Supplementary Materials: Organocatalytic Enantioselective Epoxidationof Aryl Substituted Vinylidenebisphosphonate Esters: on the Wayto Chiral Anti-Osteoporosis Drugs

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General.

^{1}H NMR, $^{31}P\{^{1}H\}$ NMR spectra were run on:
Bruker Avance 300 spectrometer operating at 300 and 122 MHz, respectively, at 298 K.
Bruker Avance 400 spectrometer operating at 400 and 162 MHz, respectively, at 298 K.
δ values in ppm are relative to $Si(CH_3)_4$ 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, °C:	80°C for 5 min
Rate, °C/min:	30°C/min
Final T, °C:	280°C for 30 min
Injector T (split), °C:	280°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, °C	280°C
Source T, °C:	200°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/UV_{254} 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).

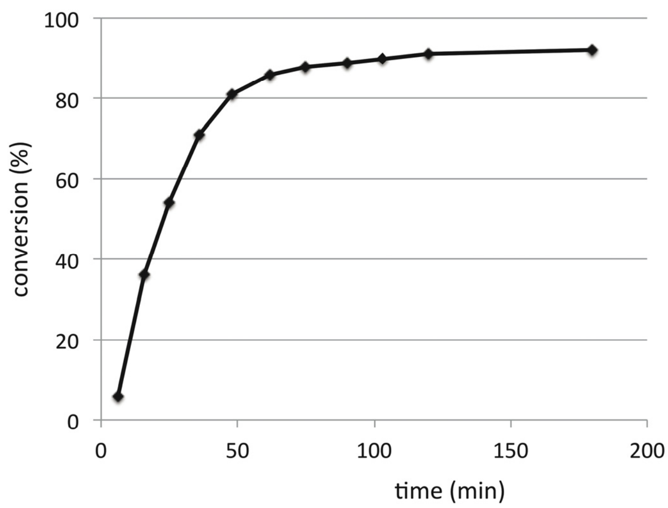
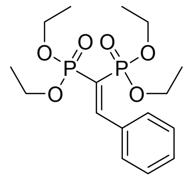


Figure S1. Stereoselective epoxidation of **PPh** with hydrogen peroxide catalyzed by sparteine.



PPh

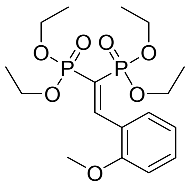
Tetraethyl 2-phenylethene-1,1-diyldiphosphonate

^{1}H 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 [M^+ -OCH_2CH_3], 239 [M^+ -$PO(OEt)_2$].

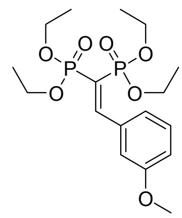


PoOMe

Tetraethyl 2-(2-methoxyphenyl)ethene-1,1-diyldiphosphonate

^{1}H 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.

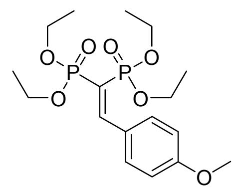


PmOMe

Tetraethyl 2-(3-methoxyphenyl)ethene-1,1-diyldiphosphonate

^{1}H 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.



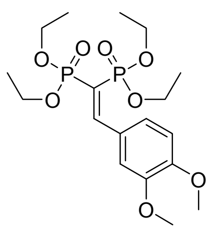
PpOMe

Tetraethyl 2-(4-methoxyphenyl)ethene-1,1-diyldiphosphonate

^{1}H 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 [M^+ -Me], 361 [M^+ -OEt], 269 [M^+ -$PO(OEt)_2$].

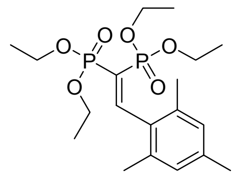


PVER

Tetraethyl 2-(3,4-dimethoxyphenyl)ethene-1,1-diyldiphosphonate

^{1}H 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-diyldiphosphonate



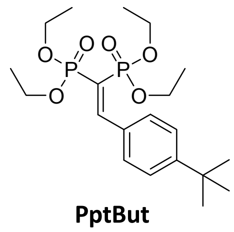
PMES

[1]H 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 [M^+ -Me], 373 [M^+ -OEt], 281 [M^+ - $PO(OEt)_2$].

Tetraethyl 2-(4-tert-butylphenyl)ethene-1,1-diyldiphosphonate



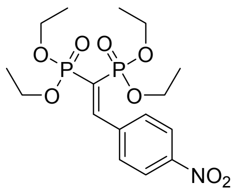
PptBut

[1]H 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 [M^+ -$PO(OEt)_2$], 239 [M^+ -$PO(OEt)_2$ –tBut +H].

Tetraethyl 2-(4-nitrophenyl)ethene-1,1-diyldiphosphonate



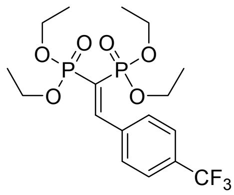
$PpNO_2$

[1]H 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 [M^+ -OEt], 284 [M^+ -$PO(OEt)_2$].

Tetraethyl 2-(4-(trifluoromethyl)phenyl)ethene-1,1-diyldiphosphonate

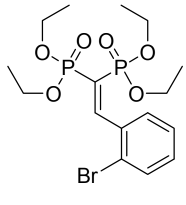


$PpCF_3$

[1]H 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-diyldiphosphonate

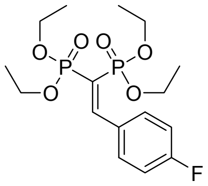


PoBr

[1]H 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 [M^+ - Br], 317 [M^+ - $PO(OEt)_2$].

Tetraethyl 2-(4-fluorophenyl)ethene-1,1-diyldiphosphonate



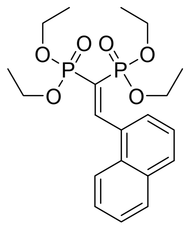
PpF

[1]H 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 [M^+ -OEt], 257 [M^+ -PO(OEt)$_2$].

Tetraethyl 2-(naphthalen-1-yl)ethene-1,1-diyldiphosphonate

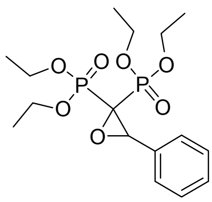


P1NAP

[1]H 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 [M^+ -Me], 381 [M^+ -OEt], 289 [M^+ -PO(OEt)$_2$].

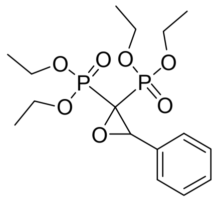


PPhO

Tetraethyl 3-phenyloxirane-2,2-diyldiphosphonate

[1]H 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.

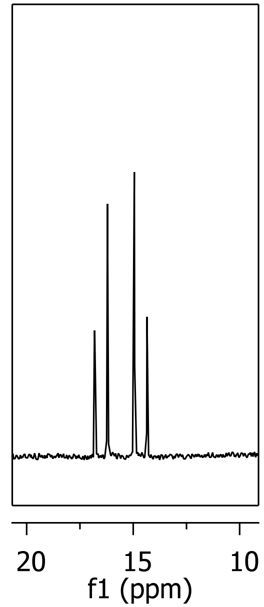


PPhO

Tetraethyl 3-phenyloxirane-2,2-diyldiphosphonate

^{1}H 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.



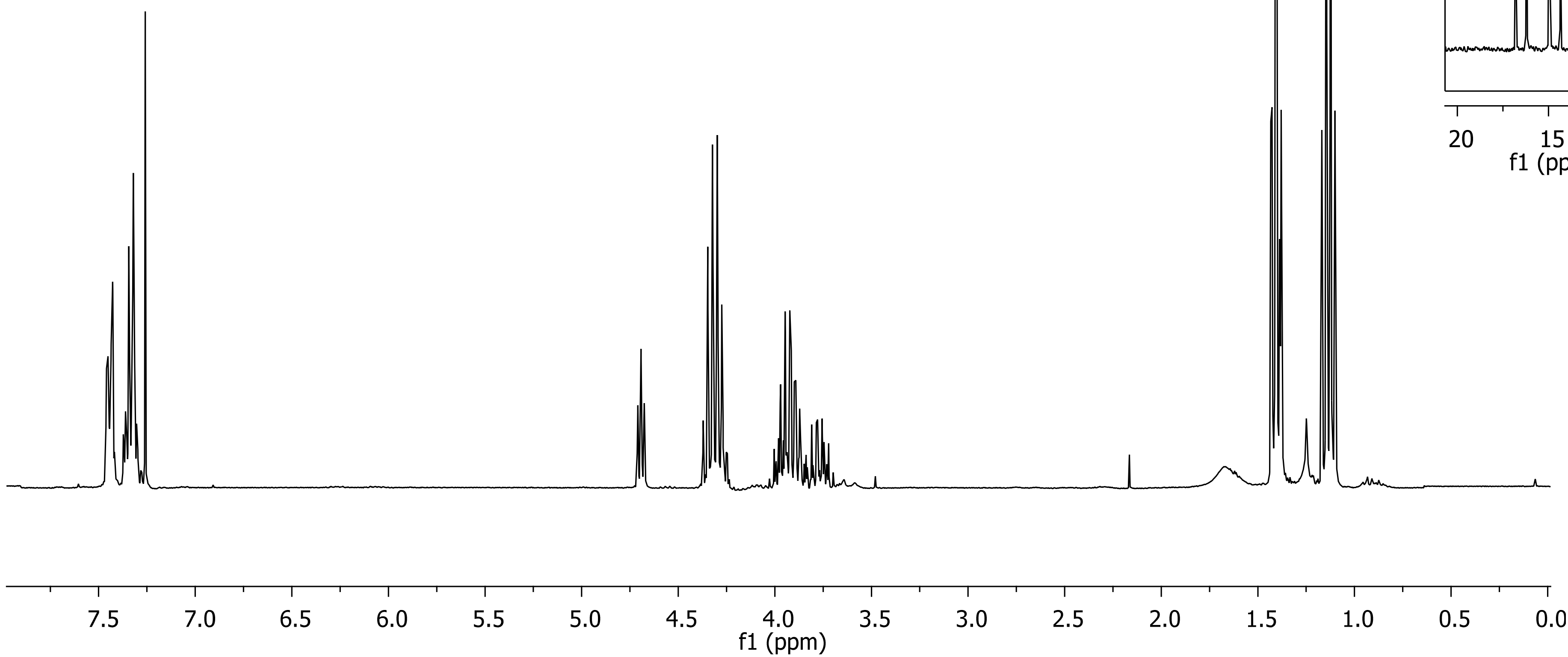


Figure S2. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PPhO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PPhO**.

GC-MS, (70 eV) m/z: 392 [M+], 377 [M+ - Me]; 347 [M+ - OEt]; 255 [M+ - $PO(OEt)_2$];

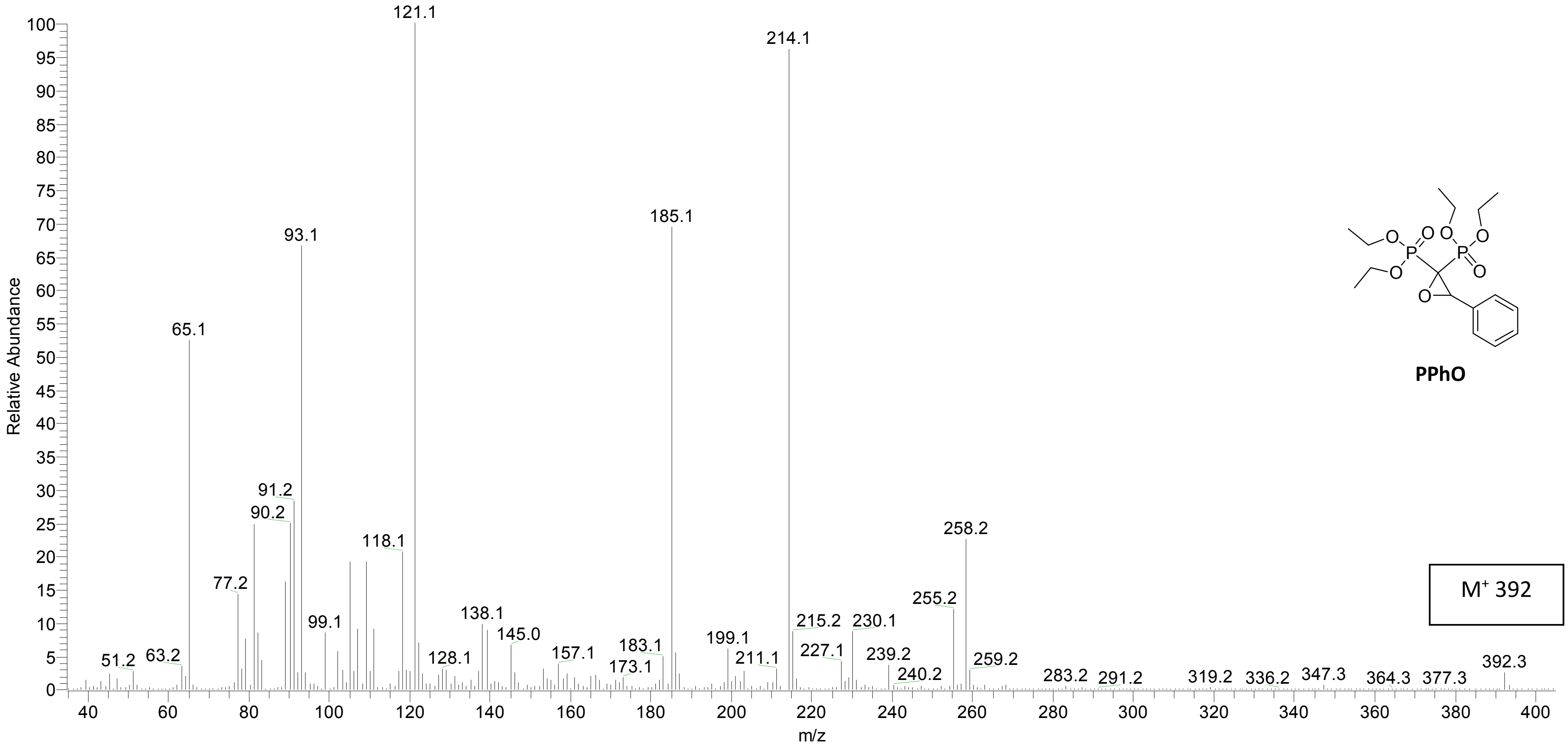
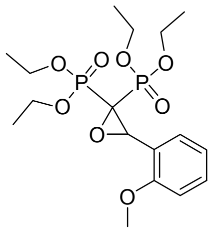


Figure S3. GC-MS spectrum of **PPhO**.



PoOMeO

Tetraethyl 3-(2-methoxyphenyl)oxirane-2,2-diyldiphosphonate

^{1}H 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.

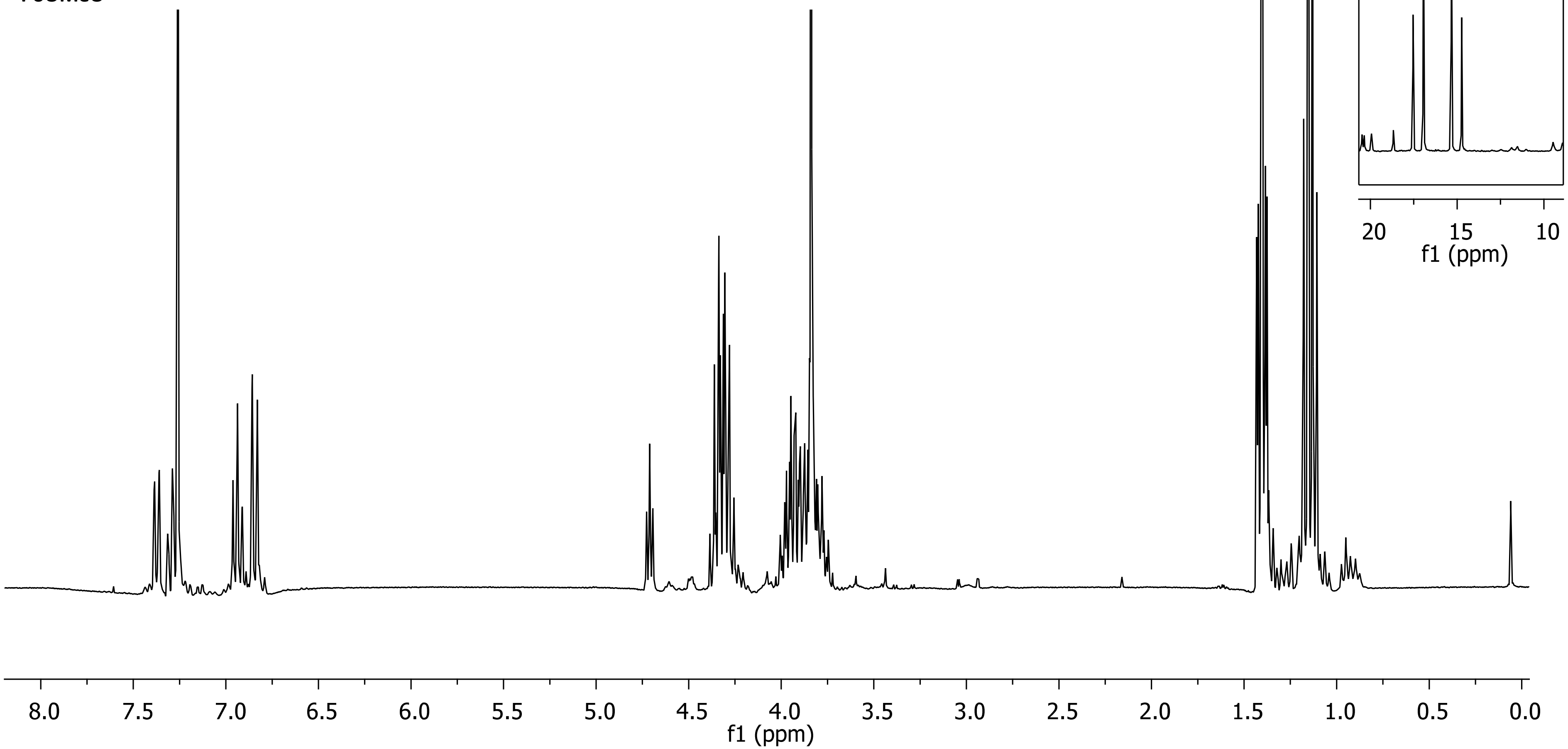


Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PoOMeO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PoOMeO**.

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

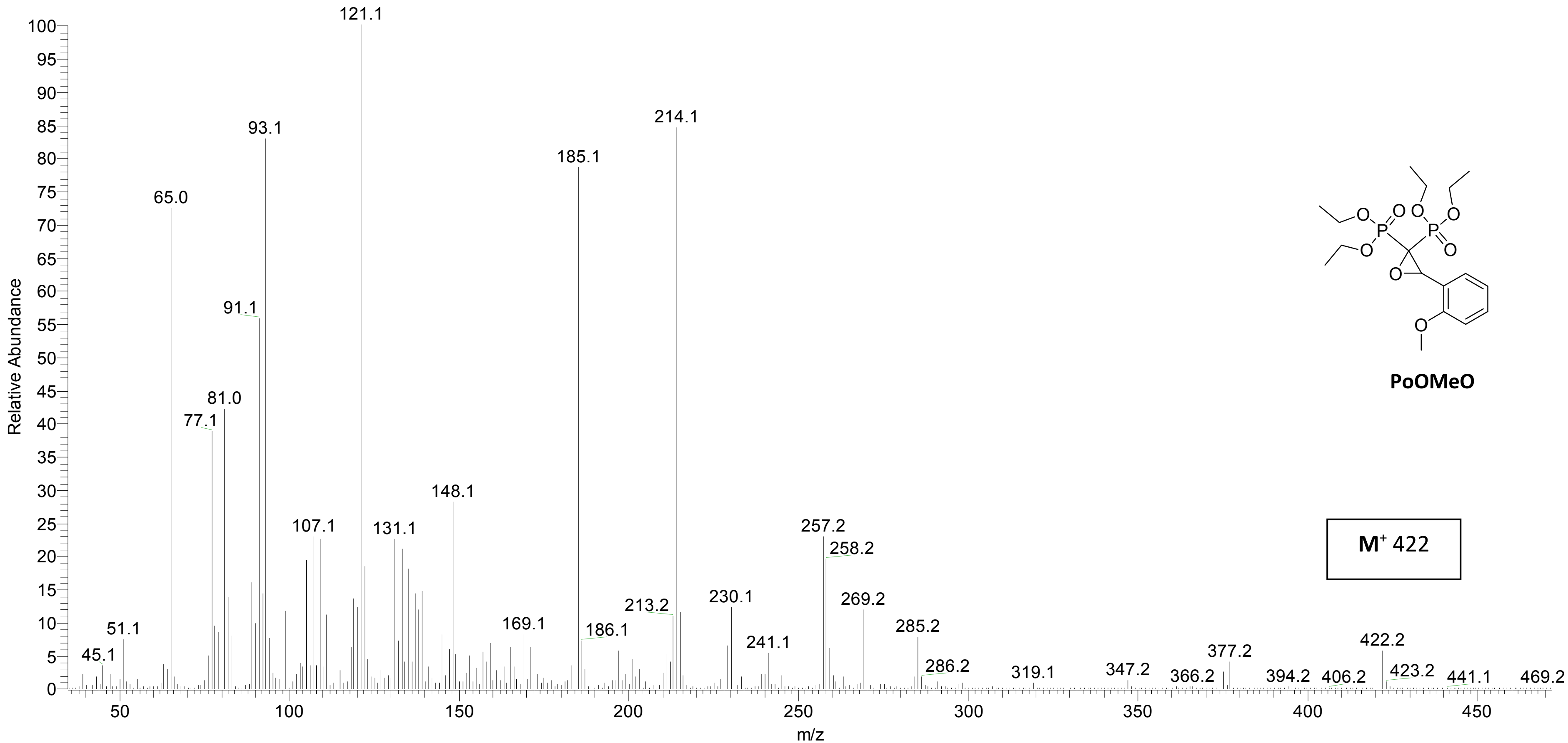
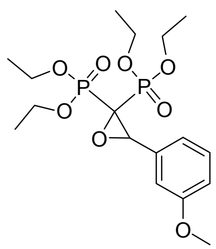


Figure S5. GC-MS spectrum of **PoOMeO**.



PmOMeO

Tetraethyl 3-(3-methoxyphenyl)oxirane-2,2-diyldiphosphonate

^{1}H 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.

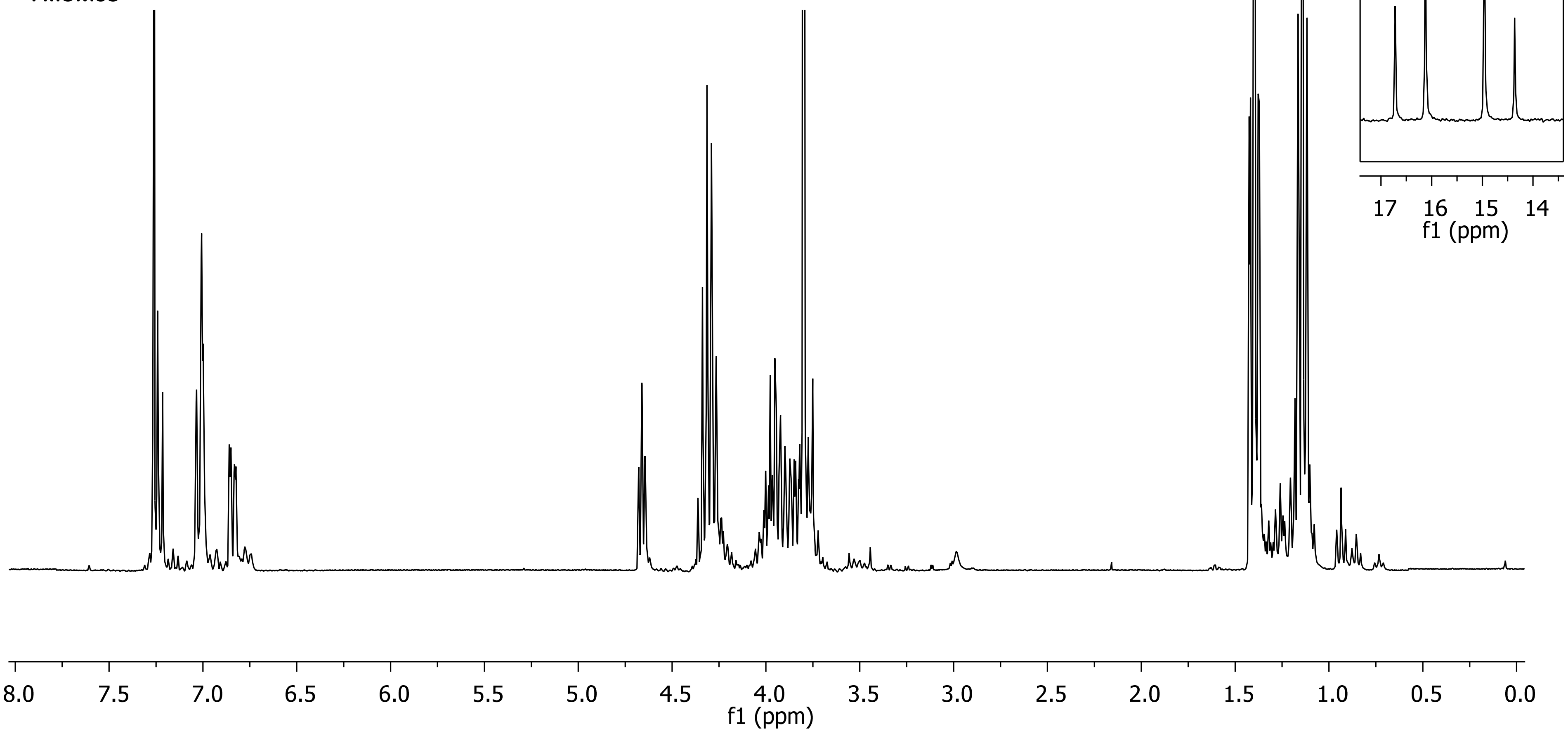


Figure S6: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PmOMeO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PmOMeO**.

GC-MS, (70 eV) m/z: 422 [M^+], 391 [M^+ -OMe], 377 [M^+ -OEt], 148 [M^+ -2PO(OEt)$_2$].

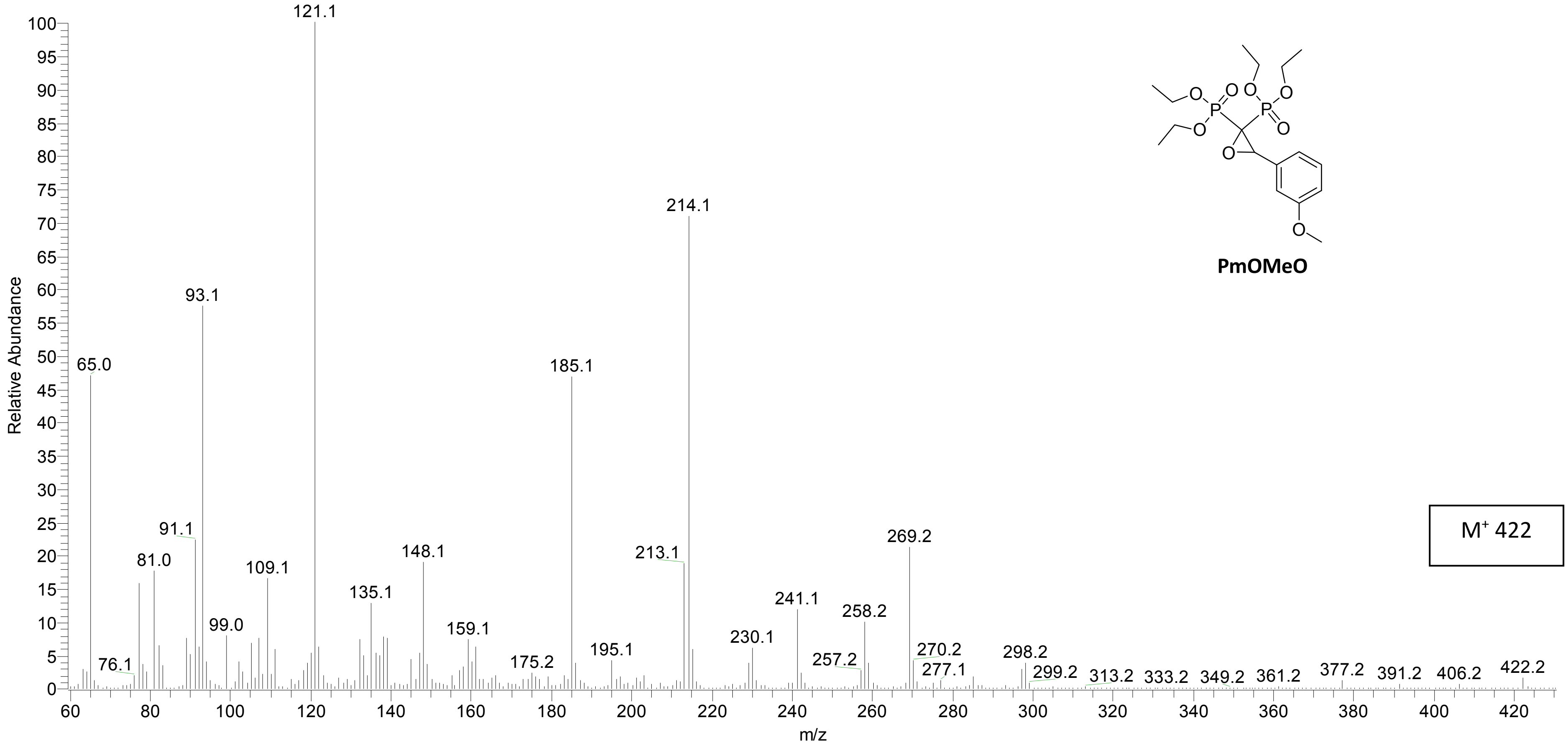
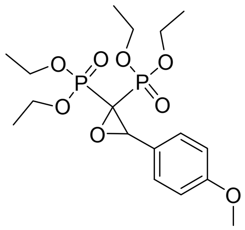


Figure S7. GC-MS spectrum of **PmOMeO.**



PpOMeO

Tetraethyl 3-(4-methoxyphenyl)oxirane-2,2-diyldiphosphonate

^{1}H 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.

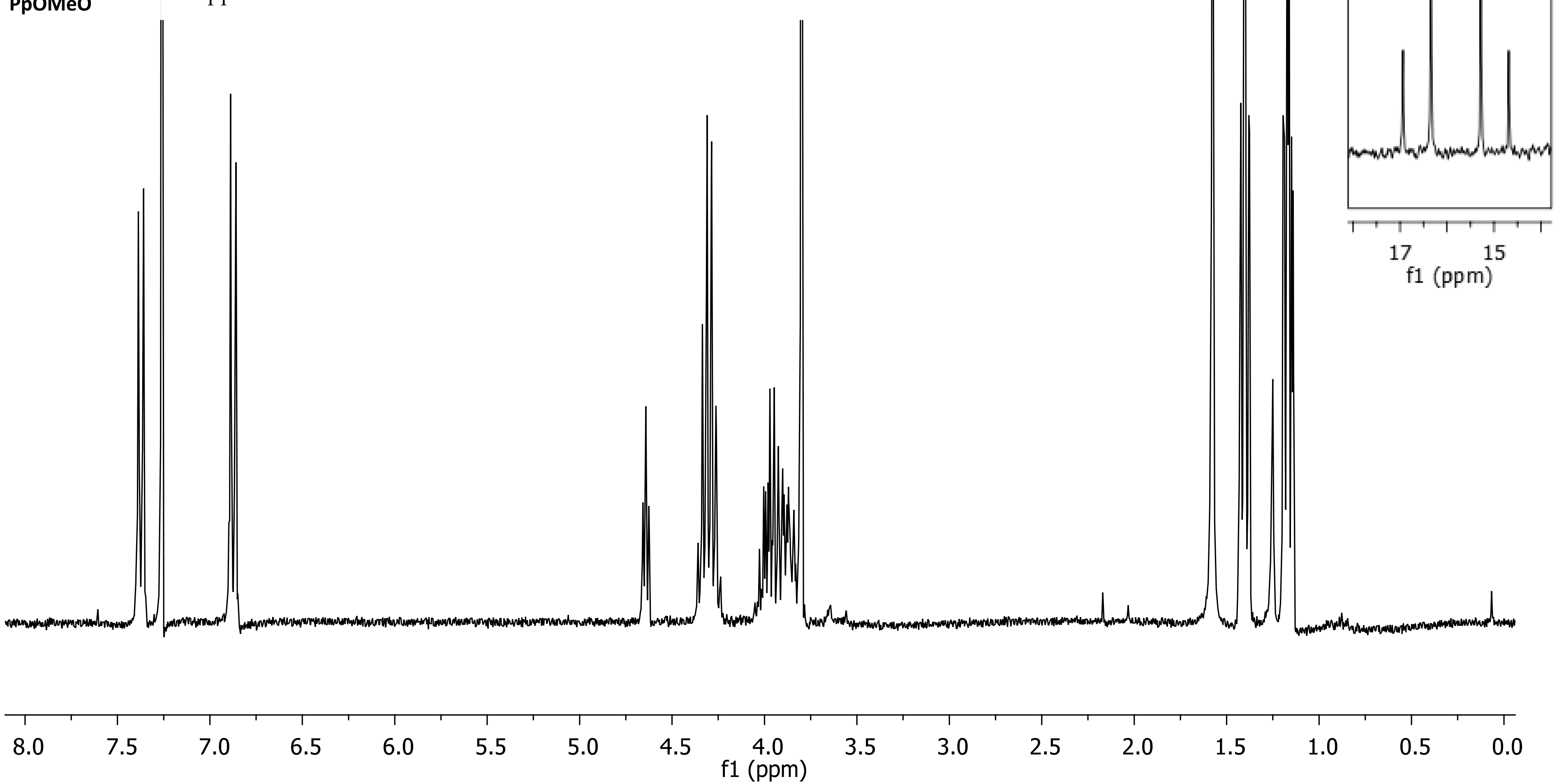


Figure S8. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PpOMeO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PpOMeO**.

GC-MS, (70 eV) m/z: 422 [M^+], 284 [M^+ -PO(OEt)$_2$ – H^+], 148 [M^+ -2PO(OEt)$_2$]

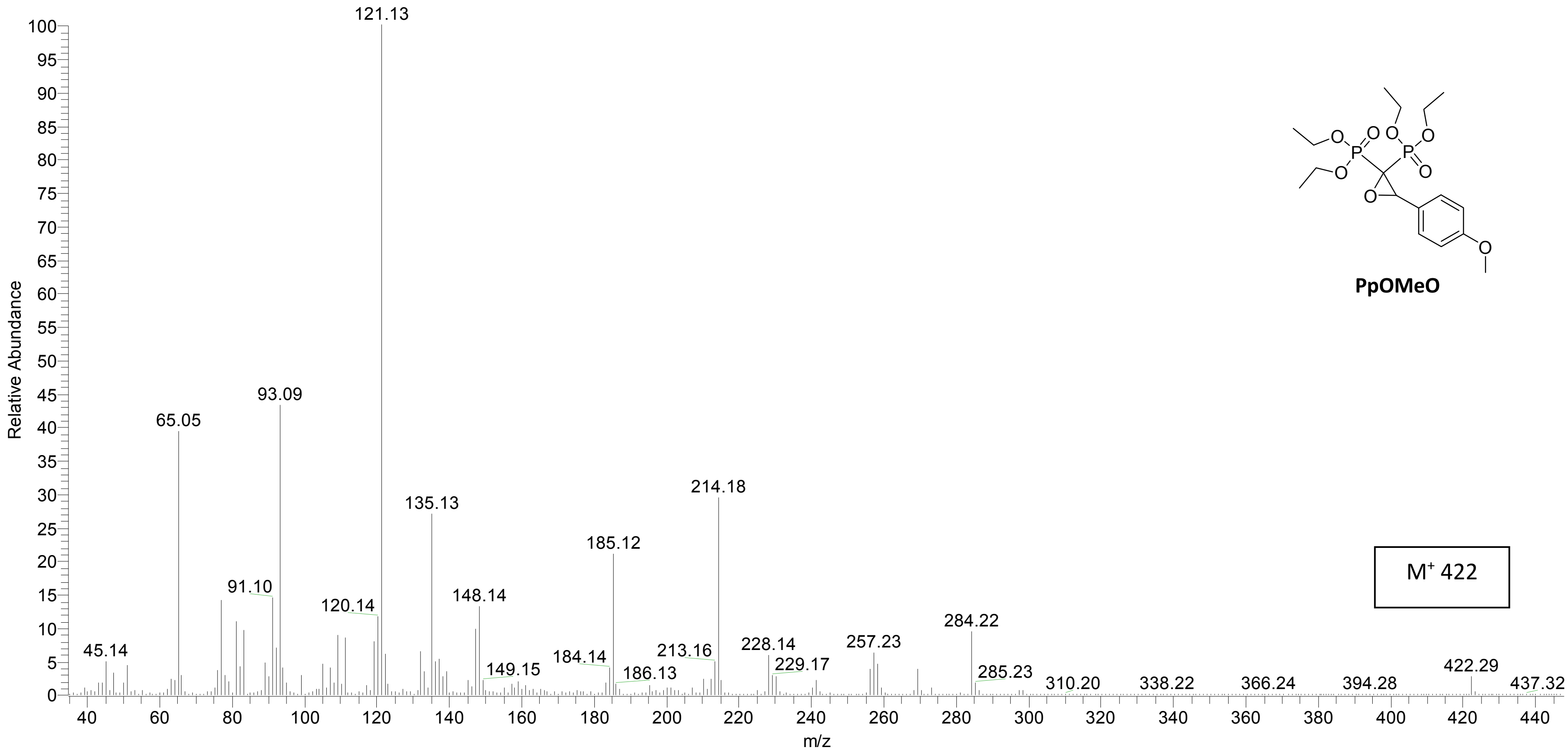
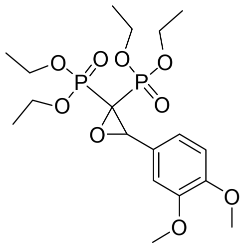


Figure S9. GC-MS spectrum of **PpOMeO**.



PVERO

Tetraethyl 3-(3,4-dimethoxyphenyl)oxirane-2,2-diyldiphosphonate

^{1}H 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.

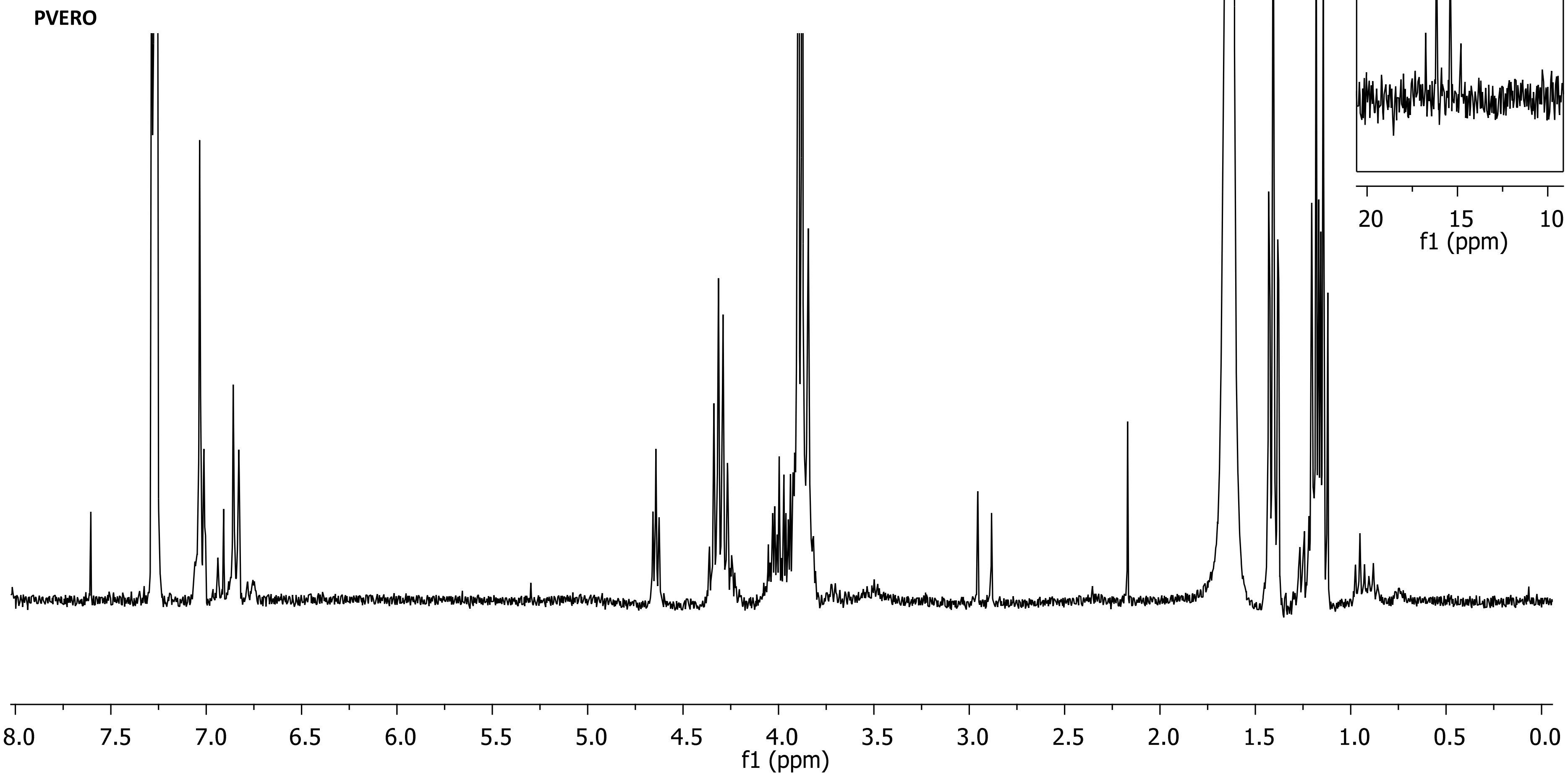


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PVERO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PVERO**.

GC-MS, (70 eV) m/z: 452 [M^+], 315 [M^+ -PO(OEt)$_2$], 314 [M^+ -PO(OEt)$_2$ - H^+], 178 [M^+ -2PO(OEt)$_2$].

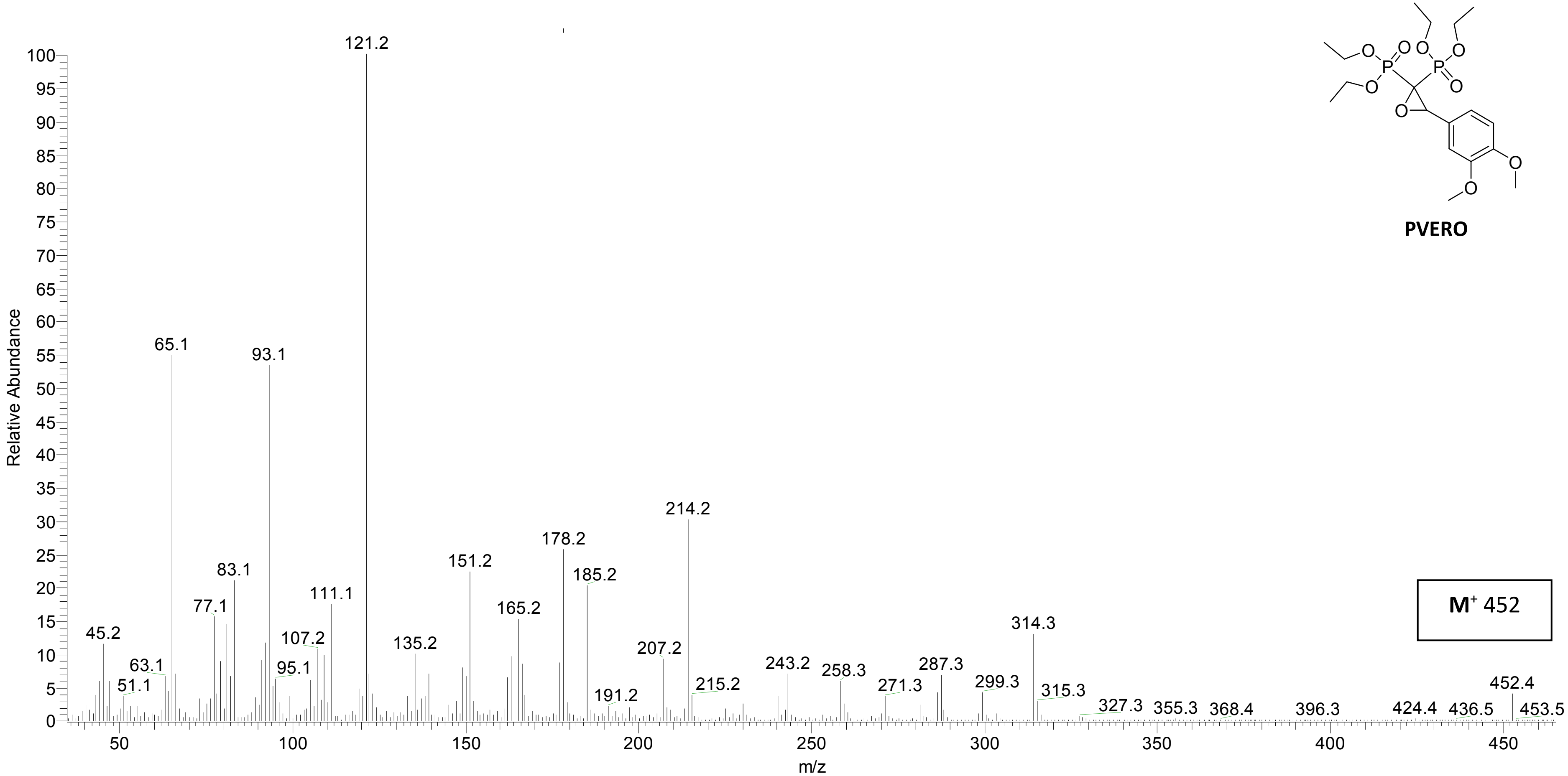
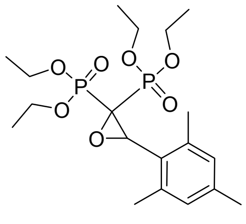


Figure S11. GC-MS spectrum of **PVERO**



PMESO

Tetraethyl 3-mesityloxirane-2,2-diyldiphosphonate

^{1}H 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.

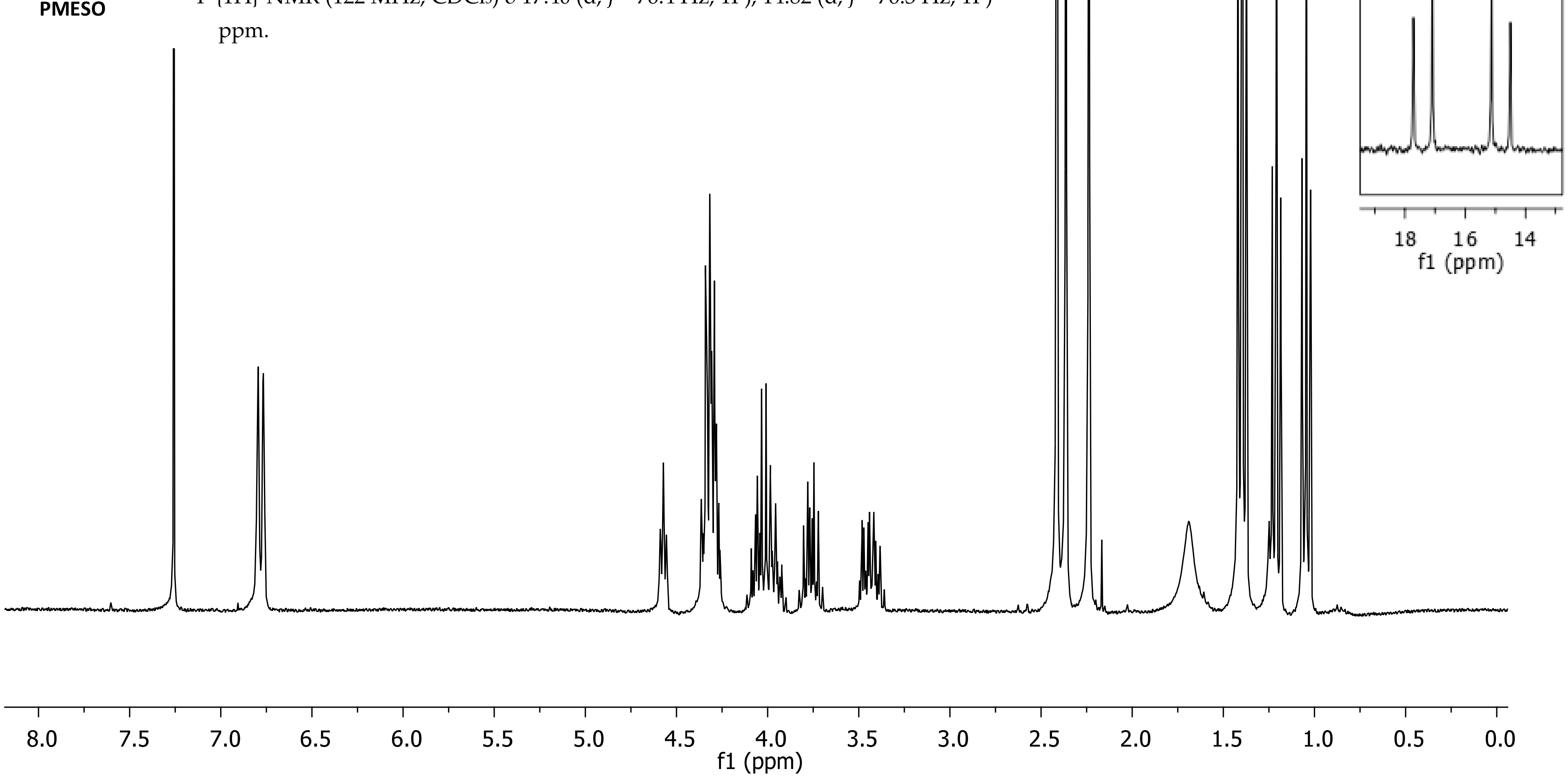


Figure S12. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PMESO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PMESO**.

GC-MS, (70 eV) m/z: 434 [M^+], 419 [M^+ - Me], 389 [M^+ -OEt], 297 [M^+ -PO(OEt)$_2$] 160 [M^+ -2PO(OEt)$_2$]

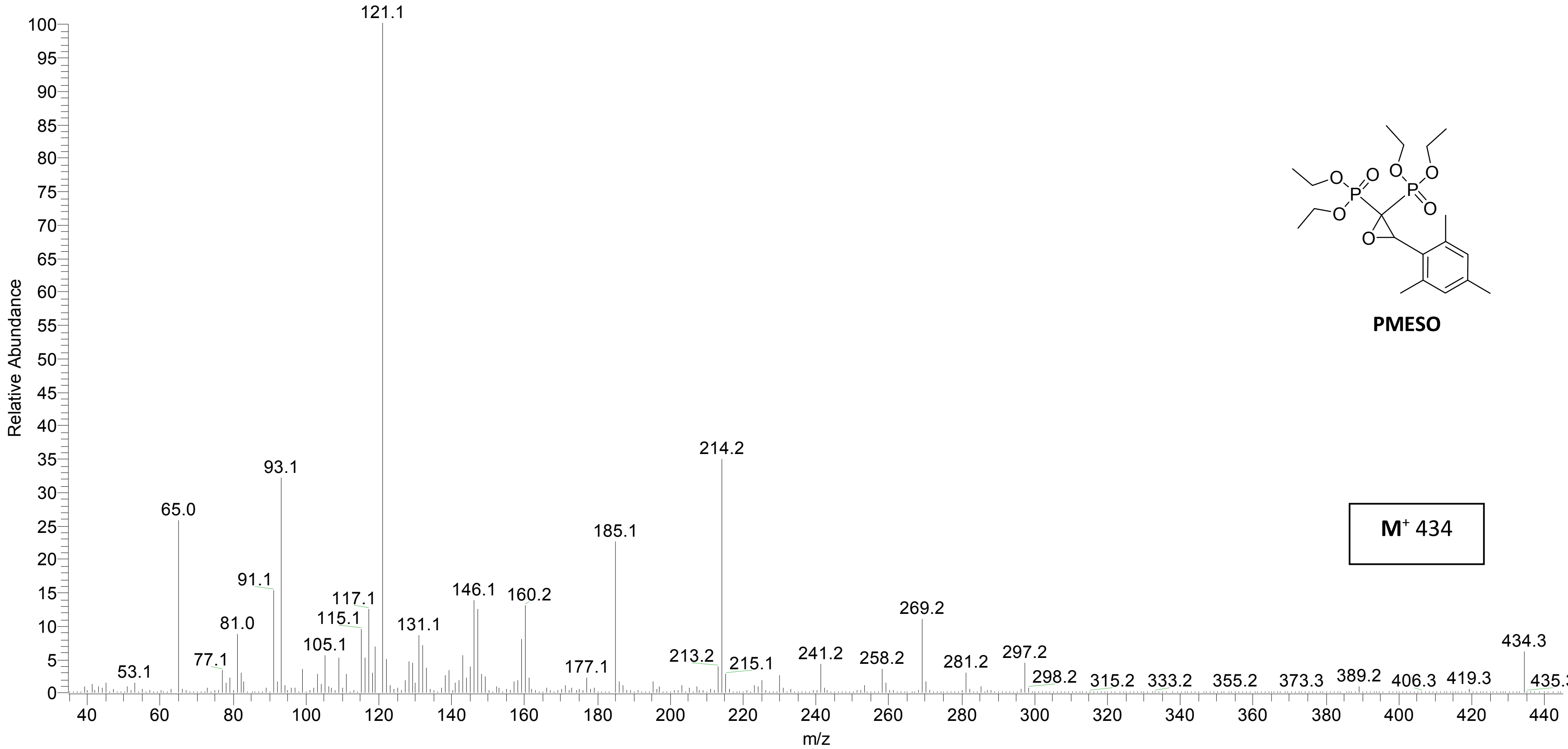
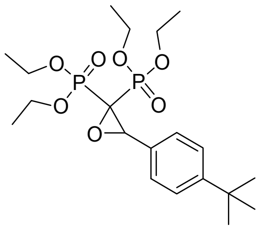


Figure S13. GC-MS spectrum of **PMESO.**



PptButO

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

^{1}H 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.

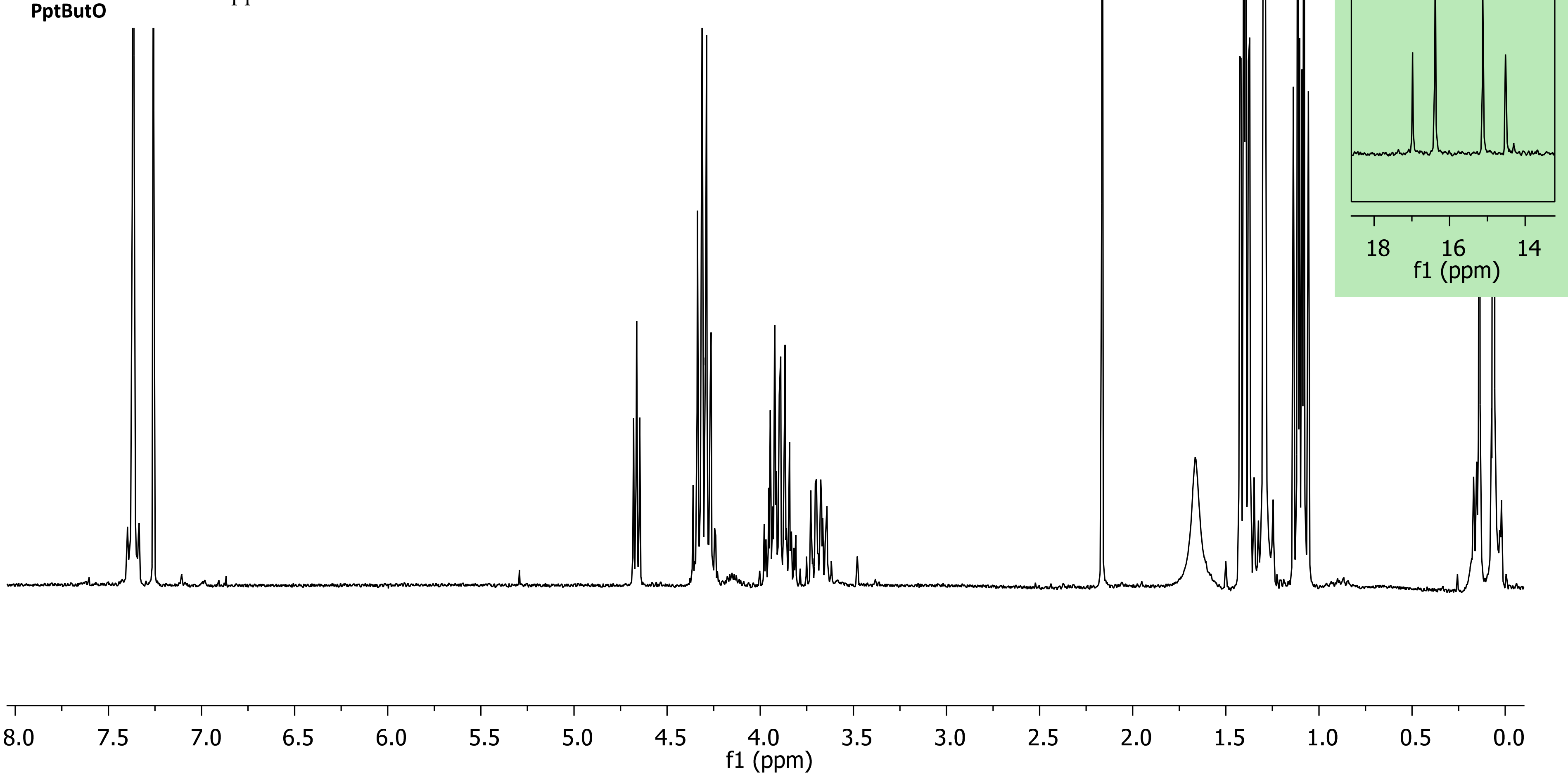


Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PtButO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PtButO**.

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

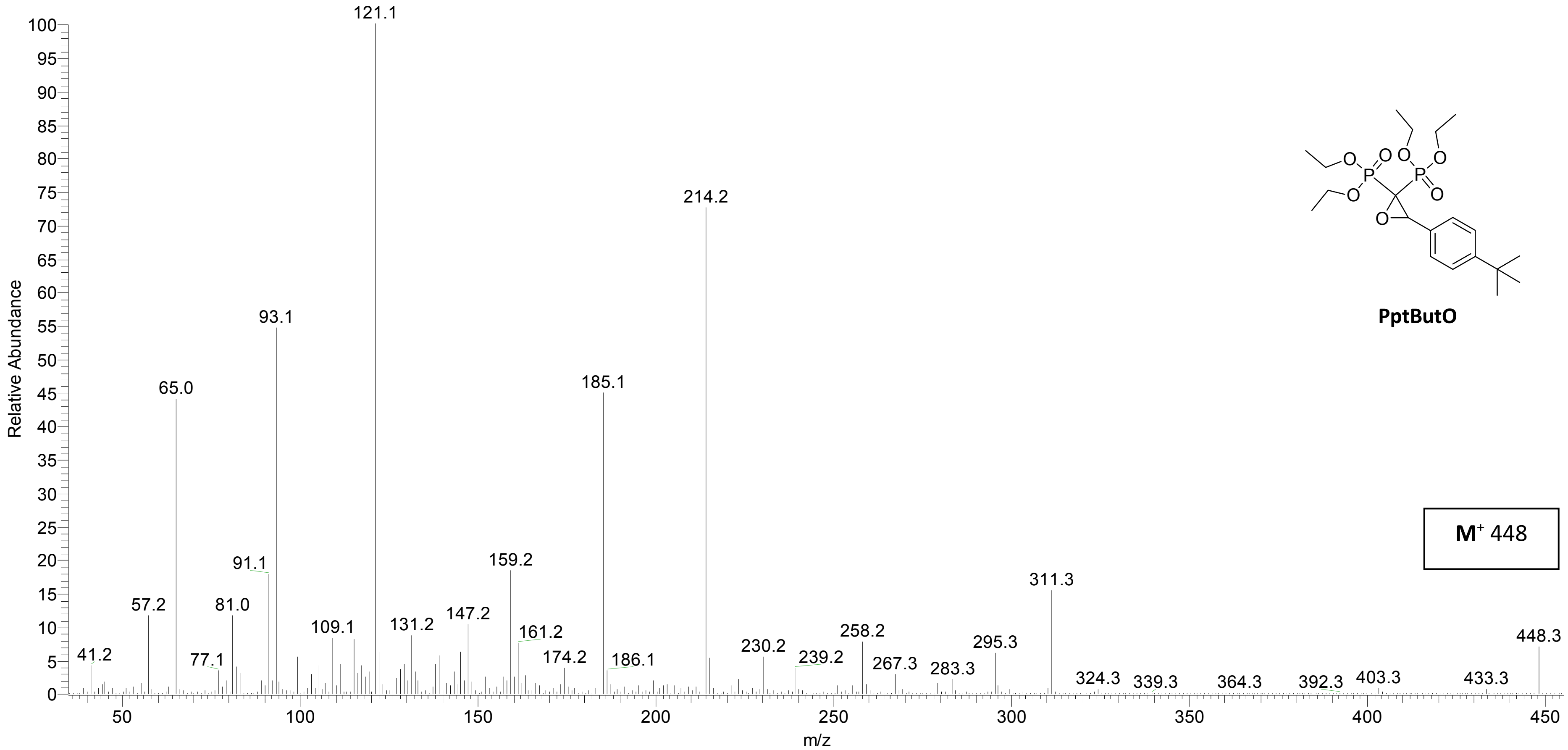
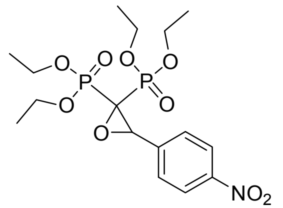


Figure S15. GC-MS spectrum of **PtButO**.



PpNO$_2$O

Tetraethyl 3-(4-nitrophenyl)oxirane-2,2-diyldiphosphonate

^{1}H NMR (300 MHz, $CDCl_3$) 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.

^{31}P {1H}-NMR (122 MHz, $CDCl_3$) δ 15.49 (d, *J* = 68.4 Hz, 1P), 13.93 (d, *J* = 68.2 Hz, 1P) ppm.

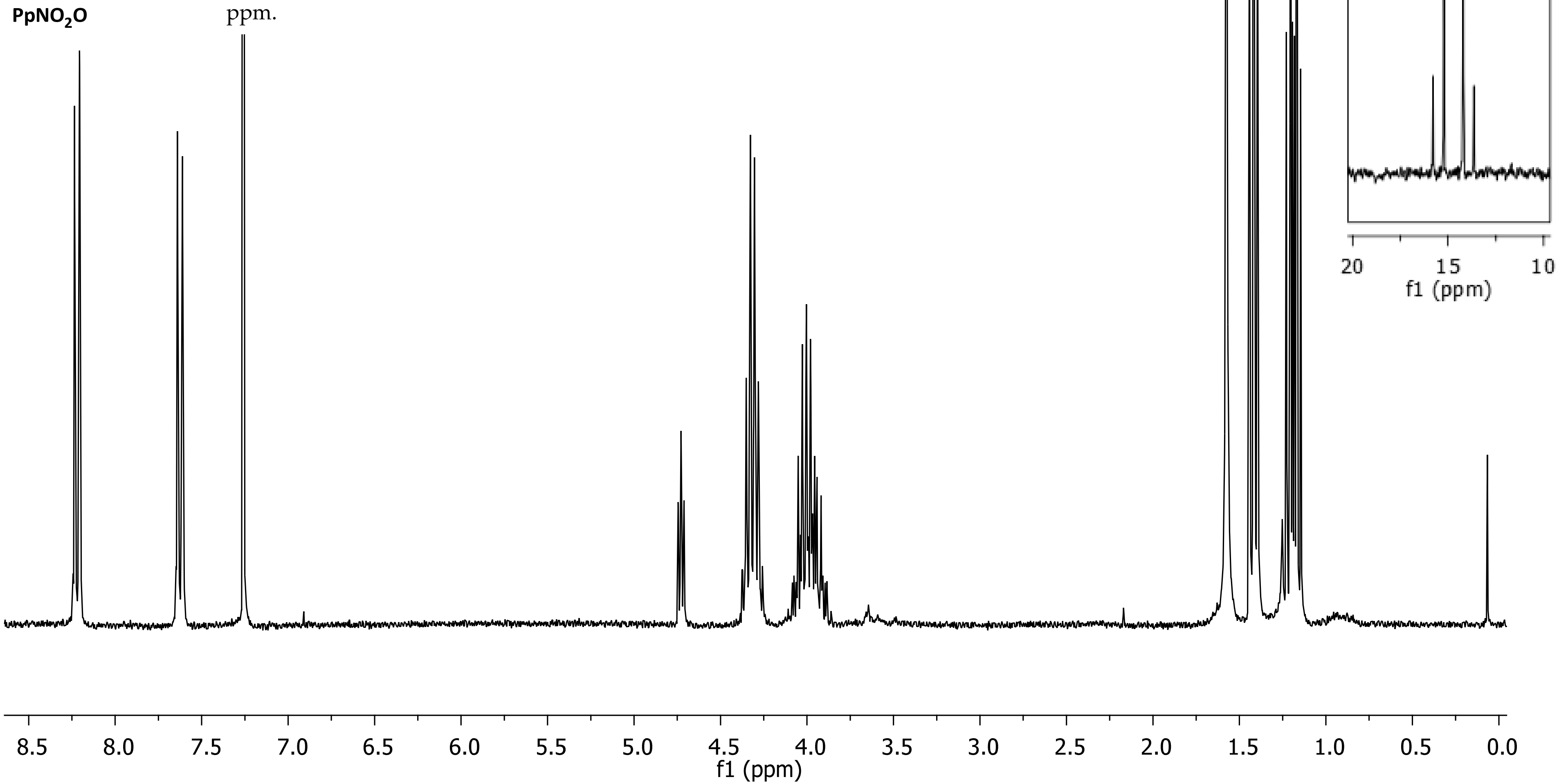


Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PpNO$_2$O**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PpNO$_2$O**.

GC-MS, (70 eV) m/z: 437 [M+], 392 [M+ -OEt], 300 [M+ -PO(OEt)2]

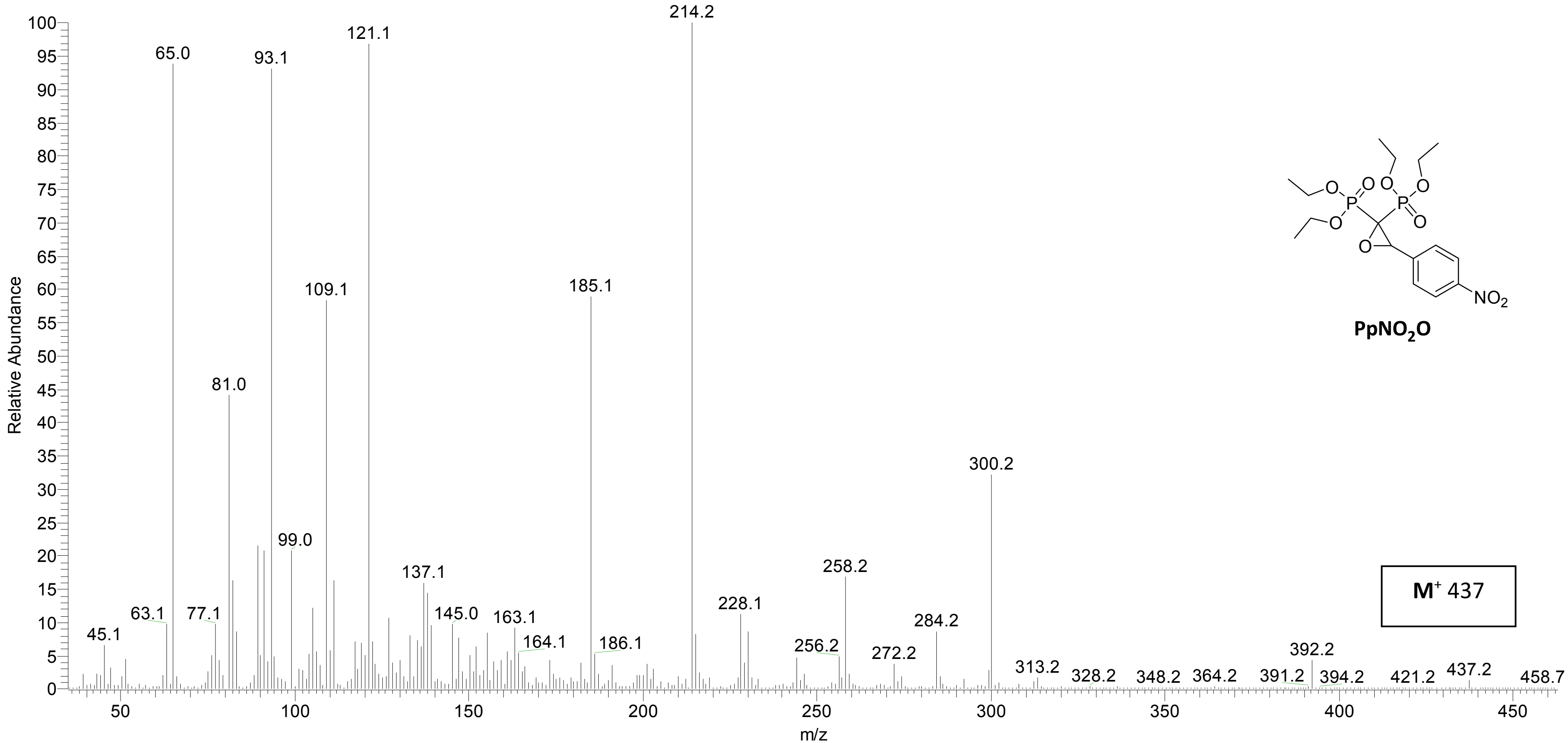
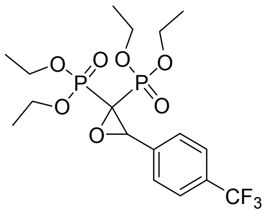


Figure S17. GC-MS spectrum of **PpNO$_2$O**.



PpCF$_3$O

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

[1]H NMR (300 MHz, D_2O) 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.

[31]P {1H}-NMR (122 MHz, $CDCl_3$) δ 15.90 (d, *J* = 70.5 Hz, 1P), 14.22 (d, *J* = 70.3 Hz, 1P) ppm.

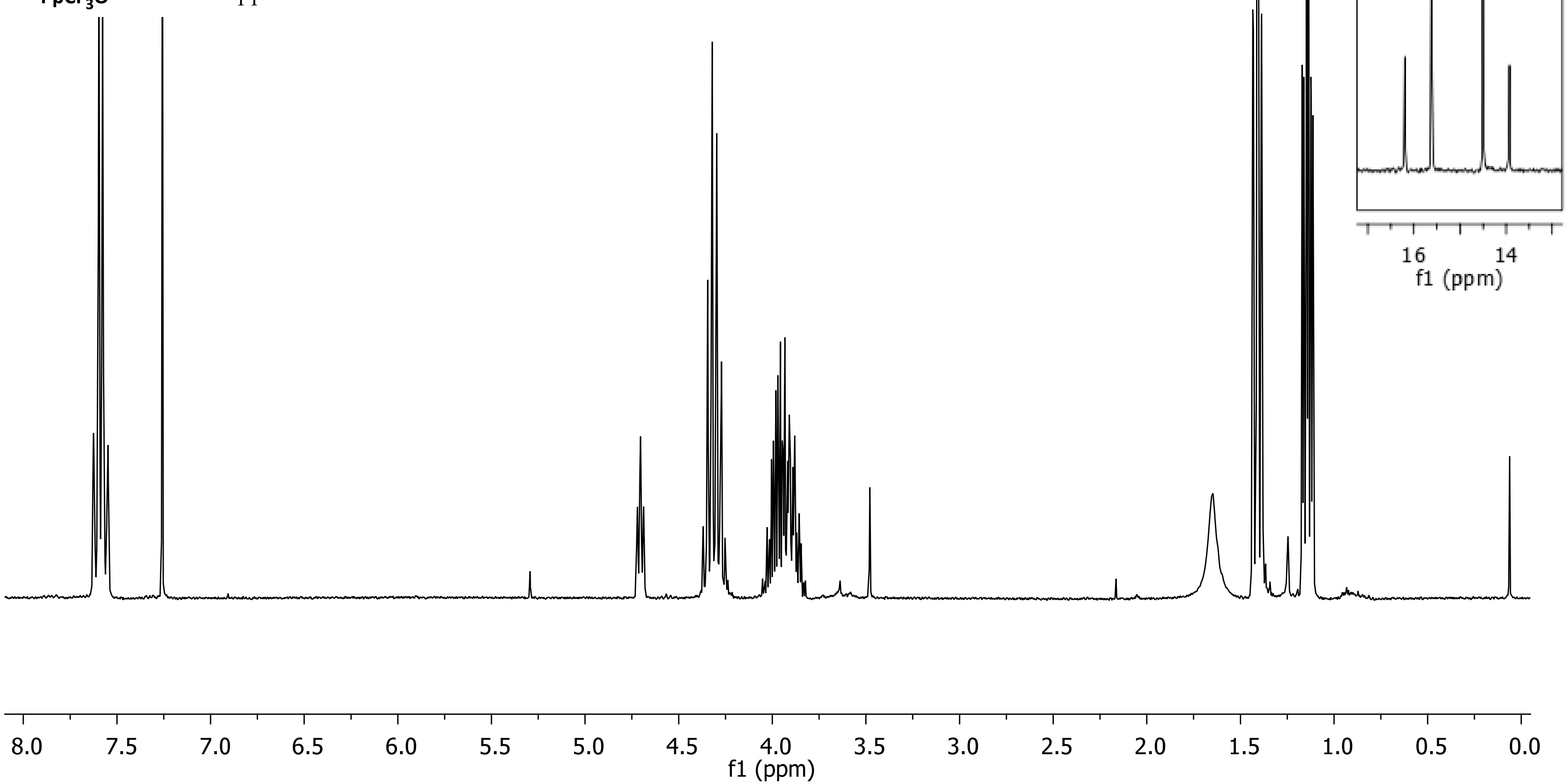


Figure S18. [1]H NMR (300 MHz, $CDCl_3$) spectrum of **PpCF$_3$O**; insert: [31]P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PpCF$_3$O**.

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+].

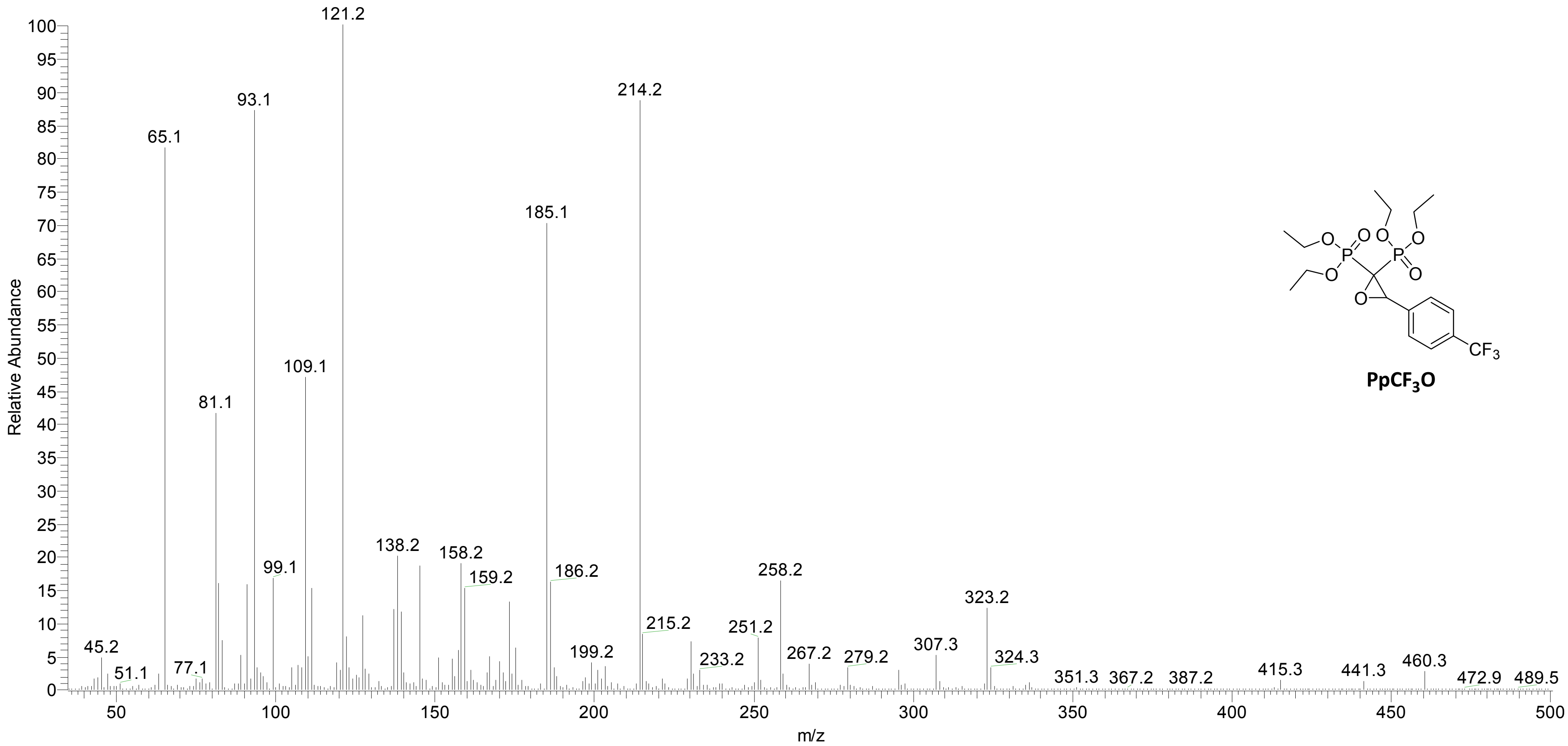
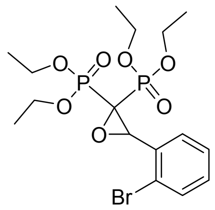


Figure S19. GC-MS spectrum of **PpCF$_3$O**.



PoBrO

Tetraethyl 3-(2-bromophenyl)oxirane-2,2-diyldiphosphonate

^{1}H 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.

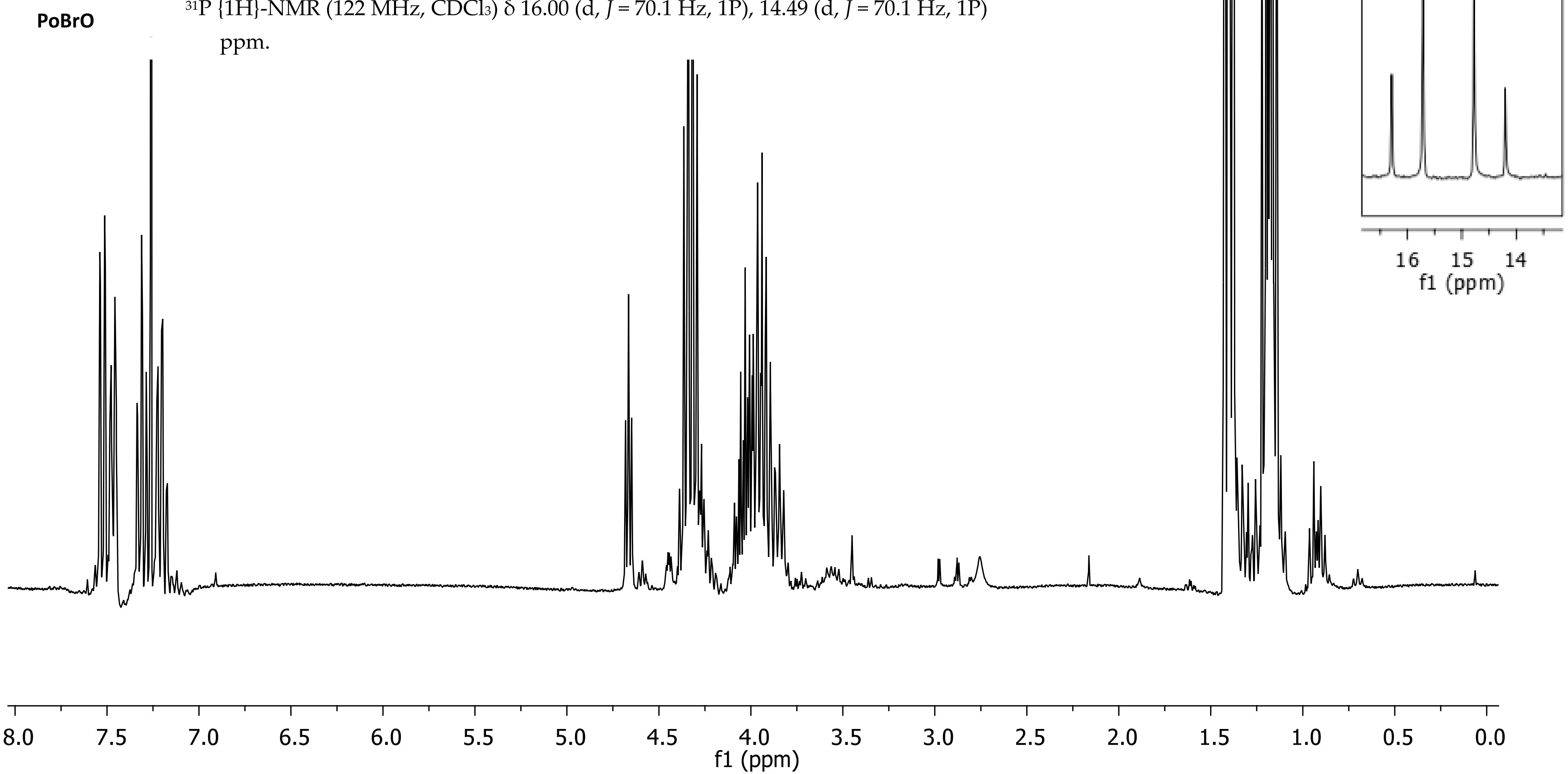


Figure S20. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **PoBrO**; insert: ^{31}P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PoBrO**.

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

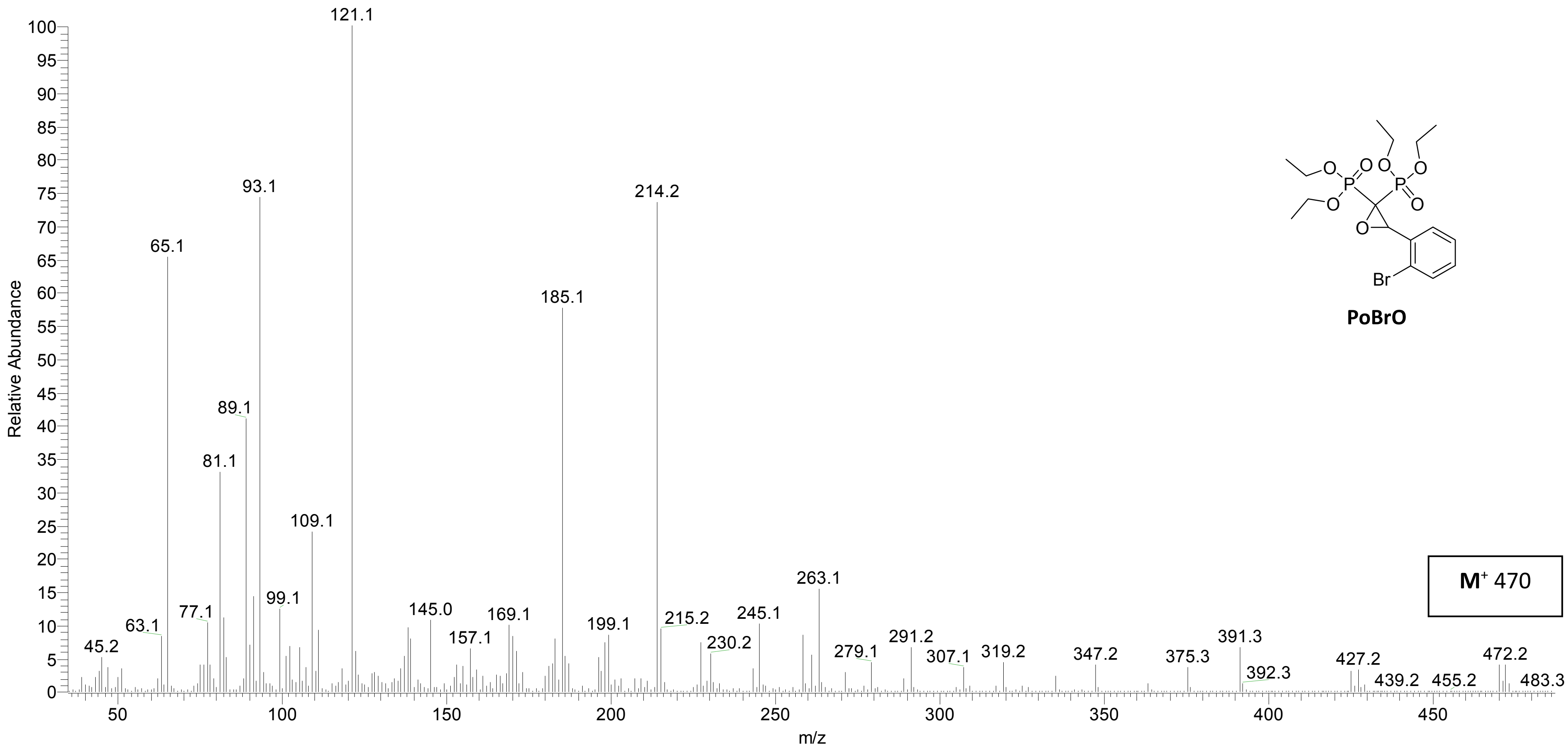
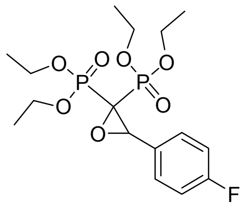


Figure S21. GC-MS spectrum of **PoBrO**.

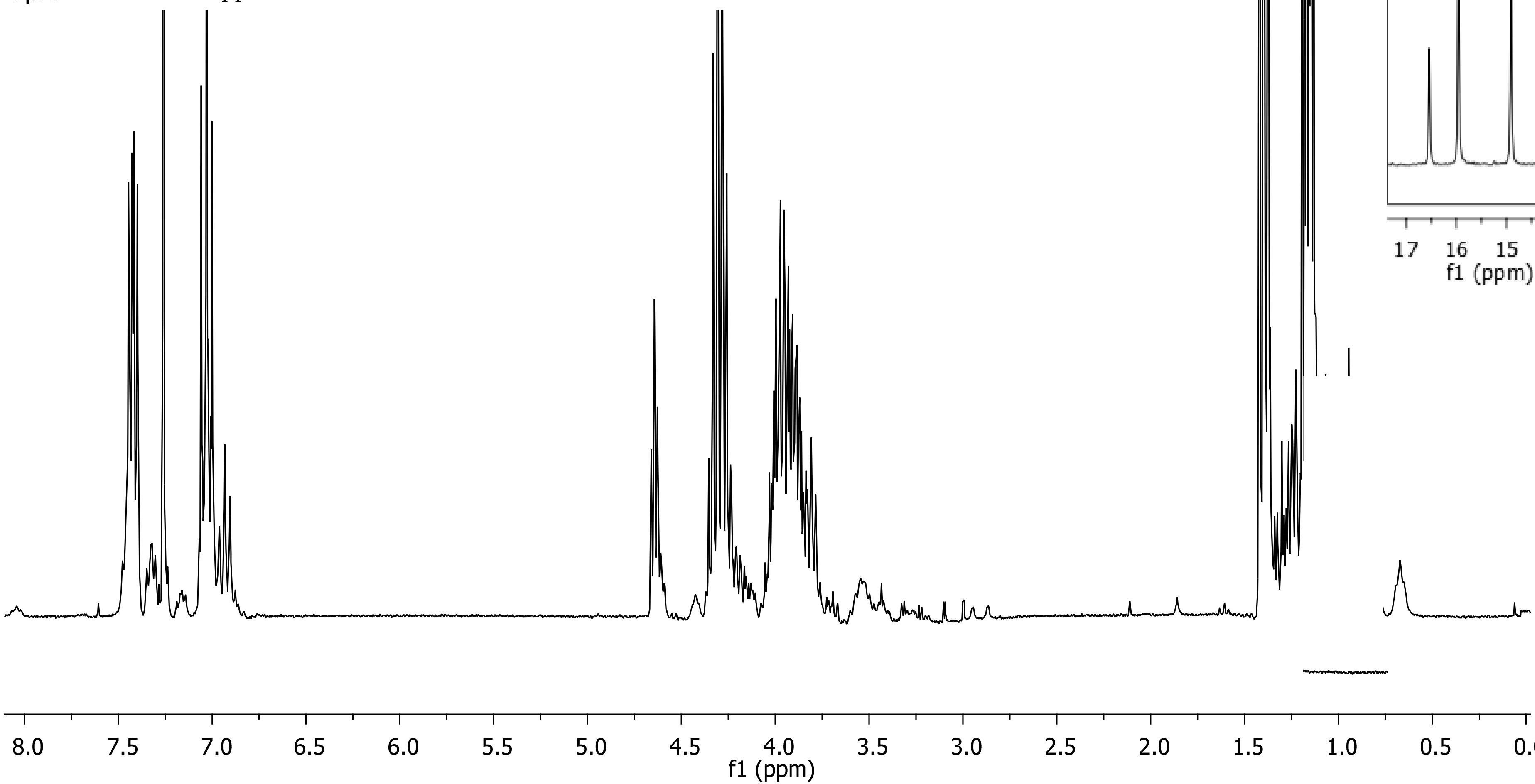


PpFO

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

[1]H 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.



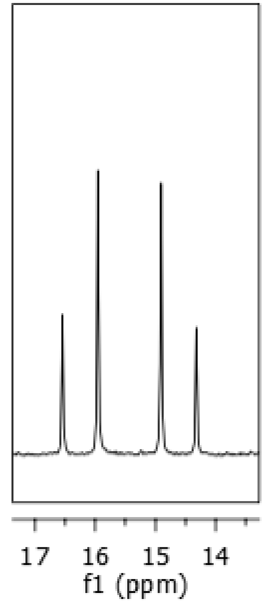


Figure S22. [1]H NMR (300 MHz, $CDCl_3$) spectrum of **PpFO**; insert: [31]P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **PpFO**.

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

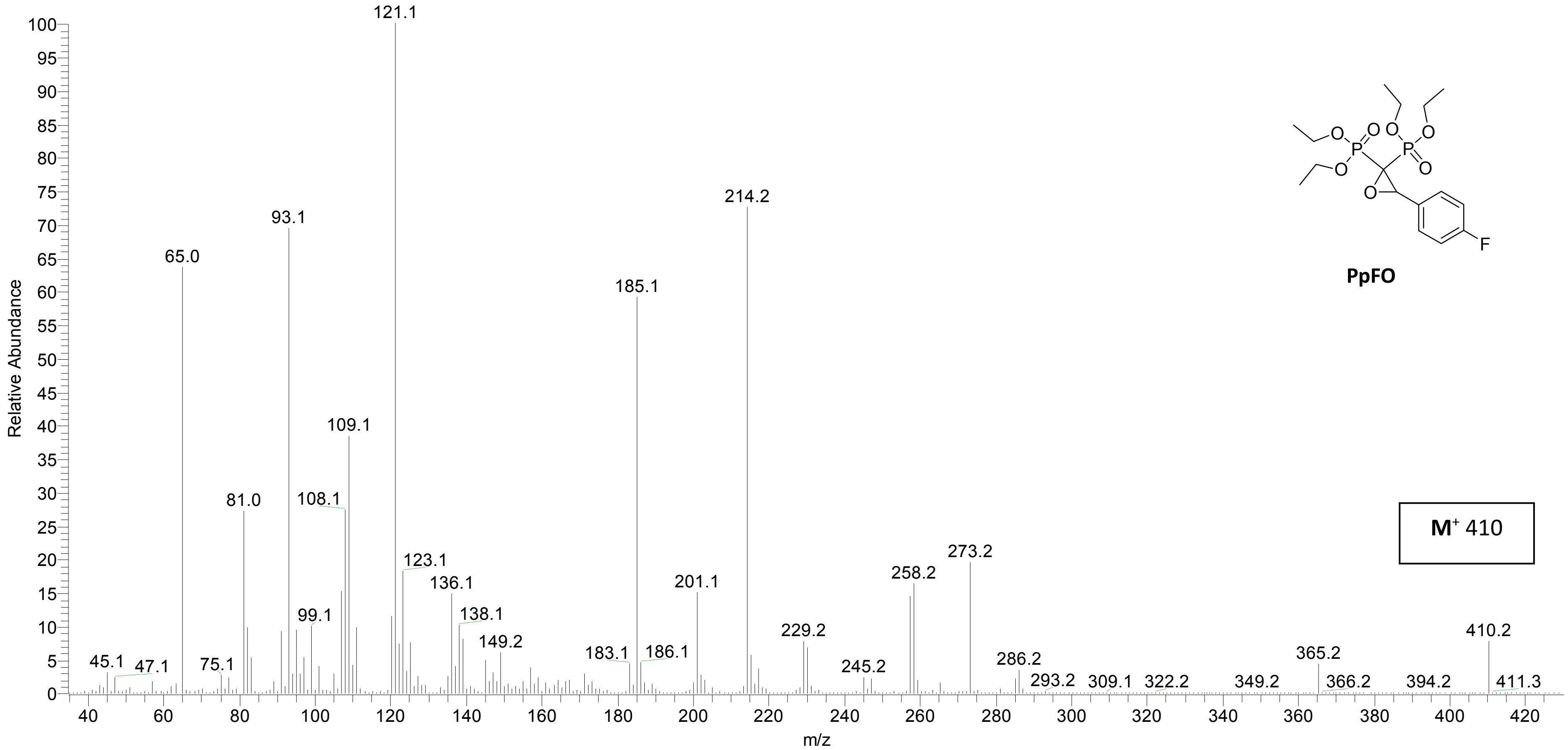
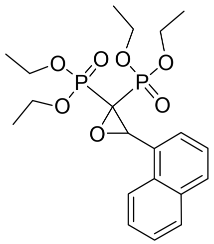


Figure S23. GC-MS spectrum of **PpFO**.

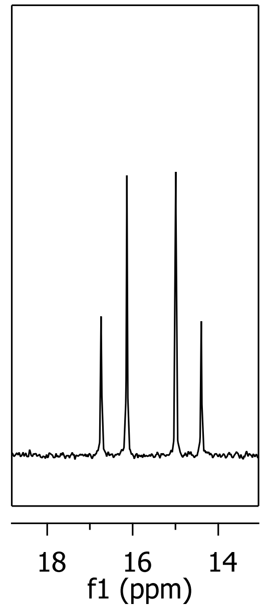


P1NAPO

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

[1]H 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.



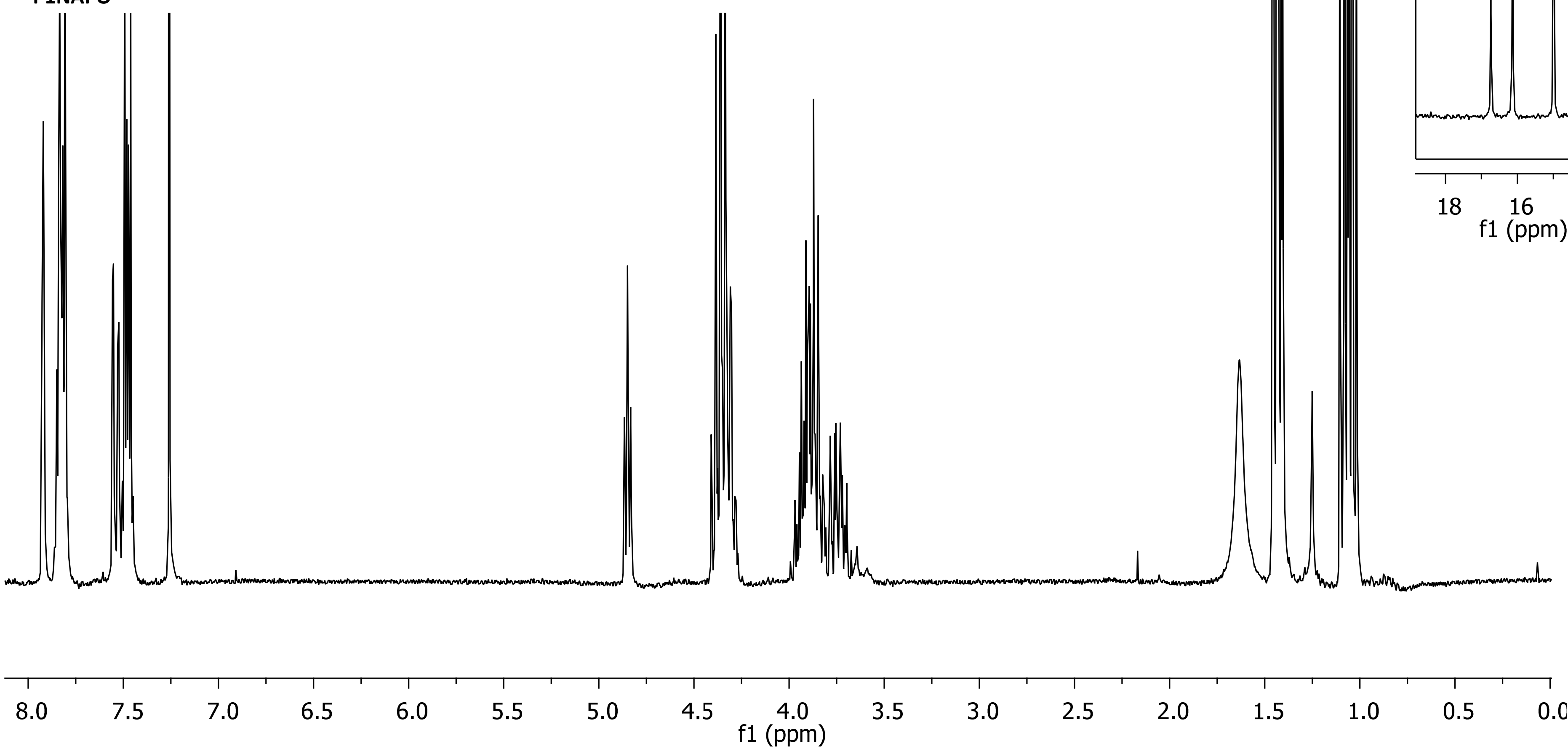


Figure S24. [1]H NMR (300 MHz, $CDCl_3$) spectrum of **P1NAPO**; insert: [31]P {1H}-NMR (122 MHz, $CDCl_3$) spectrum of **P1NAPO**.

GC-MS, (70 eV) m/z: 442 [M^+], 305 [M^+ -PO(OEt)$_2$], 127 [M^+ -CHOC$_2$PO(OEt)$_2$].

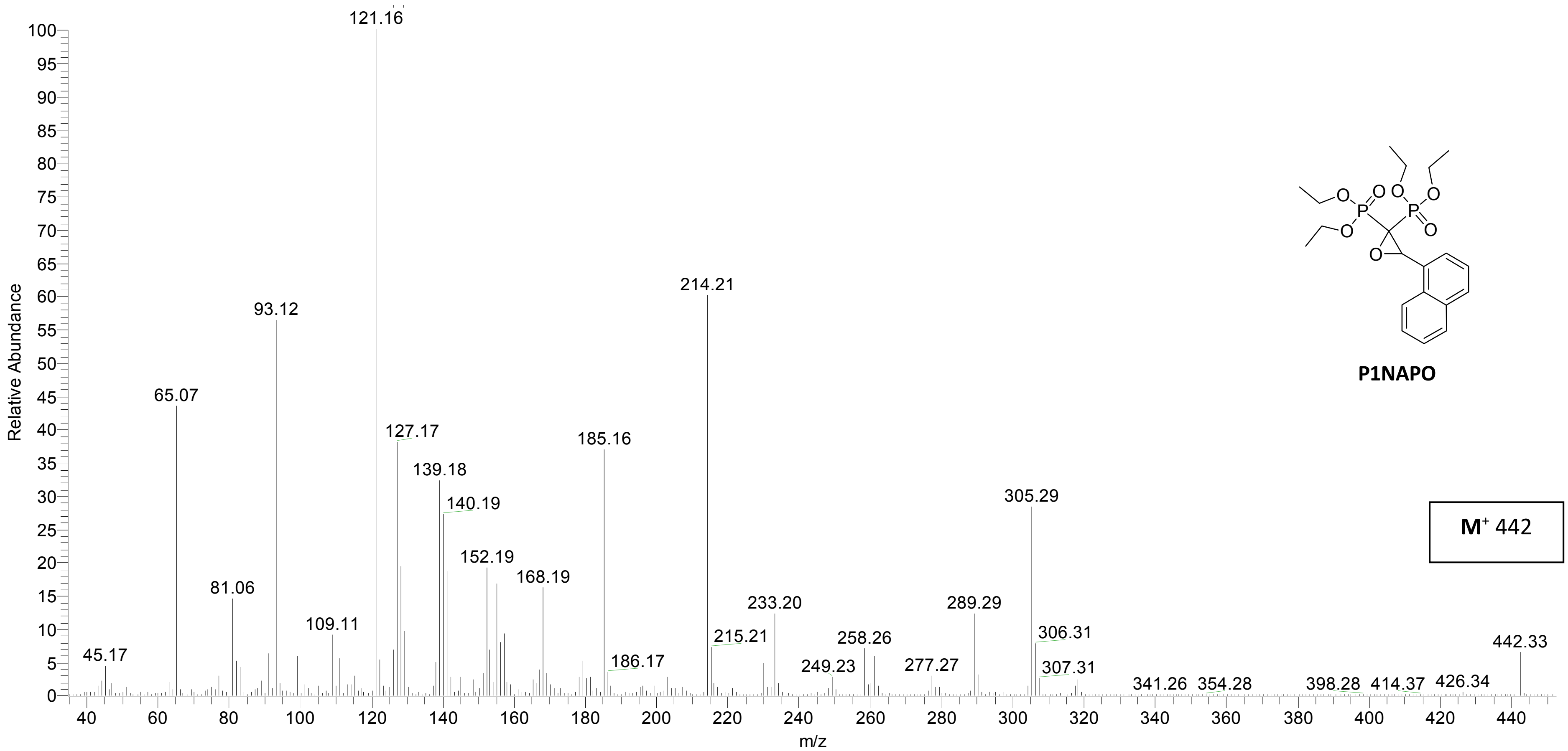
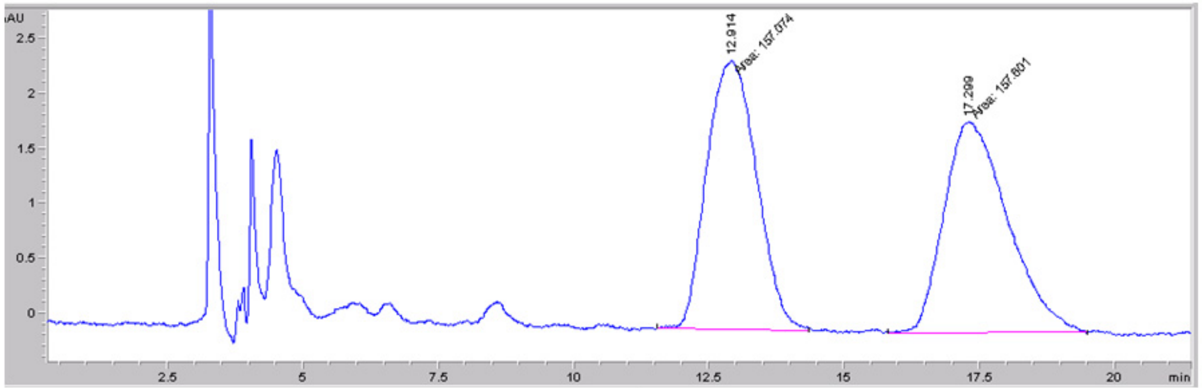


Figure S25. GC-MS spectrum of **P1NAPO**.



#	Time	Area	Height	Width	Symmetry
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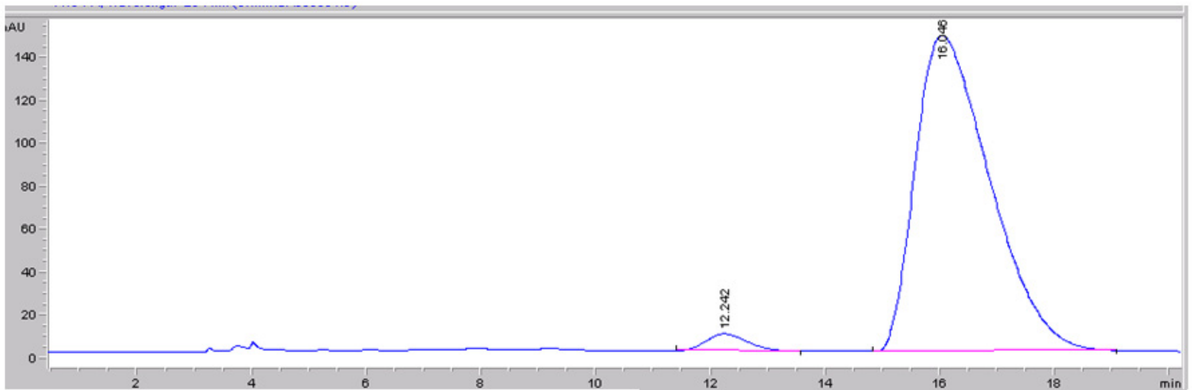
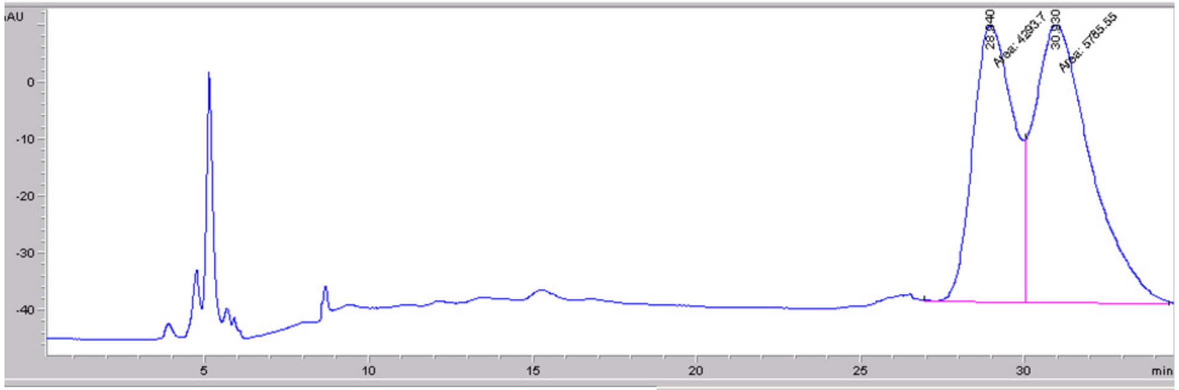
2	17.299	157.6	1.9	1.3681	0.654



#	Time	Area	Height	Width	Symmetry
1	12.242	393.4	7.9	0.7303	0.772
2	16.046	13296	147.2	1.3713	0.533

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 H_2O_2 in the presence of sparteine.



#	Time	Area	Height	Width	Symmetry
1	28.94	4293.7	48.6	1.4727	0
2	30.93	5785.6	48.7	1.9788	0.579

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 PNO2**PPH** with H_2O_2.