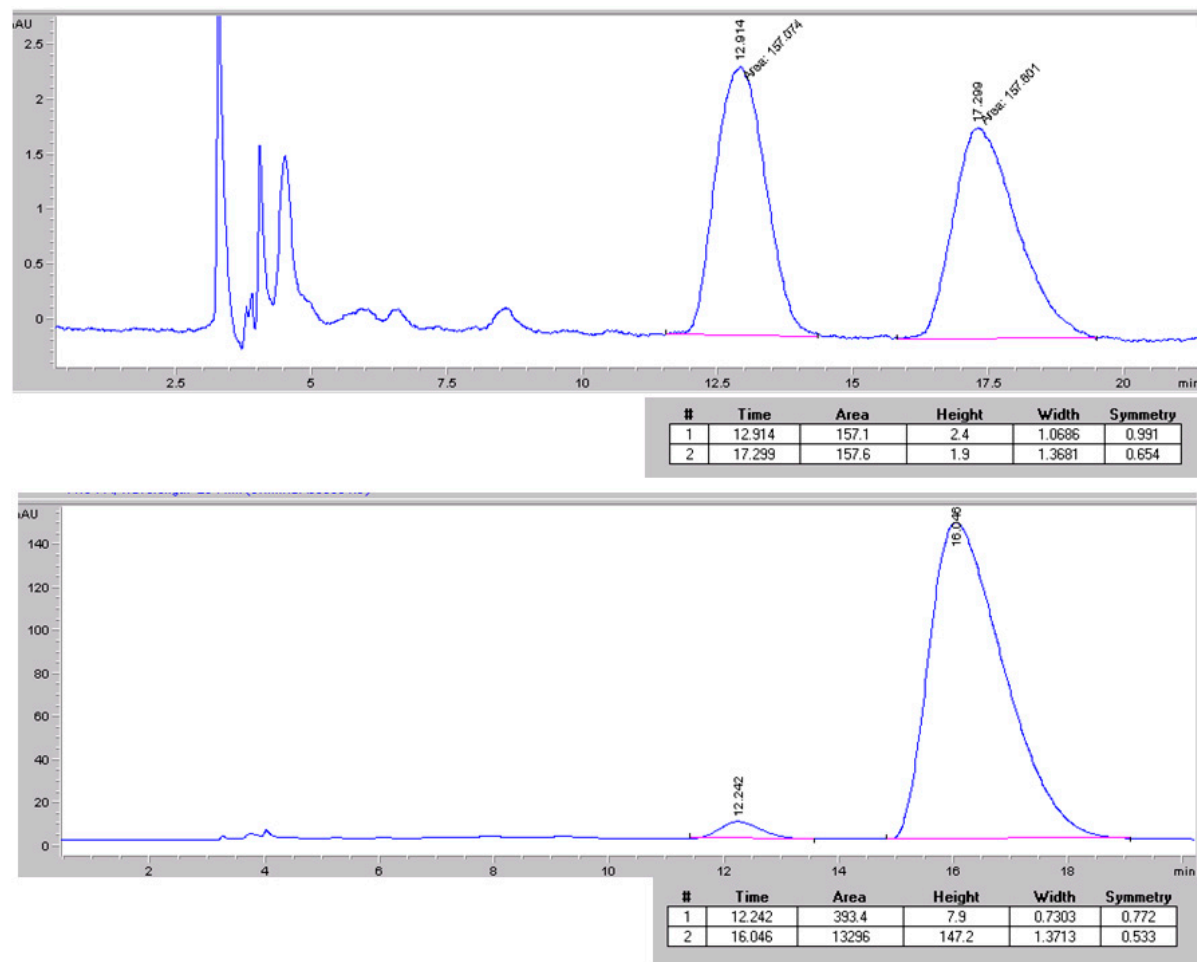


Figure S26. Example of HPLC traces for the racemic (top) and enantioenriched (bottom) PPHO (Table 1 entry 12) for the asymmetric epoxidation of PPH with H₂O₂ in the presence of sparteine.

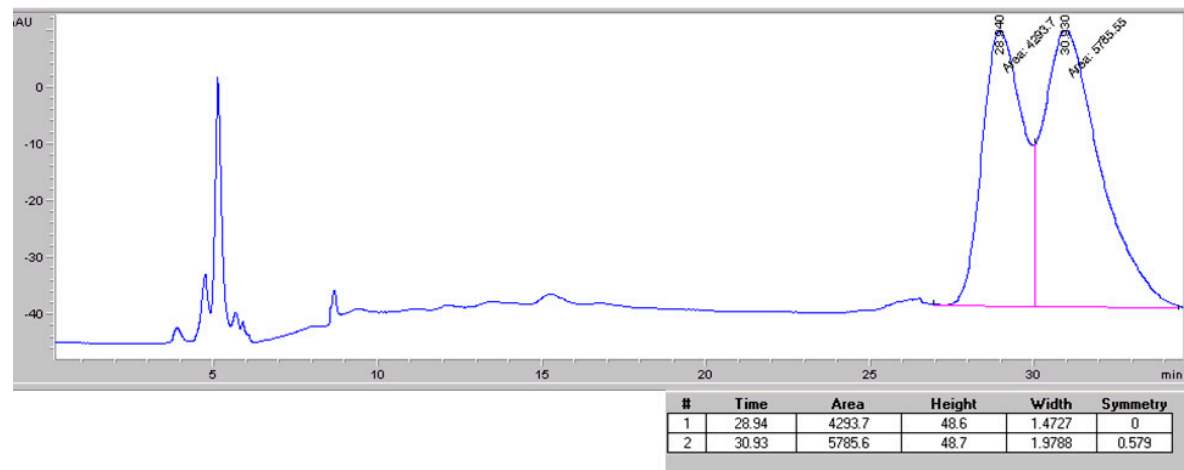


Figure S27. Example of HPLC trace characterized by difficult separation for the racemic epoxide product pNO₂PPHO (Table 2 entry 7) for the asymmetric epoxidation of PNO₂PPH with H₂O₂.