Supplementary Material (ESI) for Green Chemistry

ELECTRONIC SUPPORTING INFORMATION

Efficient and "green", microwave assisted synthesis of haloalkylphosphonates via Michaelis-Arbuzov reaction

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Experimental:

Materials.

All starting chemicals were purchased from Sigma-Aldrich (Prague, Czech Republic) and used without further purification. Solvents were purchased from Penta (Prague, Czech Republic).

Microwave (MW) syntheses were carried out in the following MW syntheses instruments:
Type I – CEM Discover®, single-mode cavity with focused MW heating (MW power supply 0-300 W, 1 W increments, IR temperature sensor, open or closed vessel mode, pressure range 0-20 bar, 10 ml or 80 ml vials).
Type II – Biotage Initiator®, single-mode cavity, not focused MW heating (MW power supply 0-400 W, 1 W increments, IR temperature sensor, closed vessel mode, pressure range 0-20 bar, 5 ml vials).
Type III – Milestone BatchSYNTH®, single-mode cavity, scale-up (MW power supply 0-1000 W, 10 W increments, internal temperature sensor, batch mode, pressure range 0-30 bar, 250 ml vessel).
Type IV – Milestone FlowSYNTH®, continuous flow microwave reactor for scale-up (MW power supply 0-1000 W, 10 W increments, two internal temperature sensors, continuous flow mode, pressure range 0-30 bar, 200 ml vessel, flow rate 10-100 ml/min).
GC/MS analyses were performed on a gas chromatographer 6890N (Agilent, Santa Clara, CA, USA) connected to a quadrupole mass spectrometer. Fused silica capillary column HP-5ms (30 m × 0.25 mm, 0.25 μm, Agilent) was used. The carrier gas was helium at 1 mL/min flow. The injector was operated in split mode (100:1) at 230 °C. Temperature program: 60°C (4 min), then 10 °C/min to 320 °C (10 min). Standard 70 eV mass spectra were recorded in the mass range of 25-800 u; 4-min solvent delay was used. Temperatures of the transfer line, ion source and quadrupole were 280 °C, 230 °C, and 150 °C, respectively. FAB mass spectra were measured on a ZAB-EQ spectrometer (VG Analytical) using FAB (ionization by Xe, accelerating voltage 8 kV, glycerol matrix). NMR spectra were measured on an FT NMR spectrometer (Bruker Avance II 500) in DMSO-d_6 (^{1}H at 500 MHz and ^{13}C at 125.7 MHz, chemical shifts given in ppm, coupling constants J given in Hz). Vacuum distillations were performed on a chemistry hybrid pump (ultimate vacuum 0.002 mbar, max. pumping speed 5.9 m^3/h, VACUUBRAND - RC6). Vacuum was measured with vacuum gauge (measuring range 1000-10^{-3} mbar, uncertainty of measurement ±10%, VACUUBRAND -VAP 5).

Securation.
Pressure vials and vessels with reaction mixtures (vigorously stirred with the magnetic stirrer) were connected to the vacuum/inert chamber through septum (using needles). The vacuum was applied until no more bubbles were formed. The reaction mixture was then saturated with the argon. This vacuum/inert cycle was repeated several times (see experimental details).

Optimization of the reaction of 1,2-dichloroethane with triisopropyl phosphite.
The optimization was performed using the MW syntheses instruments – Type I (10 ml vials). Triisopropyl phosphite (2.0 ml, 8.0 mmol) and corresponding amount of 1,2-dichloroethane (Table 1.) were added to a 10 ml MW vial. Entry 20 was performed using half amount of the starting materials to avoid overloading – 1.0 ml of triisopropyl phosphite (4.0 mmol) and 2.7 ml of 1,2-dichloroethane (40.0 mmol).

Procedure 1.1. Preparation of diisopropyl 2-chloroethylphosphonate (**1**) (Entry 19).

Triisopropyl phosphite (2.0 ml, 8 mmol) and 1,2-dichloroethane (2.2 ml, 32 mmol) were placed into a 10 ml MW vial. The vial was securated (5x). Reaction mixture was irradiated in MW syntheses instrument – Type I at 190°C for 160 min (max. power 300W). The experiment was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (65°C, 2 mbar). GC/MS analysis of the crude reaction mixture confirmed high content of the product (purity >90%), contaminated mostly by the corresponding triisopropyl phosphate. Pure diisopropyl 2-chloroethylphosphonate (**1**) was isolated in 83% yield (15.2 g) by vacuum distillation at 74-75°C/0.056 mbar. ^{1}H NMR and ^{13}C NMR spectra of the product were identical with those in Procedure **1.2**.

Procedure 1.2. Preparation of diisopropyl 2-chloroethylphosphonate (**1**) (Entry 30).

Triisopropyl phosphite (4.0 ml, 16 mmol) and 1,2-dichloroethane (1.3 ml, 19 mmol) were placed into a 10 ml MW vial. The vial was securated (5x). Reaction mixture was irradiated in MW syntheses instrument – Type I at 190°C for 190 min (max. power 300W). The experiment was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (65°C, 2 mbar). GC/MS analysis of the crude reaction mixture confirmed high content of the product (purity >88%), contaminated mostly by tetraisopropyl ethylenebisphosphonate and triisopropyl phosphate. Pure diisopropyl 2-chloroethylphosphonate (**1**) was isolated by vacuum distillation at 72-73°C/0.051 mbar in 74% yield (27.2 g) as colorless oil, b.p. 74-75°C/0.056 mbar or 72-73°C/0.051 mbar. GC/MS-EI (R_T 16.75 min), *m/z* (%): 145 [free acid$^+$] (100). FABMS, *m/z* (%): 229 [M$^+$] (26), 191 (19), 145 [free acid$^+$] (100). ^{1}H NMR (DMSO-d_6): 4.58 d of septets, 2 H, J(1',2') = 6.2, J(1',P) = 7.9 (H-1'); 3.69 dm, 2 H, J(2,P) = 11.0 (H-2); 2.26 dm, 2 H, J(1,P) = 18.3 (H-1); 1.25 d, 12 H, J(2',1') = 6.2 (H-2'). ^{13}C NMR (DMSO-d_6): 70.03 d, J(1',P) = 6.4 (C-1'); 38.66 (C-2); 30.50 d, J(1,P) = 136.3 (C-1); 23.92 d and 23.86 d, J(2',P) = 3.9 and J(2',P) = 4.8 (C-2'). For $C_8H_{18}ClO_3P$ (228.7) calculated: 42.02% C, 7.93% H, 15.51% Cl, 13.55% P; found: 41.95% C, 8.04% H, 15.47% Cl, 13.43% P.

Procedure 2.1 Preparation of diisopropyl 2-(2-chloroethoxy)ethylphosphonate (**2**) (via entry 19).

Triisopropyl phosphite (2.0 ml, 8 mmol) and 2,2'-dichlorodiethyl ether (3.8 ml, 32 mmol) were placed into a 10 ml MW vial. The vial was securated (5x). The reaction mixture was irradiated in MW syntheses instrument – Type I at 190°C for 160 min (max. power 300W), GC/MS analysis showed full conversion (yield >85%). The experiment was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (70°C, 2 mbar). GC/MS analysis of the crude reaction mixture confirmed high content of the product (purity >90%). Pure diisopropyl 2-(2-chloroethoxy)ethylphosphonate (**2**) was isolated by vacuum distillation at 102-104°C/0.5 mbar in 81% yield (17.7 g).

Scaling up procedures:

Procedure 2.2. Preparation of diisopropyl 2-(2-chloroethoxy)ethylphosphonate (**2**) (via entry 30).

Triisopropyl phosphite (32.0 ml, 130 mmol) and 2,2'-dichlorodiethyl ether (18.3 ml, 156 mmol) were placed into a 80 ml MW vial. The vial was securated (5x). The reaction mixture was irradiated in MW syntheses instrument – Type I at 190°C for 190 min (max. power 300W), GC/MS analysis showed full conversion (yield >75%). The reaction mixture was evaporated (70°C, 2 mbar) to give product (purity >85% by GC/MS), contaminated mostly by the corresponding bisphosphonate. Pure diisopropyl 2-(2-chloroethoxy)ethylphosphonate (**2**) was isolated by vacuum distillation at 101-102°C/0.47 mbar in 73% yield (25.9 g).

Procedure 2.3. Preparation of diisopropyl 2-(2-chloroethoxy)ethylphosphonate (**2**) (via entry 30).

Triisopropyl phosphite (320 ml, 1.30 mol) and 2,2'-dichlorodiethyl ether (183 ml, 1.56 mol) were pleaced into a 1 L flask. The flask was securated (5x) and connected to the continuous flow MW reactor – Type IV, which was filled with CH_3CN (apparatus tightness check up, see Results and Discussion). The reaction mixture was irradiated (power max. 500W) and the reaction temperature was elevated from 120 to 210°C during 7 h in 45 min intervals (see Table 2 and Graph 1). Pumping speed was 40ml/min. GC/MS analyses showed full conversion (yield ~70%). The reaction mixture was evaporated (70°C, 2 mbar) to give the crude product (purity >85% by GC/MS). Pure diisopropyl 2-(2-chloroethoxy)ethylphosphonate (**2**) was isolated by vacuum distillation at 85-87°C/0.32 mbar in 70% yield (249 g) as colorless oil, b.p. 102-104°C/0.5 mbar, 101-102°C/0.47 mbar or 85-87°C/0.32 mbar. GC/MS-EI (R_T 16.58 min), *m/z* (%): 189 [free acid$^+$] (76), 125 [free acid$^+$-C_2H_4Cl] (100). FABMS, *m/z* (%): 295 [M+Na$^+$] (49), 273 [M$^+$] (81), 189 [free acid$^+$] (100). ^{1}H NMR (DMSO-d_6): 4.56 d of septets, 2 H, J(1",2") = 6.2, J(1",P) = 8.0 (H-1"); 3.57-3.74 m, 6 H, (H-2; H-1'; H-2'); 2.01 dm, 2H, J(1,P) = 18.7 (H-1); 1.23 d, 6 H and 1.23 d, 6 H, J(2",1") = 6.2 and J(2",1") = 6.2 (H-2"). ^{13}C NMR (DMSO-d_6): 70.34 (C-1'); 69.60 d, J(1",P) = 6.2 (C-1"); 64.80 (C-2); 43.79 (C-2'); 27.42 d, J(1,P) = 138.2 (C-1); 24.03 d and 23.97 d, J(2",P) = 3.7 and J(2",P) = 4.9 (C-2"). For $C_{10}H_{22}ClO_4P$ (272.7) calculated: 44.04% C, 8.13% H, 13.00% Cl, 11.36% P; found: 43.93% C, 8.18% H, 13.11% Cl, 11.38% P.

Procedure 3. Preparation of diisopropyl 2-bromoethylphosphonate (**3**).

Triisopropyl phosphite (4.0 ml, 16.0 mmol) and 1,2-dibromoethane (1.7 ml, 19.2 mmol) were placed into a 10 ml MW vial. The vial was then securated (5x). The reaction mixture was irradiated in MW syntheses instruments – Type I at 130°C, 150°C, and 170°C (max. power 300W). Composition of the reaction mixtures was determined by GC/MS and the results are summarized in Table 3 (Entry 1, 2, 3, 4, 5, 6).
Experiment at 170°C was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (65°C, 2 mbar). GC/MS analysis of the crude reaction mixture confirmed high content of the product (purity>95%), contaminated mostly by corresponding bisphosphonate and triisopropyl phosphate. Pure diisopropyl 2-bromoethylphosphonate was isolated by vacuum distillation at 82-83°C/0.053 mbar in 84% yield (36.6 g). According to GC/MS analysis, the final product (97.4%) contained 2.6% of the corresponding bisphosphonate.
Diisopropyl 2-bromoethylphosphonate (**3**): colorless oil, b.p. 82-83°C/0.053 mbar. GC/MS-EI (R_T 13.93 min), *m/z* (%): 191, 189 [free acid$^+$] (100). FABMS, *m/z* (%): 297, 295 [M+Na$^+$] (9), 275, 273 [M$^+$] (23), 191, 189 [free acid$^+$] (100). ^{1}H NMR (DMSO-d_6): 4.58 d of septets, 2 H, J(1',2') = 6.2, J(1',P) = 7.9 (H-1'); 3.52 dm, 2 H, J(2,P) = 10.1 (H-2); 2.36 dm, 2 H, J(1,P) = 18.5 (H-1); 1.24 d, 12 H, J(2',1') = 6.2 (H-2'). ^{13}C NMR (DMSO-d_6): 70.21 d, J(1',P) = 6.4 (C-1'); 30.90 d, J(1,P) = 133.8 (C-1); 25.81 (C-2); 23.99 d and 23.93 d, J(2',P) = 3.9 and J(2',P) = 4.7 (C-2'). For $C_8H_{18}BrO_3P$ (273.1) calculated: 35.18% C, 6.64% H, 29.26% Br, 11.34% P; found: 35.24% C, 6.57% H, 29.05% Br, 11.47% P.

Procedure 4. Preparation of diisopropyl bromomethylphosphonate (**4**).

Triisopropyl phosphite (4.0 ml, 16.0 mmol) and dibromomethane (1.4 ml, 19.2 mmol) were placed into a 10 ml MW vial. The vial was then securated (5x). The reaction mixture was irradiated in MW syntheses instruments – Type I at 150°C for 30 min (max. power 300W). The experiment was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (65°C, 2 mbar) to afford diisopropyl bromomethylphosphonate (purity >95% by GC/MS), contaminated by corresponding bisphosphonate and triisopropyl phosphate. Pure product was isolated by vacuum distillation at 93-95°C/0.26 mbar in 78% yield (32.2 g): colorless oil, b.p. 93-95°C/0.26 mbar. GC/MS-EI (R_T 12.58 min), *m/z* (%): 177, 175 [free acid$^+$] (100). FABMS, *m/z* (%): 261, 259 [M$^+$] (11), 177, 175 [free acid$^+$] (100). ^{1}H NMR (DMSO-d_6): 4.62 d of septets, 2 H, J(1',2') = 6.2, J(1',P) = 7.1 (H-1'); 3.25 d, 2 H, J(1,P) = 9.7 (H-1); 1.37 d, 6 H and 1.37 d, 6 H, J(2',1') = 6.2, J(2',1') = 6.2 (H-2'). ^{13}C NMR (DMSO-d_6): 72.10 d, J(1',P) = 6.9 (C-1'); 23.96 d and 23.76 d, J(2',P) = 4.1 and J(2',P) = 5.3 (C-2'); 18.74 d, J(1,P) = 159.5 (C-1). For $C_7H_{16}BrO_3P$ (259.1) calculated: 32.45% C, 6.22% H, 30.84% Br, 11.96% P; found: 32.57% C, 6.20% H, 30.75% Br, 11.84% P.

Procedure 5.1. Preparation of diisopropyl iodomethylphosphonate (**5**).

Triisopropyl phosphite (4.0 ml, 16.0 mmol), diiodomethane (1.3 ml, 16.0 mmol), and diisopropyl iodomethylphosphonate (0.1 ml, 0.5 mmol) were placed into a 10 ml MW vial. The vial was then securated (5x). The reaction mixture was irradiated in MW syntheses instruments – Type I at 90°C for 200 min, maximum power 50 W. The experiment was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (65°C, 2 mbar) to afford diisopropyl iodomethylphosphonate (**5**) (purity >90% by GC/MS),

contaminated mostly by corresponding bisphosphonate and triisopropyl phosphate. Pure product was isolated by vacuum distillation at 76-77°C/0.05 mbar with 86% yield (43.3 g).

Scaling up procedure:

Procedure 5.2.
Triisopropyl phosphite (113 ml, 470 mmol), diiodomethane (38 ml, 470 mmol), and diisopropyl iodomethylphosphonate (1 ml, 5 mmol) were placed into a 250 ml MW vessel. The vessel was securated (5x). Reaction mixture was irradiated in MW syntheses instrument – Type III at 120°C for 120 min and maximum power 100 W. The reaction mixture was evaporated (69°C, 2 mbar) to give relatively pure product (purity >90% GC/MS), contaminated mostly by the corresponding bisphosphonate and triisopropyl phosphate. Pure diisopropyl iodomethylphosphonate (**5**) was isolated by vacuum distillation at 75-76°C/0.05 mbar in 80% yield (116 g) as colorless oil, b.p. 76-77°C (75-76°C)/0.05 mbar. GC/MS-EI (R_T 13.95 min), *m/z* (%): 223 [free acid$^+$] (100). FABMS, *m/z* (%): 329 [M+Na$^+$] (17), 307 [M$^+$] (34), 223 [free acid$^+$] (100). ^{1}H NMR (DMSO-d_6): 4.76 d of septets, 2 H, J(1',2') = 6.2, J(1',P) = 7.6 (H-1'); 3.01 d, 2 H, J(1,P) = 10.3 (H-1); 1.36 m, 12 H, (H-2'). ^{13}C NMR (DMSO-d_6): 71.99 d, J(1',P) = 6.5 (C-1'); 23.97 d and 23.80 d, J(2',P) = 3.7 and J(2',P) = 5.3 (C-2'); 12.70 d, J(1,P) = 156.8 (C-1). For $C_7H_{16}IO_3P$ (306.1) calculated: 27.47% C, 5.27% H, 41.46% I, 10.12% P; found: 27.58% C, 5.34% H, 41.40% I, 10.19% P.

Procedure 6. Preparation of diethyl 2-chloroethylphosphonate (**6**).
Triethyl phosphite (2.8 ml, 16 mmol) and 1,2-dichloroethane (4.5 ml, 64 mmol) were placed into a 10 ml MW vial. The vial was securated (5x). The reaction mixture was irradiated in MW syntheses instrument – Type I at 190°C for 120 min (max. power 300W). The experiment was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (65°C, 2 mbar) to afford a mixture of diethyl 2-chloroethylphosphonate and diethyl methyphosphonate. Diethyl 2-chloroethylphosphonate (**6**) was isolated by vacuum distillation at 74-75°C/0.082 mbar in 62% yield (19.8 g) as colorless oil, b.p. 74-75°C/0.082 mbar. GC/MS-EI (R_T 12.10 min), *m/z* (%): 145 [free acid$^+$] (90), 138 [M$^+$-C_2H_4Cl] (100). FABMS, *m/z* (%): 201 [M$^+$] (100), 145 [free acid$^+$] (38). ^{1}H NMR (DMSO-d_6): 4.13 m, 4 H, (H-1'); 3.72 dm, 2 H, J(2,P) = 9.4 (H-2); 2.30 dm, 2 H, J(1,P) = 18.5 (H-1); 1.34 t, 6 H, J(2',1') = 7.0 (H-2'). ^{13}C NMR (DMSO-d_6): 61.97 d, J(1',P) = 6.5 (C-1'); 37.59 (C-2); 30.29 d, J(1,P) = 136.9 (C-1); 16.37 d, (2',P) = 5.9 (C-2'). For $C_6H_{14}ClO_3P$ (200.6) calculated: 35.92% C, 7.03% H, 17.67% Cl, 15.44% P; found: 36.18% C, 7.14% H, 17.49% Cl, 15.53% P.

Procedure 7. Formation of *bis*(2-chloroethyl) 2-chloroethylphosphonate (**7**) by MW heating of reaction mixture containing *tris*(2-chloroethyl) phosphite and dibromomethane.
Tris(2-chloroethyl) phosphite (4.3 g, 16 mmol) and dibromomethane (1.4 ml, 19.2 mmol) were placed into a 10 ml MW vial. The vial was securated (5x). The reaction mixture was irradiated in MW syntheses instrument – Type I at 170°C for 60 min, max. power 300W. The experiment was repeated 10 times. All 10 reaction mixtures were combined and evaporated to dryness (65°C, 2 mbar). Vacuum distillation at 83-84°C/0.054 mbar afforded *bis*(2-chloroethyl) 2-chloroethylphosphonate (**7**) as the only product in 83% yield (35.5 g): colorless oil, b.p. 83-84°C/0.054 mbar. GC/MS-EI (R_T 17.86 min), *m/z* (%): 235, 233 [M$^+$-HCl] (100). FABMS, *m/z* (%): 293, 291 [M+Na$^+$] (13), 271, 269 [M$^+$] (54), 154 (100), 145 [free acid$^+$] (31). ^{1}H NMR (DMSO-d_6): 4.33 m, 4 H, (H-1'); 3.77 dm, 2 H, J(2,P) = 11.3 (H-2); 3.73 t, 4 H, J(2',1') = 5.5 (H-2'); 2.42 dm, 2 H, J(1,P) = 18.7 (H-1). ^{13}C NMR (DMSO-d_6): 65.54 d, J(1',P) = 6.3 (C-1'); 42.85 d, J(2',P) = 6.5 (C-2'); 37.10 (C-2); 30.08 d, J(1,P) = 138.3 (C-1).

For $C_6H_{12}Cl_3O_3P$ (269.5) calculated: 26.74% C, 4.49% H, 39.47% Cl, 11.49% P; found: 26.53% C, 4.51% H, 39.26% Cl, 11.65% P.

Procedure 8. Preparation of diisopropyl 2-iodoethylphosphonate (**8**) by Finkelstein reaction. Mixture of dry sodium iodide (15 g, 100 mmol) and diisopropyl 2-chloroethylphosphonate (2.3 g, 10 mmol) in dry acetone (30ml) was refluxed for 16 h. The resulting pale yellow reaction mixture was cooled to room temperature and acetone was removed on rotary evaporator. The residue was taken up in diethyl ether (30 ml) and washed with saturated aqueous solution of sodium thiosulfate (3x10 ml). Organics were dried over anhydrous magnesium sulfate, filtered, and ether was removed on rotary evaporator. Vacuum distillation at 89-91°C/0.05 mbar afforded diisopropyl 2-iodoethylphosphonate (**8**) in 88% yield (2.8 g) as colorless oil, b.p. 89-91°C/0.05 mbar. FABMS, *m/z* (%): 321 [M^+] (9), 181 (100). ^{1}H NMR (DMSO-d_6): 4.57 d of septets, 2 H, J(1',2') = 6.2, J(1',P) = 7.9 (H-1'); 3.21 m, 2 H, (H-2); 2.37 dm, 2 H, J(1,P) = 18.4 (H-1); 1.24 d, 12 H, J(2',1') = 6.2 (H-2'). ^{13}C NMR (DMSO-d_6): 70.04 d, J(1',P) = 6.4 (C-1'); 31.92 d, J(1,P) = 132.3 (C-1); 23.89 m (C-2'); 5.06 d, J(2,P) = 3.7 (C-2); For $C_8H_{18}IO_3P$ (320.1) calculated: 30.02% C, 5.67% H, 39.64% I, 9.68% P; found: 30.23% C, 5.83% H, 39.25% I, 9.87% P.

GC/MS analysis of diisopropyl 2-chloroethylphosphonate (**1**)

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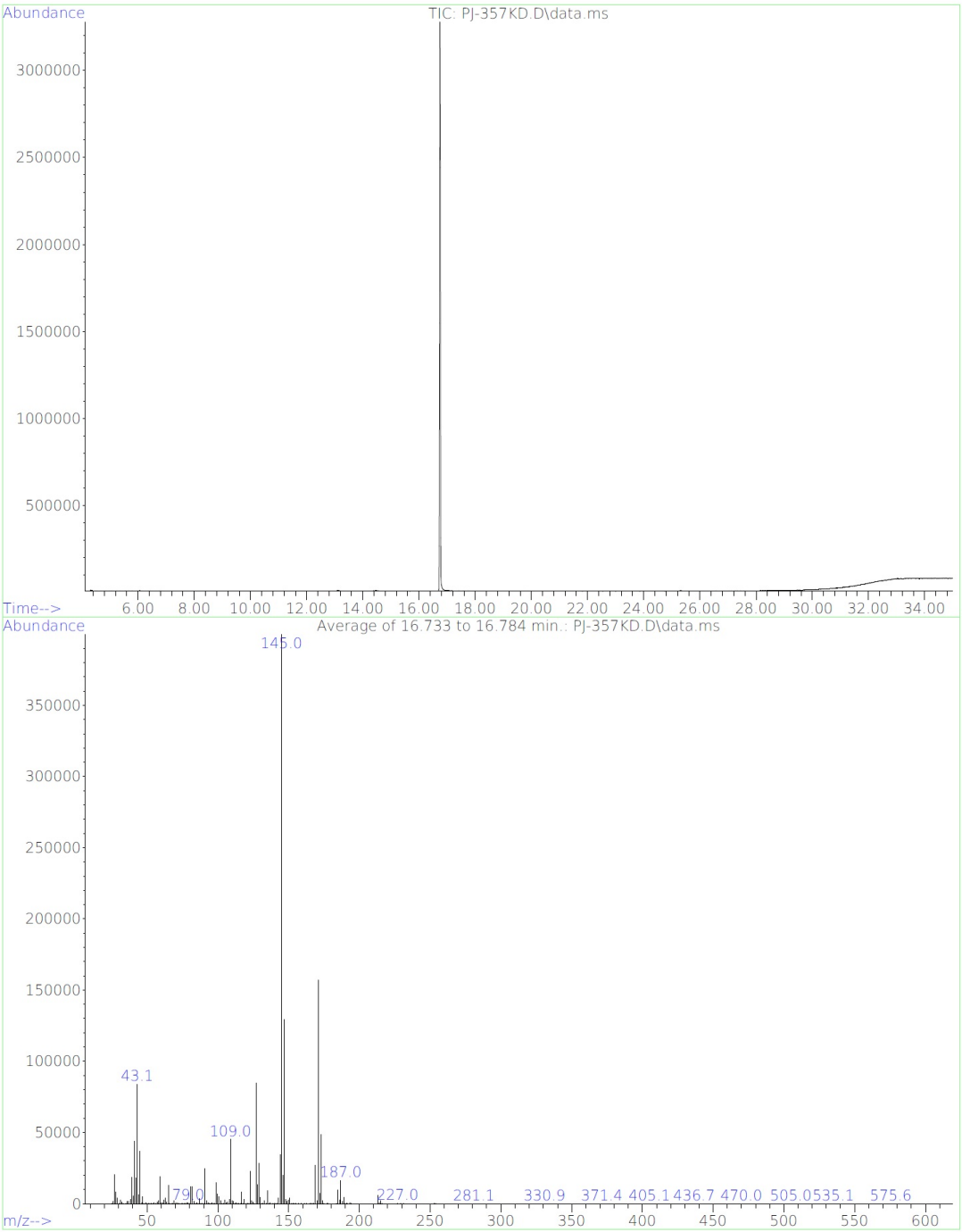

GC/MS analysis of diisopropyl 2-(2-chloroethoxy)ethylphosphonate (**2**)

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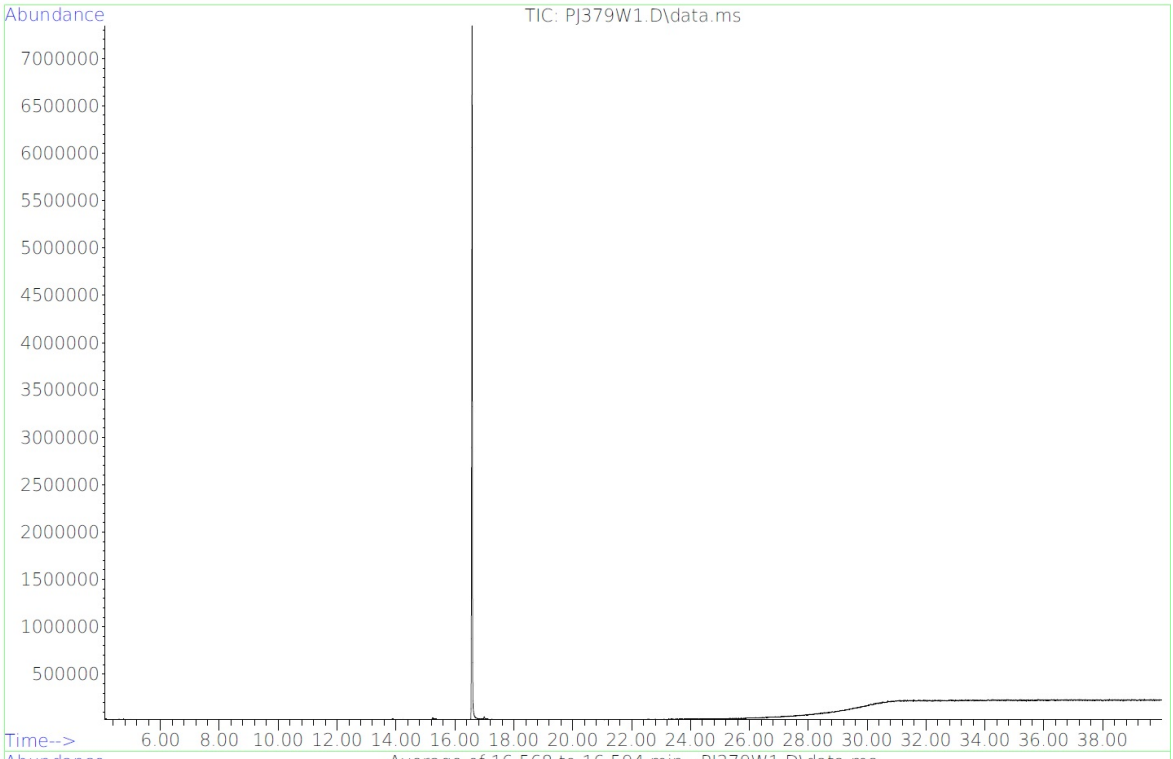

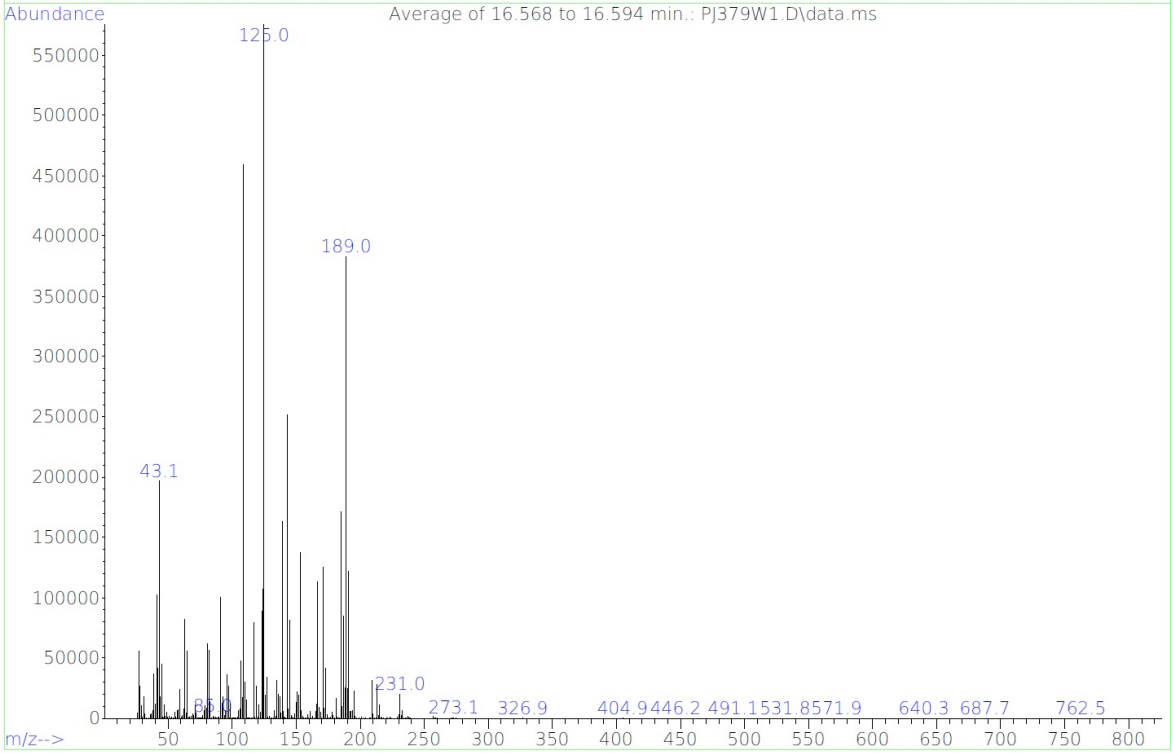

GC/MS analysis of diisopropyl 2-bromoethylphosphonate (**3**)

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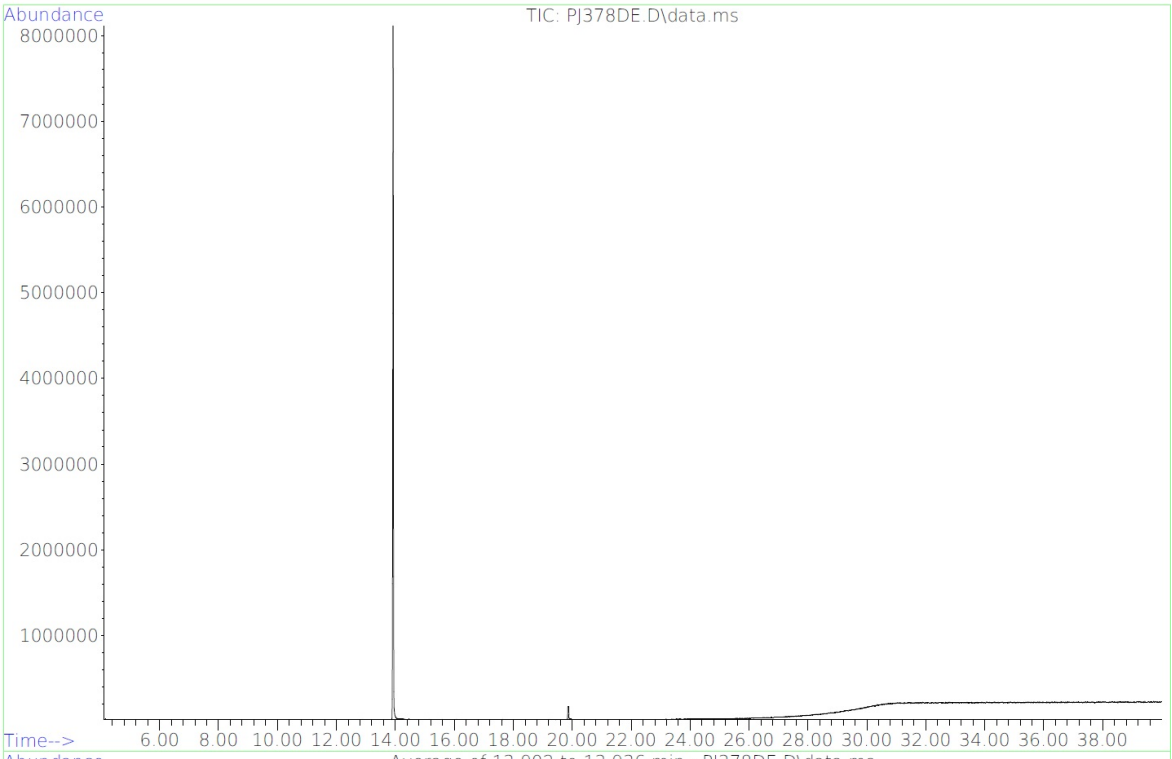

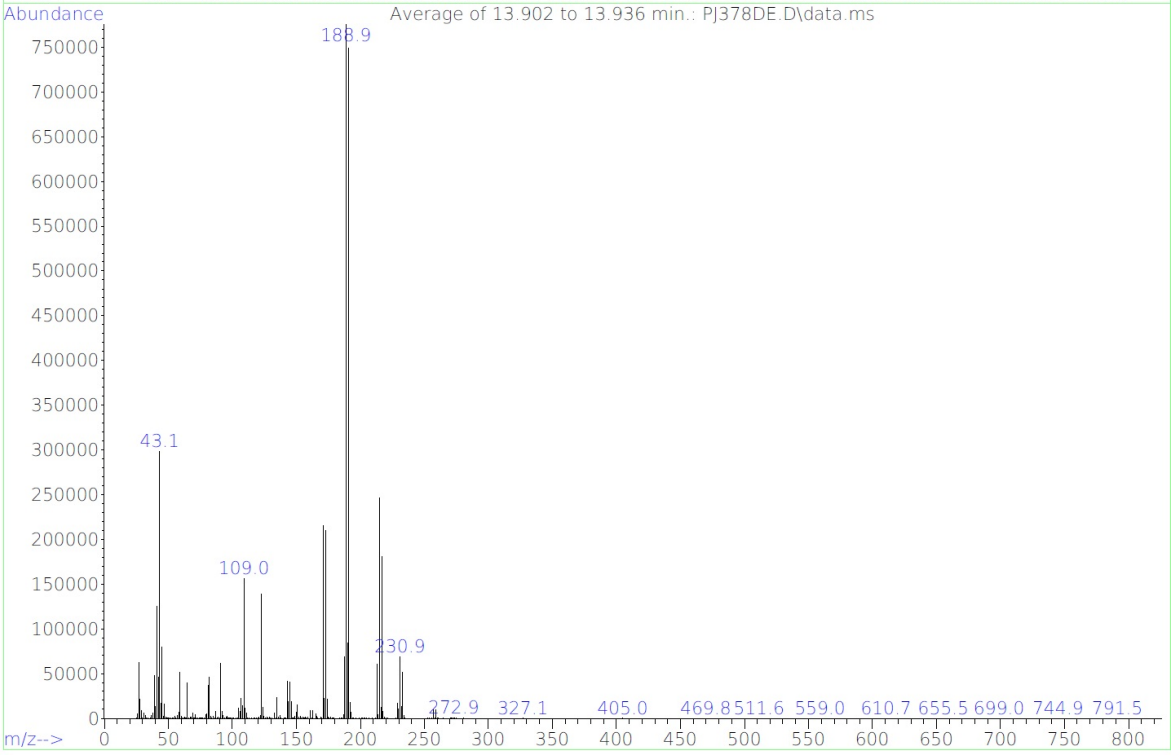

GC/MS analysis of diisopropyl bromomethylphosphonate (**4**)

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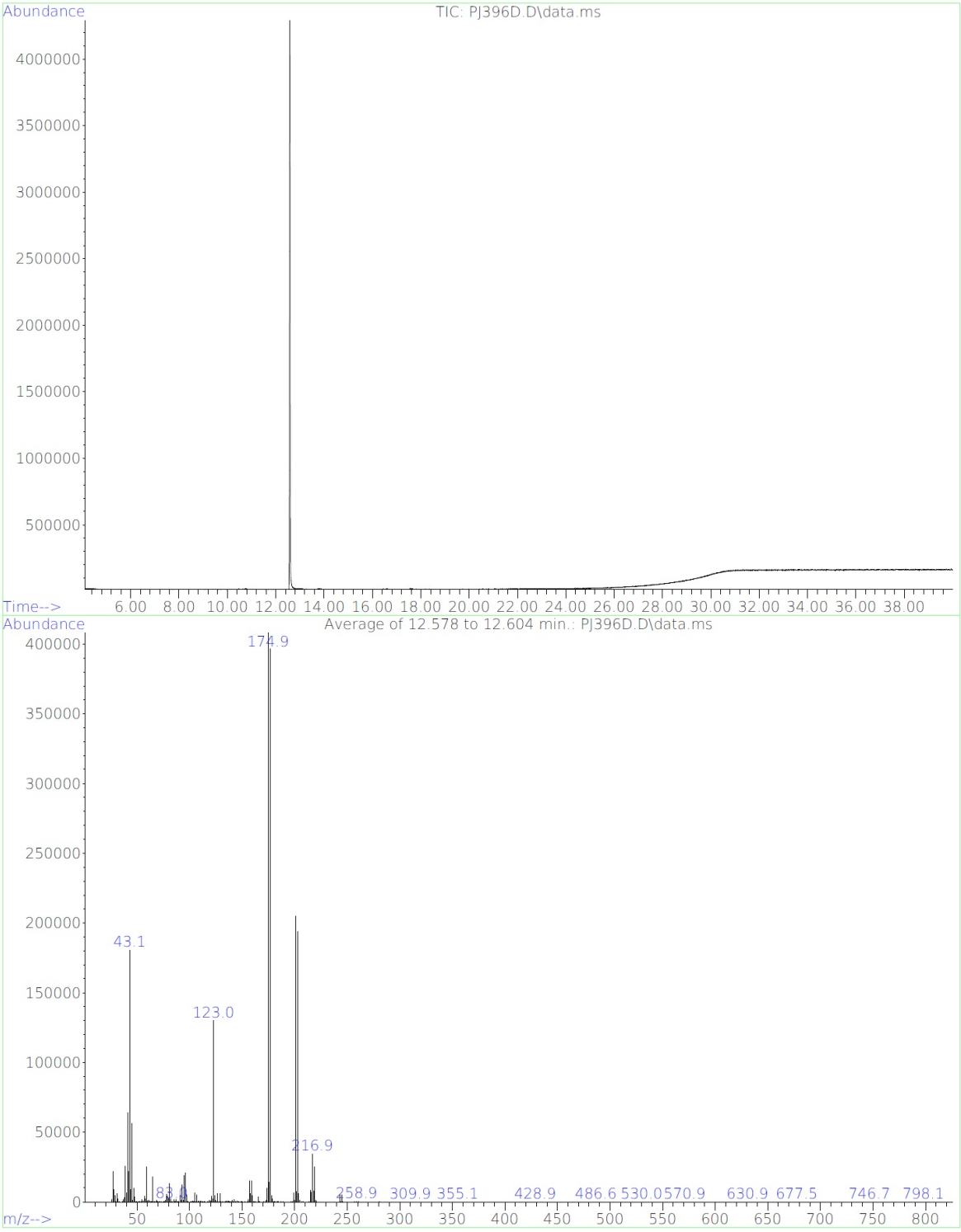

GC/MS analysis of diisopropyl iodomethylphosphonate (**5**)

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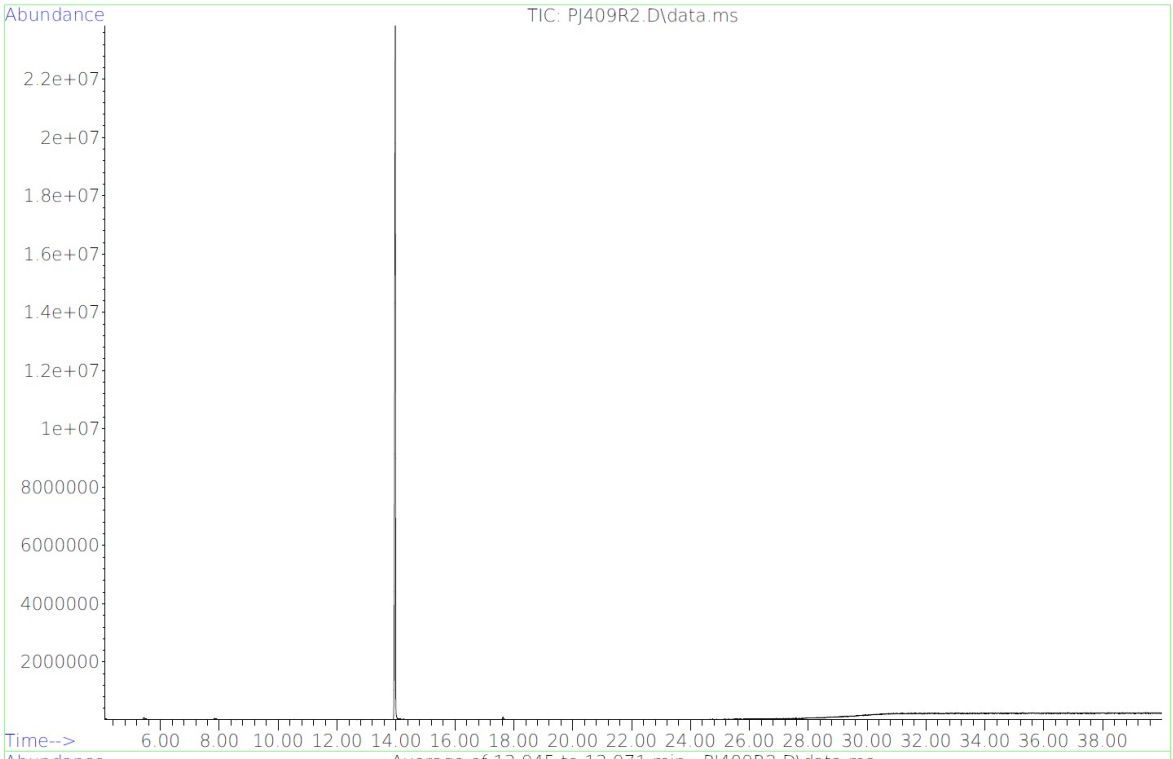

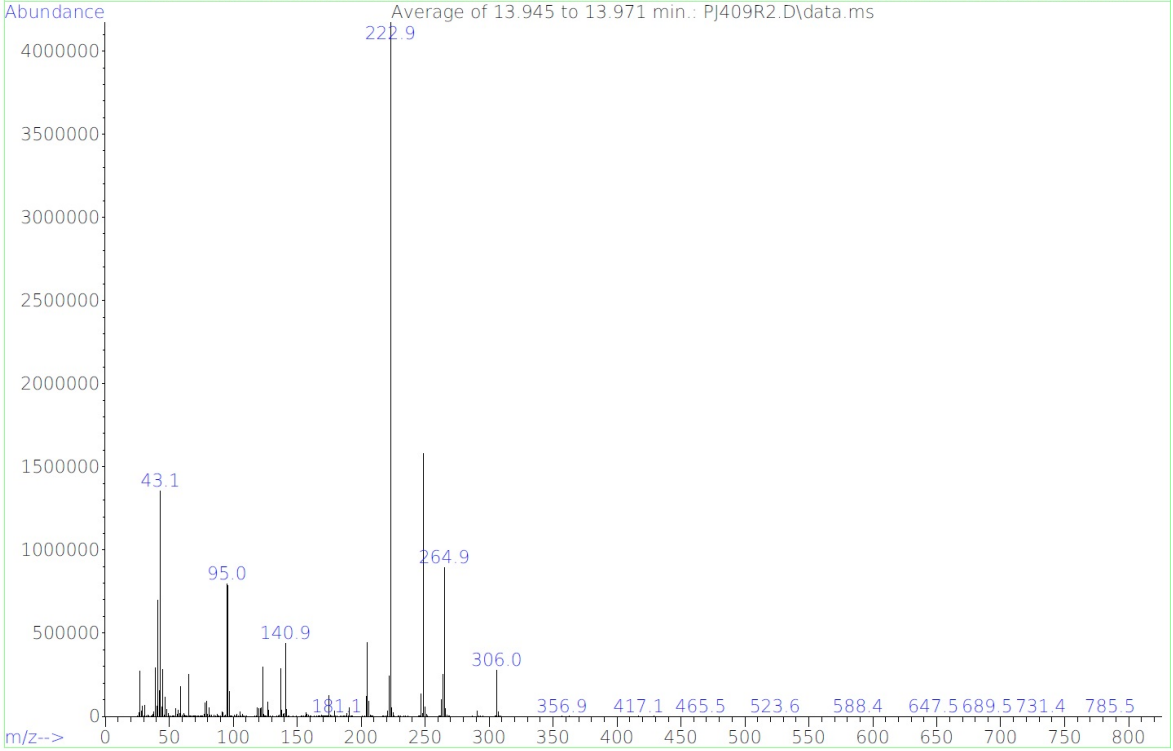

GC/MS analysis of diethyl 2-chloroethylphosphonate (**6**)

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File       :H:\jansa\PJ407D.D
Operator   : Jansa
Acquired   : 21 Feb 2008  21:21     using AcqMethod AS_M-VYSOKE_C-VYSOKE.M
Instrument :    6890N + 5975B
Sample Name: PJ407D
Misc Info  :
Vial Number: 3
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