Supporting Information for:

Selective Phosphoramidation and Phosphonation of Benzoxazoles via Sequence Control

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CONTENTS

1. General experiment detail and metrials

Experimental: All non-aqueous reactions and manipulations were performed in air atmosphere using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen. All reactions were monitored by TLC with silica gel-coated plates.

NMR spectra were recorded on Agilent Technologies 400 and AVANCE Ⅲ 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Daltonics APEX II 47e Specification (ESI). Infrared Radiations were recorded on Nicolet 5700 FT-IR.

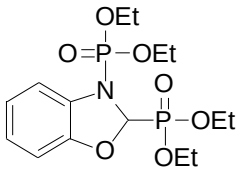
2. General Procedure

To a 100 mL round-bottom flask with a stir bar added iodine (3.68 g, 15 mmol) and CH_3CN (10 mL), the mixture was red. Then $P(OEt)_3$ (5 g, 30 mmol) and benzoxazole

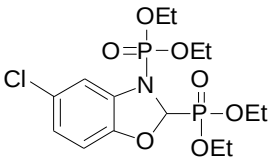
(1.19 g, 10 mmol) were added. The mixture was stirred at room temperature for 10 minutes, and monitored by TLC. The solution was then evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ester/ethyl acetate = 20:1-5:1) to get product **3a** with 3.66g

Iodine (197 mg, 0.775 mmol) and CH_3CN (2 mL) were added to a 50 mL Schlenk tube with a stir bar. Followed by $P(OEt)_3$ (125 mg, 0.75 mmol). The mixture was stirred at room temperature for 5 minutes. Then, $P(OMe)_3$ (93 mg, 0.75 mmol), benzoxazole (59.5 mg, 0.5 mmol), were added to the mixture in sequence. The mixture was stirred at room temperature for 10 minutes. The solution was then evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ester/ethyl acetate = 20:1-5:1) to get product **4a**.

1. **[2-(Diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (3a)** The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 180.7 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.2 Hz, 1H), 6.86 (m, 3H), 6.27 (dd, *J* = 19.2, 8.0 Hz, 1H), 4.30 – 3.95 (m, 8H), 1.40 – 1.14 (m, 12H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 151.30 (d, *J* = 8.7 Hz), 131.87 (s), 123.61 (s), 121.87 (s), 113.57 (s), 109.04 (s), 91.08 (d, *J* = 5.2 Hz), 89.12 (d, *J* = 5.2 Hz), 63.93 – 63.27 (m), 16.04 (ddd, *J* = 22.9, 19.7, 6.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.24 (s), -1.67 (s); IR(neat) v 3445, 2985, 2932, 1722, 1648, 1482, 1394, 1363, 1263, 1162, 1019, 796, 747, 656 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{26}NP_2O_7$ $[M+H]^+$: 394.1179, found: 394.1176.

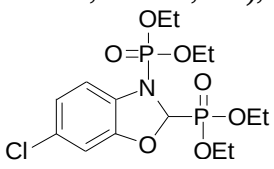


2. **[5-Chloro-2-(diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (3b)** The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 202.8 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.29 (dd, *J* = 19.2, 7.2 Hz, 1H), 4.33 – 4.01 (m, 8H), 1.44 – 1.21 (m, 12H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 133.42 (s), 130.45 (s), 126.73 (s), 123.12 (s), 113.93 (s), 109.44 (s), 91.92 (d, *J* = 5.2 Hz), 89.97 (d, *J* = 5.6 Hz), 64.13 – 63.70 (m), 63.55 (d, *J* = 6.7 Hz), 16.35 (d, *J* = 5.6 Hz), 15.98 (dd, *J* = 20.0, 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.70 (d, *J* = 18.9 Hz), -2.51 (d, *J* = 18.9 Hz); IR(neat) v 3442, 2984, 2363, 1781, 1629, 1480, 1396, 1250, 1162, 1023, 977, 864, 801, 702, 627 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}NP_2O_7Cl$ $[M+H]^+$: 428.0789, found: 428.0786.



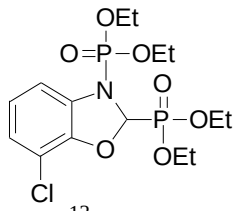
3. [6-Chloro-2-(diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (3c) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 196.4 mg, 92% yield. ^{1}H

NMR (400 MHz, cdcl$_3$) δ 6.90 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 4.3 Hz, 2H), 6.26 (dd, *J* = 18.1, 7.4 Hz, 1H), 4.27 – 3.95 (m, 8H), 1.39 – 1.17 (m, 12H); ^{13}C NMR (101 MHz,

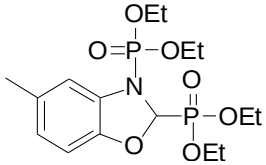


cdcl$_3$) δ 152.15 (d, *J* = 8.2 Hz), 131.12 (d, *J* = 1.8 Hz), 128.51 (s), 121.70 (s), 113.86 (s), 109.98 (s), 91.95 (d, *J* = 4.8 Hz), 89.99 (d, *J* = 4.7 Hz), 64.10 – 63.43 (m), 16.34 (d, *J* = 5.5 Hz), 15.97 (dd, *J* = 18.2, 6.8 Hz); ^{31}P NMR (162 MHz, CDCl$_3$) δ 10.21 (d, *J* = 7.3 Hz), -2.51 (d, *J* = 5.9 Hz); IR(neat) v 3481, 2984, 2933, 1602, 1481, 1394, 1344, 1271, 1163, 1020, 976, 876, 803, 711, 551 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}NP_2O_7Cl$ $[M+H]^+$: 428.0789, found: 428.0785.

4. [7-Chloro-2-(diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (3d) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 198.6 mg, 93% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.91 (t, *J* = 7.2 Hz, 2H), 6.81 (t, *J* = 8.0 Hz, 1H), 6.34 (dd, *J* = 18.4, 7.6 Hz, 1H), 4.32 – 3.98 (m, 8H), 1.46 – 1.19 (m, 12H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 147.80 (d, *J* = 8.7 Hz), 133.59, 124.19, 122.82, 114.66, 111.91, 91.68 (d, *J* = 5.1 Hz), 90.38 (d, *J* = 5.1 Hz), 64.20 (d, *J* = 6.6 Hz), 64.09 – 63.72 (m), 16.35 (d, *J* = 5.4 Hz), 16.10 (d, *J* = 6.8Hz), 15.93 (d, *J* = 6.8, Hz); ^{31}P NMR (243 MHz, CDCl$_3$) δ 9.94 (d, *J* = 19.8 Hz), -2.43 (d, *J* = 19.9 Hz); IR(neat) v 3426, 2985, 1807, 1616, 1460, 1395, 1362, 1270, 1163, 1019, 869, 768, 722, 652, 558 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}NP_2O_7Cl$ $[M+H]^+$: 428.0789, found: 428.0784.



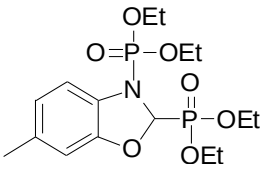
5. [2-(Diethoxy-phosphoryl)-5-fluoro-benzooxazol-3-yl]-phosphonic acid diethyl ester (3e) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 172.6 mg, 84% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.80 – 6.70 (m, 2H), 6.58 (td, *J* = 9.2, 2.4 Hz, 1H), 6.28 (dd, *J* = 19.2, 7.6 Hz, 1H), 4.32 – 4.00 (m, 8H), 1.44 – 1.20 (m, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 159.25 (s), 156.86 (s), 147.45 (s), 133.21 (s), 108.91 (s), 108.62 (d, *J* = 9.7 Hz), 102.94 – 102.47 (m), 102.27 (d, *J* = 29.2 Hz), 91.98 (d, *J* = 5.1 Hz), 90.03 (d, *J* = 4.7 Hz), 64.32 – 63.70 (m), 63.51 (d, *J* = 6.8 Hz), 16.54 – 15.73 (m); ^{31}P NMR (162 MHz, CDCl$_3$) δ 10.38 (s), -3.05 (s); IR(neat) v 3444, 2983, 1630, 1486, 1443, 1398, 1251, 1171, 1098, 1019, 976, 800, 704, 647, 551 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}NP_2O_7F$ $[M+H]^+$: 412.1085, found: 412.1082.



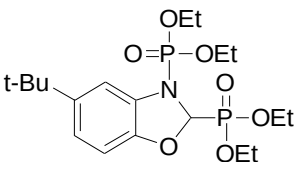
6. [2-(Diethoxy-phosphoryl)-5-methyl-benzooxazol-3-yl]-phosphonic acid diethyl ester (3f) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 189.3 mg, 93% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.85 (s, 1H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.26 (dd, *J* = 19.2, 8.4 Hz, 1H), 4.32 – 3.97 (m, 8H), 2.27 (s, 3H), 1.29 (ddd,

J = 10.5, 9.8, 5.1 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.74, 123.87, 114.63, 108.67, 91.38 (d, *J* = 4.9 Hz), 89.42 (d, *J* = 5.7 Hz), 63.89 (d, *J* = 6.0 Hz), 63.71 – 63.46 (m), 21.25, 16.31 (m); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.39, 11.30, -1.52, -1.61; IR(neat) v 3443, 2925, 1631, 1492, 1398, 1259, 1162, 1021, 976, 800, 703, 652, 552 cm^{-1}; HRMS (m/z): calcd for $C_{16}H_{28}NP_2O_7$ $[M+H]^+$: 408.1336, found: 408.1332.

7. [2-(Diethoxy-phosphoryl)-6-methyl-benzooxazol-3-yl]-phosphonic acid diethyl ester (3g) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 193.3 mg, 95% yield. ^{1}H NMR (400 MHz, cdcl$_3$) δ 6.81 (d, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 10.0 Hz, 2H), 6.19 (dd, *J* = 18.8, 8.4 Hz, 1H), 4.07 (ddd, *J* = 40.3, 23.7, 7.5 Hz, 8H), 2.19 (s, 3H), 1.34 – 1.09 (m, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 151.40 (d, *J* = 8.8 Hz), 133.72 (s), 129.32 (s), 121.98 (s), 113.17 (s), 109.89 (s), 91.13 (d, *J* = 5.0 Hz), 89.17 (d, *J* = 4.9 Hz), 64.01 – 63.19 (m), 21.16 (s), 16.45 – 15.67 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.81 (s), -1.84 (d, *J* = 6.1 Hz); IR(neat) v 3453, 2983, 2929, 1631, 1496, 1440, 1395, 1267, 1163, 1022, 975, 804, 594, 552 cm^{-1}; HRMS (m/z): calcd for $C_{16}H_{28}NP_2O_7$ $[M+H]^+$: 408.1336, found: 408.1331.



8. [2-(Diethoxy-phosphoryl)-7-methyl-benzooxazol-3-yl]-phosphonic acid diethyl ester (3h) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 191.3 mg, 94% yield. ^{1}H NMR (400 MHz, cdcl$_3$) δ 6.81 (d, *J* = 6.8 Hz, 1H), 6.72 (dd, *J* = 18.2, 7.5 Hz, 2H), 6.27 (dd, *J* = 19.5, 7.9 Hz, 1H), 4.30 – 3.89 (m, 8H), 2.19 (s, 3H), 1.40 – 1.13 (m, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 149.51 (d, *J* = 8.4 Hz), 131.20 (s), 125.34 (s), 121.63 (s), 119.30 (s), 111.05 (s), 90.97 (d, *J* = 5.4 Hz), 89.02 (d, *J* = 5.5 Hz), 63.57 (dt, *J* = 10.6, 5.6 Hz), 16.49 – 15.71 (m), 14.67 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.59 (s), -2.27 (s); IR(neat) v 3448, 2983, 1632, 1465, 1396, 1272, 1166, 1101, 1020, 975, 770, 655, 554 cm^{-1}; HRMS (m/z): calcd for $C_{16}H_{28}NP_2O_7$ $[M+H]^+$ 408.1336, found: 408.1333.



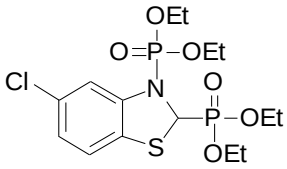
9. [5-tert-Butyl-2-(diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (3i) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 179.5 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.28 (dd, *J* = 19.2, 8.0 Hz, 1H), 4.33 – 3.94 (m, 8H), 1.39 (t, *J* = 7.2 Hz, 4H), 1.28 (s, 9H), 1.24 – 1.15 (m, 8H); ^{13}C NMR (151 MHz, $CDCl_3$) δ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.17 (d, *J* = 8.4 Hz), 145.41, 131.77, 119.98, 111.32, 108.11, 91.01 (d, *J* = 5.3 Hz), 89.72 (d, *J* = 5.3 Hz), 63.77 (dd, *J* = 9.4, 5.9 Hz), 63.63 – 63.35 (m), 34.58, 31.57, 16.39 – 16.01 (m), 15.89 (d, *J* = 7.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.30 (d, *J* = 21.9 Hz), -1.69 (d, *J* = 21.9 Hz); IR(neat) v 3476, 2967, 1779, 1615, 1492, 1434, 1393, 1366, 1339, 1262,

1165, 1125, 1019, 975, 884, 804, 639, 553 cm^{-1}; HRMS (m/z): calcd for $C_{19}H_{33}NP_2NaO_7$ $[M+Na]^+$: 472.1624, found: 472.1619.

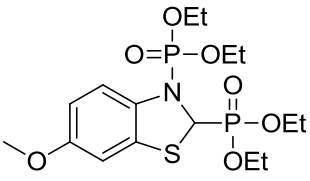
10. [2-(Diethoxy-phosphoryl)-5-nitro-benzooxazol-3-yl]-phosphonic acid diethyl ester (3j) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 127 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 1H), 7.79 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.40 (dd, *J* = 19.2, 6.8 Hz, 1H), 4.35 – 4.03 (m, 8H), 1.47 – 1.19 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.81 (d, *J* = 8.4 Hz), 143.23, 133.87 (d, *J* = 2.1 Hz), 121.34, 108.75, 108.32, 92.92 (d, *J* = 5.8 Hz), 91.62 (d, *J* = 5.8 Hz), 64.62 – 64.09 (m), 63.88 (d, *J* = 7.2 Hz), 16.48 (d, *J* = 5.4 Hz), 16.19 (d, *J* = 6.7 Hz), 16.01 (d, *J* = 6.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 9.84 (d, *J* = 16.1 Hz), -3.30 (d, *J* = 16.1 Hz); IR(neat) v 3432, 2979, 2621, 1631, 1524, 1482, 1399, 1341, 1274, 1163, 1018, 830, 747, 702, 621, 559 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}N_2P_2O_9$ $[M+H]^+$:439.1030, found: 439.1027.

11. [2-(Diethoxy-phosphoryl)-5-sulfamoyl-benzooxazol-3-yl]-phosphonic acid diethyl ester (3k) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 147.3 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 2H), 7.58 – 7.45 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.33 (dd, *J* = 18.4, 7.2 Hz, 1H), 4.31 – 4.04 (m, 8H), 1.41 – 1.19 (m, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 156.00 (d, *J* = 1.4 Hz), 124.55, 123.57, 111.90, 109.01, 92.60 (d, *J* = 5.0 Hz), 90.63 (d, *J* = 5.1 Hz), 64.70 – 64.06 (m), 63.88 (d, *J* = 7.2 Hz), 16.37 (d, *J* = 5.5 Hz), 16.08 (d, *J* = 5.5 Hz), 15.92 (d, *J* = 15.5 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 9.65 (d, *J* = 17.7 Hz), -3.22 (d, *J* = 17.7 Hz); IR(neat) v 3429, 2926, 2621, 1631, 1400, 1265, 1154, 1014, 831, 703, 581 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{26}N_2P_2NaO_9S$ $[M+Na]^+$: 495.0726, found: 495.0723 .

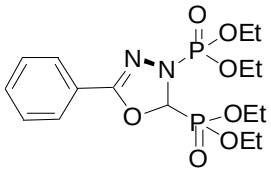
12. [2-(Diethoxy-phosphoryl)-benzothiazol-3-yl]-phosphonic acid diethyl ester (3l) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 194.2 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 7.6 Hz, 1H), 6.98 (m, 3H), 5.87 (d, *J* = 9.6 Hz, 1H), 4.34 – 3.76 (m, 8H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.16 – 0.96 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.55 (d, *J* = 5.0 Hz), 129.44 (d, *J* = 7.8 Hz), 124.77, 123.19, 121.29, 114.78, 63.03 (d, *J* = 7.2 Hz), 62.71 (t, *J* = 5.5 Hz), 62.07 (d, *J* = 4.7 Hz), 61.09 (d, *J* = 3.8 Hz), 59.92 (d, *J* = 3.8 Hz), 15.44 – 15.11 (m), 14.75 (d, *J* = 7.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 15.54 (d, *J* = 17.9 Hz), 0.93 (d, *J* = 18.0 Hz); IR(neat) v 3479, 2983, 1720, 1634, 1580, 1465, 1394, 1262, 1219, 1162, 1099, 1020, 977, 796, 752, 595, 535, 483 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{26}NP_2O_6S$ $[M+H]^+$: 410.0951, found: 410.0948.

13. [5-Chloro-2-(diethoxy-phosphoryl)-benzothiazol-3-yl]-phosphonic acid diethyl ester (3m) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 205.9 mg, 93% yield. 

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 10.8 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.90 (d, *J* = 9.2 Hz, 1H), 4.37 – 3.87 (m, 8H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 6.8 Hz, 3H), 1.17 (dt, *J* = 14.4, 7.2Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.96 (d, *J* = 3.2 Hz), 131.34, 129.15 (d, *J* = 8.0 Hz), 124.00, 122.67, 116.08, 64.15 – 63.78 (m), 63.40 (d, *J* = 4.9 Hz), 62.72 (d, *J* = 3.8 Hz), 61.55 (d, *J* = 3.8 Hz), 16.47 – 16.10 (m), 15.80 (d, *J* = 7.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 15.22 (d, *J* = 16.1 Hz), 0.14 (d, *J* = 16.1 Hz); IR(neat) v 3456, 2983, 1631, 1575, 1463, 1399, 1264, 1162, 1096, 1015, 979, 849, 804, 700, 594, 527, 463 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}NP_2O_6ClS[M+H]^+$: 444.0561, found: 444.0558.

14. [2-(Diethoxy-phosphoryl)-6-methoxy-benzothiazol-3-yl]-phosphonic acid diethyl ester (3n) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 210.7 mg, 96% yield. 

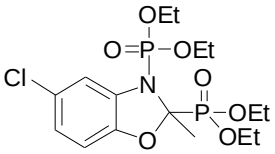
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.8 Hz, 1H), 6.76 (s, 1H), 6.55 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.87 (d, *J* = 10.4 Hz, 1H), 4.33 – 3.84 (m, 8H), 3.75 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 156.71 (s), 133.94 (d, *J* = 3.7 Hz), 131.98 (d, *J* = 7.3 Hz), 116.17 (s), 110.46 (s), 108.59 (s), 64.08 – 63.32 (m), 63.05 – 62.71 (m), 61.06 (d, *J* = 3.3 Hz), 55.61 (s), 16.46 – 15.97 (m), 15.70 (d, *J* = 7.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 15.71 (d, *J* = 21.8 Hz), 1.62 (d, *J* = 21.8 Hz); IR(neat) v 3442, 2980, 1632, 1479, 1398, 1262, 1210, 1160 1020, 976, 796, 703, 498 cm^{-1}; HRMS (m/z): calcd for $C_{16}H_{28}NP_2O_7S$ $[M+H]^+$: 440.1056, found: 440.1054.

15. [2-(Diethoxy-phosphoryl)-5-phenyl-[1,3,4]oxadiazol-3-yl]-phosphonic acid diethyl ester (3o) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 92.4 mg, 44% yield. 

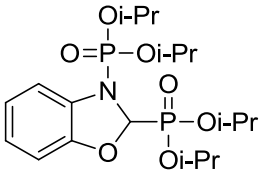
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.0 Hz, 2H), 7.39 (m, 3H), 6.23 (m, 1H), 4.36 – 3.95 (m, 8H), 1.28 (ddd, *J* = 22.4, 12.0, 5.2 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ131.72, 128.72, 127.34, 124.15, 89.04 (d, *J* = 4.6 Hz), 87.05 (d, *J* = 3.9 Hz), 64.84 – 63.81 (m), 16.63 (dd, *J* = 5.0, 3.2 Hz), 16.25 (t, *J* = 6.8 Hz); ^{31}P NMR (162 MHz, D_2O) δ 0.19, -13.41; IR(neat) v 3436, 2929, 2621, 1631, 1401, 1008, 831, 702, 666, 480 cm^{-1}; HRMS (m/z): calcd for $C_{16}H_{27}N_2P_2O_7$ $[M+H]^+$: 421.1288, found: 421.1284.

16. [5-Chloro-2-(diethoxy-phosphoryl)-2-methyl-benzooxazol-3-yl]-phosphonic acid diethyl ester (3p) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 141.1 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.64

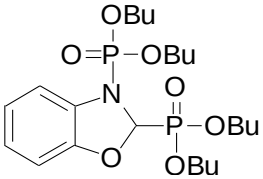
(d, *J* = 8.0 Hz, 1H), 4.36 – 4.00 (m, 8H), 2.13 (d, *J* = 12.0 Hz, 3H), 1.30 (ddt, *J* = 45.2, 21.6, 7.2 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.88 (d, *J* = 10.9 Hz), 134.73 (d, *J* = 4.5 Hz), 126.46, 122.05, 112.71, 108.76, 101.74 (d, *J* = 9.4 Hz), 100.46 (d, *J* = 9.3 Hz), 63.97 (dd, *J* = 23.2, 6.0 Hz), 63.68 (d, *J* = 7.4 Hz), 63.48 (d, *J* = 5.4 Hz), 58.52, 22.31 (d, *J* = 17.7 Hz), 18.54 (s), 16.51 (dd, *J* = 10.1, 5.4 Hz), 16.16 (dd, *J* = 11.2, 7.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.30, -4.70; IR(neat) v 3419, 2985, 2935, 1628, 1483, 1444, 1393, 1344, 1230, 1165, 1017, 855, 806, 748, 660, 532 cm^{-1}; HRMS (m/z): calcd for $C_{16}H_{27}NP_2O_7Cl[M+H]^+$: 442.0946, found: 442.0945.



17. [2-(Diisopropoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diisopropyl ester (3q) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 208.8 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 7.2 Hz, 1H), 6.78 (m, 3H), 6.21 (dd, *J* = 19.2, 8.4 Hz, 1H), 4.89 (tt, *J* = 12.4, 6.4 Hz, 1H), 4.76 – 4.59 (m, 2H), 4.46 (td, *J* = 12.4, 6.0 Hz, 1H), 1.35 (d, *J* = 6.0 Hz, 3H), 1.25 (ddd, *J* = 9.2, 8.0, 4.4 Hz, 12H), 1.10 (d, *J* = 6.0 Hz, 3H), 1.04 (d, *J* = 6.0 Hz, 3H), 0.93 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 132.60 (s), 123.33 (s), 121.51 (s), 113.72 (s), 108.95 (s), 91.87 (s), 89.89 (s), 72.64 (d, *J* = 6.2 Hz), 72.32 (dd, *J* = 10.5, 1.6 Hz), 24.74 – 24.16 (m), 24.16 – 23.79 (m), 23.57 (dd, *J* = 16.1, 5.2 Hz), 23.11 (d, *J* = 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.34 (s), 9.27 (d, *J* = 22.5 Hz), 2.77 (d, *J*, 22.5 Hz); IR(neat) v 3448, 2979, 2932, 2358, 1649, 1482, 1382, 1268, 1177, 1105, 991, 890, 744, 587 cm^{-1}; HRMS (m/z): calcd for $C_{19}H_{33}NP_2NaO_7$ $[M+Na]^+$: 472.1624, found: 472.1622.



18. [2-(Dibutoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid dibutyl ester (3r) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 209.6 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 7.2 Hz, 1H), 6.79 (m, 3H), 6.23 (dd, *J* = 19.6, 8.0 Hz, 1H), 4.19 – 3.78 (m, 8H), 1.73 – 1.11 (m, 16H), 1.10 – 0.53 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.28 (d, *J* = 8.5 Hz), 131.80, 123.40, 121.65, 113.31, 108.86, 90.66 (d, *J* = 5.2 Hz), 89.35 (d, *J* = 5.3 Hz), 67.12 (dd, *J* = 7.9, 6.2 Hz), 66.82 (dd, *J* = 11.2, 6.4 Hz), 32.40 – 32.13 (m), 32.04 (d, *J* = 7.1 Hz), 31.84 (d, *J* = 6.9 Hz), 18.55, 18.42 – 18.23 (m), 13.30 (dd, *J* = 12.6, 7.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.29 (d, *J* = 21.7 Hz), -1.47 (d, *J* = 26.7 Hz); IR(neat) v 3439, 2960, 2873, 1781, 1631, 1480, 1399, 1256, 1119, 1021, 832, 739, 703, 659, 549 cm^{-1}; HRMS (m/z): calcd for $C_{23}H_{42}NP_2O_7$ $[M+H]^+$: 506.2431, found: 506.2427.



19. [2-(Dimethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid dimethyl ester (3s) The title compound was prepared according to the general procedure and purified

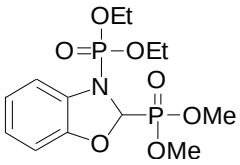
by column chromatography to give a yellow oil, 141.54mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 6.8 Hz, 1H), 6.91 (m, 3H), 6.31 (dd, *J* = 19.6, 7.6 Hz, 1H), 3.79 (ddd, *J* = 28.0, 14.4, 9.6 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.94 (d, *J* = 8.8 Hz), 131.27, 123.87, 122.16, 113.41, 109.15, 90.36 (d, *J* = 5.6 Hz), 89.06 (d, *J* = 5.6 Hz), 54.16 – 53.77 (m), 53.68 (d, *J* = 7.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 13.52 (d, *J* = 21.7 Hz), 0.77 (d, *J* = 19.4Hz); IR(neat) v 3430, 2959, 1633, 1481, 1451, 1401, 1264, 1187, 1038, 839, 752, 542 cm^{-1}; HRMS (m/z): calcd for $C_{11}H_{17}NaNP_2O_7$ $[M+Na]^{+}$: 360.0372, found: 360.0371.

20. [6-bromo-2-(diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (3u) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil. 188 mg, 80% yield. ^{1}H NMR (400 MHz, cdcl$_3$) δ 6.97 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.26 (dd, *J* = 18.8, 7.7 Hz, 1H), 4.30 – 3.96 (m, 8H), 1.41 – 1.17 (m, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 152.29 (d, *J* = 8.1 Hz), 131.64 (d, *J* = 1.9 Hz), 124.71 (s), 115.49 (s), 114.38 (s), 112.67 (s), 91.86 (d, *J* = 4.9 Hz), 89.90 (d, *J* = 5.3 Hz), 64.17 – 63.30 (m), 16.34 (d, *J* = 5.4 Hz), 15.98 (dd, *J* = 17.8, 6.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.03 (s), -2.83 (s); IR (neat) v 3445, 2981, 2363, 1631, 1478, 1398, 1269, 1162, 1022, 976, 801, 699, 553 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}BrNO_7P_2$ $[M+H]^{+}$: 472.0284, found: 472.0282.

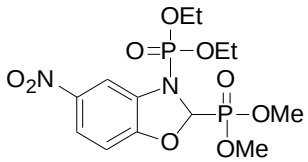
21. [6-bromo-2-(diethoxy-phosphoryl)-benzothiazol-3-yl]-phosphonic acid diethyl ester (3v) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil. 202 mg, 83% yield. 1H NMR (400 MHz, cdcl$_3$) δ 7.25 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 5.85 (d, *J* = 9.4 Hz, 1H), 4.34 – 3.98 (m, 8H), 1.39 – 1.10 (m, 12H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 139.90 (s), 128.50 (s), 124.82 (s), 116.63 (s), 116.29 (s), 109.99 (s), 64.11 – 63.57 (m), 63.24 (d, *J* = 5.1 Hz), 62.77 (d, *J* = 3.5 Hz), 61.02 (s), 16.45 – 15.75 (m), 15.71 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.05 (s), -0.80 (s); IR(neat) v 3447, 2982, 2362, 1646, 1460, 1394, 1313, 1265, 1220, 1161, 1100, 1019, 976, 800, 623 cm^{-1}; HRMS (m/z): calcd for $C_{15}H_{25}BrNO_6P_2S$ $[M+H]^{+}$: 488.0056, found: 488.0052.

22. [2-(Diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid dimethyl ester (4a) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 153.3 mg, 84% yield. ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.00 (d, *J* = 7.2 Hz, 1H), 6.87 (dt, *J* = 16.7, 7.5 Hz, 3H), 6.24 (dd, *J* = 19.3, 8.2 Hz, 1H), 4.12 (ddd, *J* = 22.4, 15.4, 7.6 Hz, 4H), 3.79 (dd, *J* = 56.3, 11.5 Hz, 6H), 1.19 (dd, *J* = 16.2, 7.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.36 (dd, *J* = 8.8, 1.4 Hz), 131.75 (d, *J* = 1.7 Hz), 123.96, 122.18 (d, *J* =

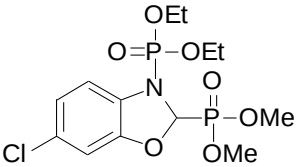
0.7 Hz), 113.68, 109.30, 91.09 (d, *J* = 5.1 Hz), 89.14 (d, *J* = 5.3 Hz), 64.01 (d, *J* = 6.5 Hz), 63.65 (d, *J* = 7.0 Hz), 54.17 (dd, *J* = 22.1, 5.5 Hz), 16.42 (dd, *J* = 5.6, 3.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 11.68(d, *J* = 21.7 Hz), 1.68(d, *J* = 21,7 Hz); IR(neat) v 2988, 1778, 1626, 1482, 1397, 1362, 1251, 1035, 844, 751, 658, 545 cm^{-1}; HRMS (m/z): calcd for $C_{13}H_{22}NO_7P_2$ $[M+H]^+$: 366.0866, found: 366.0864.

23. [2-(Dimethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (4b) 

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 158.8 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 7.2 Hz, 1H), 6.83 (m, 3H), 6.26 (dd, *J* = 19.6, 7.6 Hz, 1H), 4.24 – 4.13 (m, 2H), 4.10 – 3.90 (m, 2H), 3.70 (t, *J* = 11.2 Hz, 6H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.27, 131.79, 123.86, 122.23, 113.69, 109.28, 63.85 (dd, *J* = 21.8, 5.5 Hz), 54.21, 54.21 – 53.65 (m), 16.13 (ddd, *J* = 8.6, 6.7, 1.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 14.36 (d, *J* = 19.4 Hz), -1.28(d, *J* = 21.9 Hz); IR(neat) v 3420, 2986, 1779, 1628, 1482, 1398, 1253, 1036, 814, 748, 657, 545 cm^{-1}; HRMS (m/z): calcd for $C_{13}H_{22}NO_7P_2$ $[M+H^]^+$: 366.0866, found: 366.0865.

24. [2-(Dimethoxy-phosphoryl)-5-nitro-benzooxazol-3-yl]-phosphonic acid diethyl ester (4c) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 143.5 mg, 70% yield. 

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 48.4, 9.6 Hz, 2H), 6.96 – 6.81 (m, 1H), 6.44 (dd, *J* = 17.6, 6.4 Hz, 1H), 4.36 – 4.00 (m, 4H), 3.81 (dt, *J* = 12.4, 10.0 Hz, 6H), 1.35 (dd, *J* = 56.8, 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.47, 143.20 (d, *J* = 1.0 Hz), 133.45 (d, *J* = 1.8 Hz), 121.29, 108.59, 108.29, 92.85 (d, *J* = 5.8 Hz), 90.89 (d, *J* = 5.9 Hz), 64.39 (dd, *J* = 11.7, 5.6 Hz), 54.33 (d, *J* = 6.4 Hz), 53.93 (d, *J* = 7.3 Hz), 16.00 (dd, *J* = 18.5, 6.7 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 12.96 (d, *J* = 15.5 Hz), -2.86 (d, *J* = 15.5 Hz); IR(neat) v 3415, 2986, 1623, 1528, 1484, 1447, 1395, 1342, 1225, 1032, 817, 747, 624 , 488 cm^{-1}; HRMS (m/z): calcd for $C_{13}H_{21}N_2O_9P_2$ $[M+H]^+$: 411.0717, found: 411.0713.

25. [6-Chloro-2-(dimethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diethyl ester (4d) 

The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 151.6 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (t, *J* = 7.2 Hz, 1H), 6.78 (s, 2H), 6.27 (dd, *J* = 18.8, 7.6 Hz, 1H), 4.23 – 4.13 (m, 2H), 4.03 (ddd, *J* = 28.8, 20.0, 7.4 Hz, 2H), 3.73 (dt, *J* = 12.6, 6.3 Hz, 6H), 1.36 – 1.27 (m, 3H), 1.24 – 1.15 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.05 (d, *J* = 8.7 Hz), 130.98 (d, *J* = 2.7 Hz), 128.72 (d, *J* = 1.0 Hz), 122.03, 113.94, 110.19, 91.86 (d, *J* = 5.3 Hz), 89.90 (d, *J* = 5.3 Hz), 64.03 (dd, *J* = 15.6, 5.4 Hz), 54.29 (d, *J* = 6.3 Hz), 53.93 (d, *J* = 7.1 Hz), 16.11 (dd, *J* = 18.8, 6.9 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ

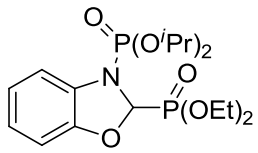
13.73 (d, *J* = 19.7 Hz), -1.68 (d, *J* = 20.4 Hz); IR(neat) v 3418, 2986, 2361, 1776, 1630, 1481, 1443, 1398, 1251, 1017, 815, 757, 711, 592, 548 cm^{-1}; HRMS (m/z): calcd for $C_{13}H_{21}ClNO_7P_2$ $[M+H]^+$: 400.0476, found: 400.0474.

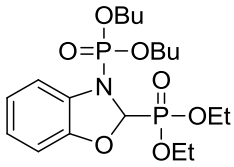
26. [2-(Dimethoxy-phosphoryl)-6-methyl-benzooxazol-3-yl]-phosphonic acid diethyl ester (4e) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 94.7 mg, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 11.2 Hz, 2H), 6.23 (dd, *J* = 19.2, 8.4 Hz, 1H), 4.18 (dd, *J* = 13.6, 8.0 Hz, 2H), 4.09 – 3.90 (m, 2H), 3.70 (t, *J* = 9.6 Hz, 6H), 2.21 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 5.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.46, 134.07 (d, *J* = 1.9 Hz), 129.31 (d, *J* = 1.7 Hz), 122.40, 113.36, 110.20, 91.15 (d, *J* = 4.5 Hz), 89.22 (d, *J* = 2.3 Hz), 63.79 (dd, *J* = 19.3, 5.0 Hz), 54.18 (d, *J* = 6.2 Hz), 53.86 (d, *J* = 6.7 Hz), 21.42, 16.14 (dd, *J* = 20.7, 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.91(d, *J* = 34.2 Hz), -1.47(d, *J* = 34.2 Hz); IR(neat) v 3432, 2982, 1774, 1630, 1496, 1439, 1399, 1261, 1034, 816, 705, 593, 548 cm^{-1}; HRMS (m/z): calcd for $C_{14}H_{24}NO_7P_2$ $[M+H]^+$: 380.1023, found: 380.1021.

27. [5-Chloro-2-(dimethoxy-phosphoryl)-2-methyl-benzooxazol-3-yl]-phosphonic acid diethyl ester (4f) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 107.4 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.60 (t, *J* = 7.2 Hz, 1H), 4.30 – 3.92 (m, 4H), 3.73 (m, 6H), 2.07 (dd, *J* = 11.6, 6.4 Hz, 3H), 1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.51 (d, *J* = 11.4 Hz), 134.36 (d, *J* = 5.0 Hz), 126.64, 122.14, 112.65, 108.83, 102.10, 100.28, 64.00 (d, *J* = 5.3 Hz), 63.55 (d, *J* = 5.5 Hz), 54.37 (d, *J* = 6.5 Hz), 54.03 (d, *J* = 6.9 Hz), 22.61 (d, *J* = 17.8 Hz), 16.17 (dd, *J* = 9.0, 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.90, -4.87; IR(neat) v 3755, 3442, 2966, 2621, 2290, 1632, 1400, 1273, 1015, 830, 702, 665, 584 cm^{-1}; HRMS (m/z): calcd for $C_{14}H_{23}ClNO_7P_2$$[M+H]^+$: 414.0633, found: 414.0632.

28. [2-(Dimethoxy-phosphoryl)-benzothiazol-3-yl]-phosphonic acid diethyl ester (4g) The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 114.3 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 1H), 7.11 – 6.88 (m, 3H), 5.93 (dd, *J* = 12.8, 6.8 Hz, 1H), 4.30 (dd, *J* = 14.8, 6.8 Hz, 2H), 4.08 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.90 – 3.82 (m, 1H), 3.81 – 3.61 (m, 6H), 1.46 – 1.35 (m, 3H), 1.12 (dt, *J* = 14.4, 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.35 (d, *J* = 4.0 Hz), 130.03 (d, *J* = 7.9 Hz), 126.01, 124.31, 122.42, 115.72, 63.77 (d, *J* = 4.7 Hz), 63.19 (d, *J* = 4.8 Hz), 61.98 (d, *J* = 3.4 Hz), 60.22 (d, *J* = 3.7 Hz), 54.56 (d, *J* = 6.6 Hz), 54.13 (d, *J* = 6.3 Hz), 16.31 (d, *J* = 7.3 Hz), 15.81 (d, *J* = 7.7 Hz); ^{31}P NMR (243 MHz,

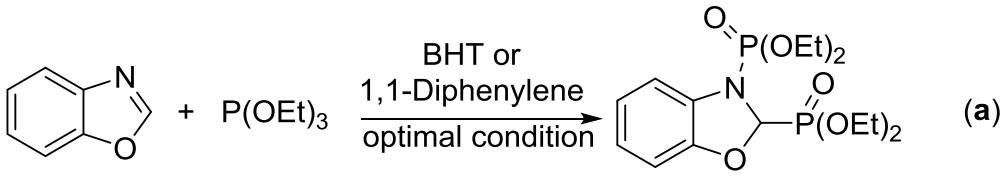
$CDCl_3$) δ 18.81 (d, *J* = 16.2 Hz), 1.36 (d, *J* = 16.3 Hz); IR(neat) v 3477, 2983, 2856, 1643, 1580, 1464, 1394, 1261, 1167, 1023, 979, 824, 752, 595, 533, 481 cm^{-1}; HRMS (m/z): calcd for $C_{13}H_{22}NO_6P_2S_7$ $[M+H]^+$: 382.0638, found: 382.0637.

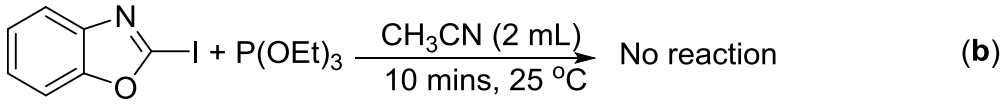
29. [2-(Diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid diisopropyl ester (4h)  The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 195.8 mg, 93% yield. ^1H NMR (400 MHz, cdcl$_3$) δ 6.92 (d, *J* = 7.2 Hz, 1H), 6.82 (dt, *J* = 17.4, 6.5 Hz, 3H), 6.30 (dd, *J* = 19.6, 8.0 Hz, 1H), 4.87 (dd, *J* = 13.7, 6.3 Hz, 1H), 4.51 (dd, *J* = 12.8, 6.4 Hz, 1H), 4.08 (ddd, *J* = 47.0, 15.9, 8.6 Hz, 4H), 1.38 (d, *J* = 6.1 Hz, 3H), 1.32 (d, *J* = 6.1 Hz, 3H), 1.27 (d, *J* = 6.1 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 151.42 (d, *J* = 9.3 Hz), 132.20 (s), 123.39 (s), 121.68 (s), 113.56 (s), 108.96 (s), 91.26 (d, *J* = 5.6 Hz), 89.30 (d, *J* = 5.6 Hz), 72.64 – 72.30 (m), 63.49 (dd, *J* = 18.5, 6.7 Hz), 23.86 (d, *J* = 4.1 Hz), 23.53 (dd, *J* = 14.6, 5.0 Hz), 23.14 (d, *J* = 5.6 Hz), 16.24 (t, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.30, -3.95 (d, *J* = 31.6 Hz); IR(neat) v 3456, 2981, 2933, 1631, 1482, 1386, 1268, 1154, 1103, 989, 833, 789, 745, 656, 550 cm^{-1}; HRMS (m/z): calcd for $C_{17}H_{30}NO_7P_2[M+H]^+$: 422.1492, found: 422.1489.

30. [2-(Diethoxy-phosphoryl)-benzooxazol-3-yl]-phosphonic acid dibutyl ester (4i)  The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 188.6 mg, 81% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 3.6 Hz, 1H), 6.85 (m, 3H), 6.27 (m, 1H), 4.22 – 3.84 (m, 8H), 1.52 (m, 6H), 1.20 (m, 8H), 0.86 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ132.08, 123.74, 122.02, 113.68, 109.19, 91.29 (d, *J* = 5.7 Hz), 89.34 (d, *J* = 5.5 Hz), 67.51 (d, *J* = 4.9 Hz), 67.23 (d, *J* = 5.9 Hz), 32.24 (dd, *J* = 17.8, 7.0 Hz), 18.85, 18.64, 16.43 (d, *J* = 5.6 Hz), 13.63 (d, *J* = 12.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.20, -1.32 (d, *J* = 31.6 Hz); IR(neat) v 3488, 2962, 2873, 1630, 1481, 1392, 1361, 1271, 1158, 1023, 794, 741, 655, 549 cm^{-1}; HRMS (m/z): calcd for $C_{19}H_{33}NaNO_7P_2$ $[M+Na]^+$: 472.16245, found: 472.1618.

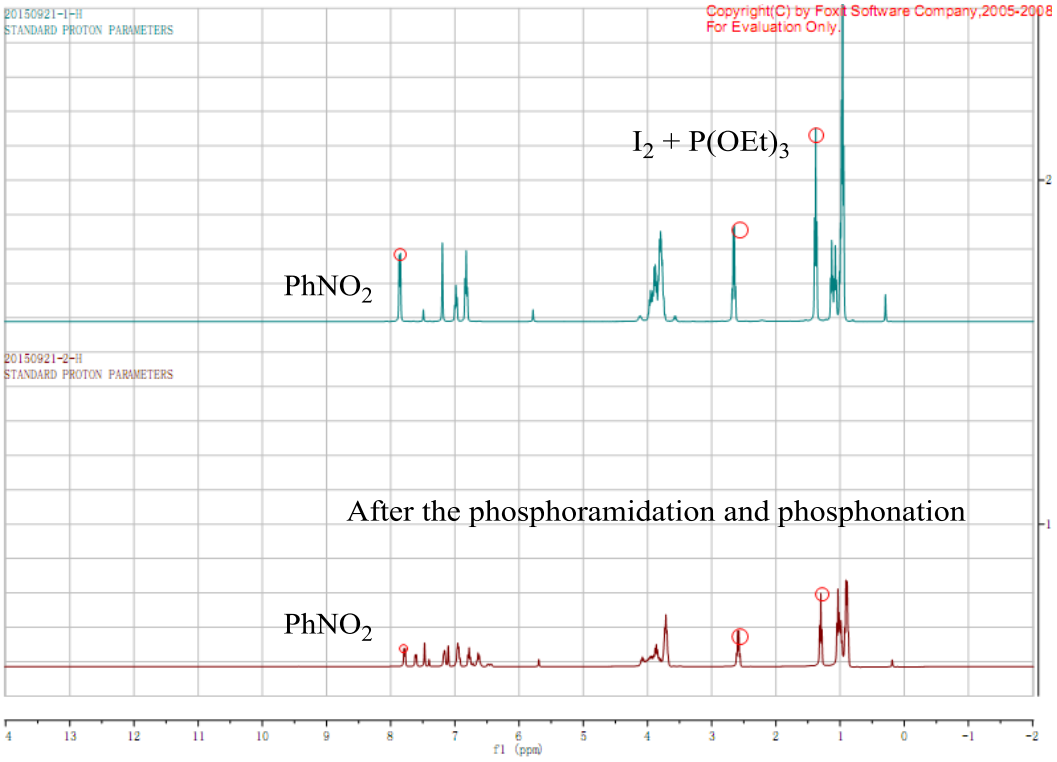
4. Control experiments

4.1 Control experiments of the reaction

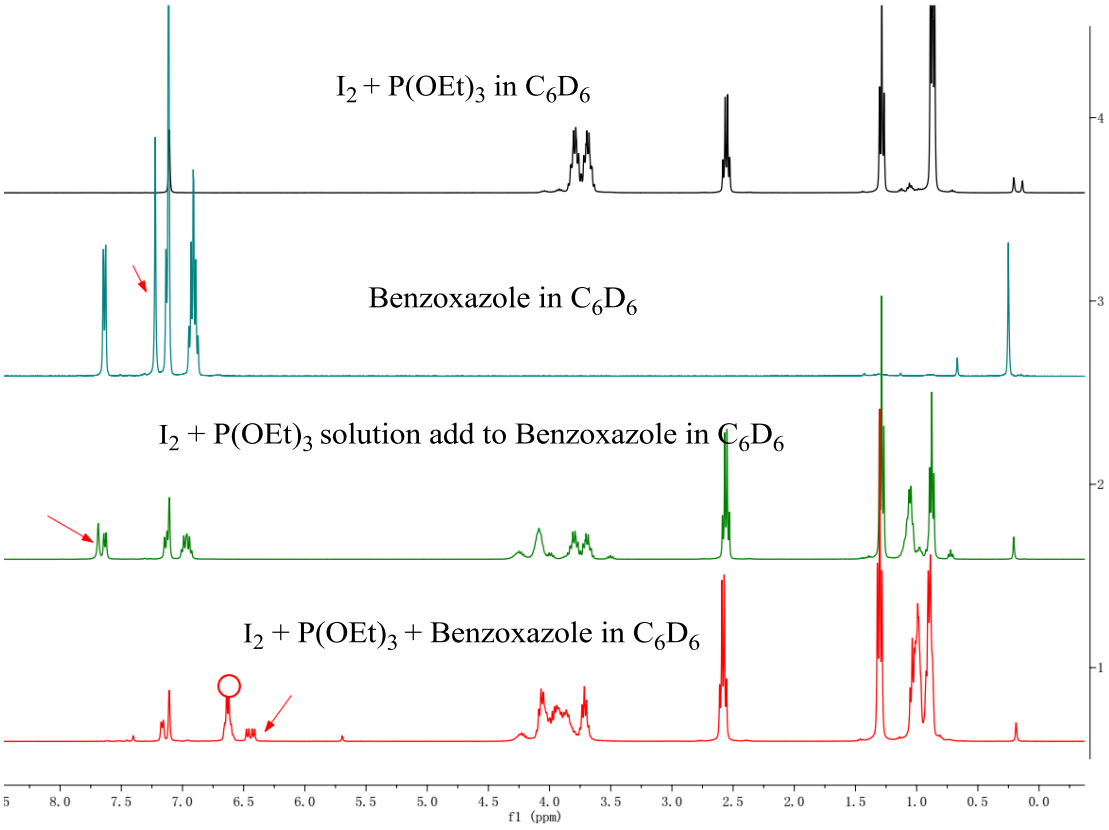




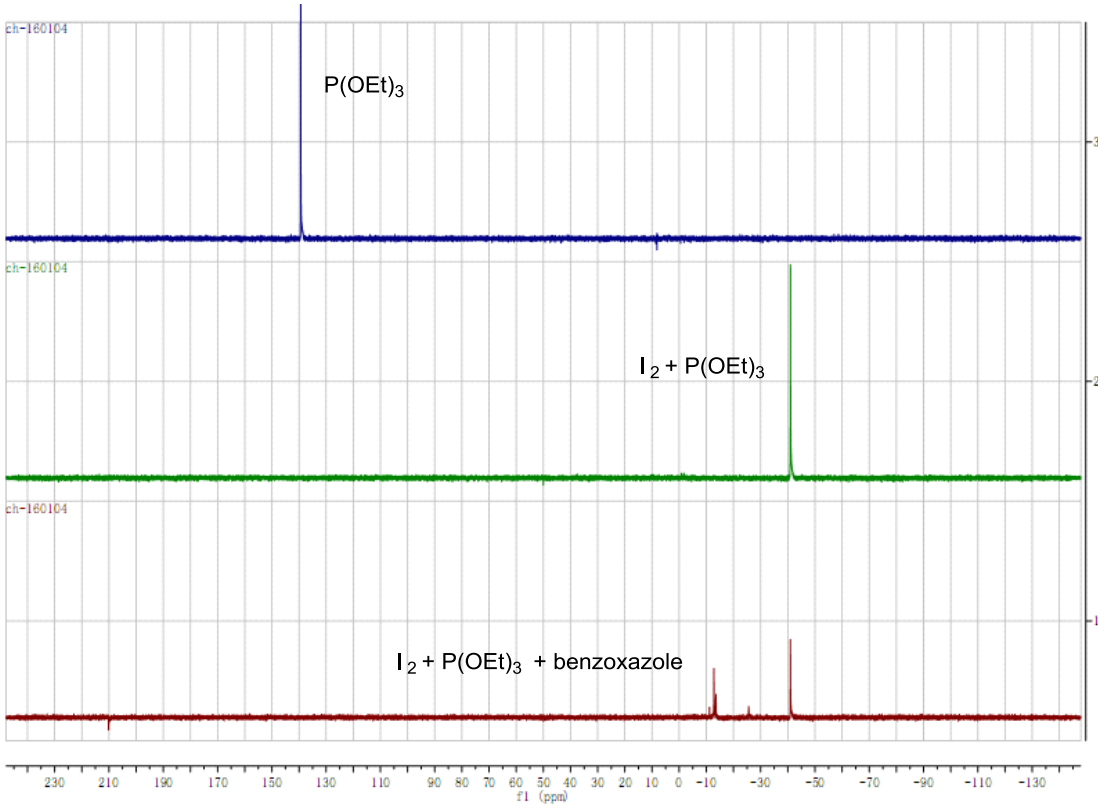
4.2 The ^{1}HNMR experiments to track the change of the mount of ICH_2CH_3 with the nitrobenzene as internal standard.



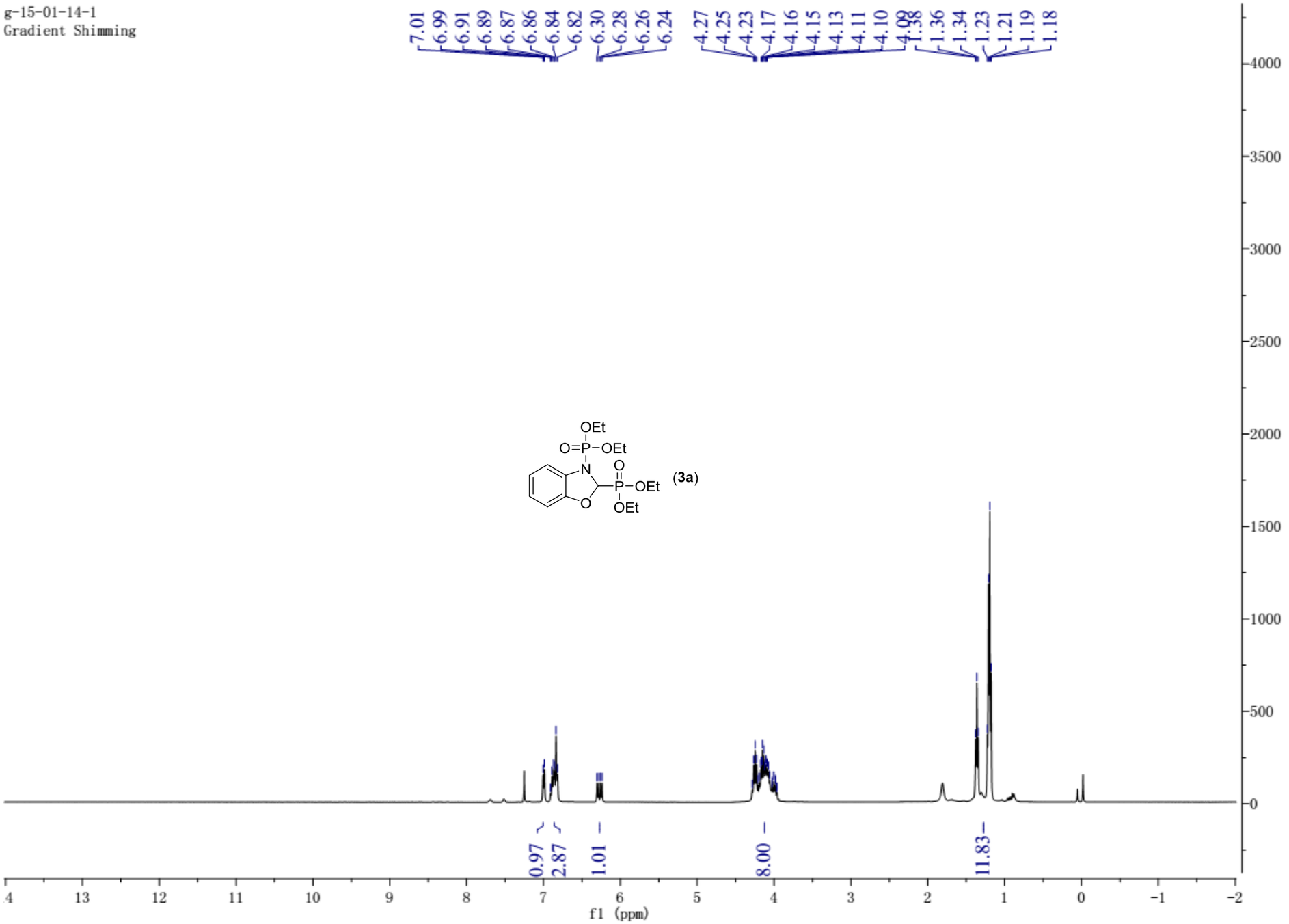
4.3 The ^{1}HNMR to track the signal of C_2-H



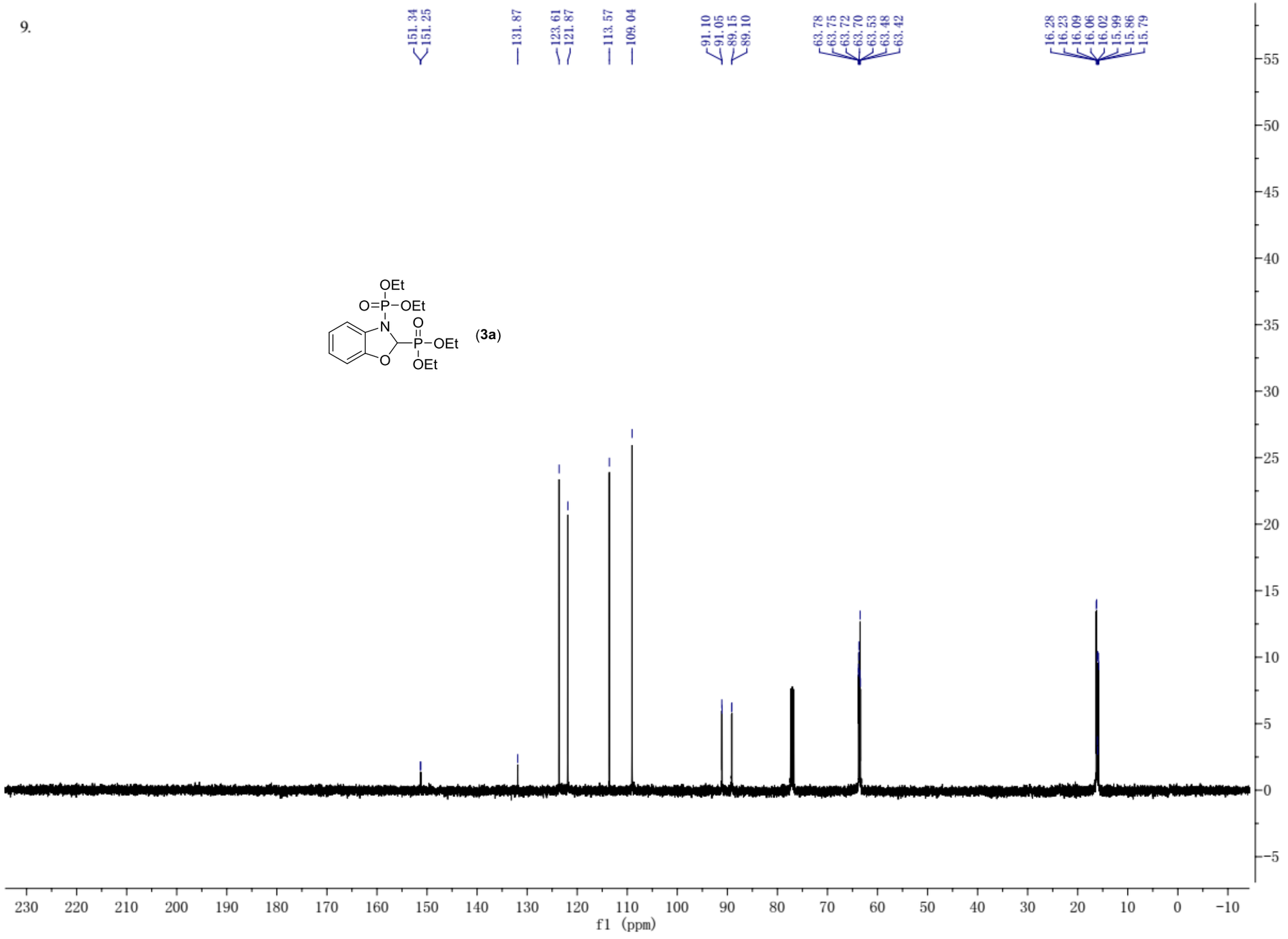
4.4 The control reaction by ^{31}PNMR

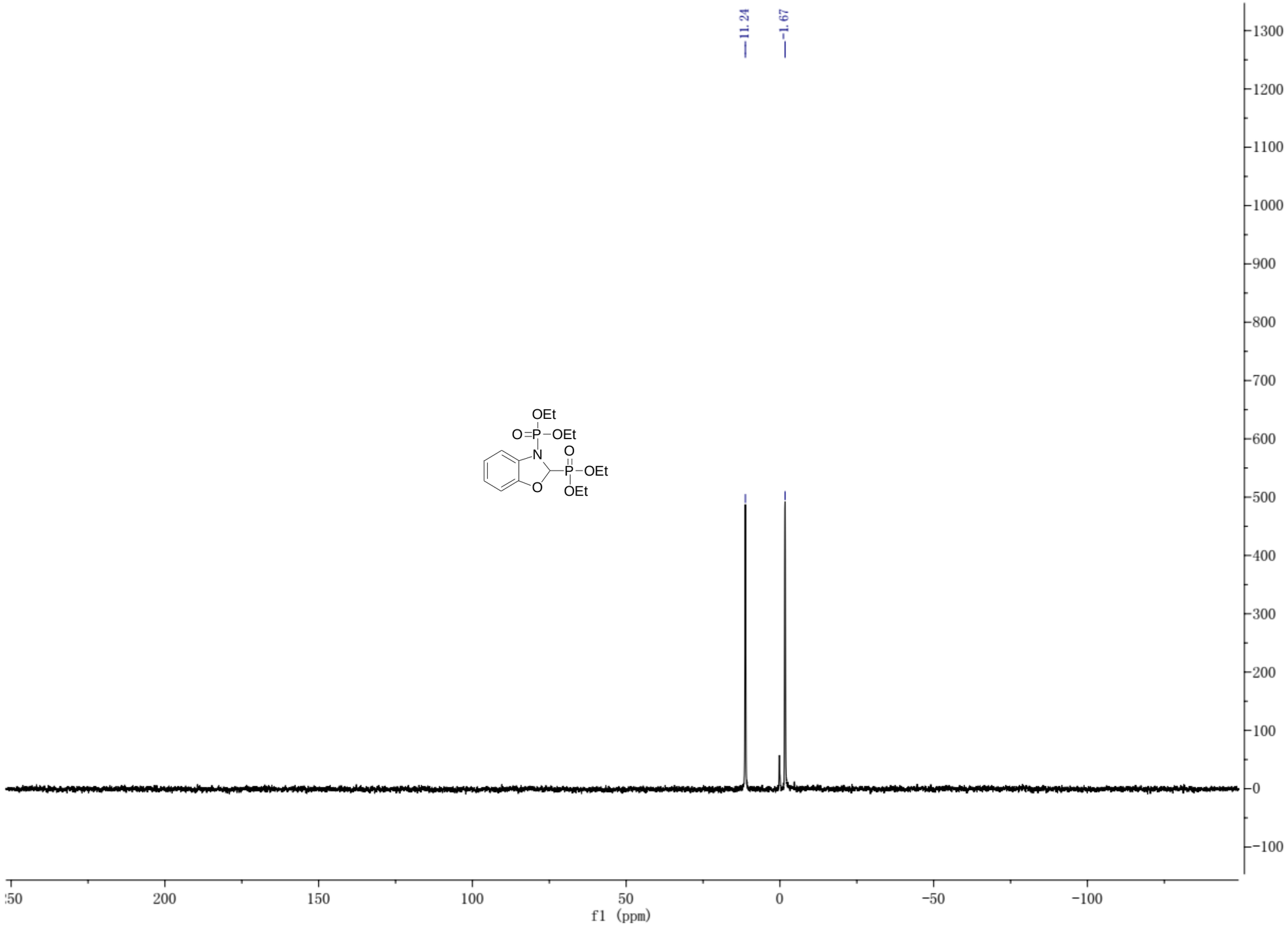


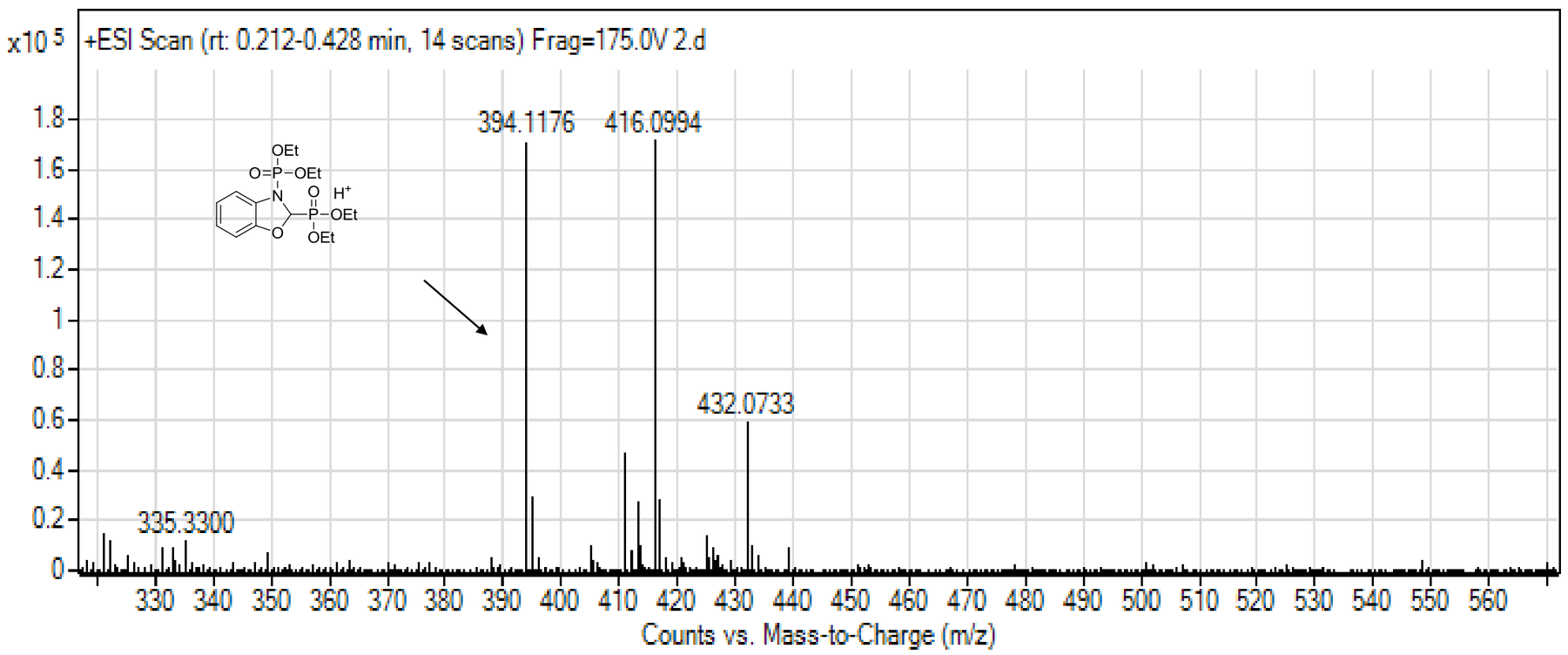
g-15-01-14-1
Gradient Shimming



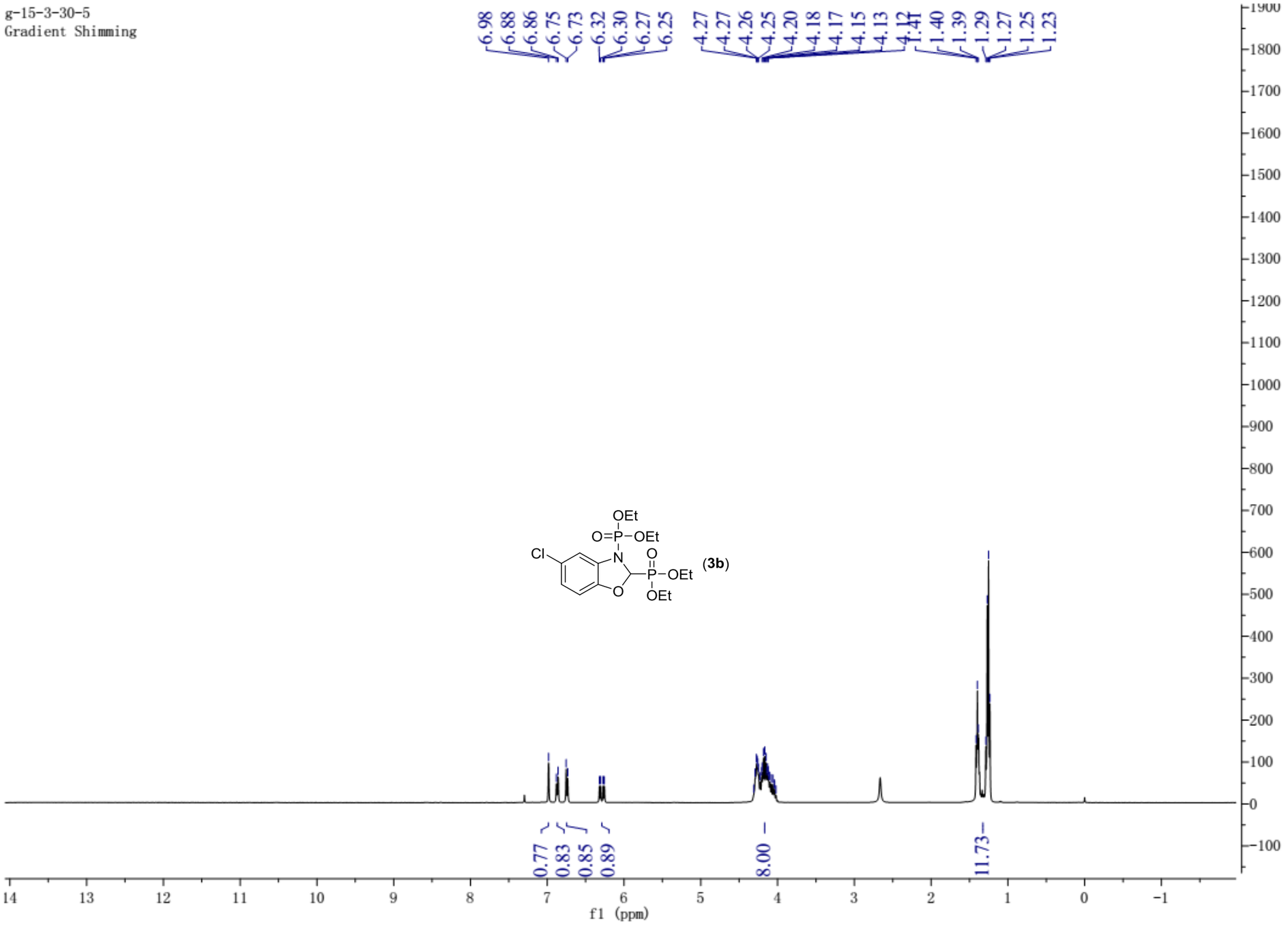
9.


151.34
151.25
131.87
123.61
121.87
113.57
109.04
91.10
91.05
89.15
89.10
63.78
63.75
63.72
63.70
63.53
63.48
63.42
16.28
16.23
16.09
16.06
16.02
15.99
15.86
15.79
OEt
O=P−OEt
N
O
P−OEt
O
OEt
(3a)
f1 (ppm)

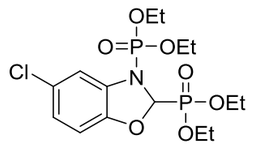

11.24
1.67
OEt
O=P–OEt
N
O
O
P–OEt
O
OEt
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
50
200
150
100
50
0
−50
−100
f1 (ppm)


x10 5
+ESI Scan (rt: 0.212-0.428 min, 14 scans) Frag=175.0V 2.d
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
394.1176
416.0994
432.0733
335.3300
330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560
Counts vs. Mass-to-Charge (m/z)

g-15-3-30-5
Gradient Shimming



133.42
130.45
126.73
123.12
113.93
109.44
91.94
91.89
90.00
89.94
64.03
63.98
63.92
63.85
63.79
63.58
63.52
16.37
16.32
16.12
16.05
15.92
15.85

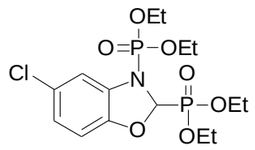


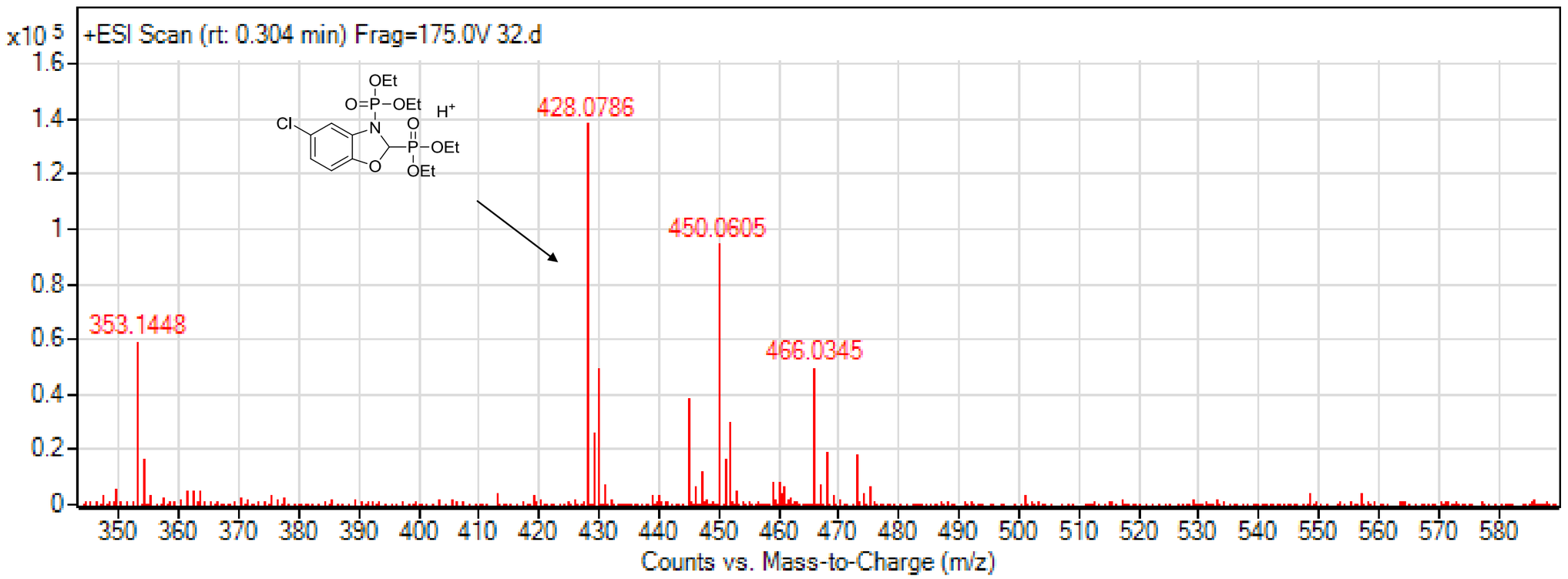
(**3b**)

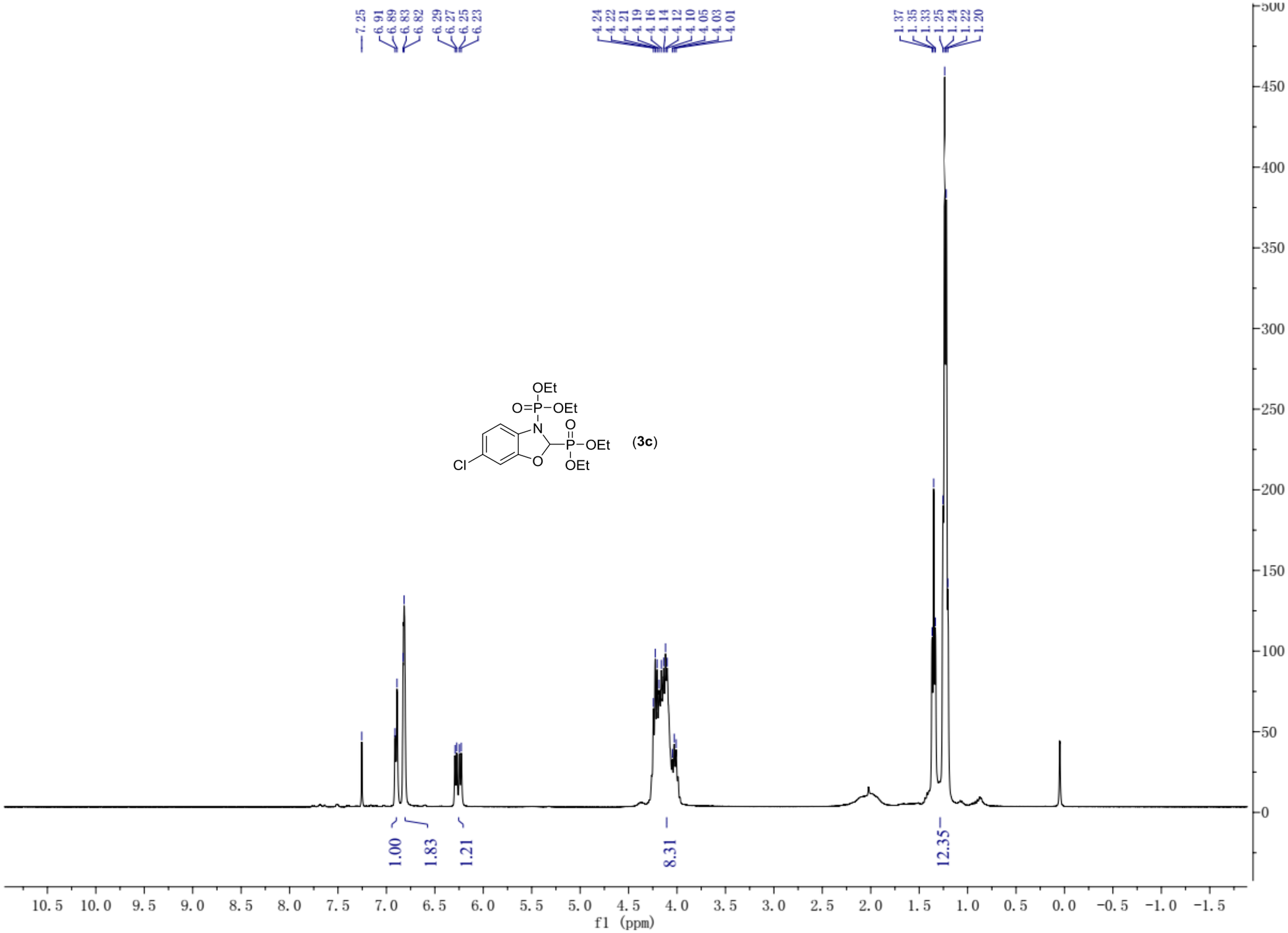
f1 (ppm)

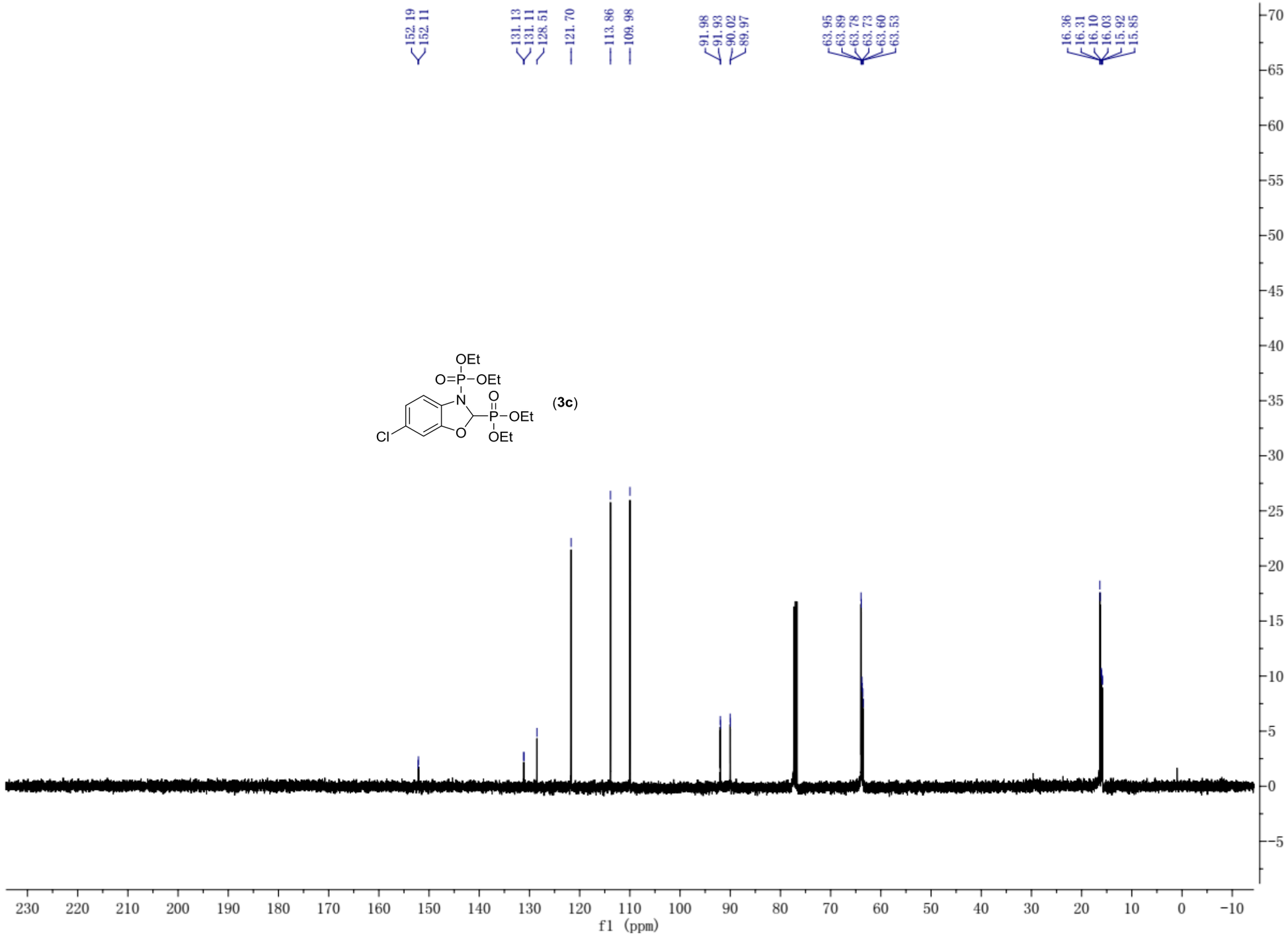
ch0522-4

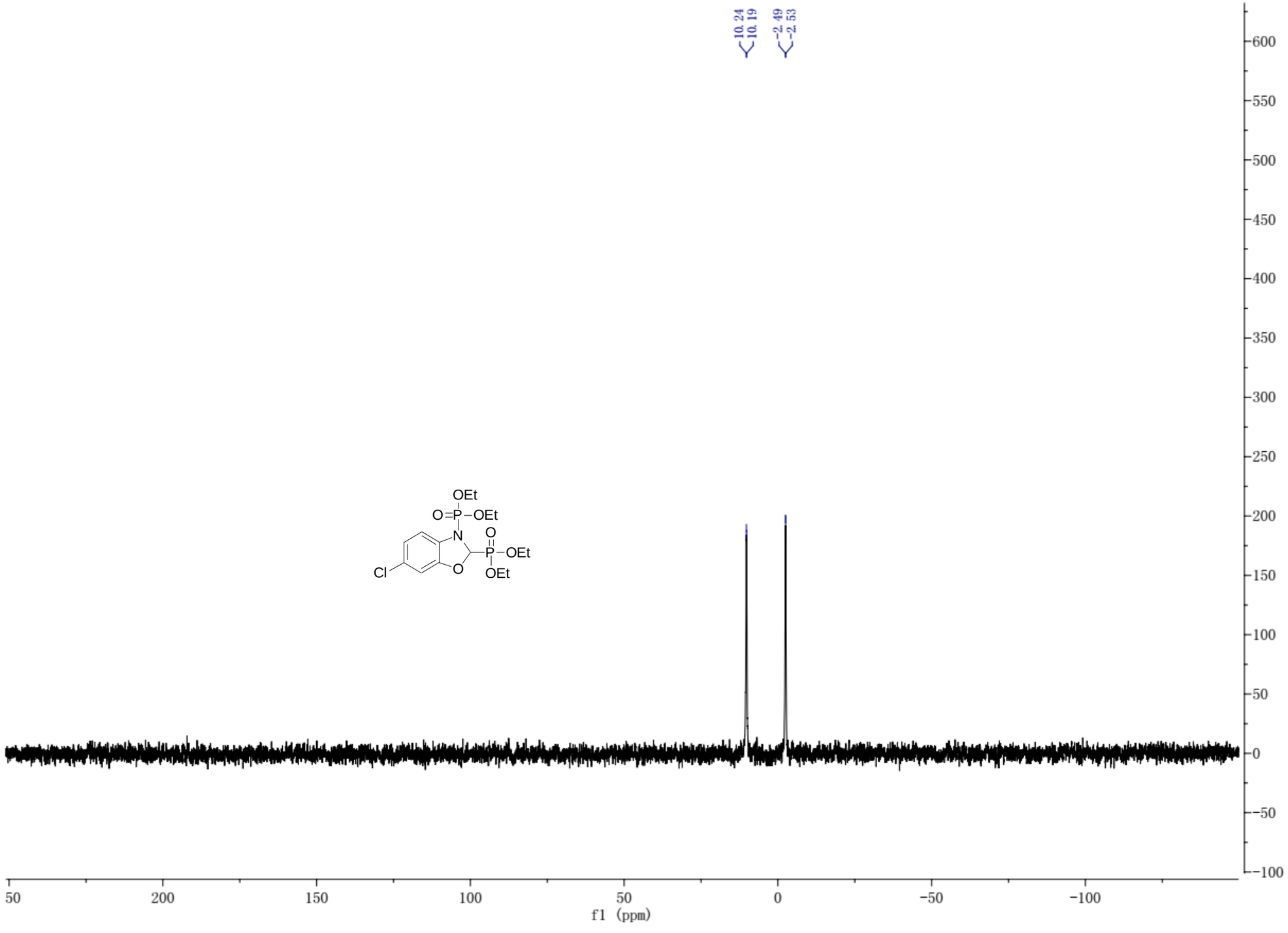
10.76
10.64
-2.45
-2.57

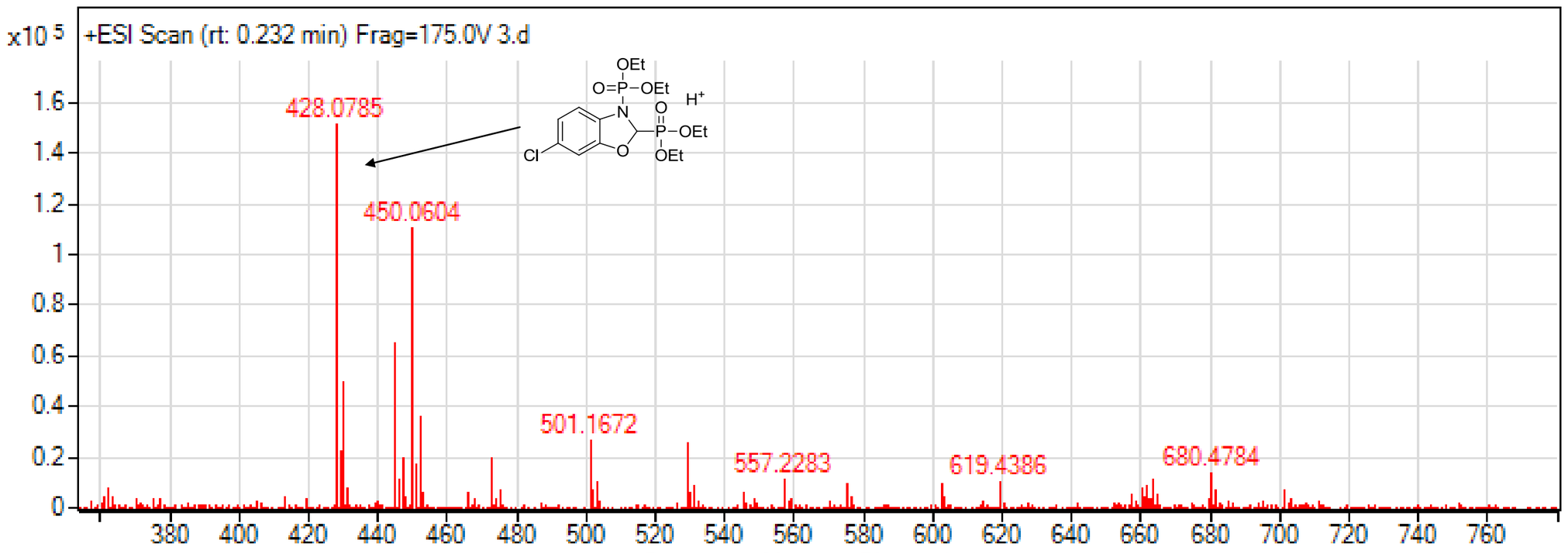



x10 5
+ESI Scan (rt: 0.304 min) Frag=175.0V 32.d
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
428.0786
450.0605
466.0345
353.1448
350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560 570 580
Counts vs. Mass-to-Charge (m/z)

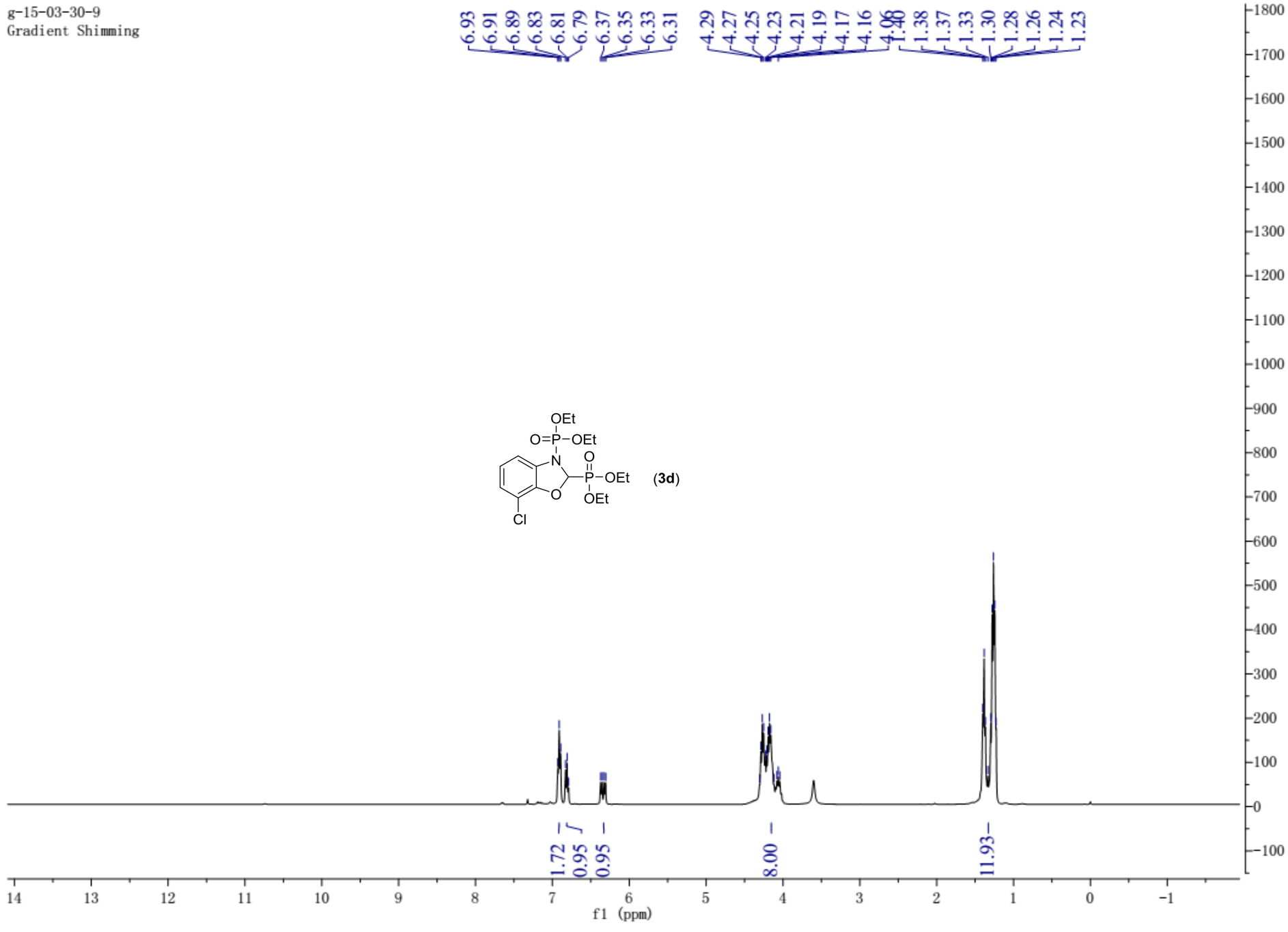

7.25
6.91
6.89
6.83
6.82
6.29
6.27
6.25
6.23
4.24
4.22
4.21
4.19
4.16
4.14
4.12
4.10
4.05
4.03
4.01
1.37
1.35
1.33
1.25
1.24
1.22
1.20
OEt
O=P−OEt
N
O
P−OEt
Cl
O
OEt
(3c)
1.00
1.83
1.21
8.31
12.35
f1 (ppm)


152.19
152.11
131.13
131.11
128.51
121.70
113.86
109.98
91.98
91.93
90.02
89.97
63.95
63.89
63.78
63.73
63.60
63.53
16.36
16.31
16.10
16.03
15.92
15.85
OEt
O=P−OEt
N
O
P−OEt
OEt
Cl
O
(3c)
f1 (ppm)

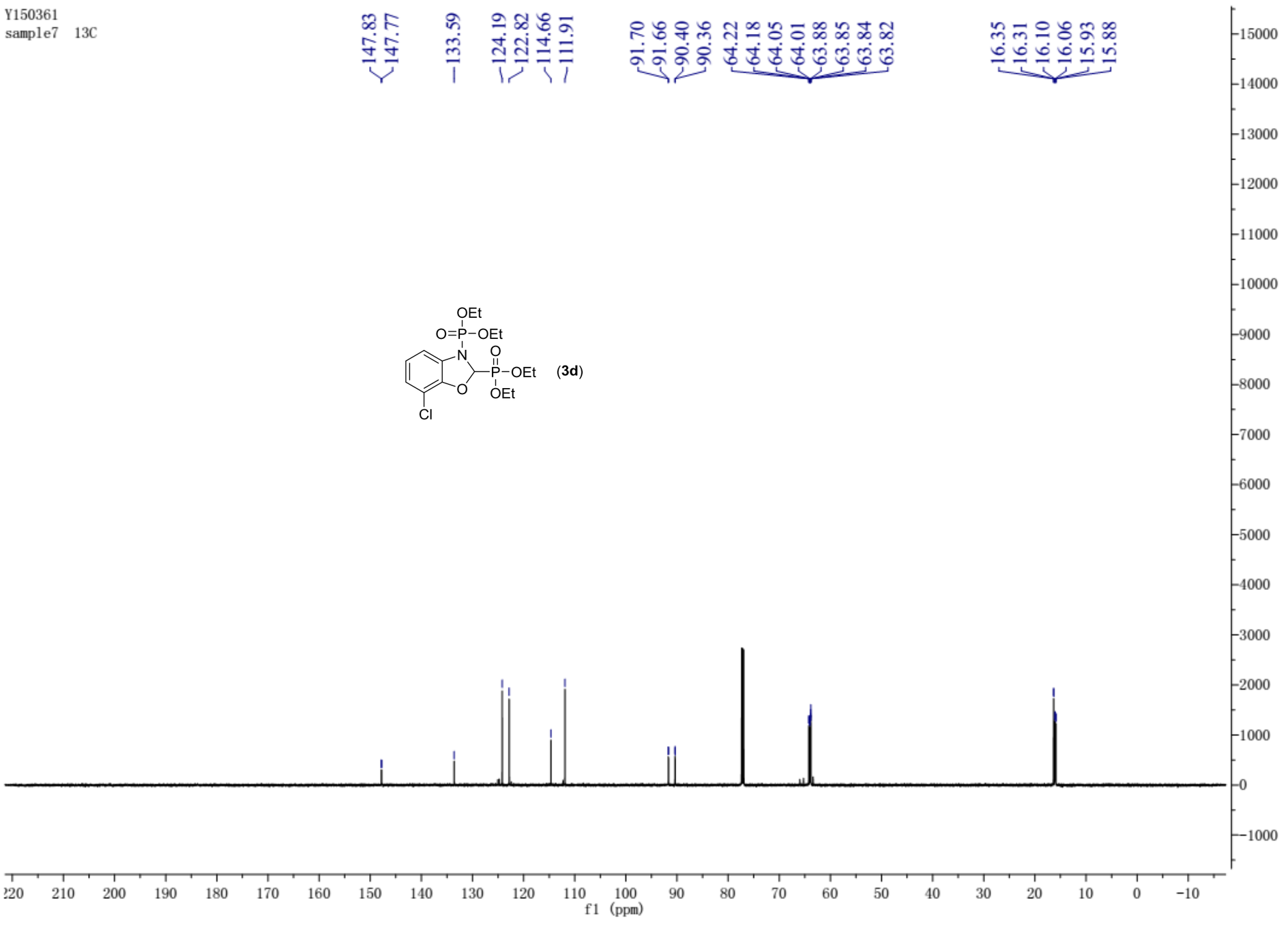

10.24
10.19
-2.49
-2.53
OEt
O=P-OEt
N
O
P-OEt
Cl
O
OEt
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
50
200
150
100
50
0
-50
-100
f1 (ppm)


x10 5
+ESI Scan (rt: 0.232 min) Frag=175.0V 3.d
428.0785
450.0604
501.1672
557.2283
619.4386
680.4784
OEt
O=P–OEt
N
O
H+
P–OEt
OEt
Cl
O
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760
Counts vs. Mass-to-Charge (m/z)

g-15-03-30-9
Gradient Shimming

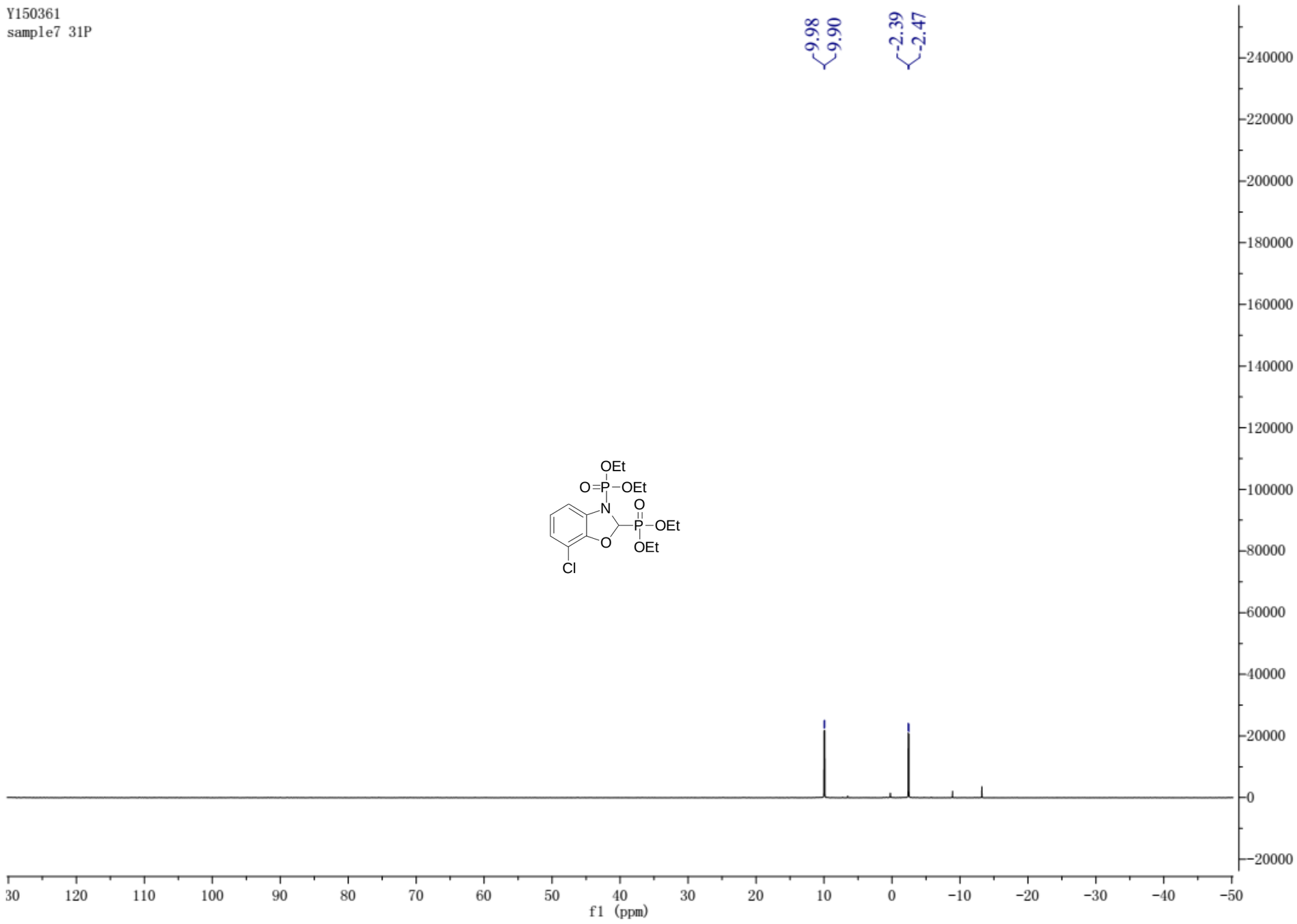


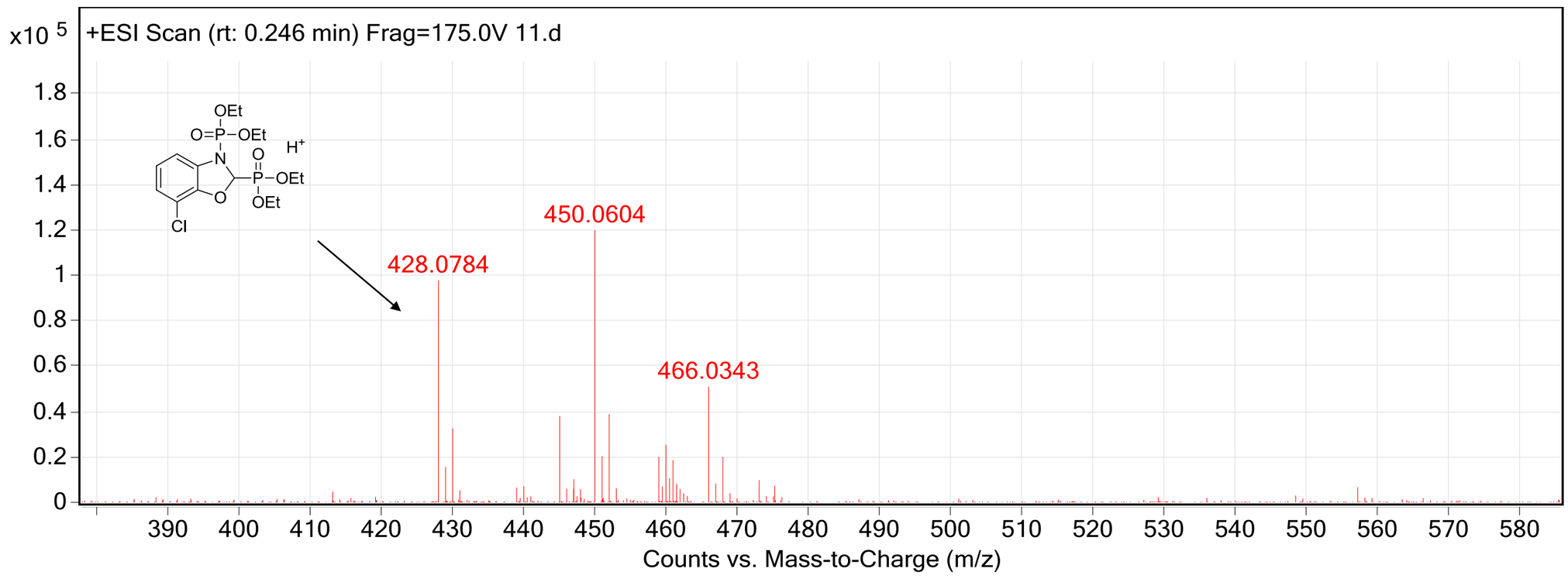
Y150361
sample7 13C



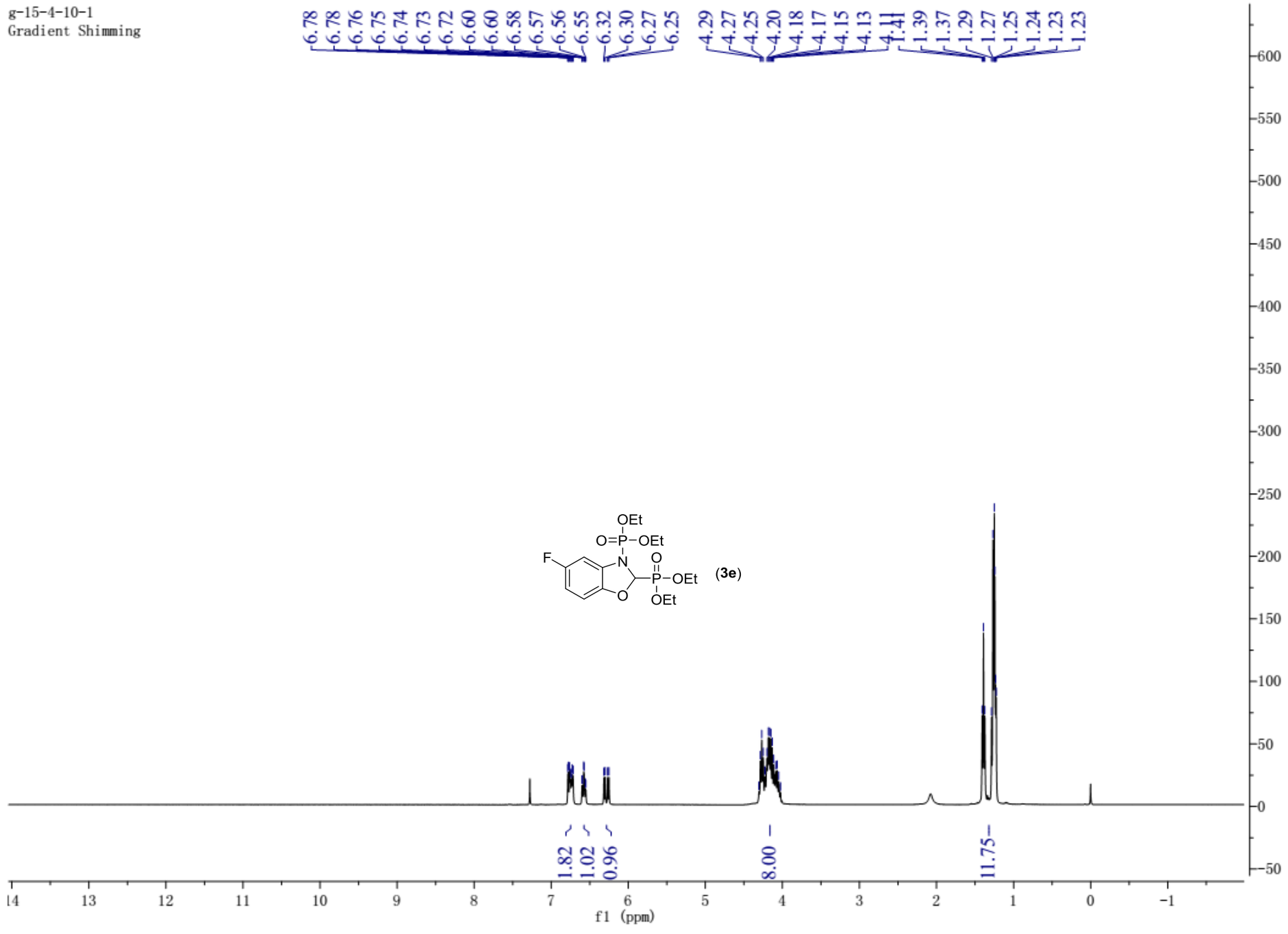
(**3d**)

Y150361
sample7 31P

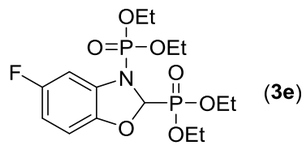



x10 5
+ESI Scan (rt: 0.246 min) Frag=175.0V 11.d
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
OEt
O=P–OEt
N
O
H+
P–OEt
OEt
O
Cl
450.0604
428.0784
466.0343
390
400
410
420
430
440
450
460
470
480
490
500
510
520
530
540
550
560
570
580
Counts vs. Mass-to-Charge (m/z)

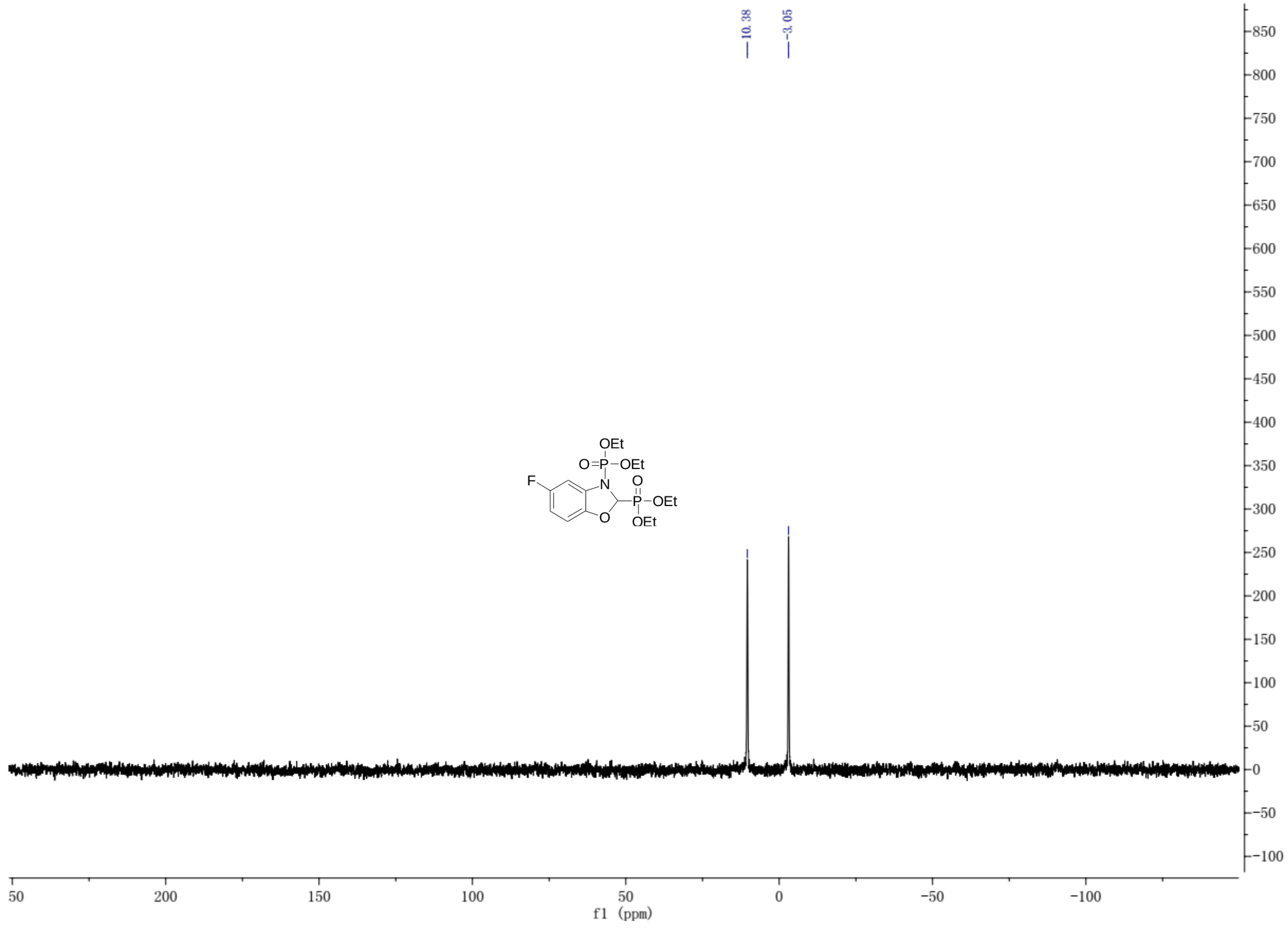
g-15-4-10-1
Gradient Shimming

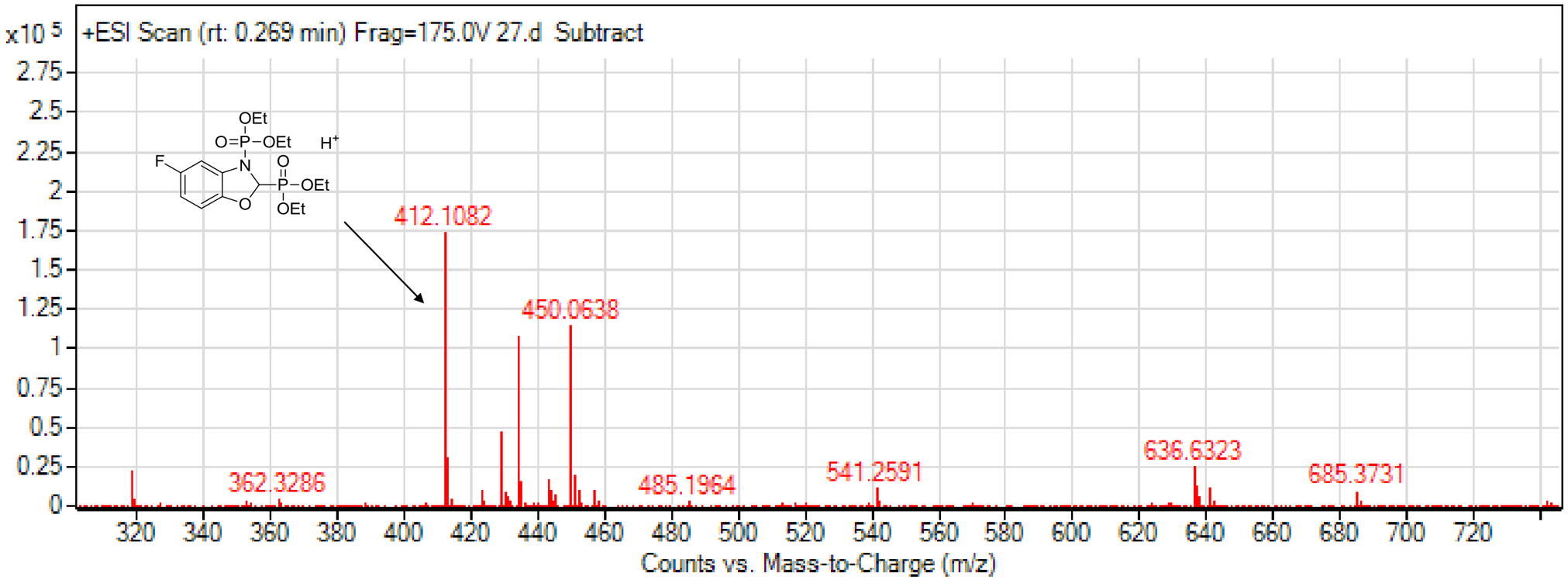


159.25
156.86
147.45
133.21
108.91
108.67
108.57
102.42
102.13
92.01
91.96
90.06
90.01
63.98
63.93
63.80
63.54
63.47
16.34
16.29
16.09
16.02
15.90
15.83

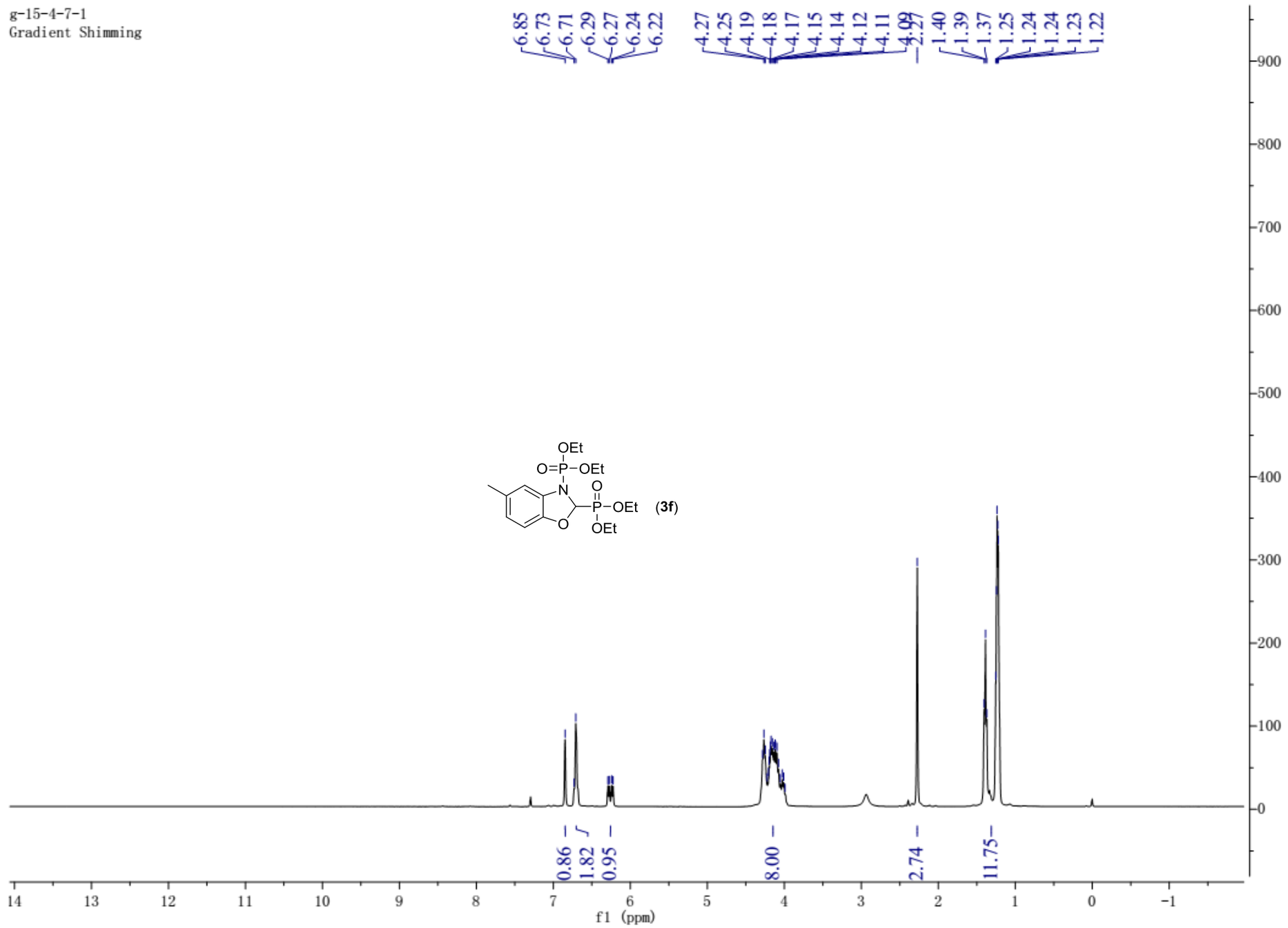


(**3e**)

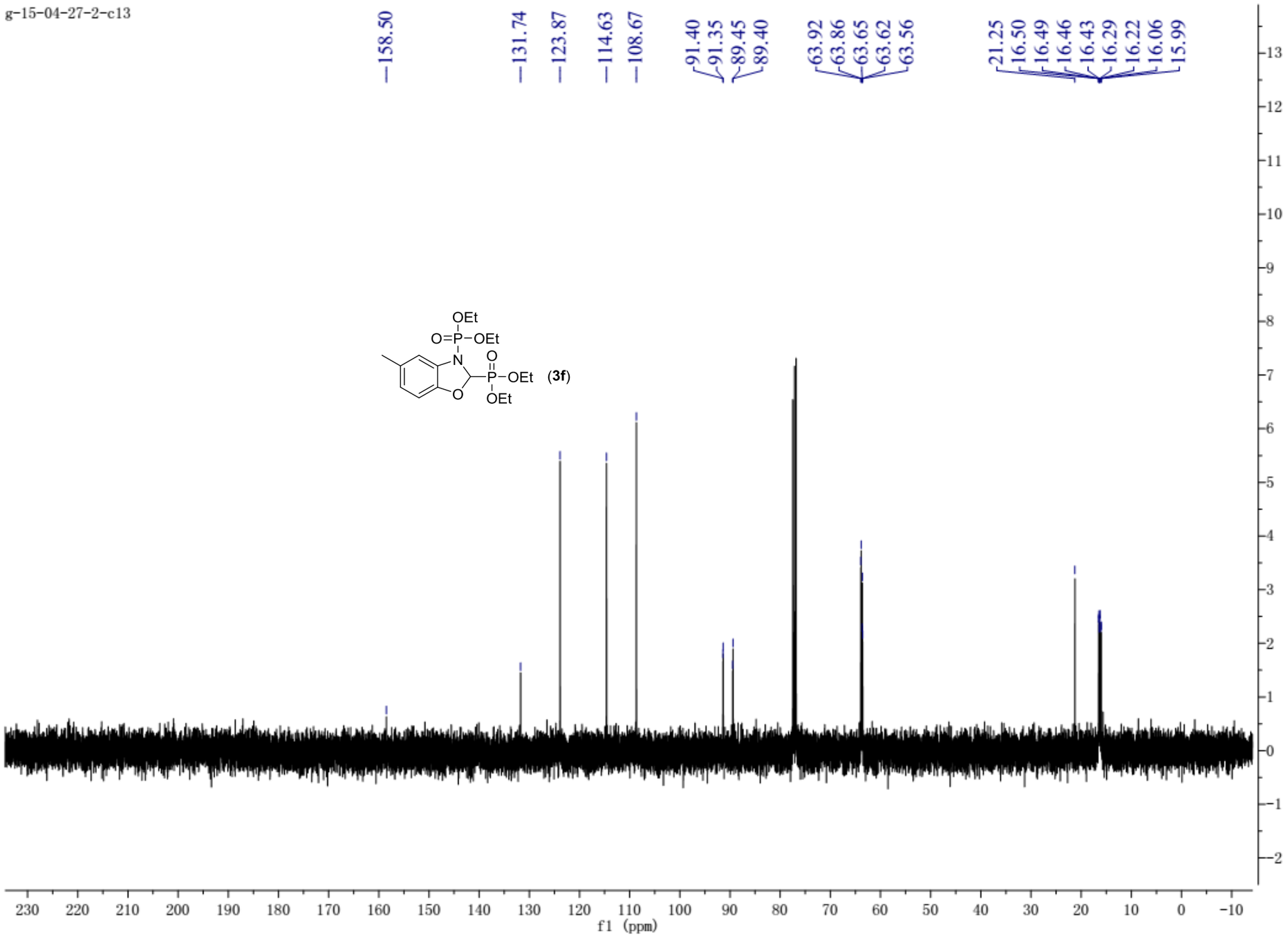

10.38
3.05
OEt
O=P–OEt
F
N
O
O
P–OEt
OEt
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
−100
50
200
150
100
50
0
−50
−100
f1 (ppm)


x10 5
+ESI Scan (rt: 0.269 min) Frag=175.0V 27.d Subtract
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
OEt
O=P–OEt
H+
F
N
O
P–OEt
O
OEt
412.1082
450.0638
362.3286
485.1964
541.2591
636.6323
685.3731
320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720
Counts vs. Mass-to-Charge (m/z)

g-15-4-7-1
Gradient Shimming

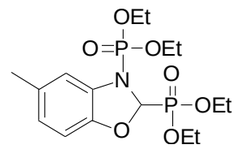


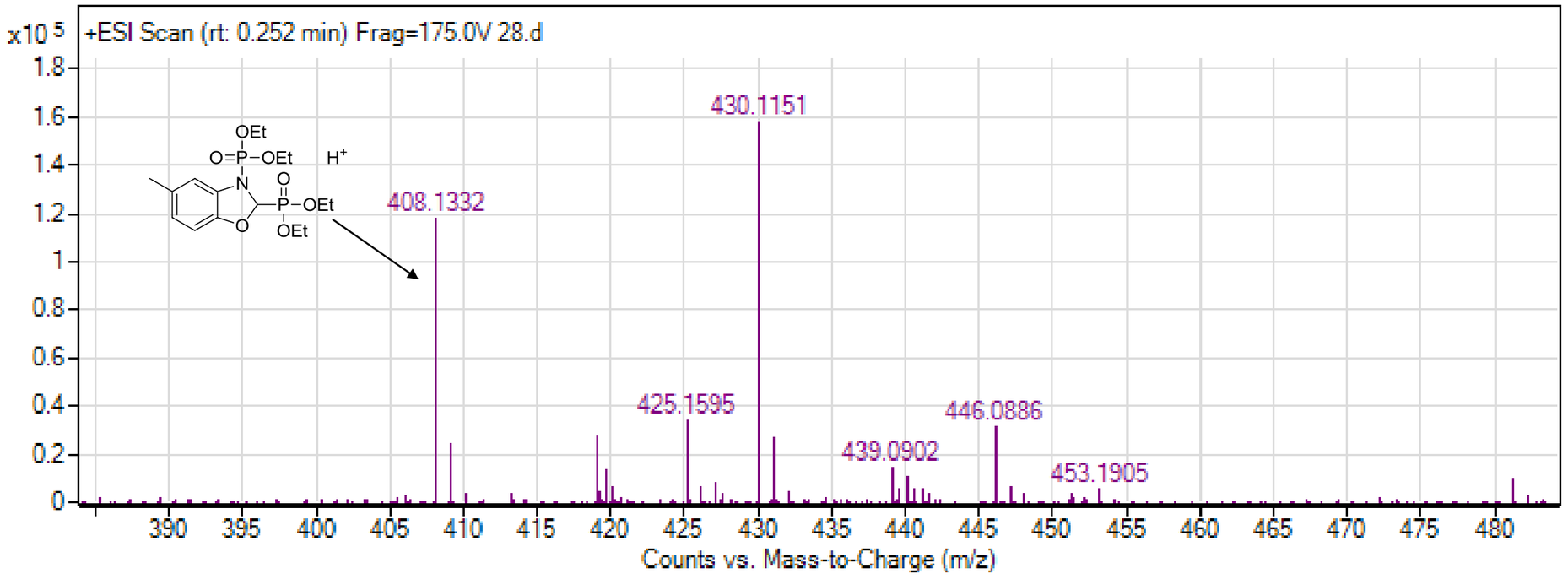
g-15-04-27-2-c13

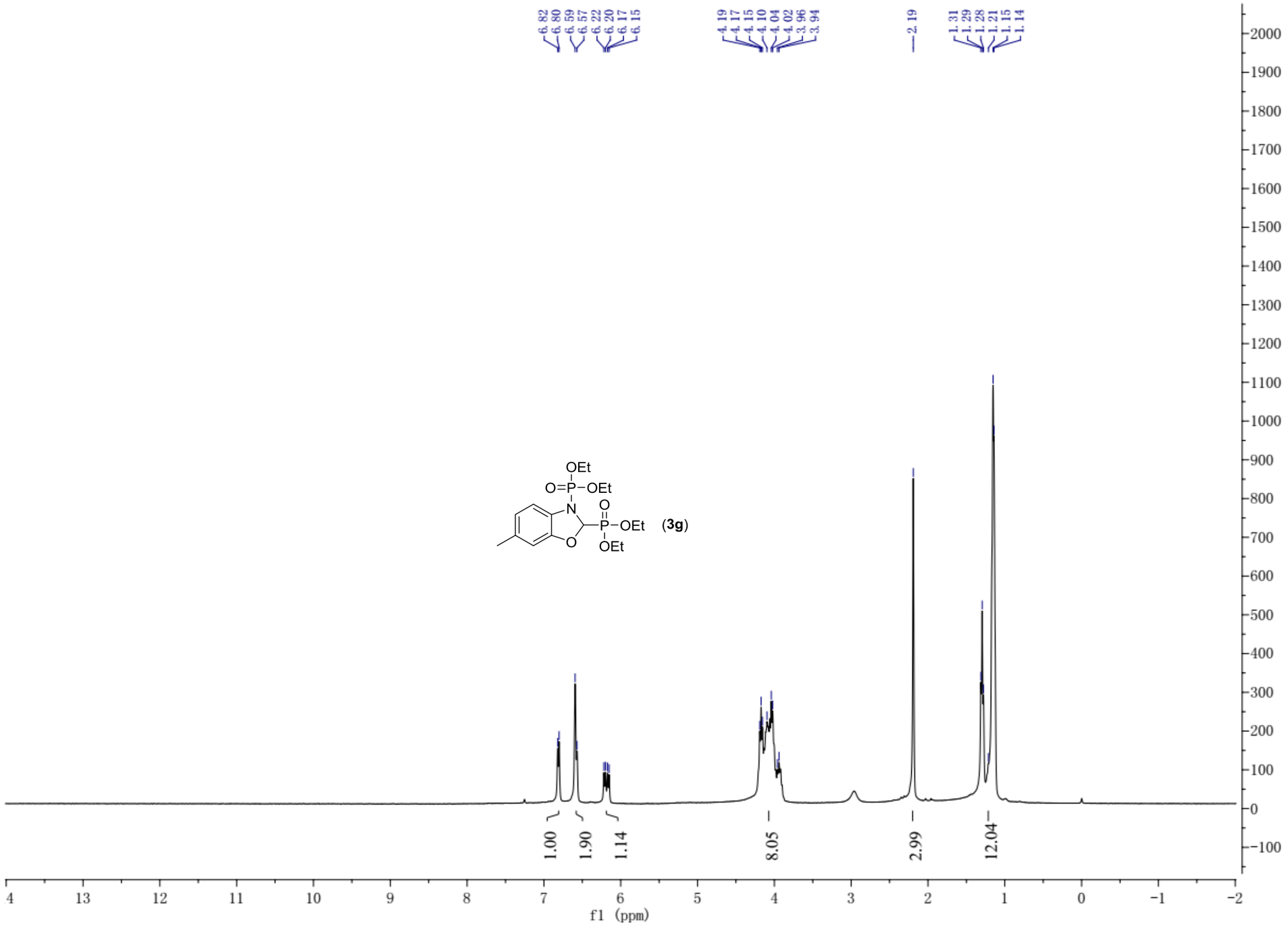


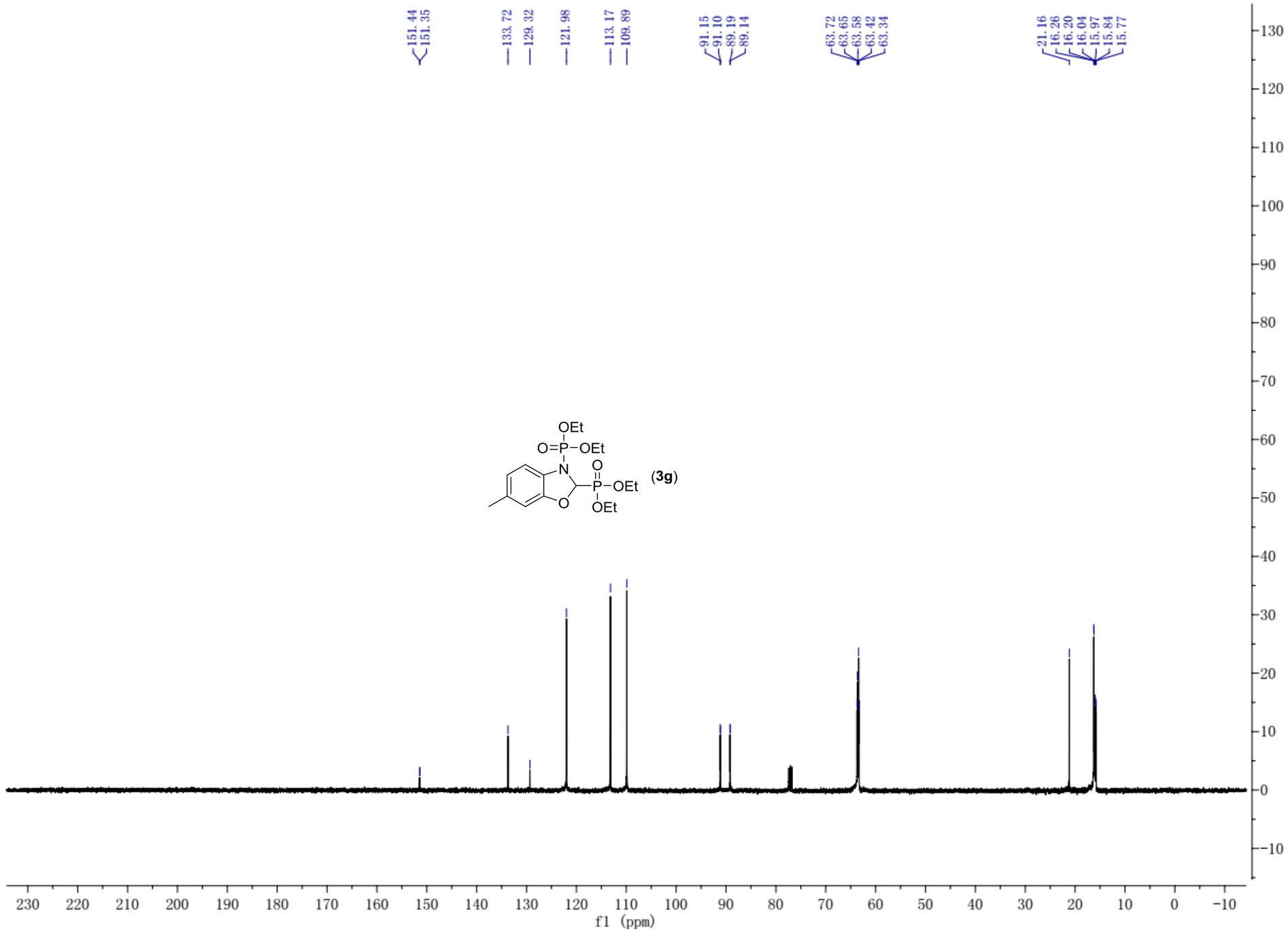
11.39
11.30

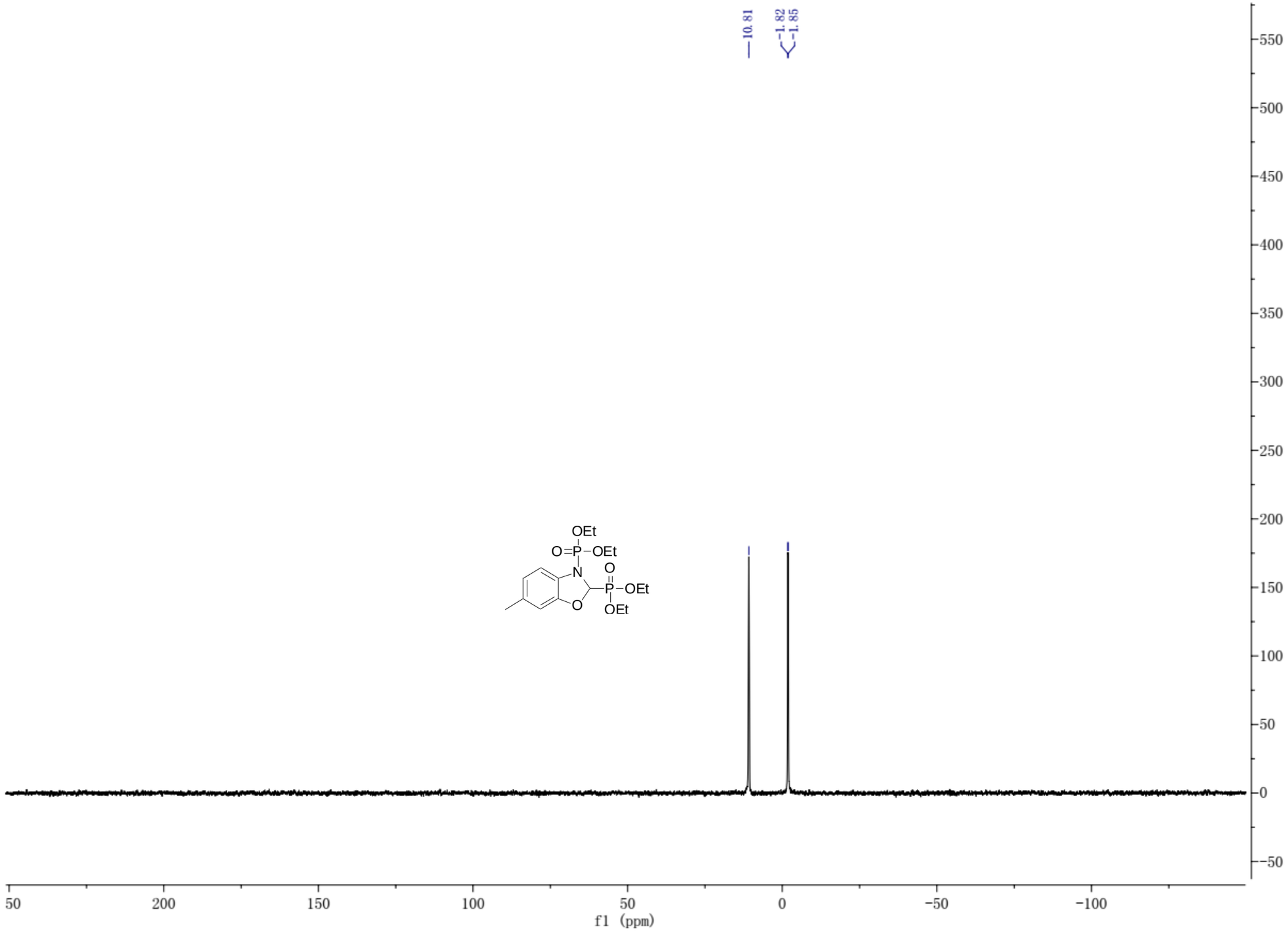
-1.52
-1.61

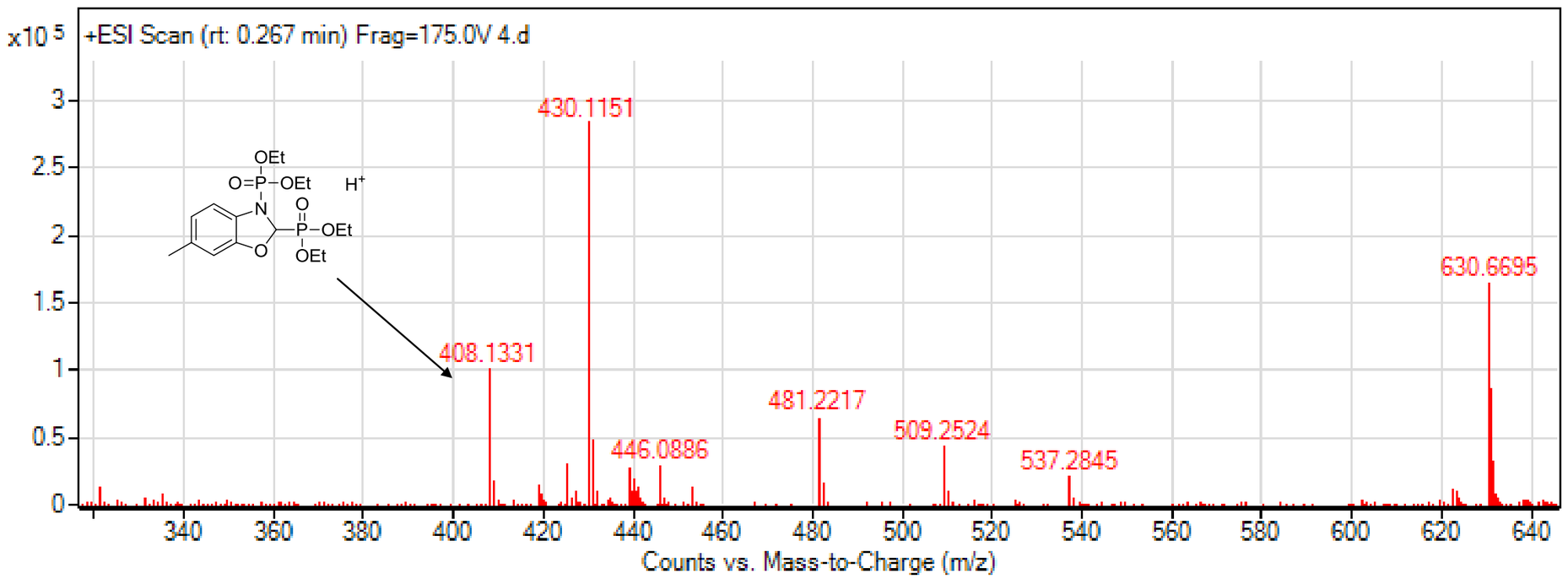


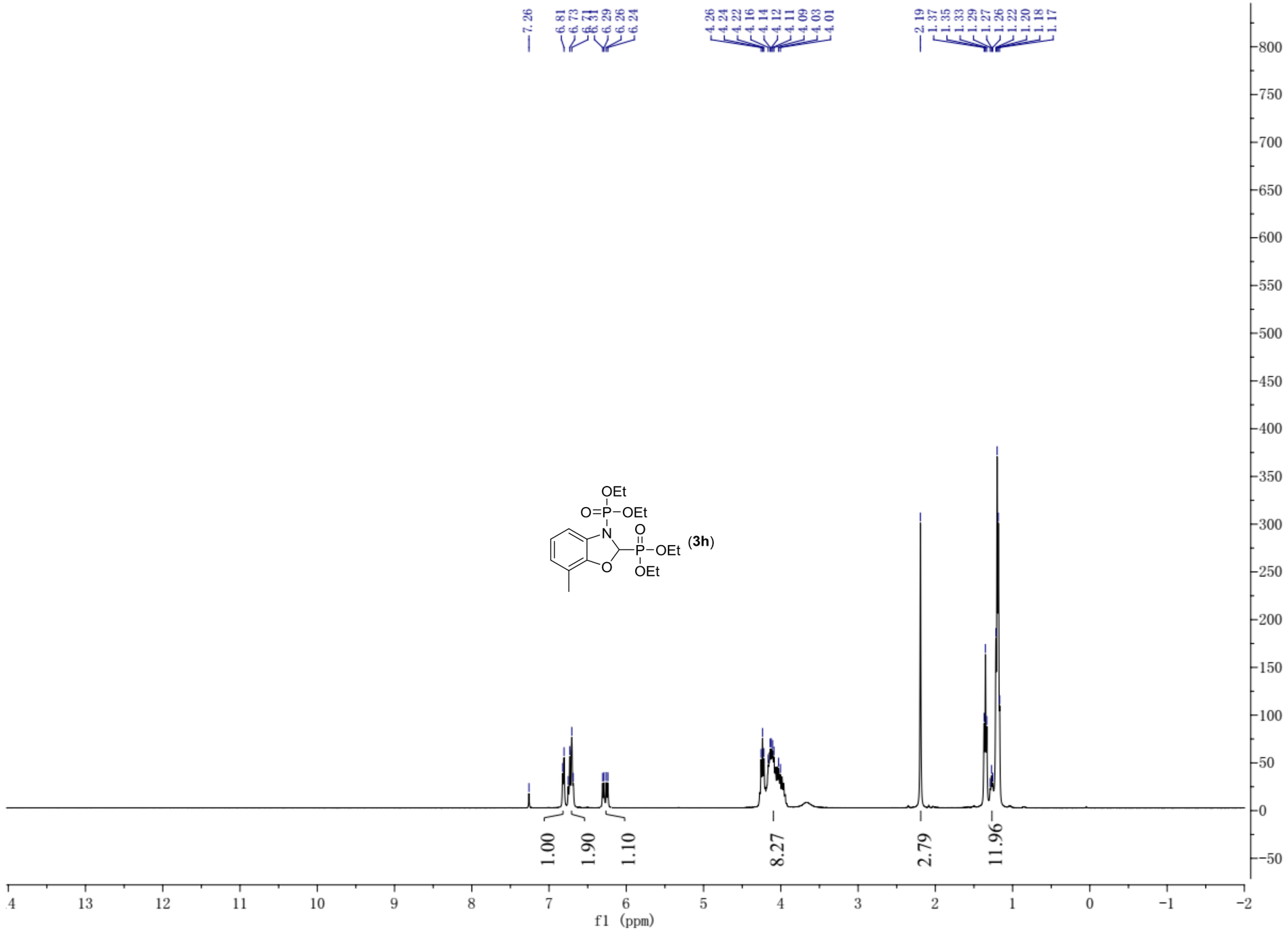

x10 5
+ESI Scan (rt: 0.252 min) Frag=175.0V 28.d
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
OEt
O=P–OEt
H+
N
O
P–OEt
O
OEt
408.1332
430.1151
425.1595
446.0886
439.0902
453.1905
390
395
400
405
410
415
420
425
430
435
440
445
450
455
460
465
470
475
480
Counts vs. Mass-to-Charge (m/z)

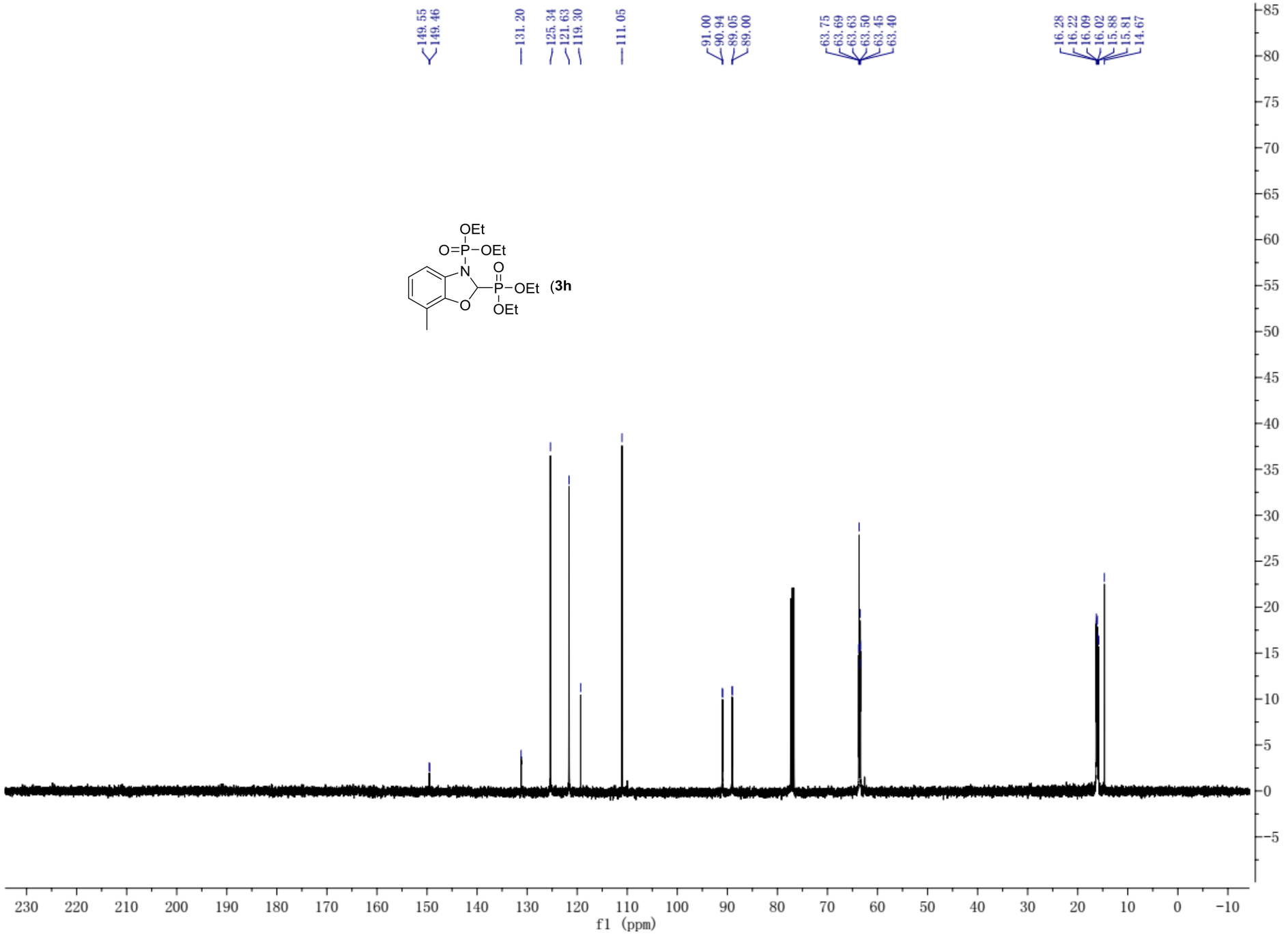

6.82
6.80
6.59
6.57
6.22
6.20
6.17
6.15
4.19
4.17
4.15
4.10
4.04
4.02
3.96
3.94
2.19
1.31
1.29
1.28
1.21
1.15
1.14
OEt
O=P–OEt
N
O
P–OEt
O
OEt
(3g)
1.00
1.90
1.14
8.05
2.99
12.04
f1 (ppm)

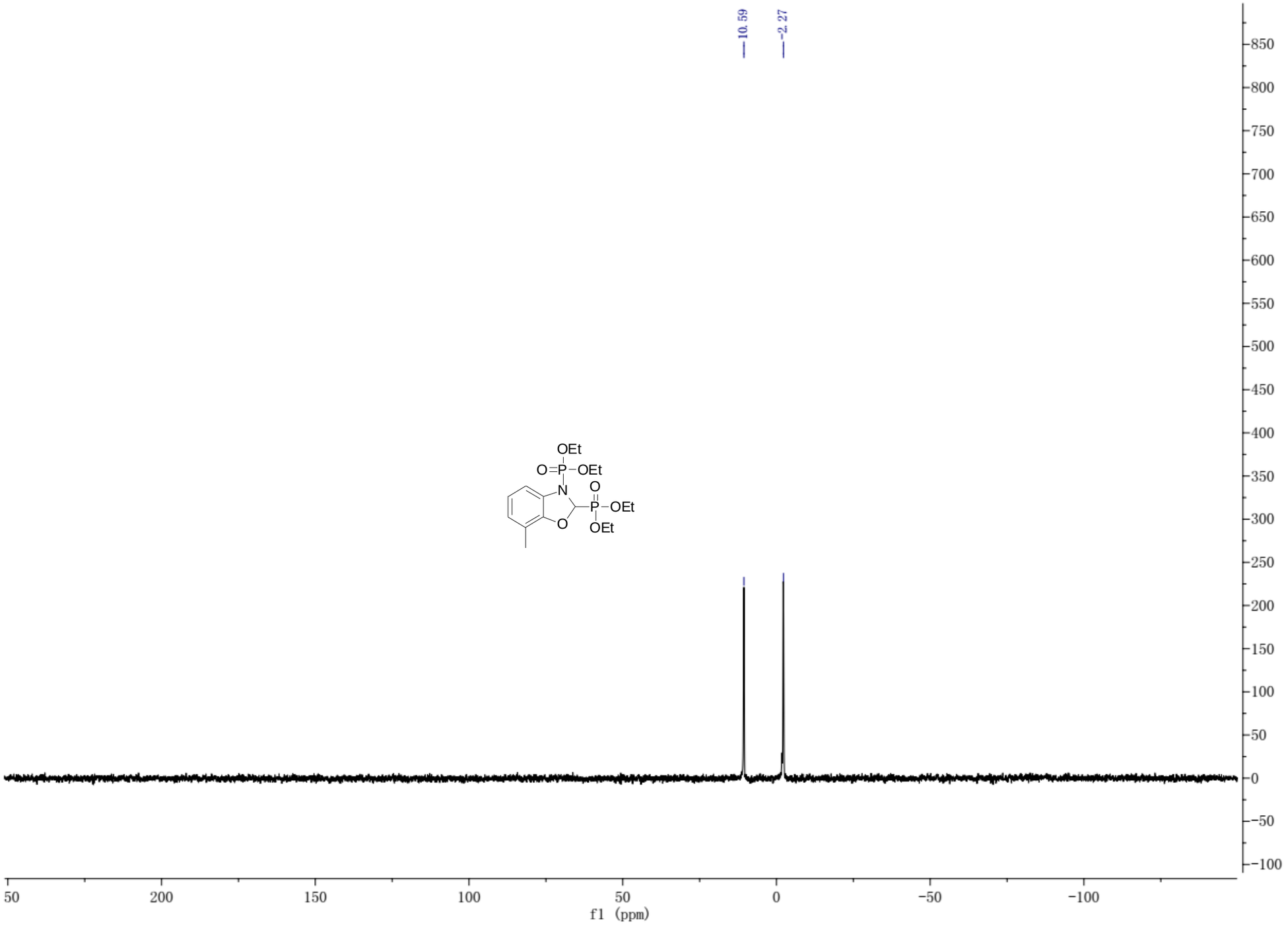

151.44
151.35
133.72
129.32
121.98
113.17
109.89
91.15
91.10
89.19
89.14
63.72
63.65
63.58
63.42
63.34
21.16
16.26
16.20
16.04
15.97
15.84
15.77
OEt
O=P−OEt
N
O
O
P−OEt
OEt
O
(3g)
f1 (ppm)

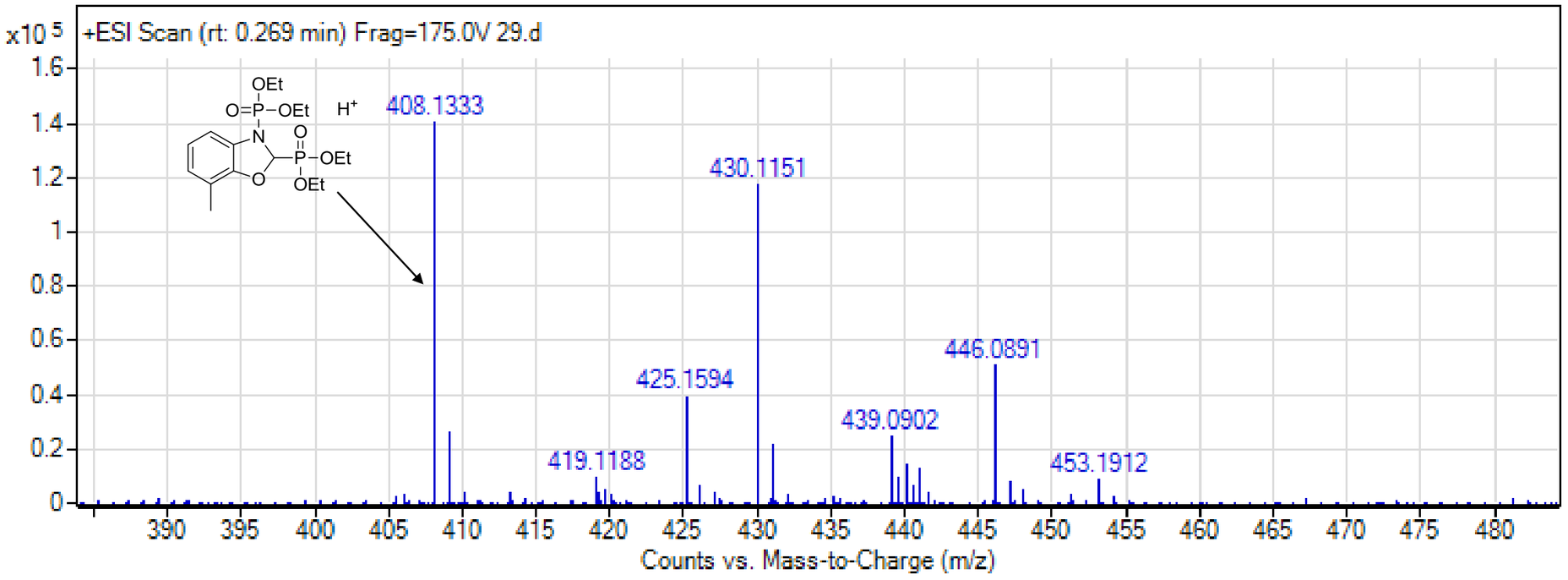

10.81
-1.82
-1.85
OEt
O=P-OEt
N
O
P-OEt
O
OEt
550
500
450
400
350
300
250
200
150
100
50
0
-50
50
200
150
100
50
0
-50
-100
f1 (ppm)


x10 5
+ESI Scan (rt: 0.267 min) Frag=175.0V 4.d
3
2.5
2
1.5
1
0.5
0
430.1151
630.6695
408.1331
481.2217
509.2524
446.0886
537.2845
340
360
380
400
420
440
460
480
500
520
540
560
580
600
620
640
Counts vs. Mass-to-Charge (m/z)
OEt
O=P–OEt
H+
N
O
P–OEt
O
OEt

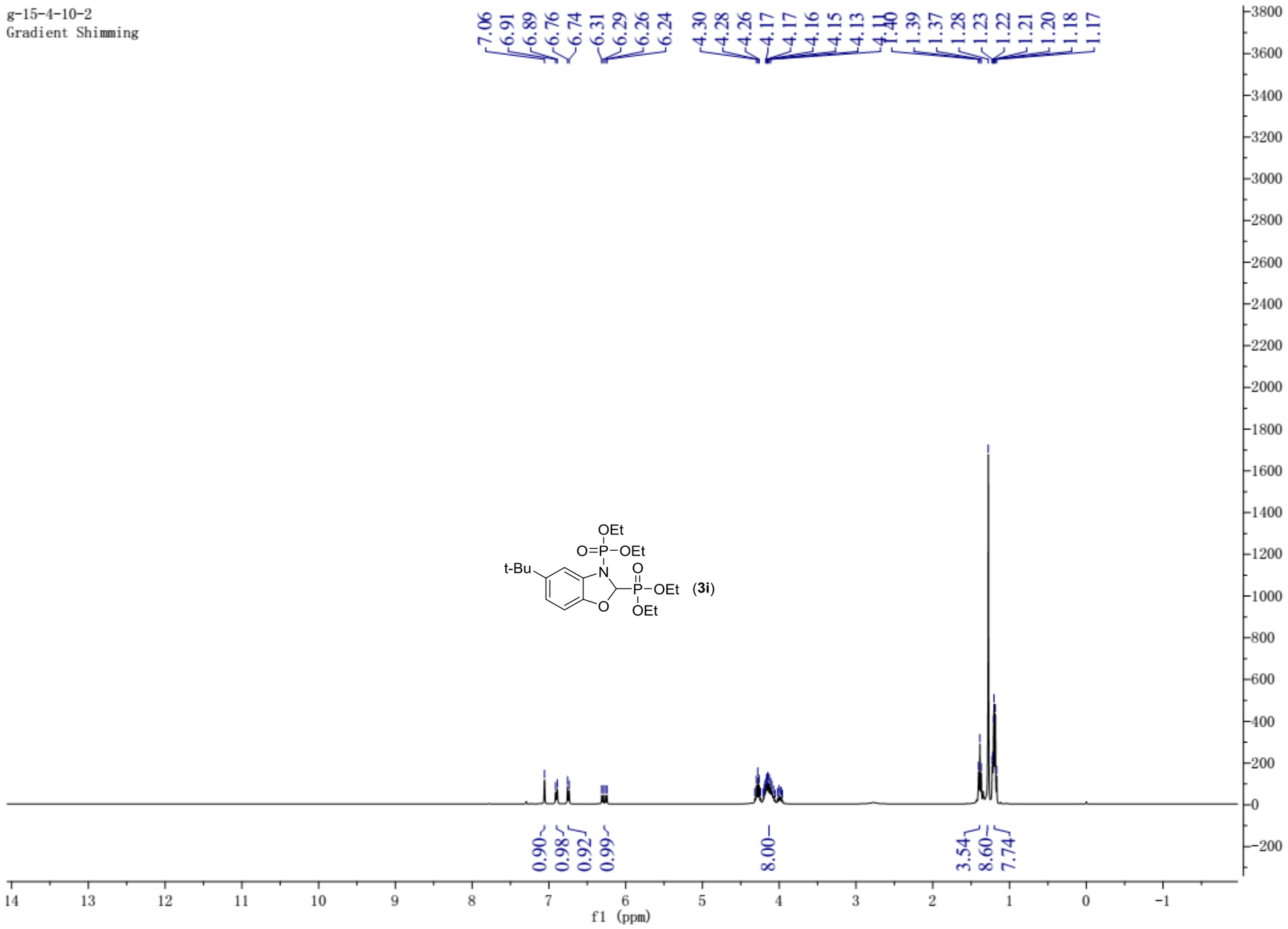

7.26
6.81
6.73
6.31
6.29
6.26
6.24
4.26
4.24
4.22
4.16
4.14
4.12
4.11
4.09
4.03
4.01
2.19
1.37
1.35
1.33
1.29
1.27
1.26
1.22
1.20
1.18
1.17
OEt
O=P−OEt
N
O
O
P−OEt
OEt
(3h)
1.00
1.90
1.10
8.27
2.79
11.96
f1 (ppm)


149.55
149.46
131.20
125.34
121.63
119.30
111.05
91.00
90.94
89.05
89.00
63.75
63.69
63.63
63.50
63.45
63.40
16.28
16.22
16.09
16.02
15.88
15.81
14.67
OEt
O=P−OEt
N
O
P−OEt
O
OEt
(3h
f1 (ppm)

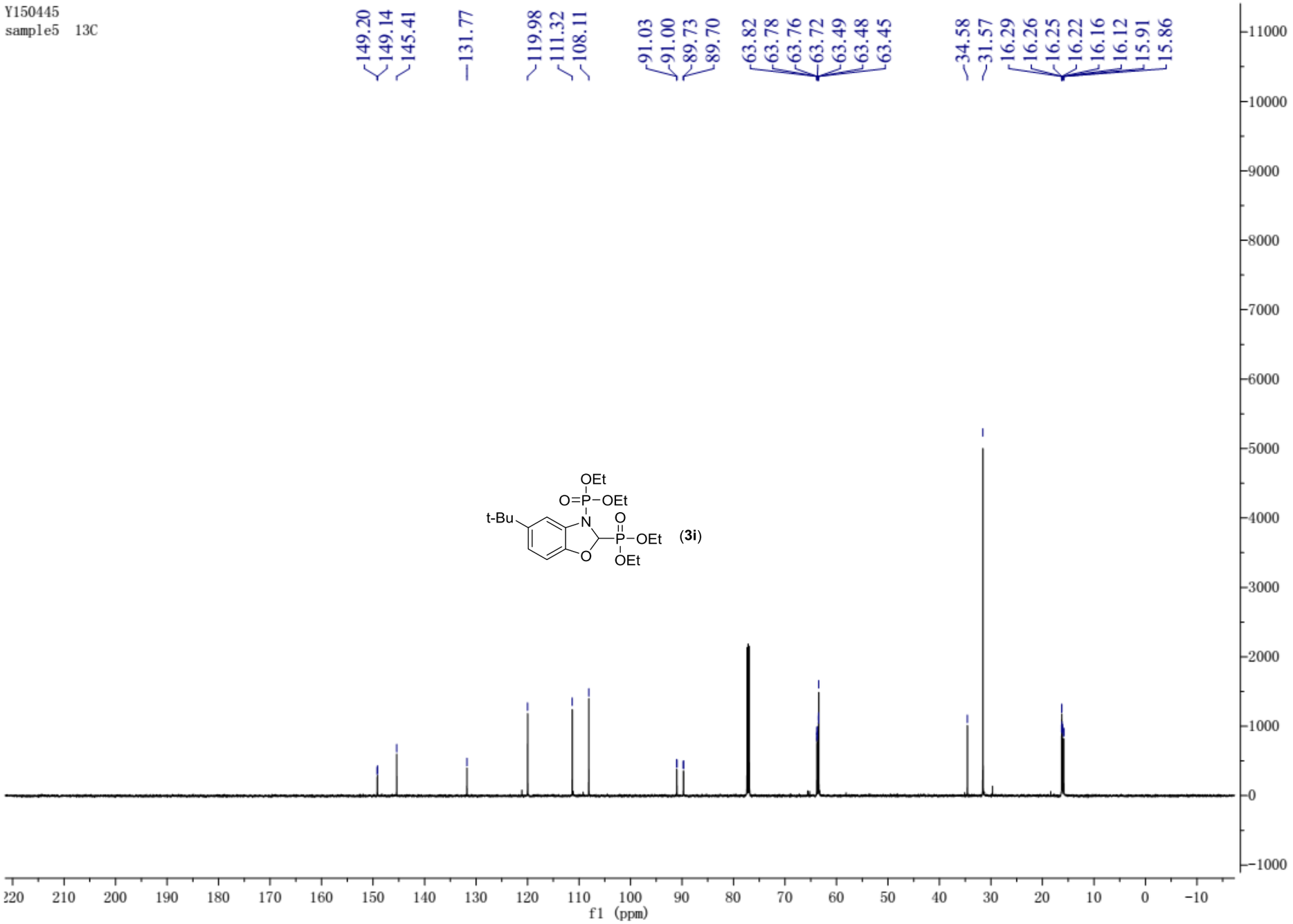

10.59
2.27
OEt
O=P−OEt
N
O
P−OEt
O
OEt
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
−100
50
200
150
100
50
0
−50
−100
f1 (ppm)


x10 5
+ESI Scan (rt: 0.269 min) Frag=175.0V 29.d
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
OEt
O=P–OEt
H+
N
O
P–OEt
O
OEt
408.1333
430.1151
446.0891
425.1594
439.0902
419.1188
453.1912
390
395
400
405
410
415
420
425
430
435
440
445
450
455
460
465
470
475
480
Counts vs. Mass-to-Charge (m/z)

g-15-4-10-2
Gradient Shimming

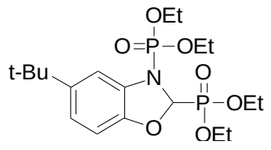


Y150445
sample5 13C



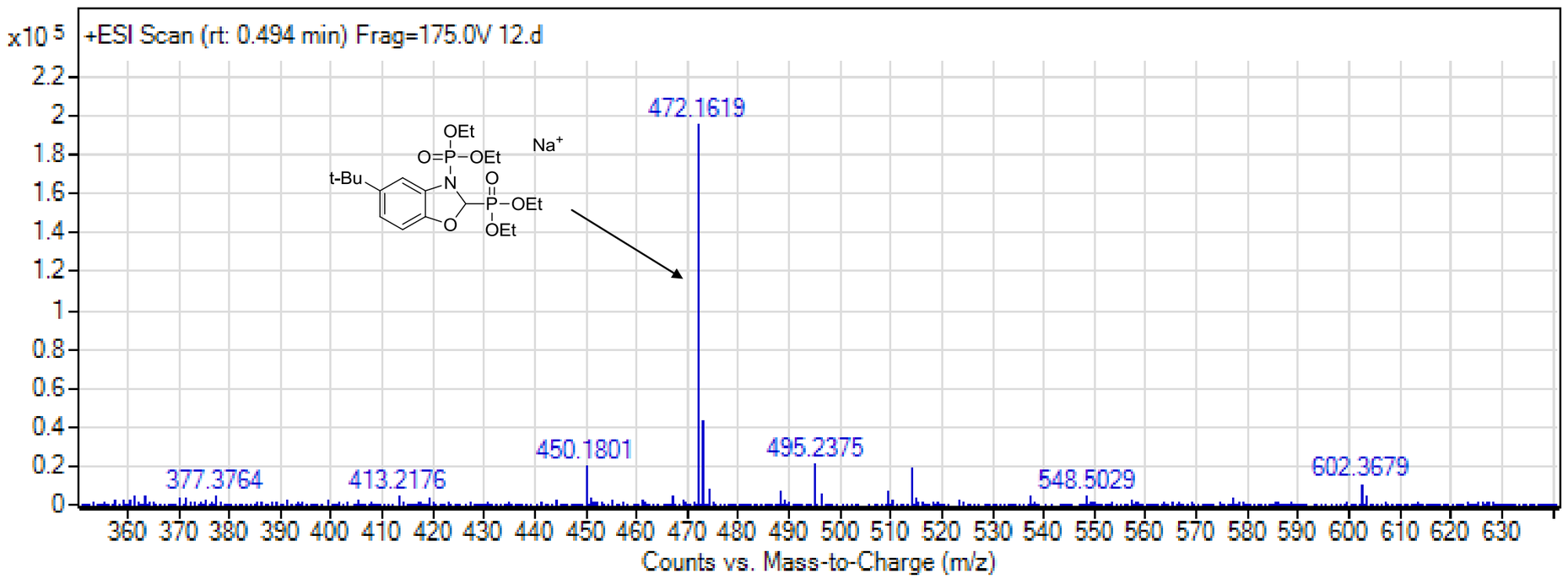
Y150445
sample5 31P

11.30
11.21
-1.64
-1.73

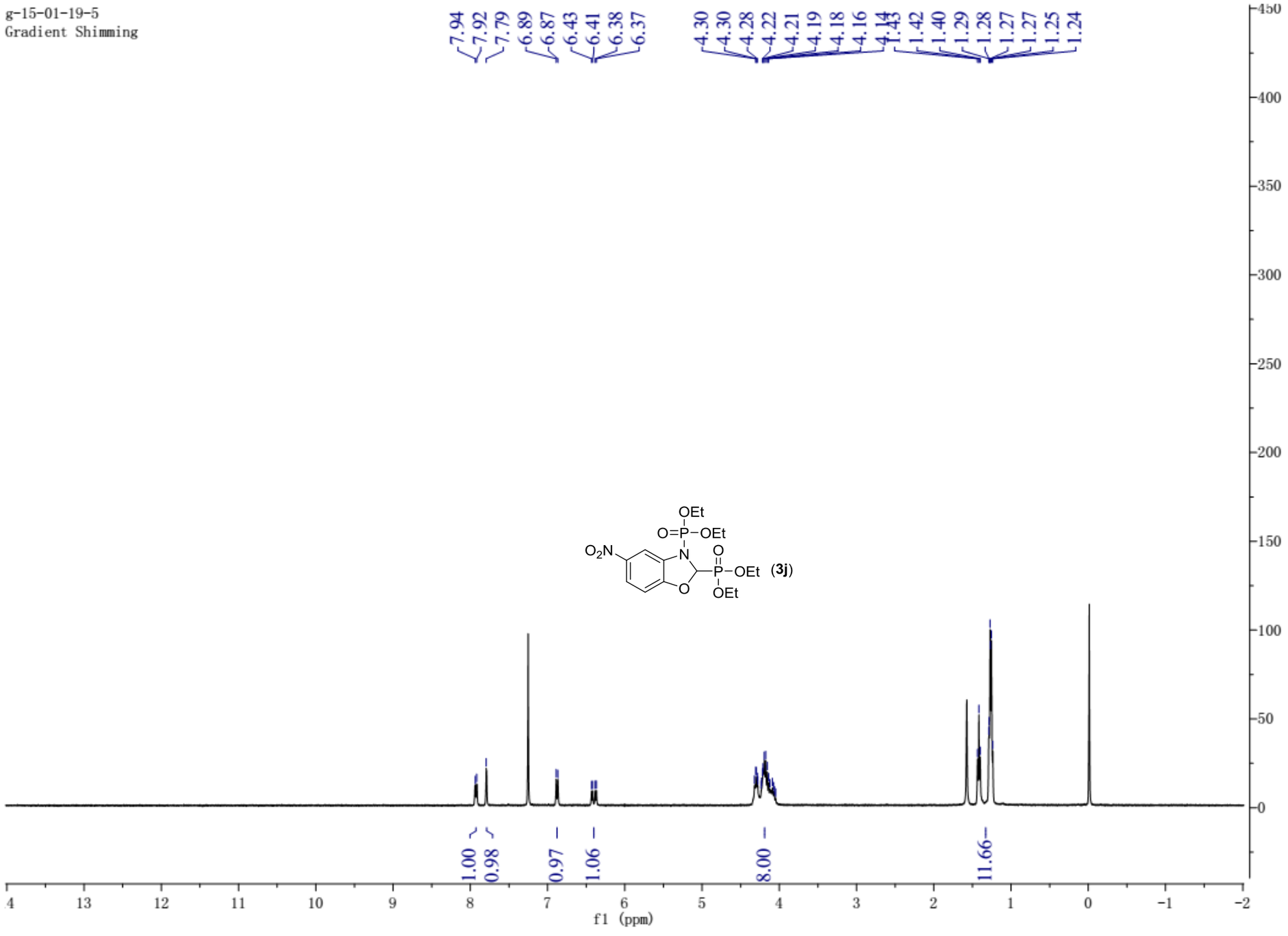


280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000

30 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

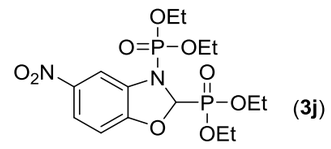

x10 5
+ESI Scan (rt: 0.494 min) Frag=175.0V 12.d
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
472.1619
450.1801
495.2375
377.3764
413.2176
548.5029
602.3679
OEt
O=P–OEt
t-Bu
N
O
P–OEt
O
OEt
Na+
360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560 570 580 590 600 610 620 630
Counts vs. Mass-to-Charge (m/z)

g-15-01-19-5
Gradient Shimming



Y150361
sample3 13C

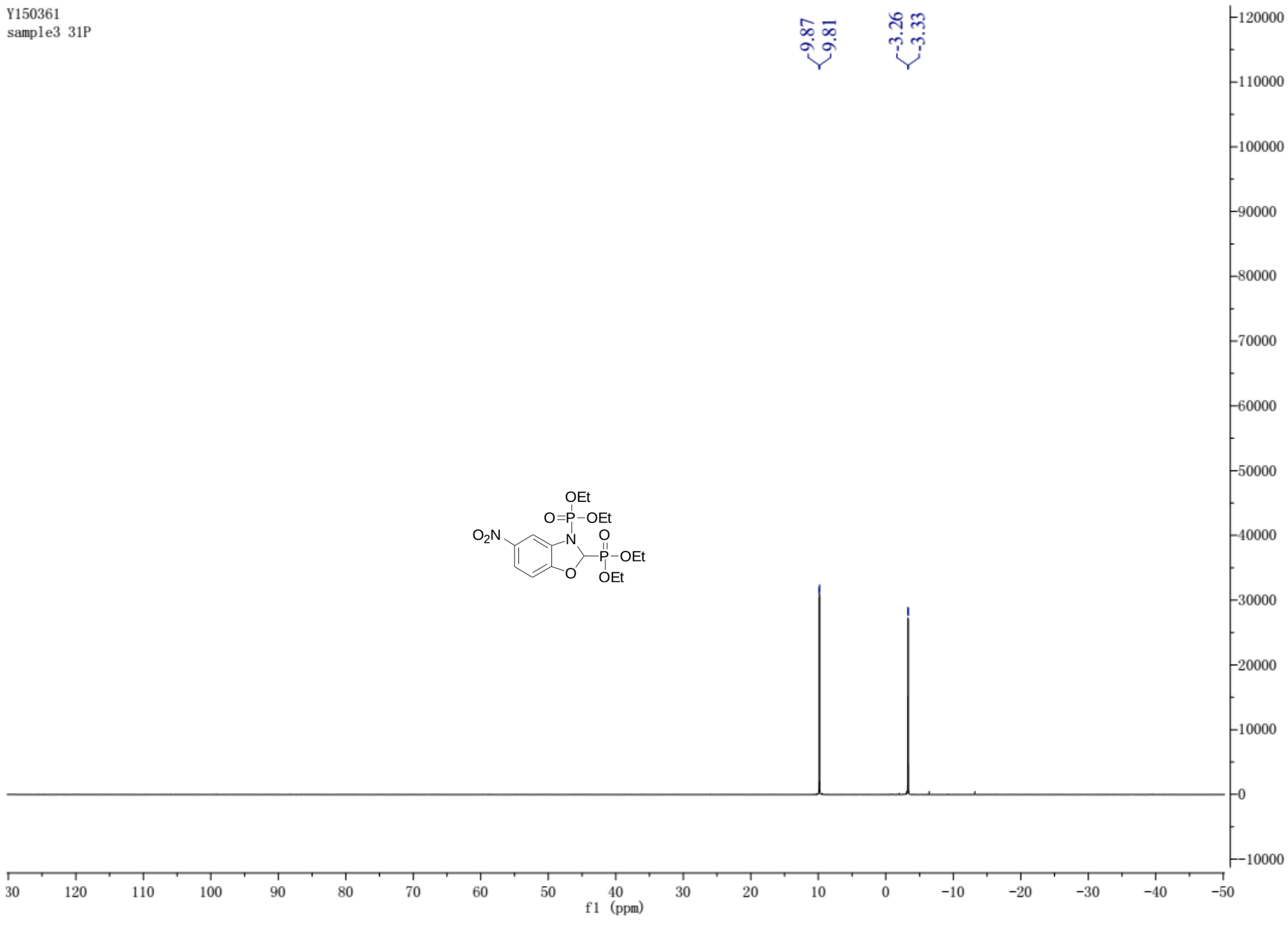
156.84
156.78
143.23
133.88
133.86
121.34
108.75
108.32
92.94
92.90
91.64
91.60
64.53
64.49
64.39
64.35
64.27
64.23
63.91
63.86
16.50
16.46
16.21
16.17
16.03
15.99

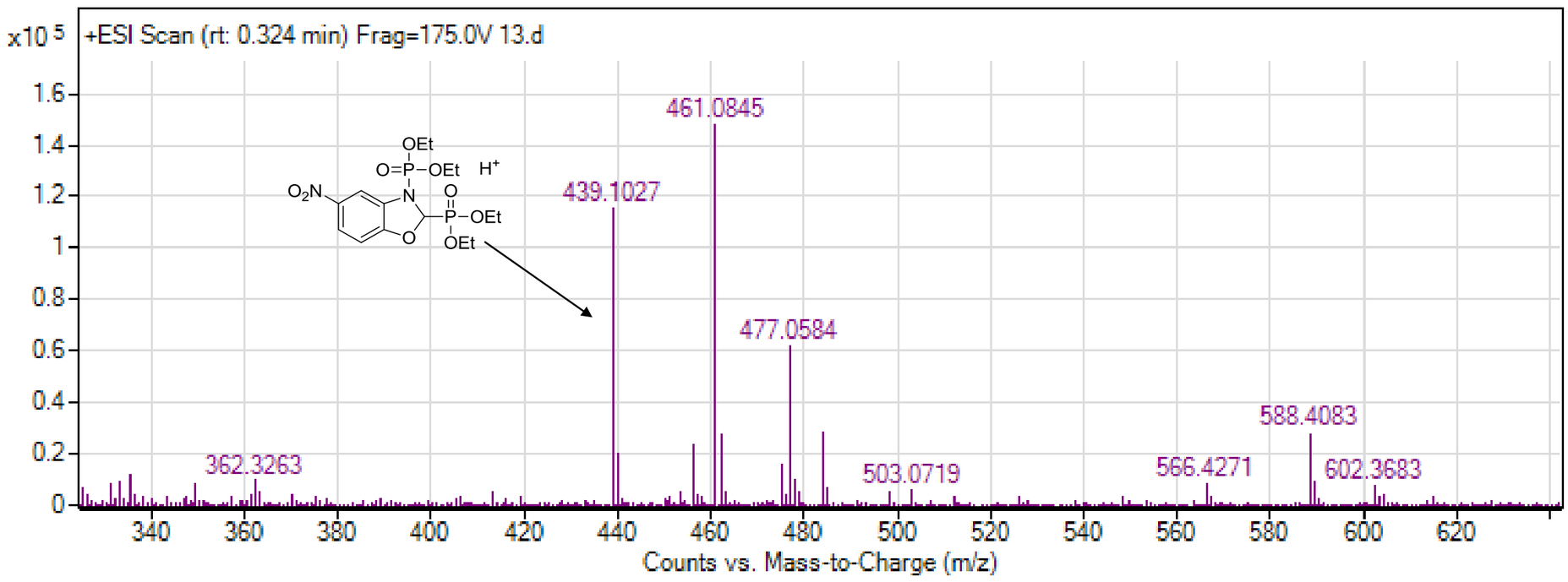


(**3j**)

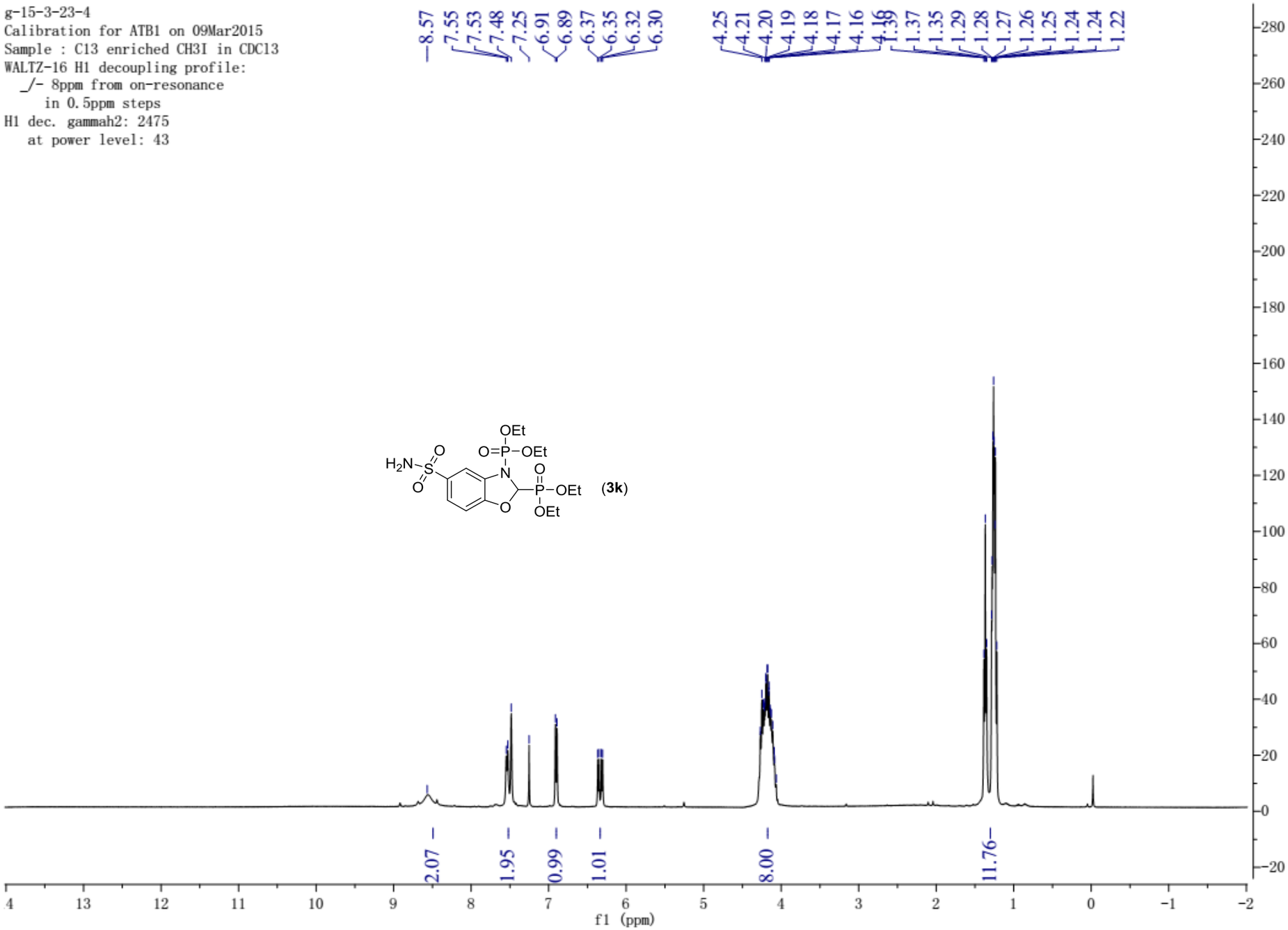
f1 (ppm)

Y150361
sample3 31P



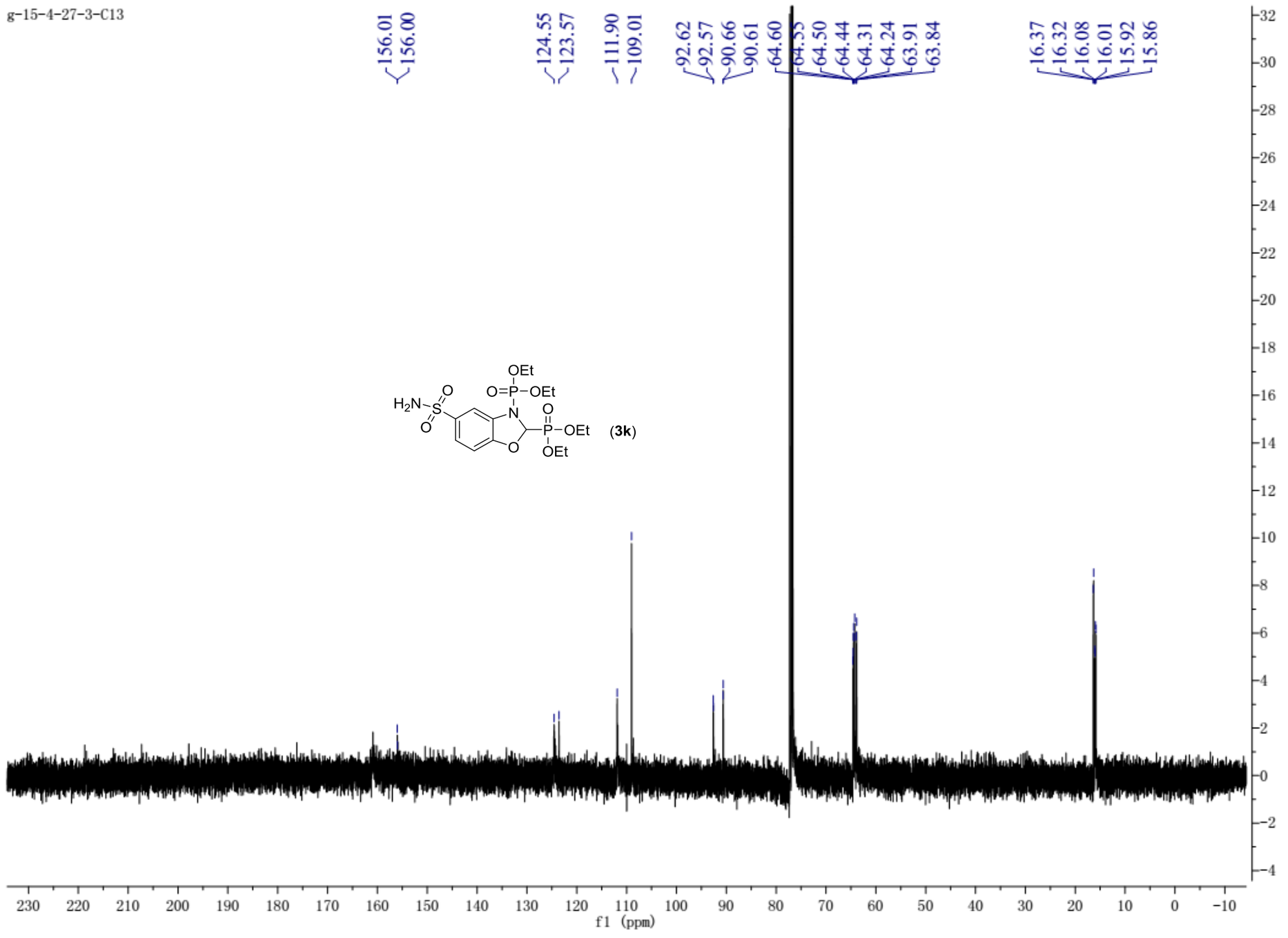

x10 5
+ESI Scan (rt: 0.324 min) Frag=175.0V 13.d
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
461.0845
439.1027
477.0584
588.4083
362.3263
503.0719
566.4271
602.3683
340
360
380
400
420
440
460
480
500
520
540
560
580
600
620
Counts vs. Mass-to-Charge (m/z)
OEt
O=P–OEt
H+
O2N
N
O
O
P–OEt
O
OEt

g-15-3-23-4
Calibration for ATB1 on 09Mar2015
Sample : C13 enriched CH3I in CDCl3
WALTZ-16 H1 decoupling profile:
  _/- 8ppm from on-resonance
      in 0.5ppm steps
H1 dec. gammah2: 2475
   at power level: 43

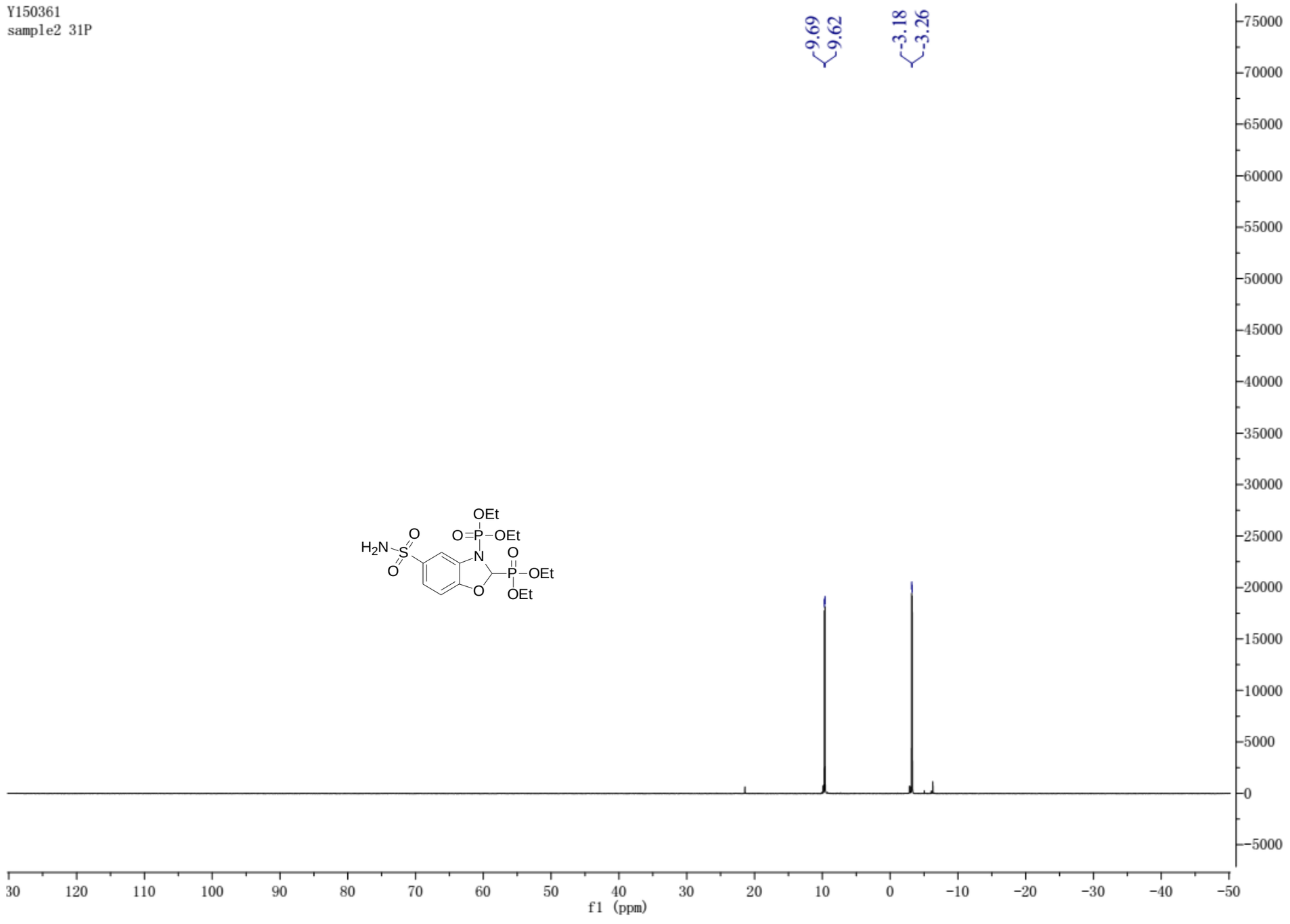


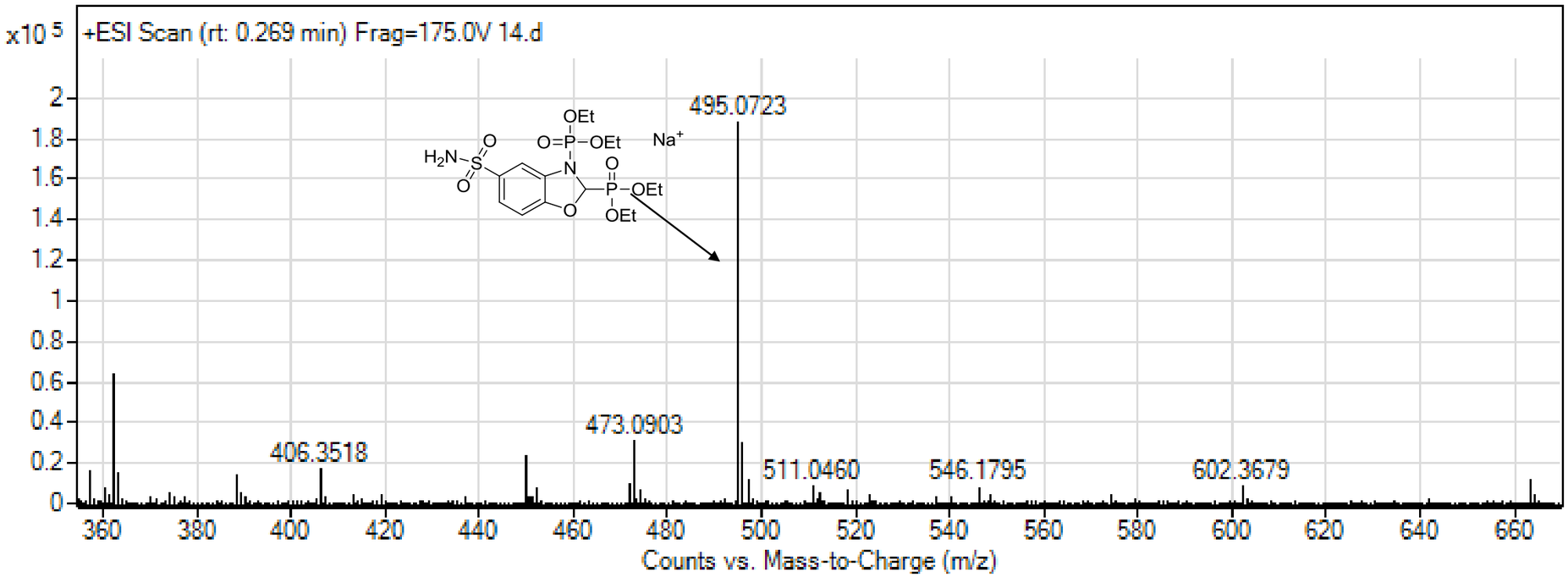
(**3k**)

g-15-4-27-3-C13

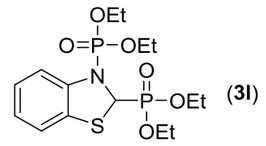

156.01
156.00
124.55
123.57
111.90
109.01
92.62
92.57
90.66
90.61
64.60
64.55
64.50
64.44
64.31
64.24
63.91
63.84
16.37
16.32
16.08
16.01
15.92
15.86
OEt
O=P–OEt
H2N
S
O
N
O
P–OEt
OEt
(3k)
f1 (ppm)

Y150361
sample2 31P



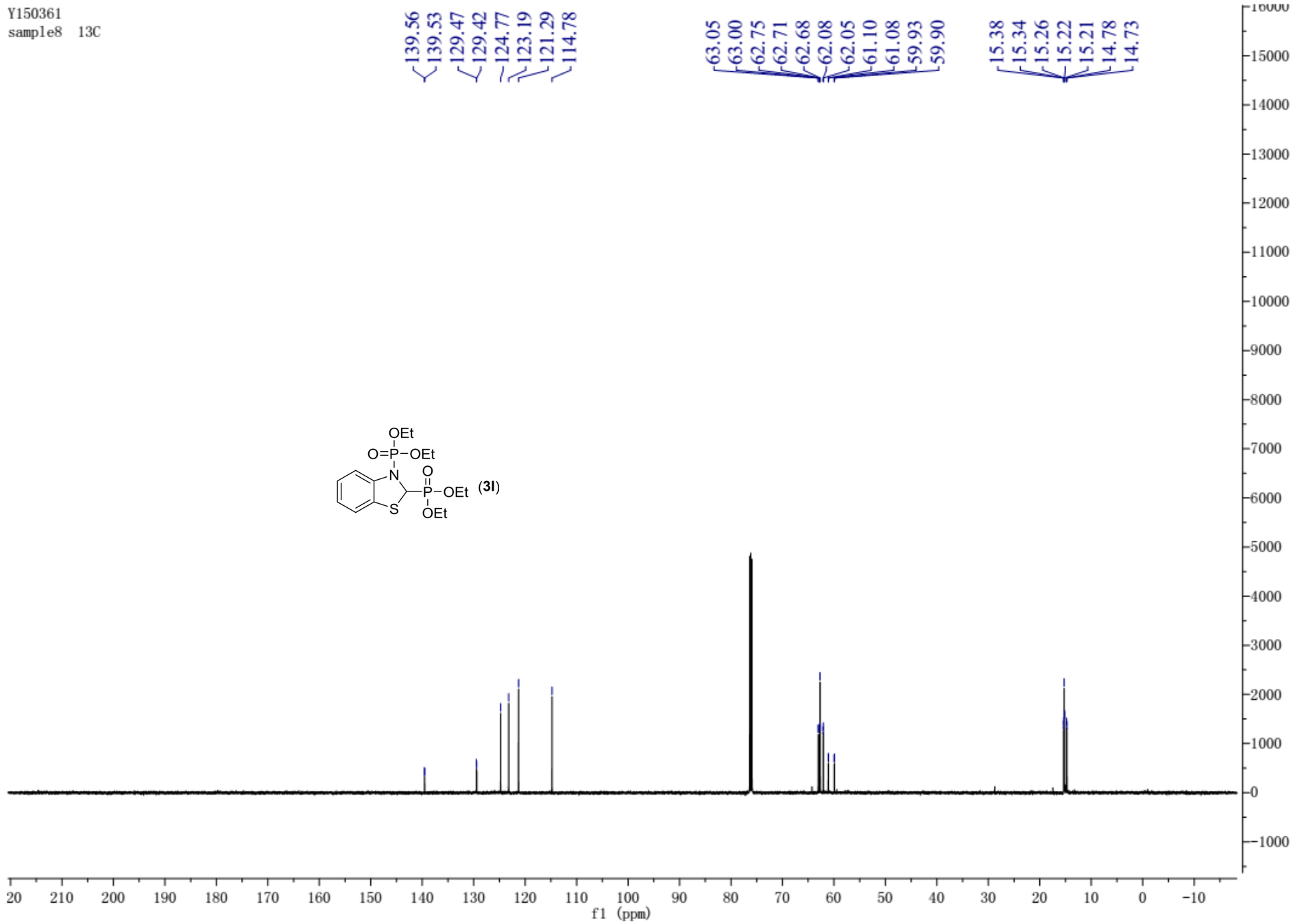

x10 5
+ESI Scan (rt: 0.269 min) Frag=175.0V 14.d
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
360
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
Counts vs. Mass-to-Charge (m/z)
495.0723
473.0903
406.3518
511.0460
546.1795
602.3679
OEt
O=P–OEt
Na+
H2N
S
O
N
O
P
OEt
OEt

g-15-3-24-1
Calibration for ATB1 on 09Mar2015
Sample : C13 enriched CH3I in CDCl3
WALTZ-16 H1 decoupling profile:
  _/- 8ppm from on-resonance
     in 0.5ppm steps
H1 dec. gammah2: 2475
   at power level: 43

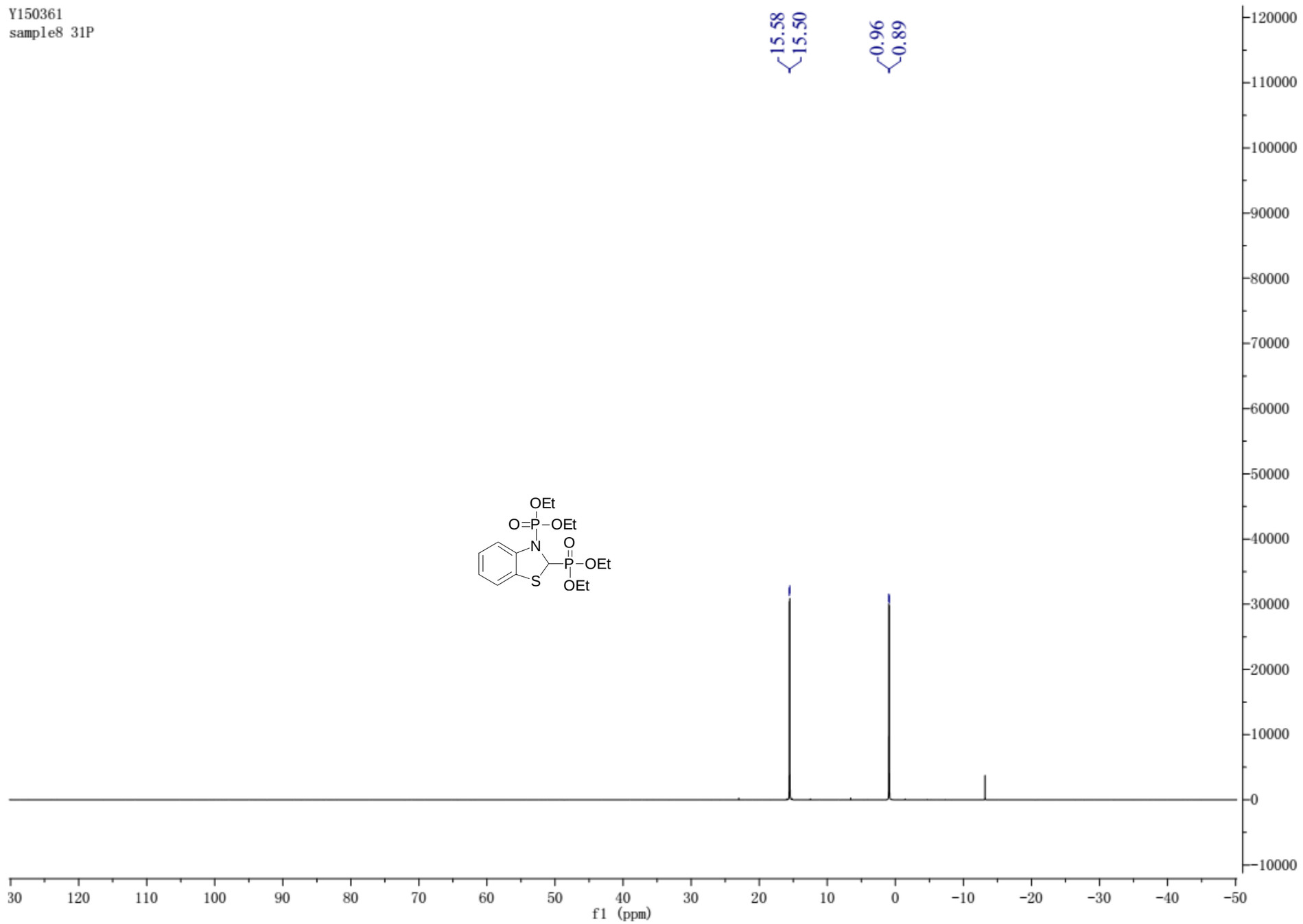


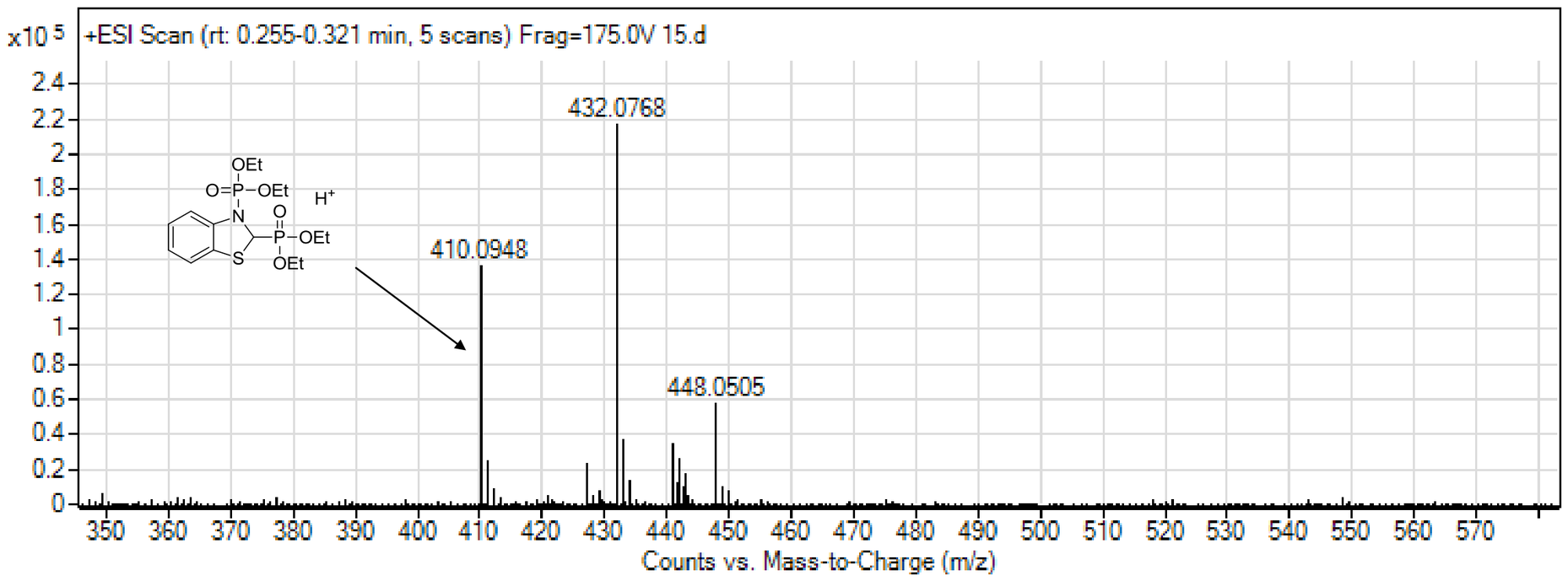
(**3l**)

Y150361
sample8 13C

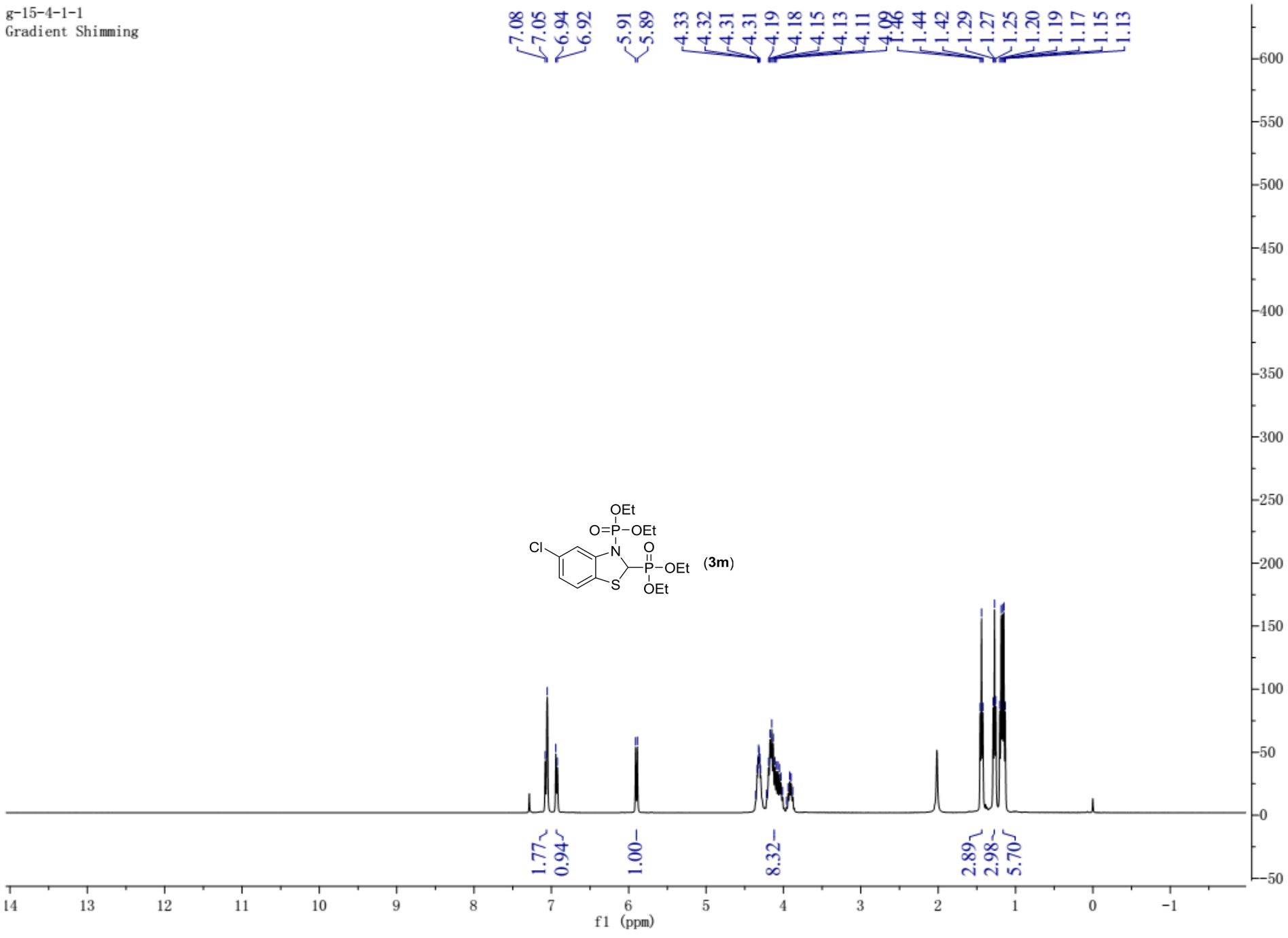


Y150361
sample8 31P




x10 5
+ESI Scan (rt: 0.255-0.321 min, 5 scans) Frag=175.0V 15.d
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
432.0768
410.0948
448.0505
OEt
O=P–OEt
N
H+
O
P–OEt
S
OEt
350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560 570
Counts vs. Mass-to-Charge (m/z)

g-15-4-1-1
Gradient Shimming

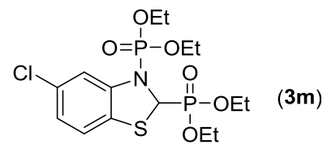


Y150361
sample10 13C

141.97
141.95
131.34
129.18
129.12
124.00
122.67
116.08

64.08
64.03
64.01
63.98
63.89
63.84
63.42
63.38
62.74
62.71
61.56
61.54

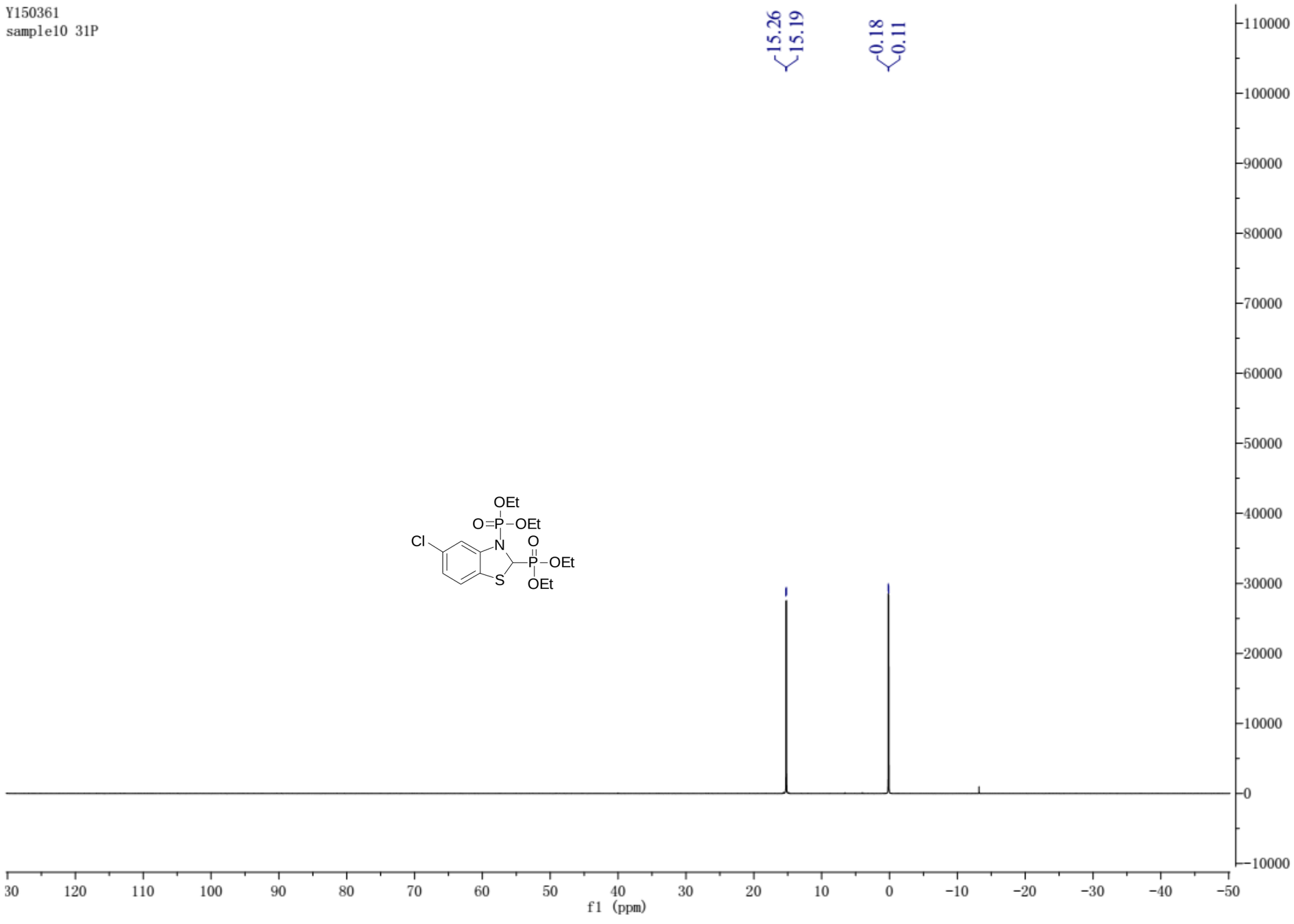
16.41
16.37
16.33
16.30
16.24
16.19
15.82
15.77

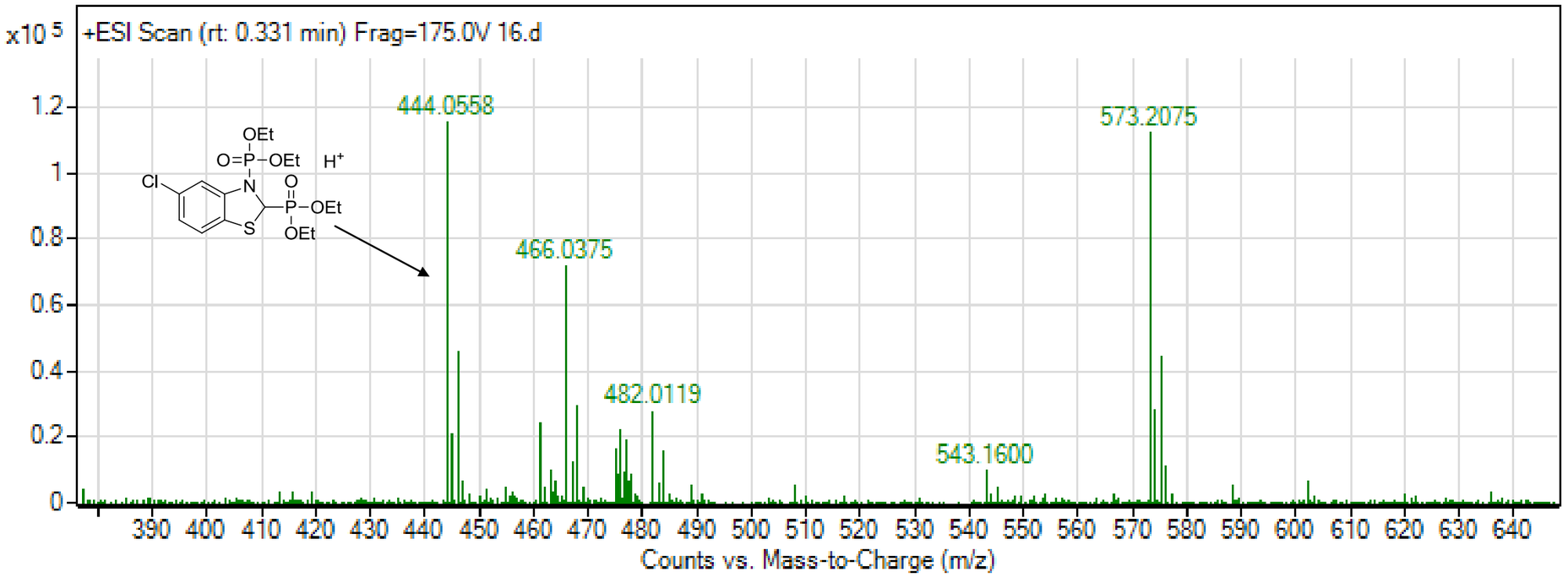


(**3m**)

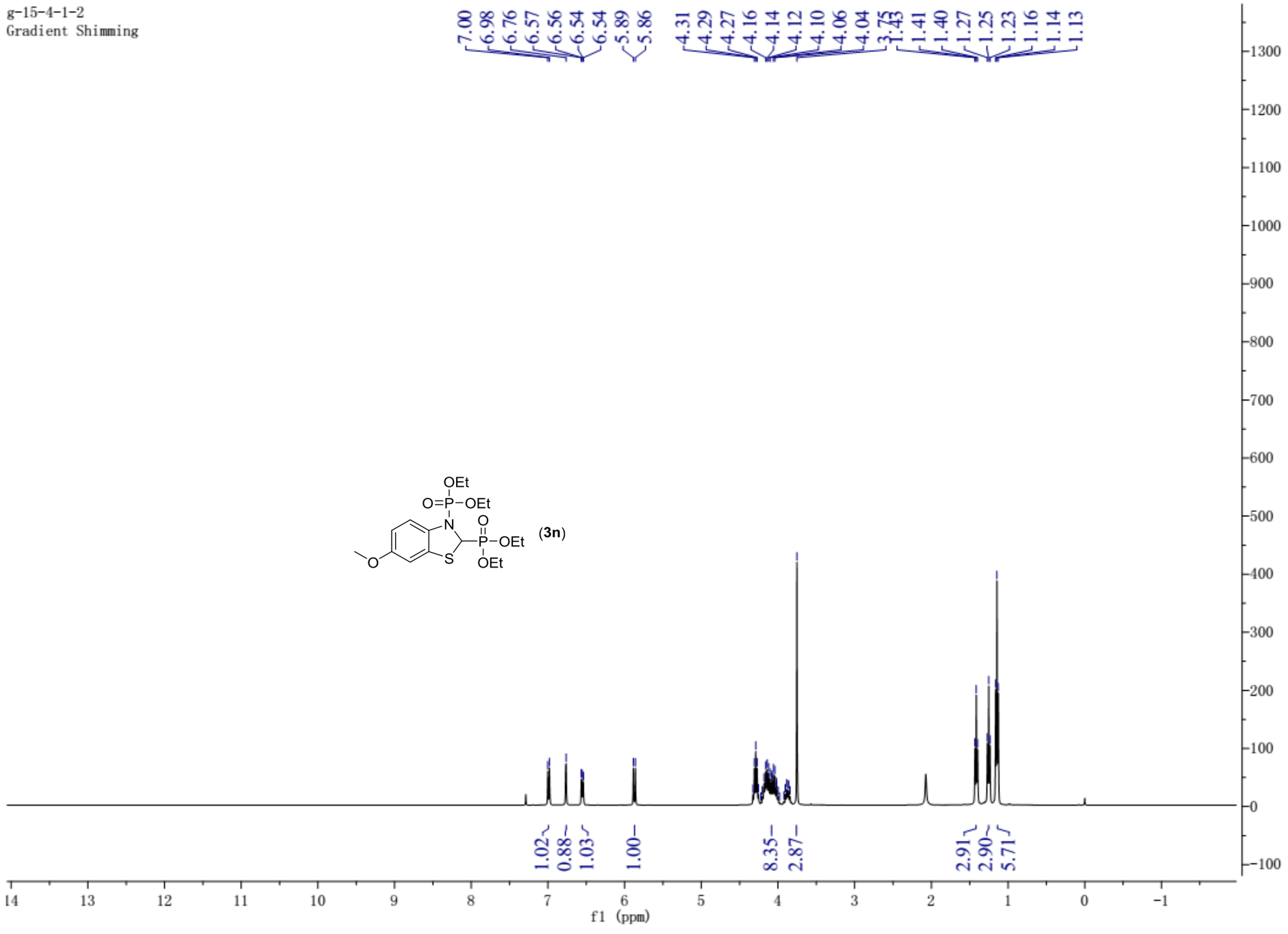
f1 (ppm)

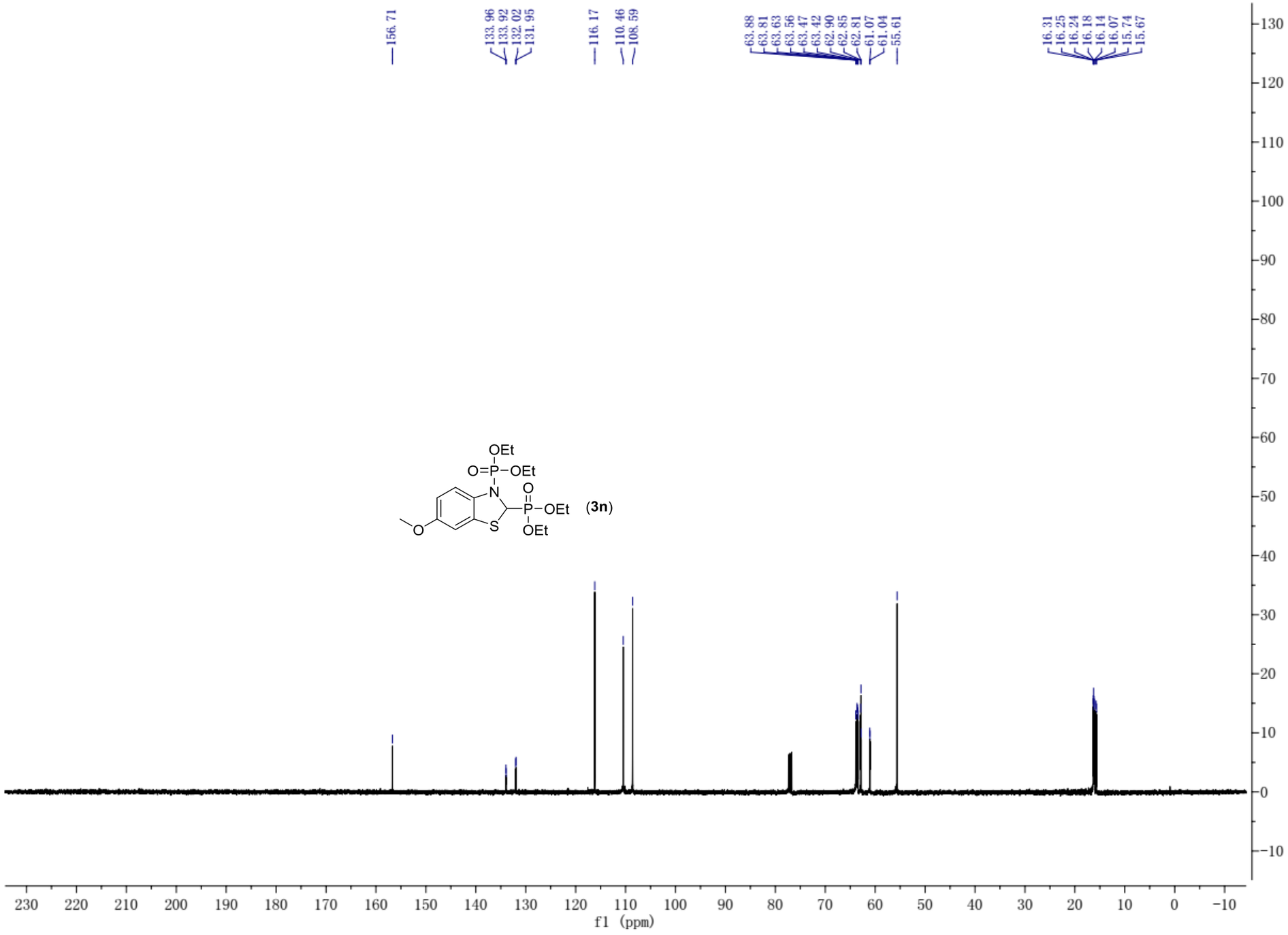
Y150361
sample10 31P




x10 5
+ESI Scan (rt: 0.331 min) Frag=175.0V 16.d
444.0558
573.2075
466.0375
482.0119
543.1600
OEt
O=P–OEt
H+
Cl
N
O
P–OEt
S
OEt
1.2
1
0.8
0.6
0.4
0.2
0
390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560 570 580 590 600 610 620 630 640
Counts vs. Mass-to-Charge (m/z)

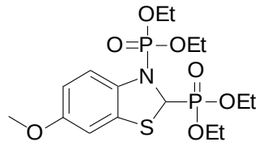
g-15-4-1-2
Gradient Shimming




156.71
133.96
133.92
132.02
131.95
116.17
110.46
108.59
63.88
63.81
63.63
63.56
63.47
63.42
62.90
62.85
62.81
61.07
61.04
55.61
16.31
16.25
16.24
16.18
16.14
16.07
15.74
15.67
OEt
O=P−OEt
N
O
P−OEt
S
OEt
O
(3n)
f1 (ppm)

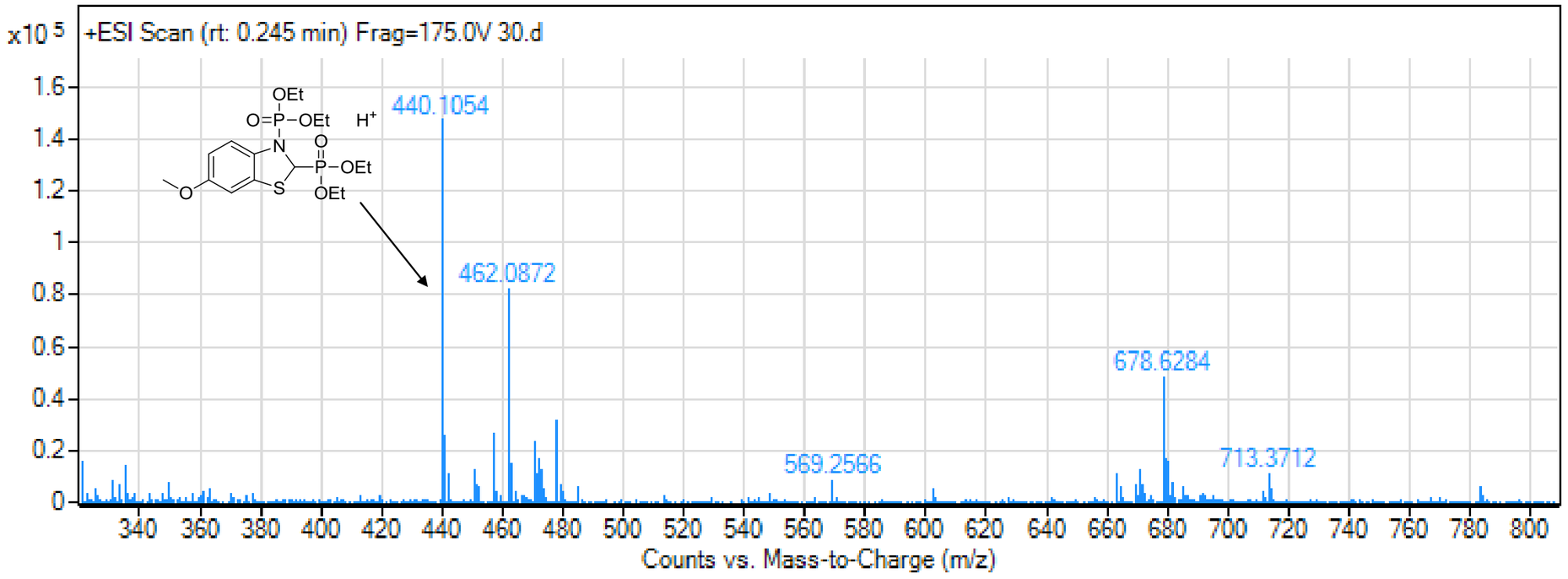
Y150361
sample11 31P

15.71
15.62
1.62
1.53

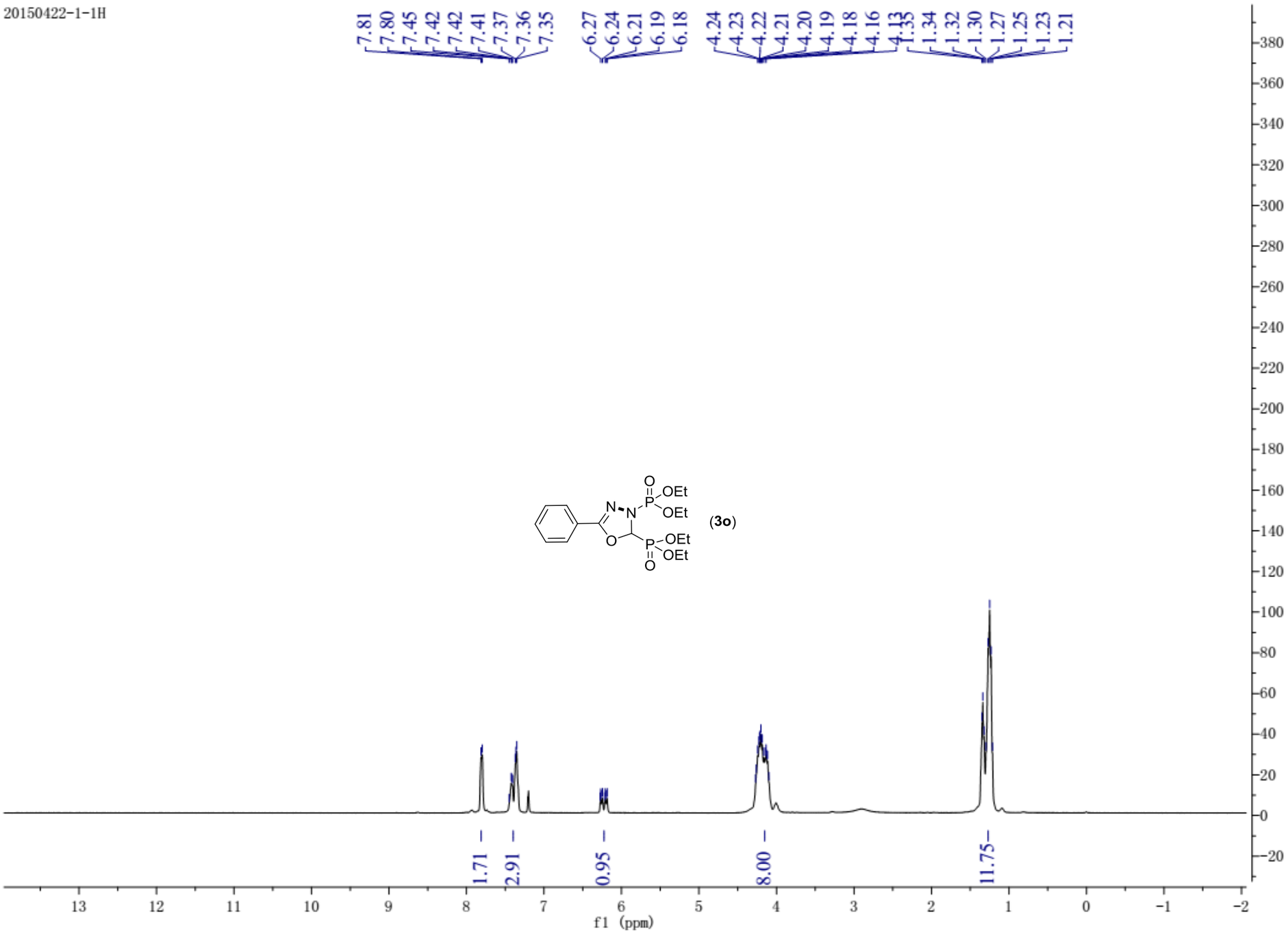


130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000

30 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50
f1 (ppm)


x10 5
+ESI Scan (rt: 0.245 min) Frag=175.0V 30.d
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
OEt
O=P–OEt
H+
N
O
P–OEt
S
OEt
O
440.1054
462.0872
678.6284
569.2566
713.3712
340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780 800
Counts vs. Mass-to-Charge (m/z)

20150422-1-1H

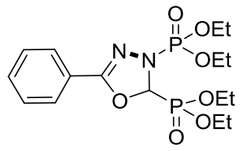


20150422-1-13C

131.72
128.72
127.34
124.15

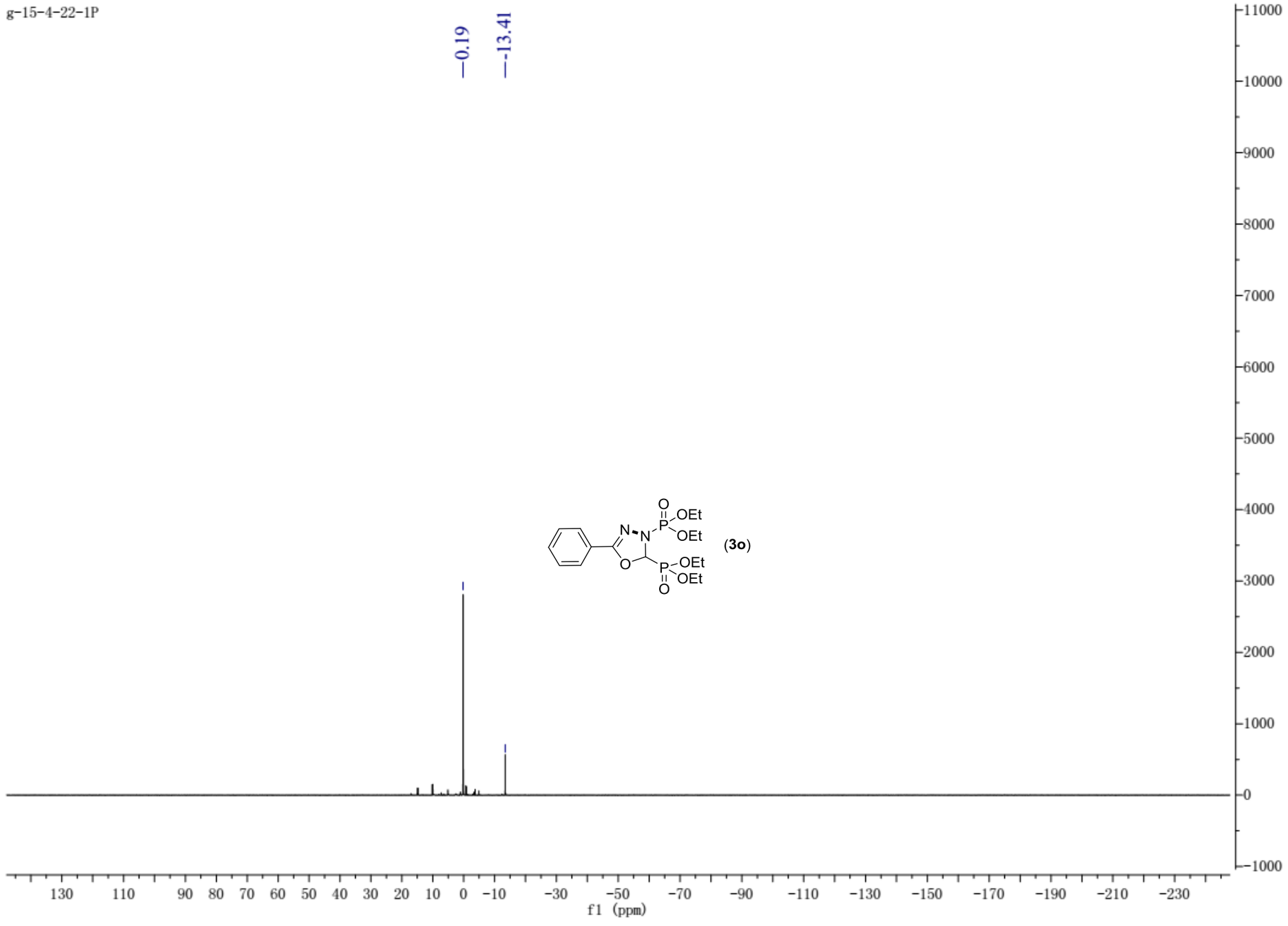
89.06
89.02
87.07
87.03
64.46
64.40
64.35
64.22
64.15
63.98
63.91

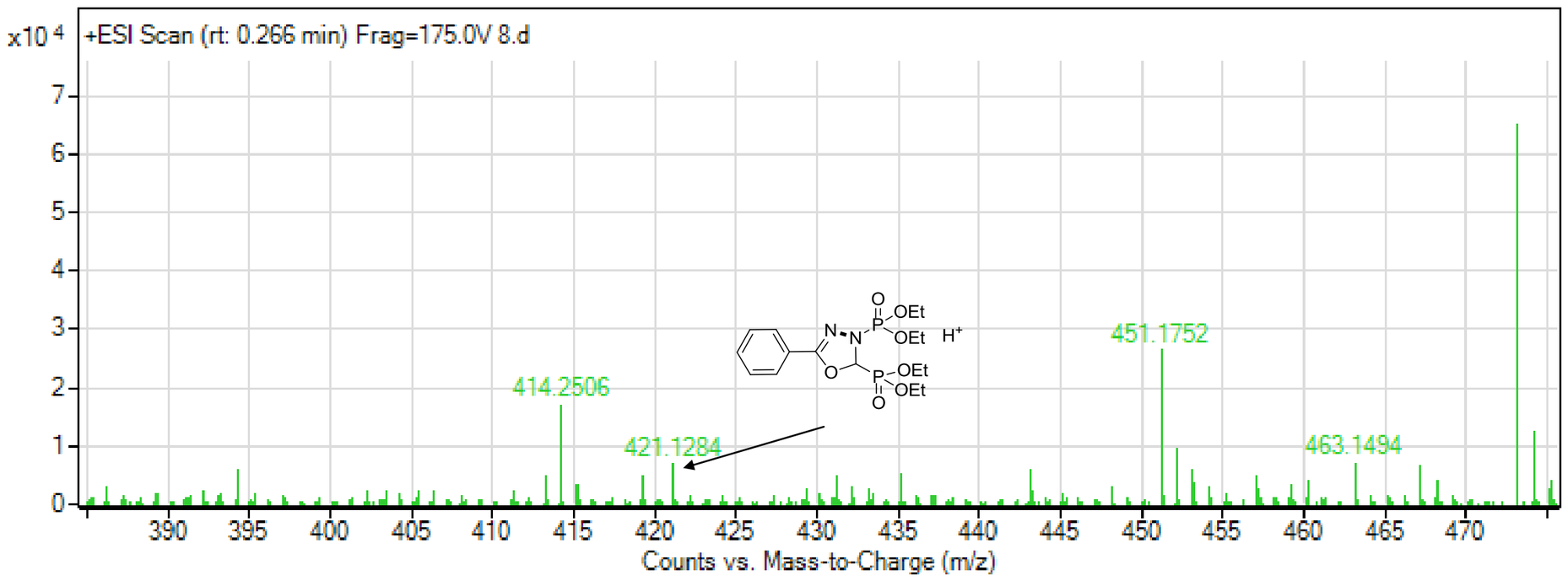
16.67
16.64
16.63
16.59
16.32
16.25
16.18



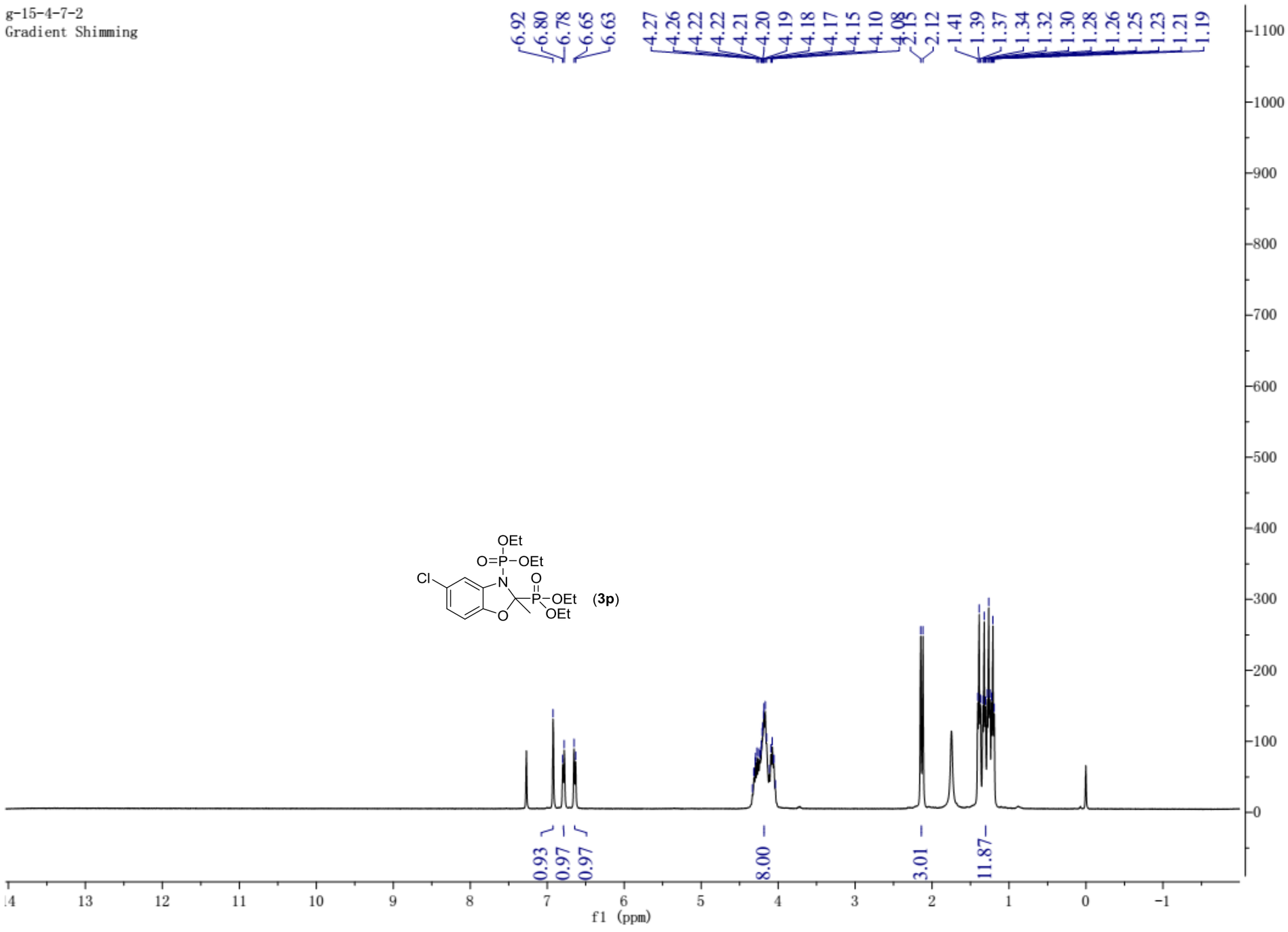
(**3o**)

g-15-4-22-1P


0.19
-13.41
O
OEt
P
OEt
N
N
O
O
OEt
P
OEt
O
(3o)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

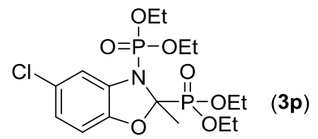

x10 4
+ESI Scan (rt: 0.266 min) Frag=175.0V 8.d
7
6
5
4
3
2
1
0
414.2506
421.1284
451.1752
463.1494
OEt
OEt
OEt
OEt
H+
390
395
400
405
410
415
420
425
430
435
440
445
450
455
460
465
470
Counts vs. Mass-to-Charge (m/z)

g-15-4-7-2
Gradient Shimming



Y150445
sample3 13C

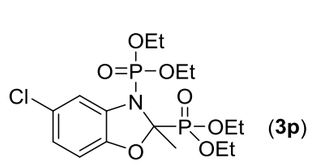
148.91
148.84
134.75
134.72
126.43
122.05
112.71
108.76
101.77
101.71
100.49
100.43
64.07
64.03
63.91
63.88
63.71
63.66
63.49
63.46
58.52
22.37
22.25
18.54
16.57
16.53
16.50
16.46
16.23
16.18
16.15
16.10



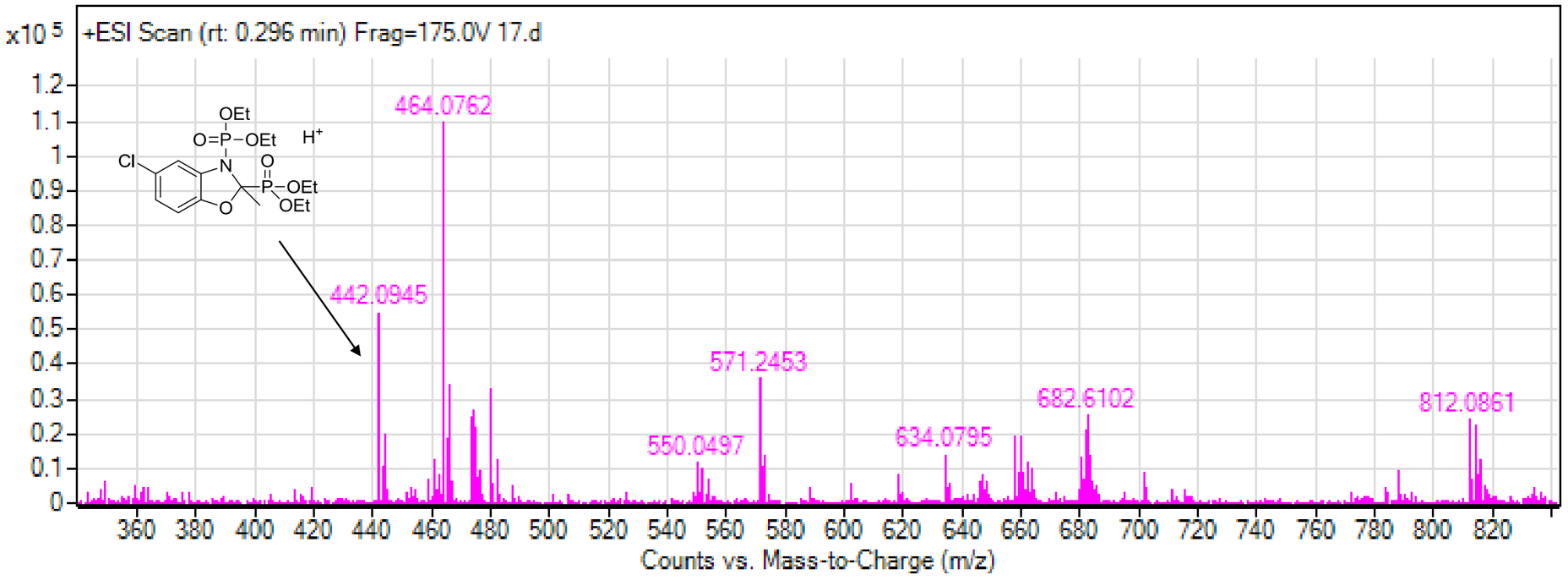
(**3p**)

f1 (ppm)

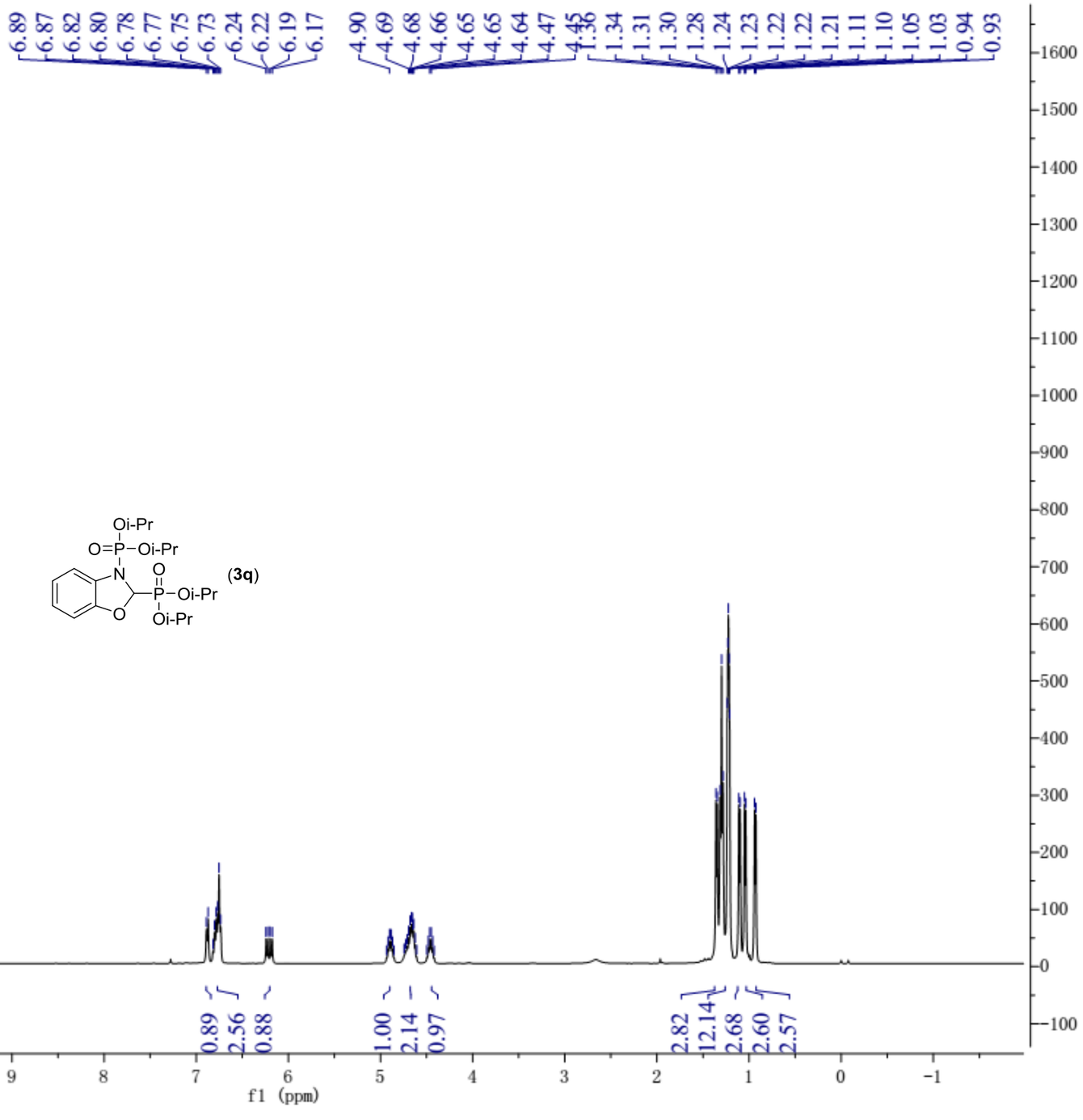
Y150445
sample3 31P

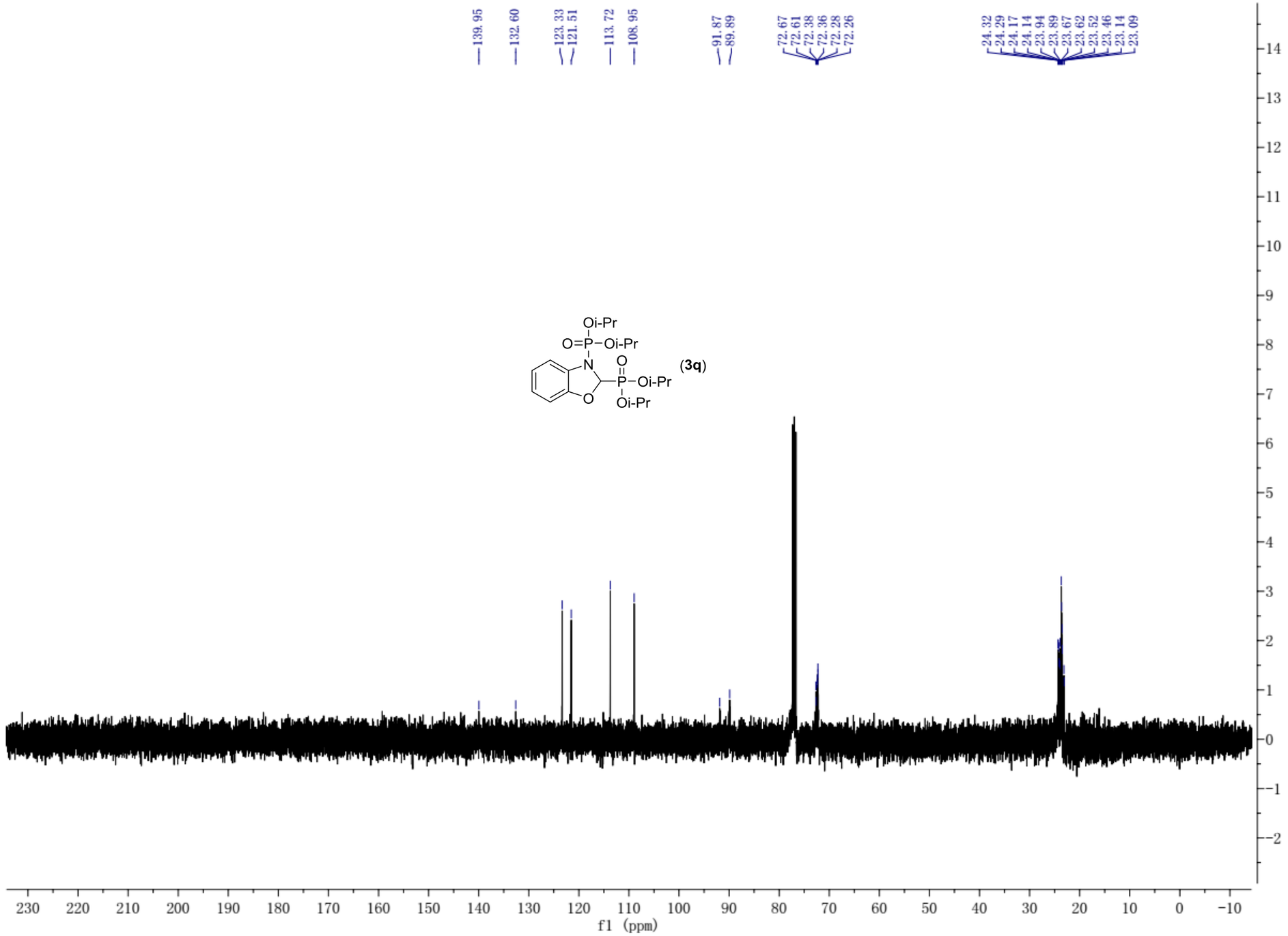


(**3p**)


x10 5
+ESI Scan (rt: 0.296 min) Frag=175.0V 17.d
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
OEt
O=P–OEt
H+
Cl
N
O
P–OEt
OEt
O
464.0762
442.0945
571.2453
682.6102
812.0861
550.0497
634.0795
360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660 680 700 720 740 760 780 800 820
Counts vs. Mass-to-Charge (m/z)

g-15-3-9-3
Calibration for ATB1 on 09Mar2015
Sample : C13 enriched CH3I in CDCl3
WALTZ-16 H1 decoupling profile:
_/- 8ppm from on-resonance
in 0.5ppm steps
H1 dec. gammah2: 2475
at power level: 43



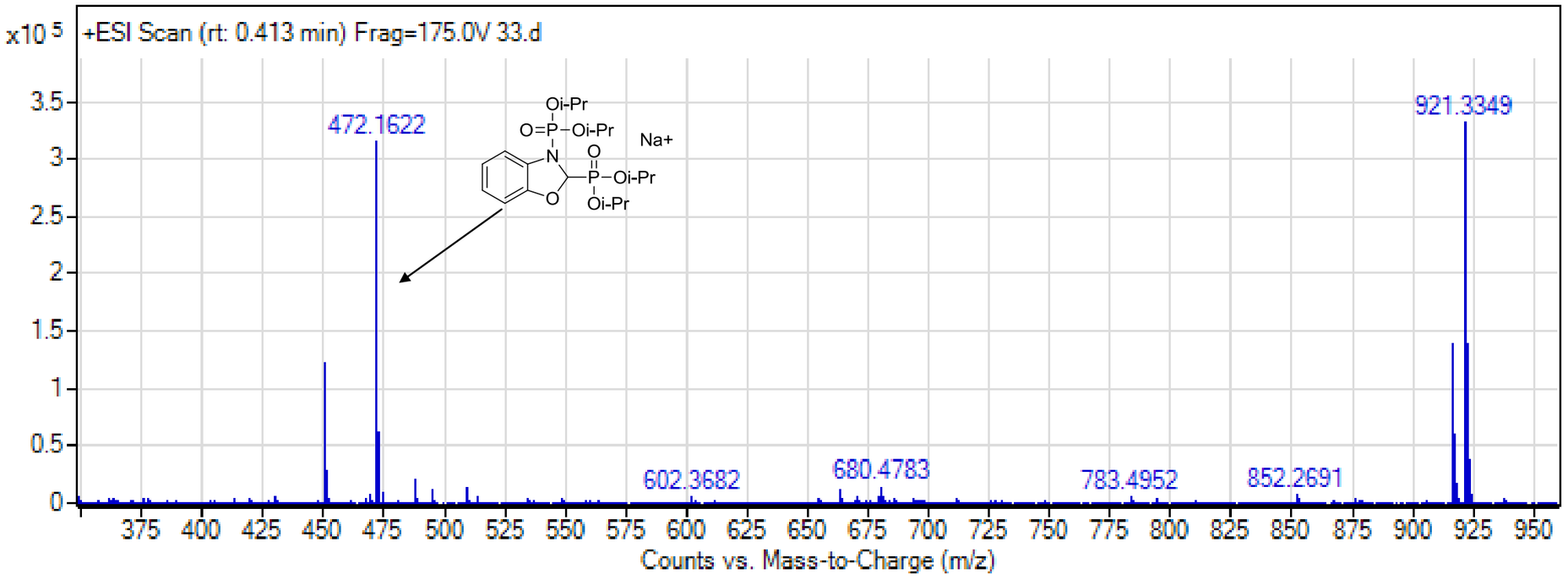

139.95
132.60
123.33
121.51
113.72
108.95
91.87
89.89
72.67
72.61
72.38
72.36
72.28
72.26
24.32
24.29
24.17
24.14
23.94
23.89
23.67
23.62
23.52
23.46
23.14
23.09
Oi-Pr
O=P
Oi-Pr
N
O
P
Oi-Pr
O
Oi-Pr
(3q)
f1 (ppm)

ch0522-3

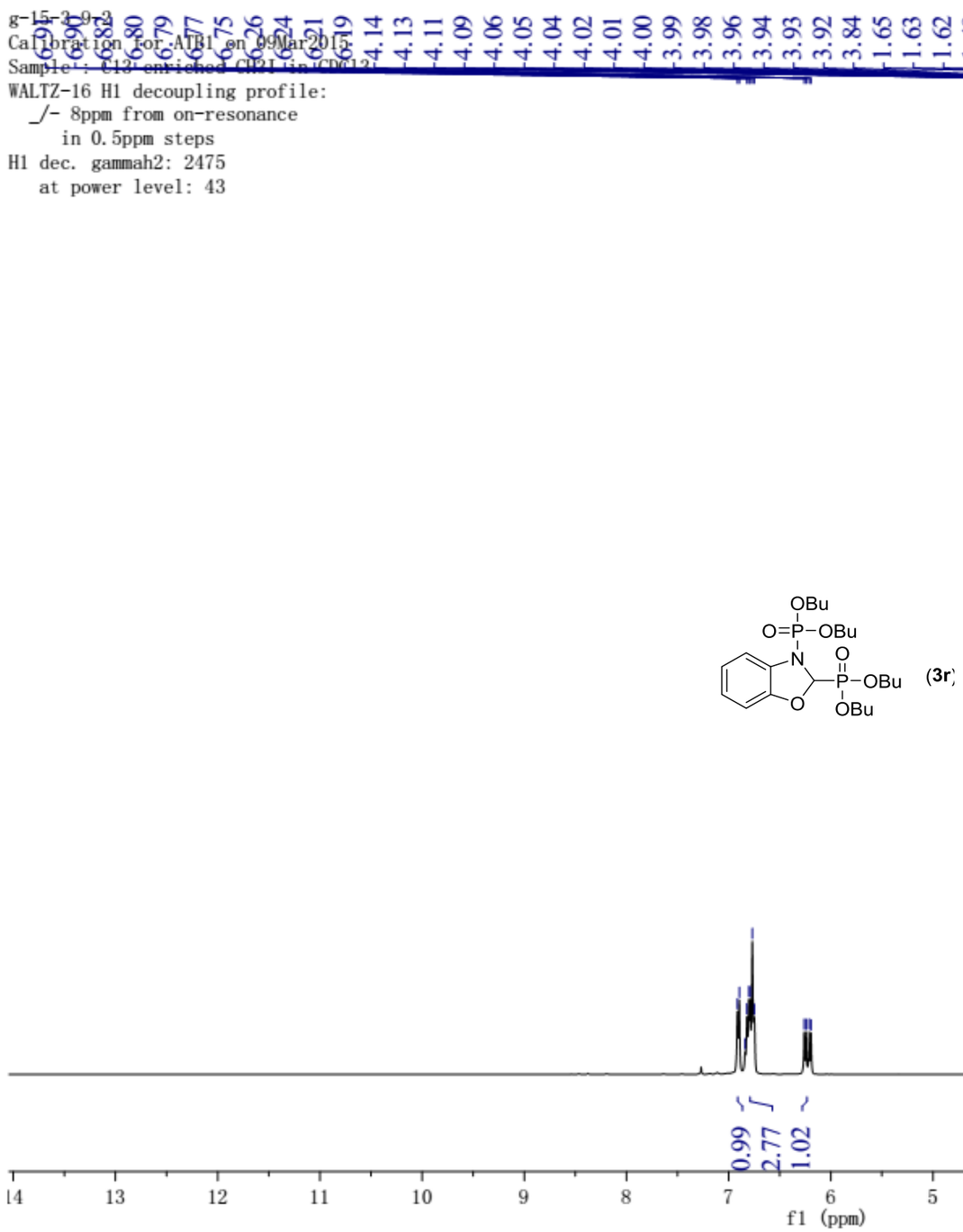
9.34
9.20
-3.66
-3.80

(**3q**)

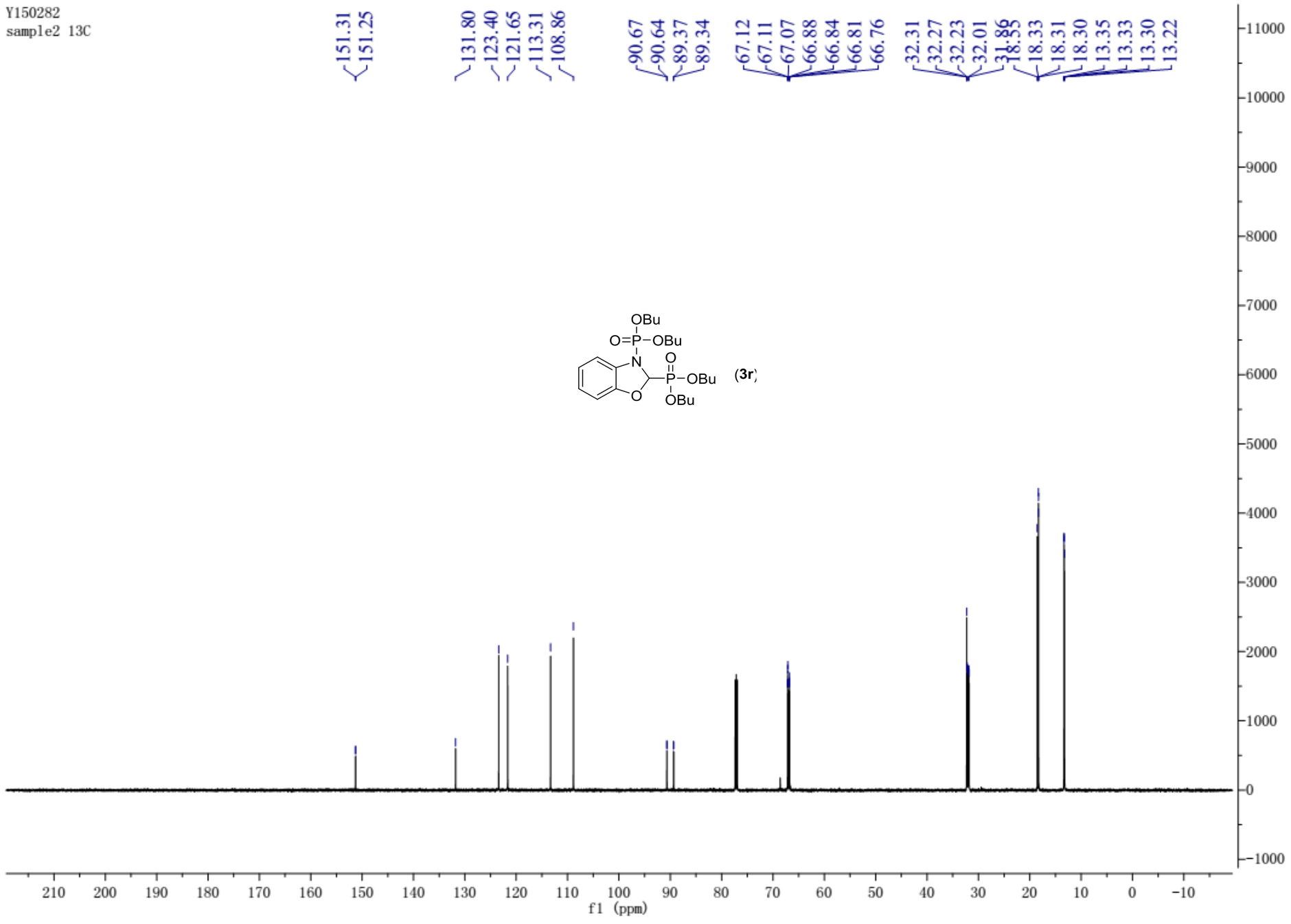
f1 (ppm)


x10 5
+ESI Scan (rt: 0.413 min) Frag=175.0V 33.d
3.5
3
2.5
2
1.5
1
0.5
0
472.1622
921.3349
602.3682
680.4783
783.4952
852.2691
Oi-Pr
O=P–Oi-Pr
Na+
N
O
P–Oi-Pr
O
Oi-Pr
375 400 425 450 475 500 525 550 575 600 625 650 675 700 725 750 775 800 825 850 875 900 925 950
Counts vs. Mass-to-Charge (m/z)

g-15-3_9-3
Calibration for AIB1 on 09Mar2015
Sample': C13 enriched CH2I in CDCl3
WALTZ-16 H1 decoupling profile:
  _/- 8ppm from on-resonance
     in 0.5ppm steps
H1 dec. gammah2: 2475
   at power level: 43

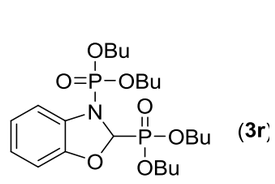


Y150282
sample2 13C



Y150282
sample2 31P

11.29
11.20
-1.47
-1.56

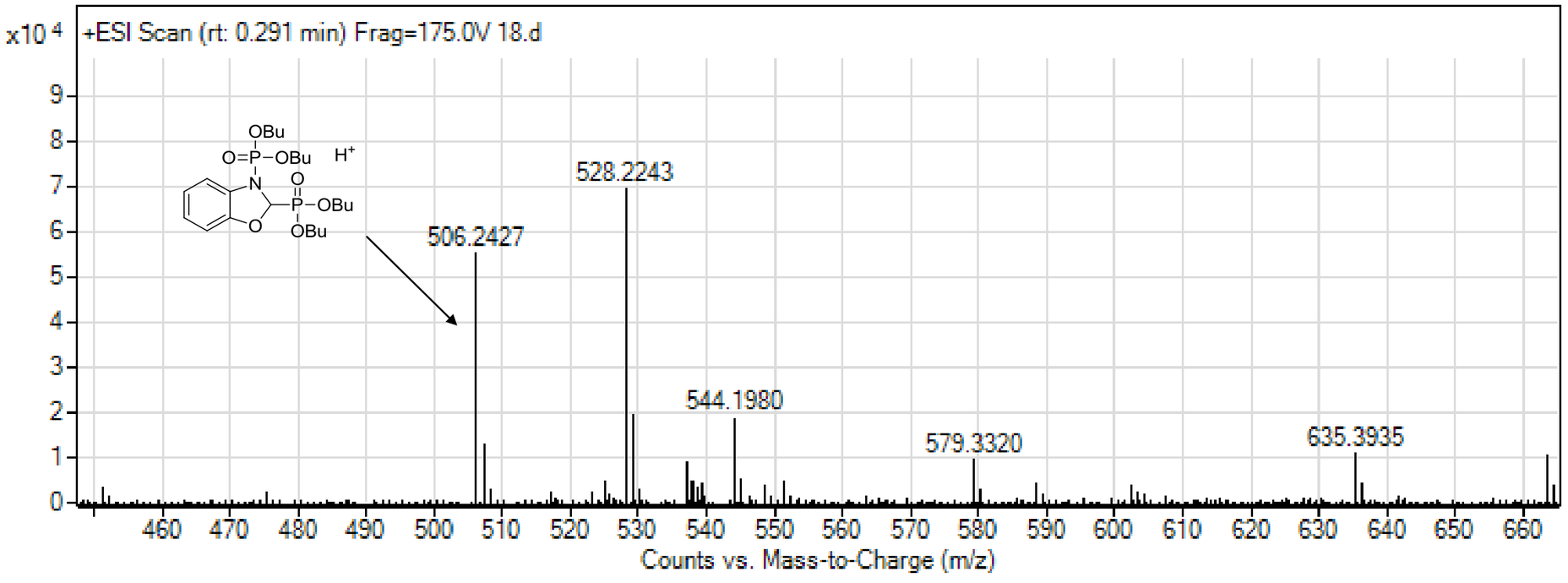


(**3r**)

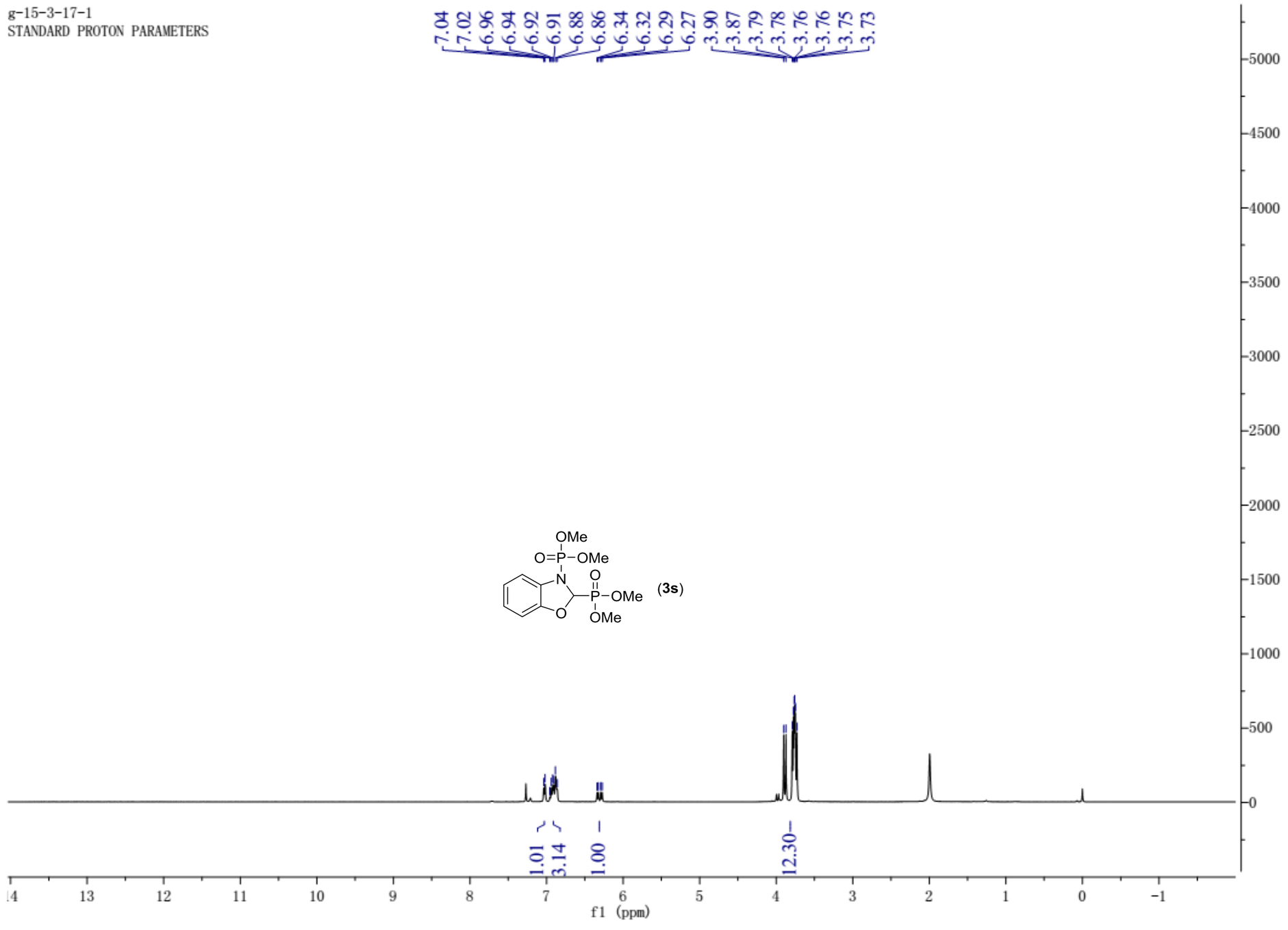
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

30 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50

f1 (ppm)

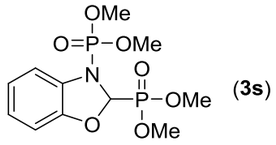

x10 4
+ESI Scan (rt: 0.291 min) Frag=175.0V 18.d
OBu
O=P–OBu
H+
N
O
P–OBu
O
OBu
506.2427
528.2243
544.1980
579.3320
635.3935
Counts vs. Mass-to-Charge (m/z)

g-15-3-17-1
STANDARD PROTON PARAMETERS



Y150282
sample4 13C

150.97
150.91
131.27
123.87
122.16
113.41
109.15
90.38
90.34
89.08
89.04
54.09
54.05
54.05
54.00
53.89
53.86
53.71
53.66

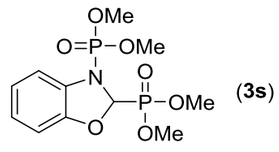


(**3s**)

Y150282
sample4 31P

13.52
13.43

0.77
0.69

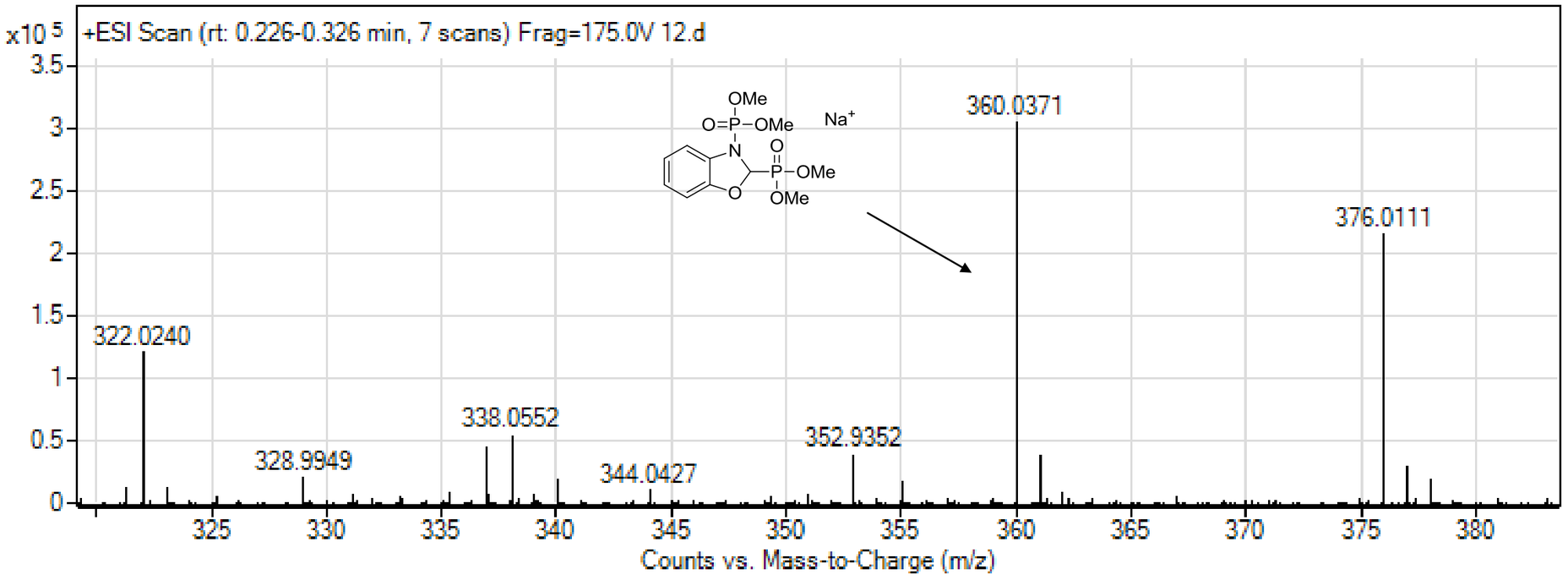


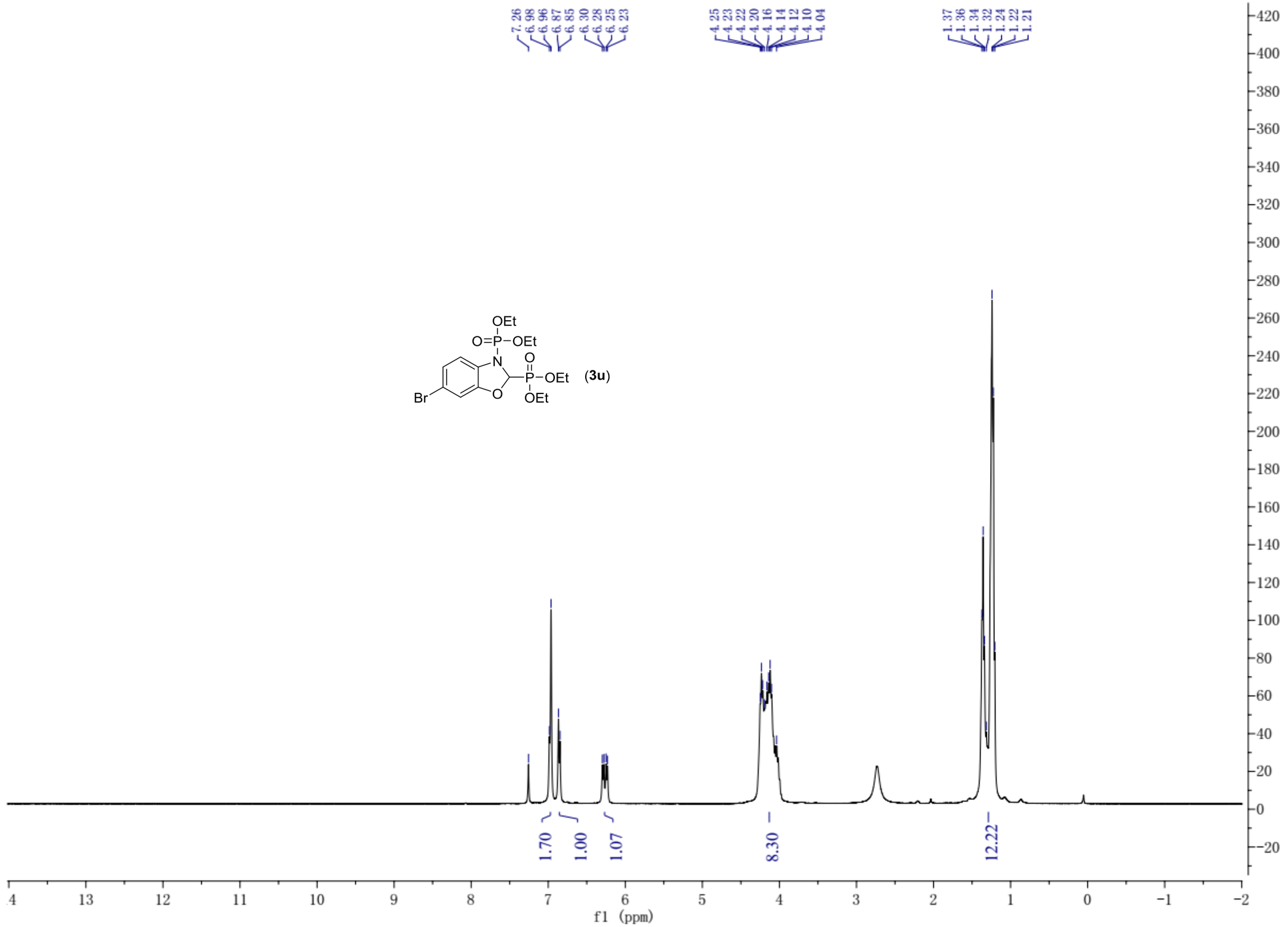
(**3s**)

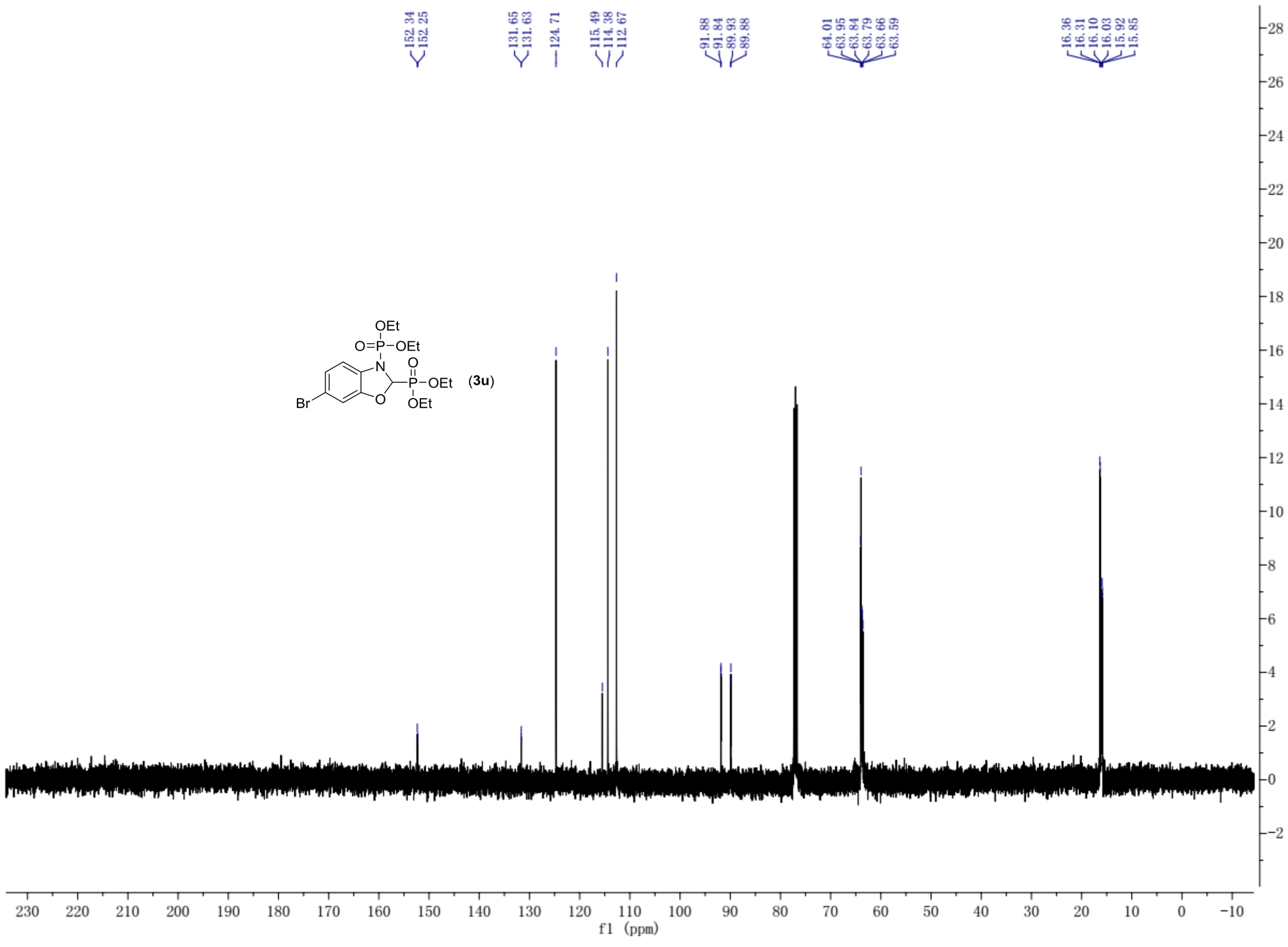
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

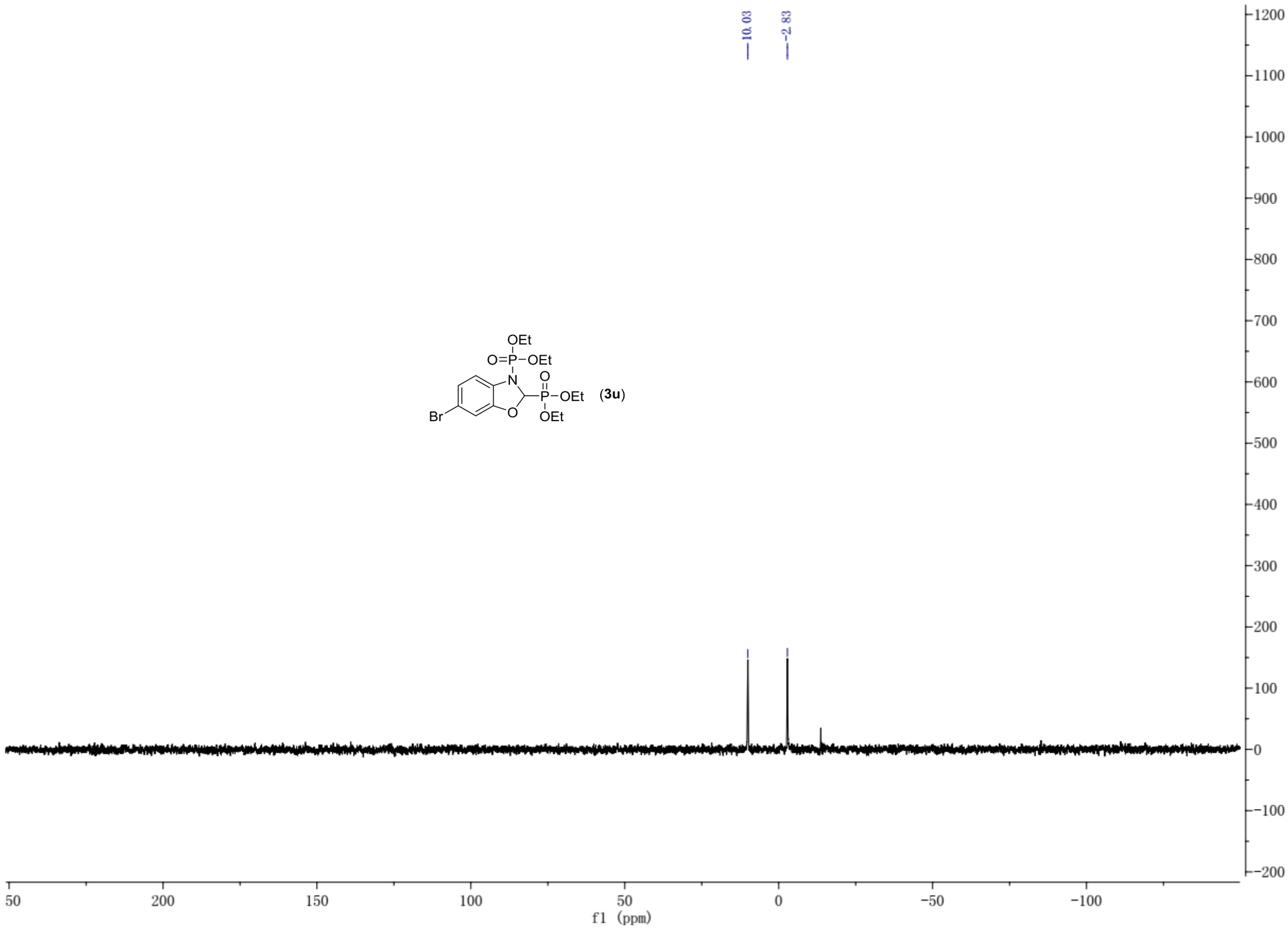
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50

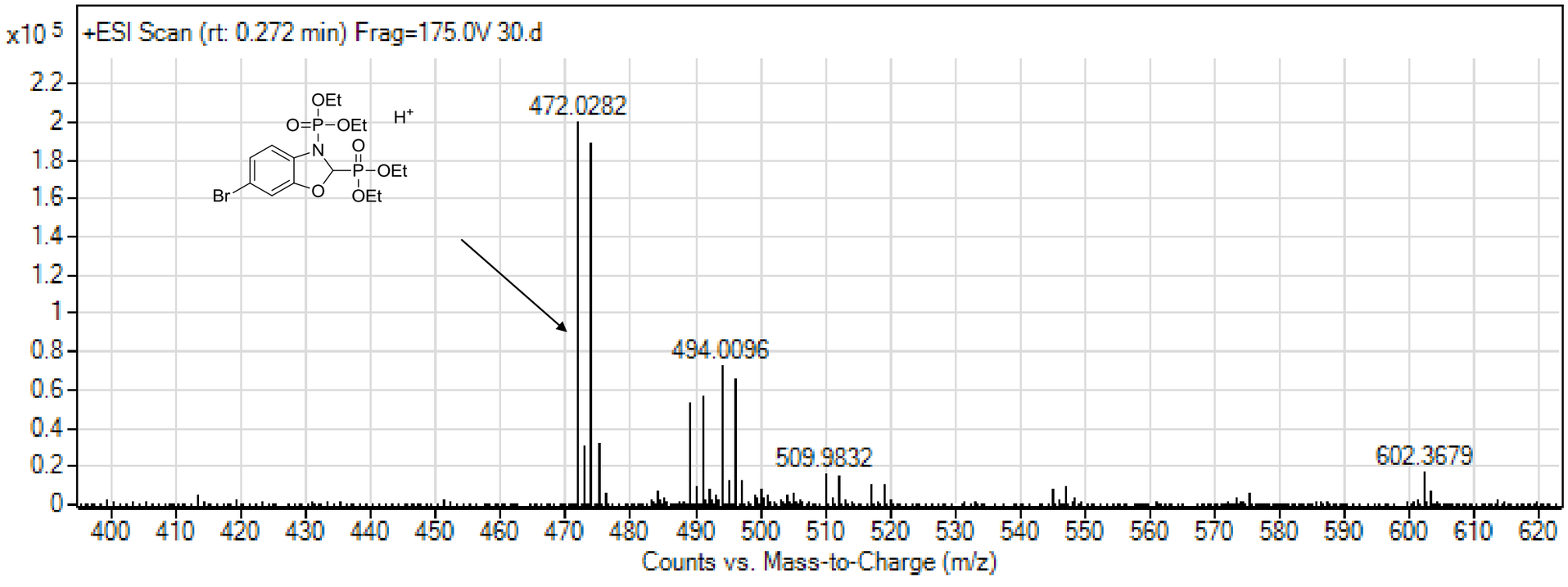
f1 (ppm)

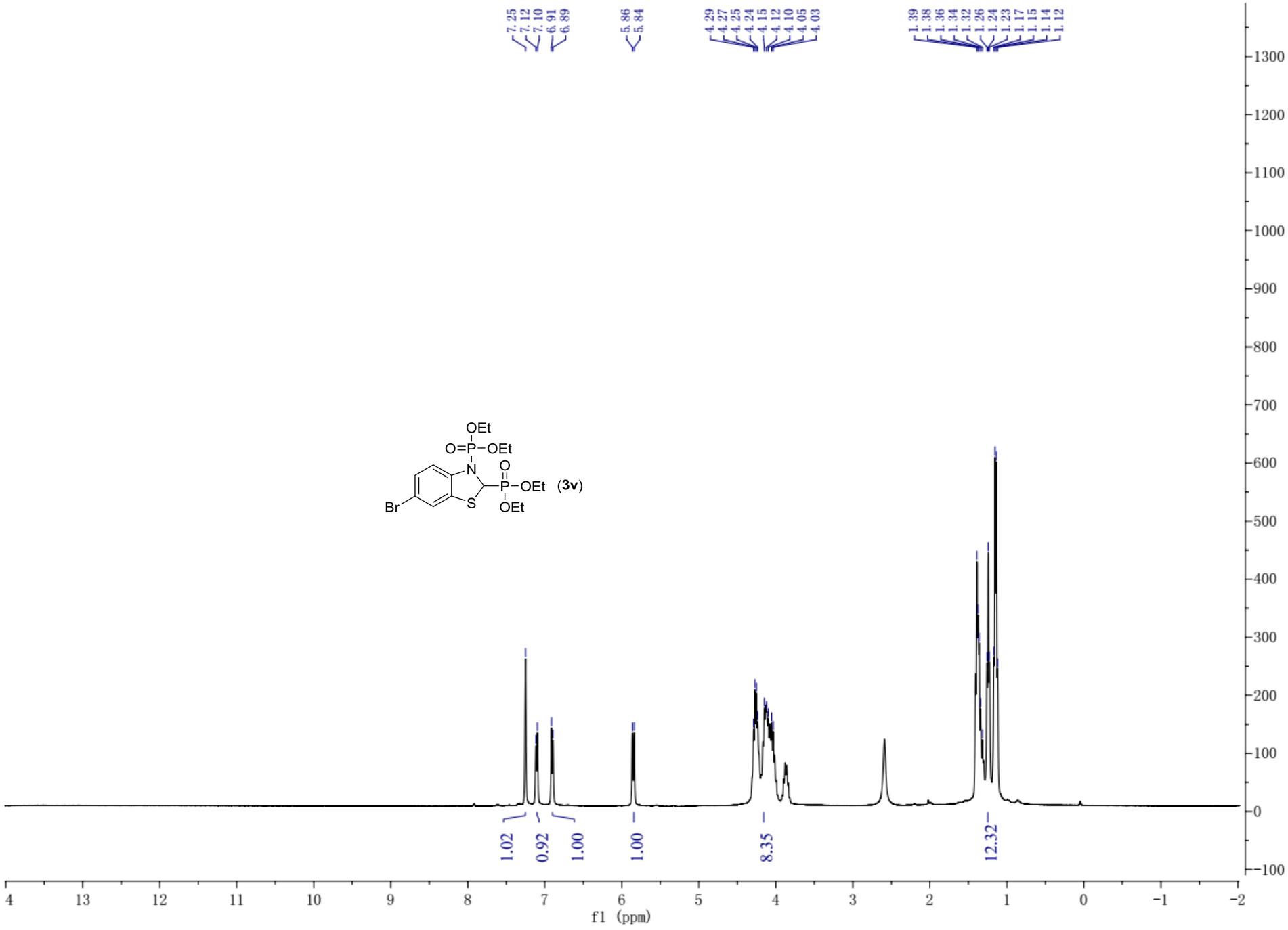

x10 5
+ESI Scan (rt: 0.226-0.326 min, 7 scans) Frag=175.0V 12.d
3.5
3
2.5
2
1.5
1
0.5
0
OMe
O=P–OMe
N
O
O
P–OMe
OMe
Na+
360.0371
376.0111
322.0240
338.0552
328.9949
344.0427
352.9352
325
330
335
340
345
350
355
360
365
370
375
380
Counts vs. Mass-to-Charge (m/z)

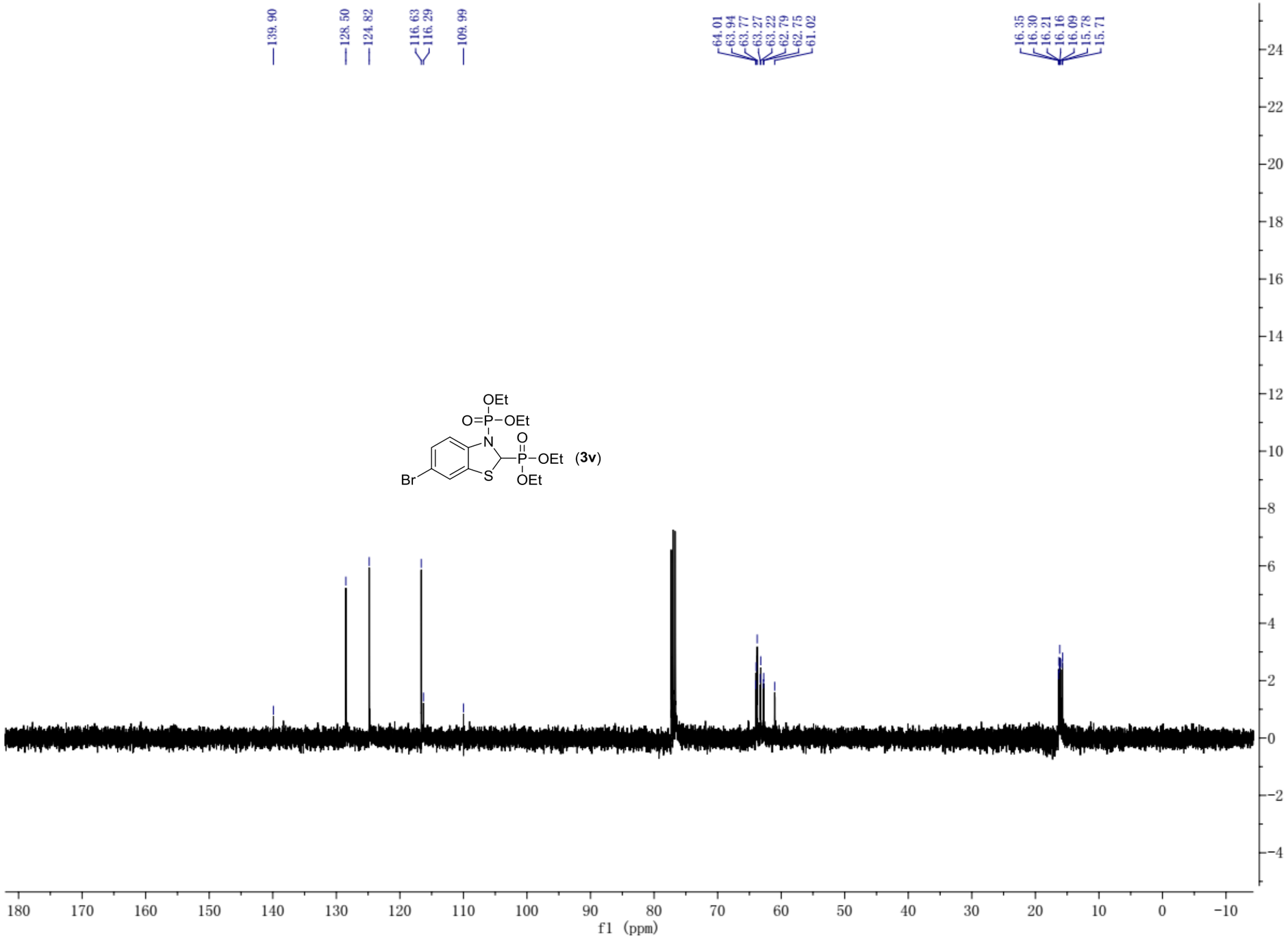

7.26
6.98
6.96
6.87
6.85
6.30
6.28
6.25
6.23
4.25
4.23
4.22
4.20
4.16
4.14
4.12
4.10
4.04
1.37
1.36
1.34
1.32
1.24
1.22
1.21
OEt
O=P−OEt
N
O
P−OEt
Br
O
OEt
(3u)
1.70
1.00
1.07
8.30
12.22
f1 (ppm)

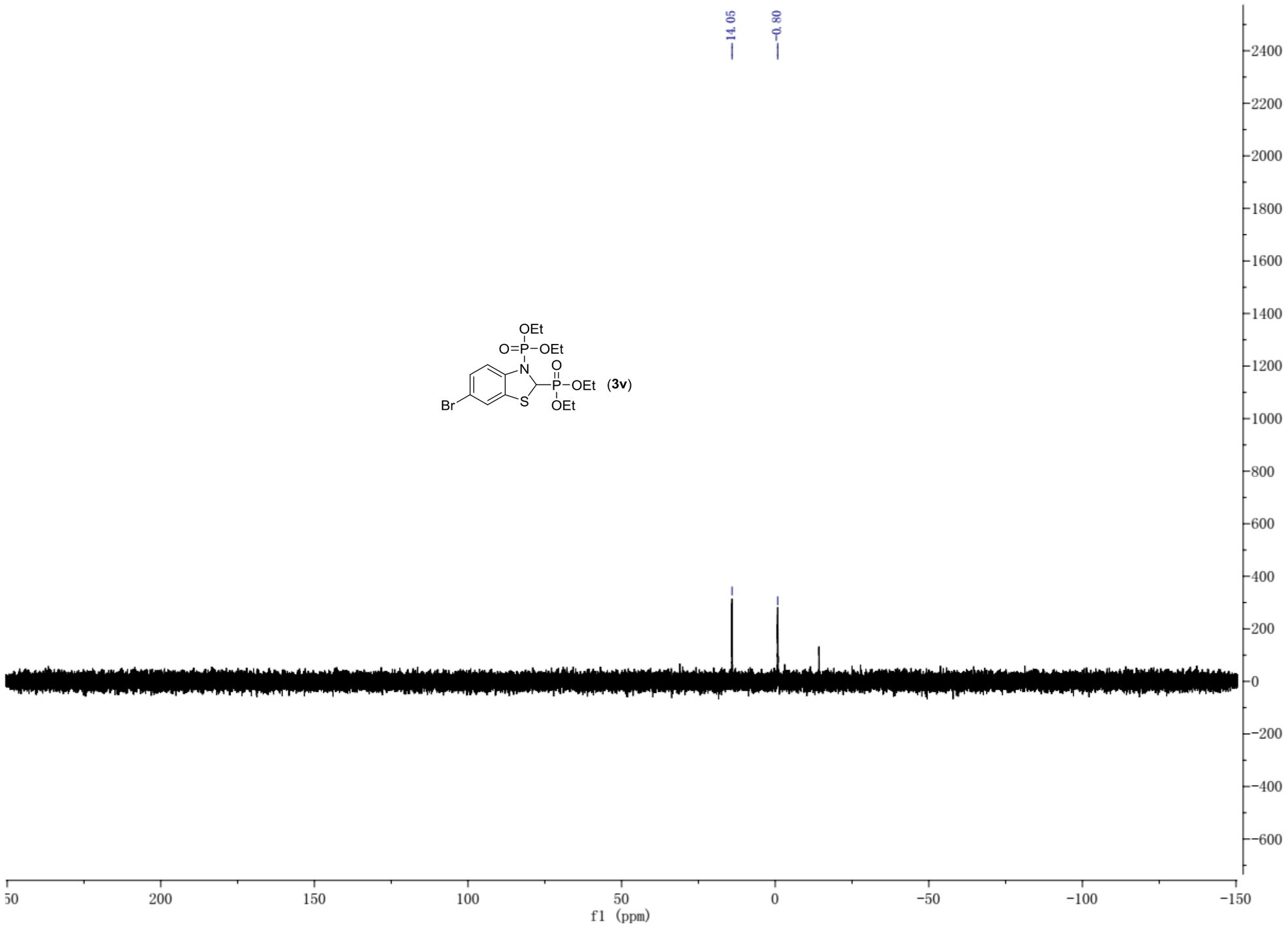

152.34
152.25
131.65
131.63
124.71
115.49
114.38
112.67
91.88
91.84
89.93
89.88
64.01
63.95
63.84
63.79
63.66
63.59
16.36
16.31
16.10
16.03
15.92
15.85
OEt
O=P–OEt
N
O
P–OEt
Br
O
OEt
(3u)
f1 (ppm)

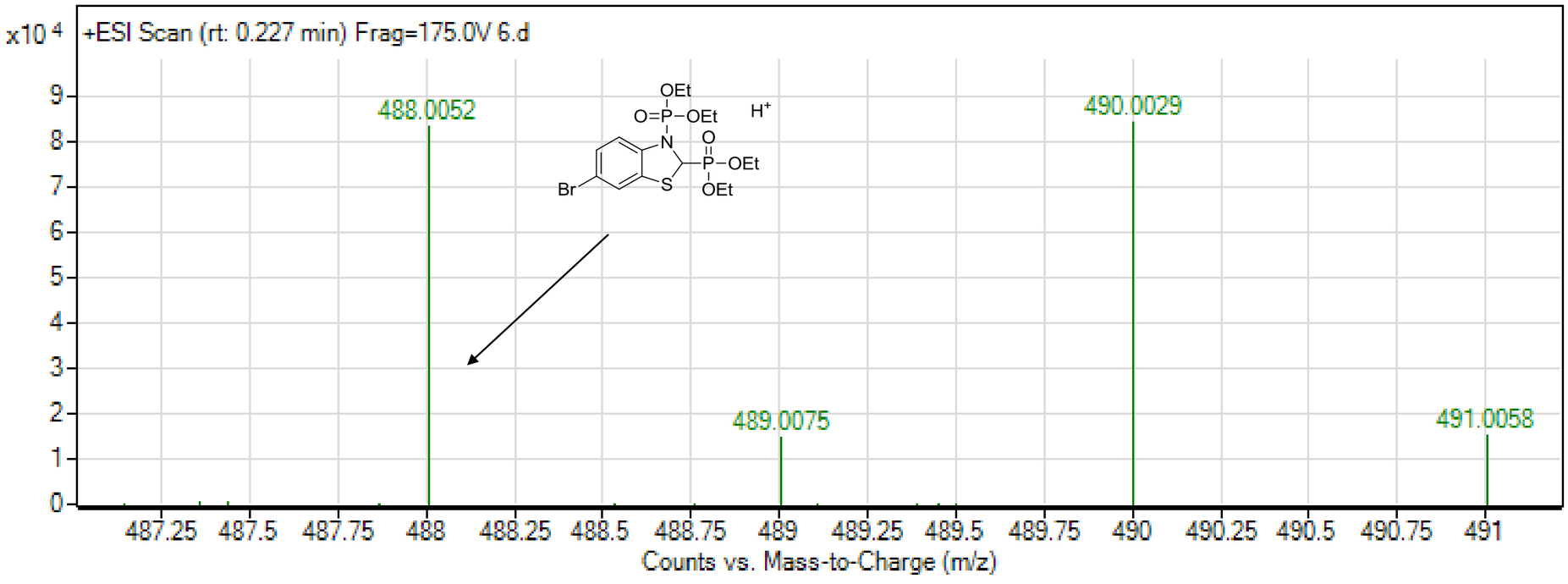

10.03
-2.83
OEt
O=P−OEt
N
O
P−OEt
Br
O
OEt
(3u)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
50
200
150
100
50
0
−50
−100
f1 (ppm)

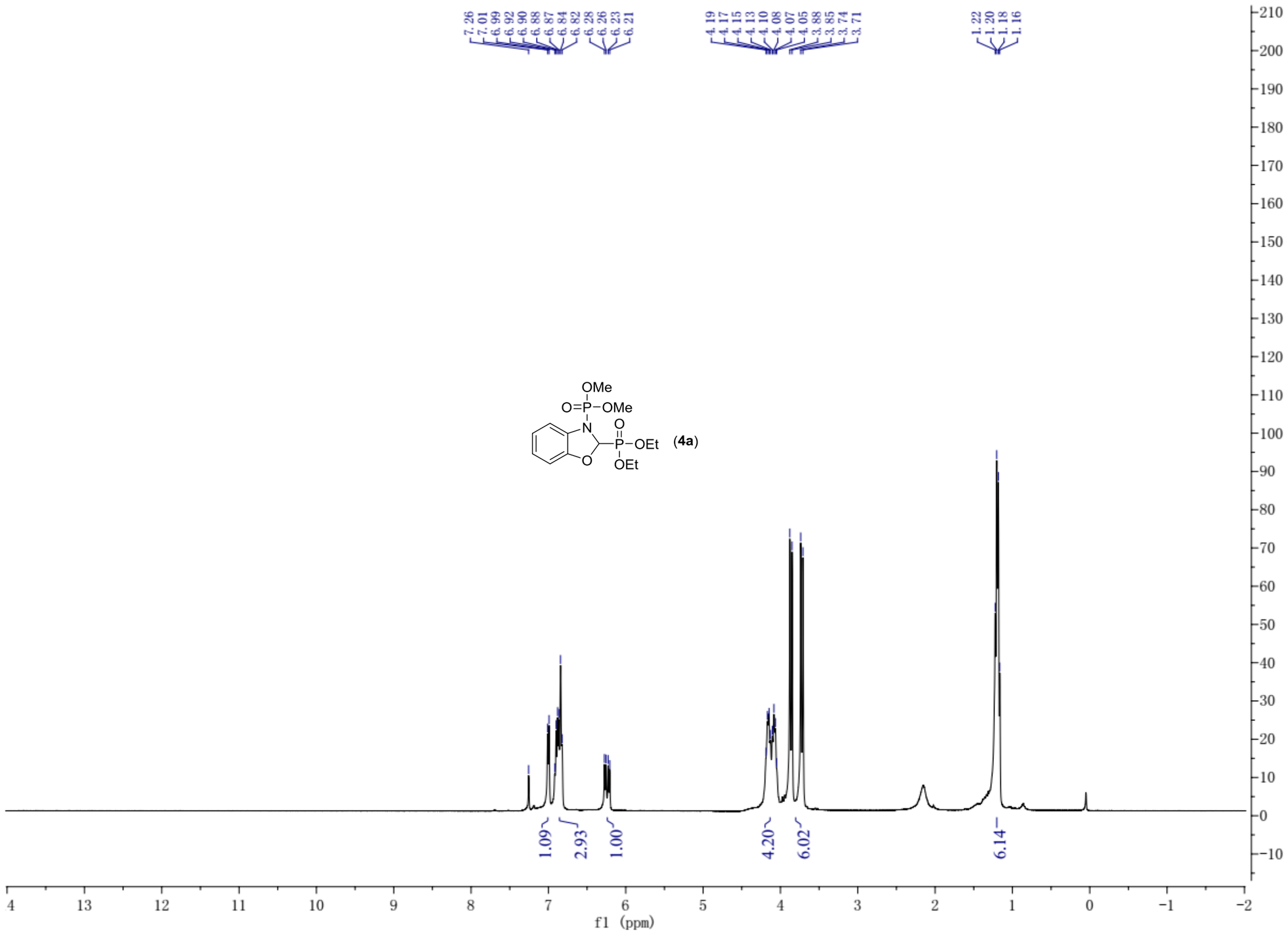

x10 5
+ESI Scan (rt: 0.272 min) Frag=175.0V 30.d
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
OEt
O=P–OEt
H+
N
O
P–OEt
Br
O
OEt
472.0282
494.0096
509.9832
602.3679
400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560 570 580 590 600 610 620
Counts vs. Mass-to-Charge (m/z)


7.25
7.12
7.10
6.91
6.89
5.86
5.84
4.29
4.27
4.25
4.24
4.15
4.12
4.10
4.05
4.03
1.39
1.38
1.36
1.34
1.32
1.26
1.24
1.23
1.17
1.15
1.14
1.12
OEt
O=P−OEt
N
O
P−OEt
Br
S
OEt
(3v)
1.02
0.92
1.00
1.00
8.35
12.32
f1 (ppm)


139.90
128.50
124.82
116.63
116.29
109.99
64.01
63.94
63.77
63.27
63.22
62.79
62.75
61.02
16.35
16.30
16.21
16.16
16.09
15.78
15.71
OEt
O=P−OEt
N
O
P−OEt
Br
S
OEt
(3v)
f1 (ppm)

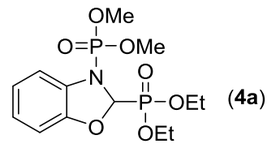

14.05
0.80
OEt
O=P−OEt
N
O
P−OEt
Br
S
OEt
(3v)
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
−400
−600
50
200
150
100
50
0
−50
−100
−150
f1 (ppm)


x10 4
+ESI Scan (rt: 0.227 min) Frag=175.0V 6.d
488.0052
489.0075
490.0029
491.0058
OEt
O=P–OEt
H+
N
O
P–OEt
Br
S
OEt
9
8
7
6
5
4
3
2
1
0
487.25
487.5
487.75
488
488.25
488.5
488.75
489
489.25
489.5
489.75
490
490.25
490.5
490.75
491
Counts vs. Mass-to-Charge (m/z)

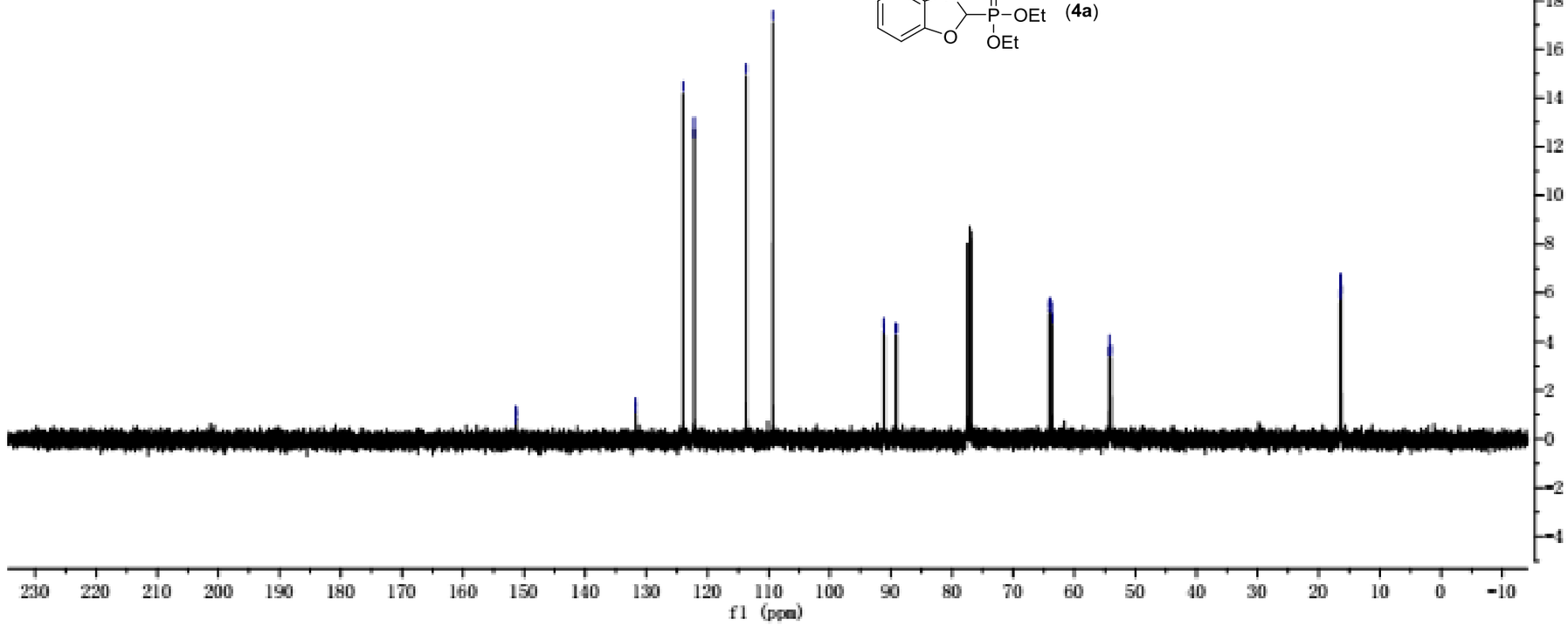

7.26
7.01
6.99
6.92
6.90
6.88
6.87
6.84
6.82
6.28
6.26
6.23
6.21
4.19
4.17
4.15
4.13
4.10
4.08
4.07
4.05
3.88
3.85
3.74
3.71
1.22
1.20
1.18
1.16
OMe
O=P–OMe
N
O
P–OEt
O
OEt
(4a)
1.09
2.93
1.00
4.20
6.02
6.14
f1 (ppm)

g-15-9-16-2-C13
STANDARD PROTON PARAMETERS

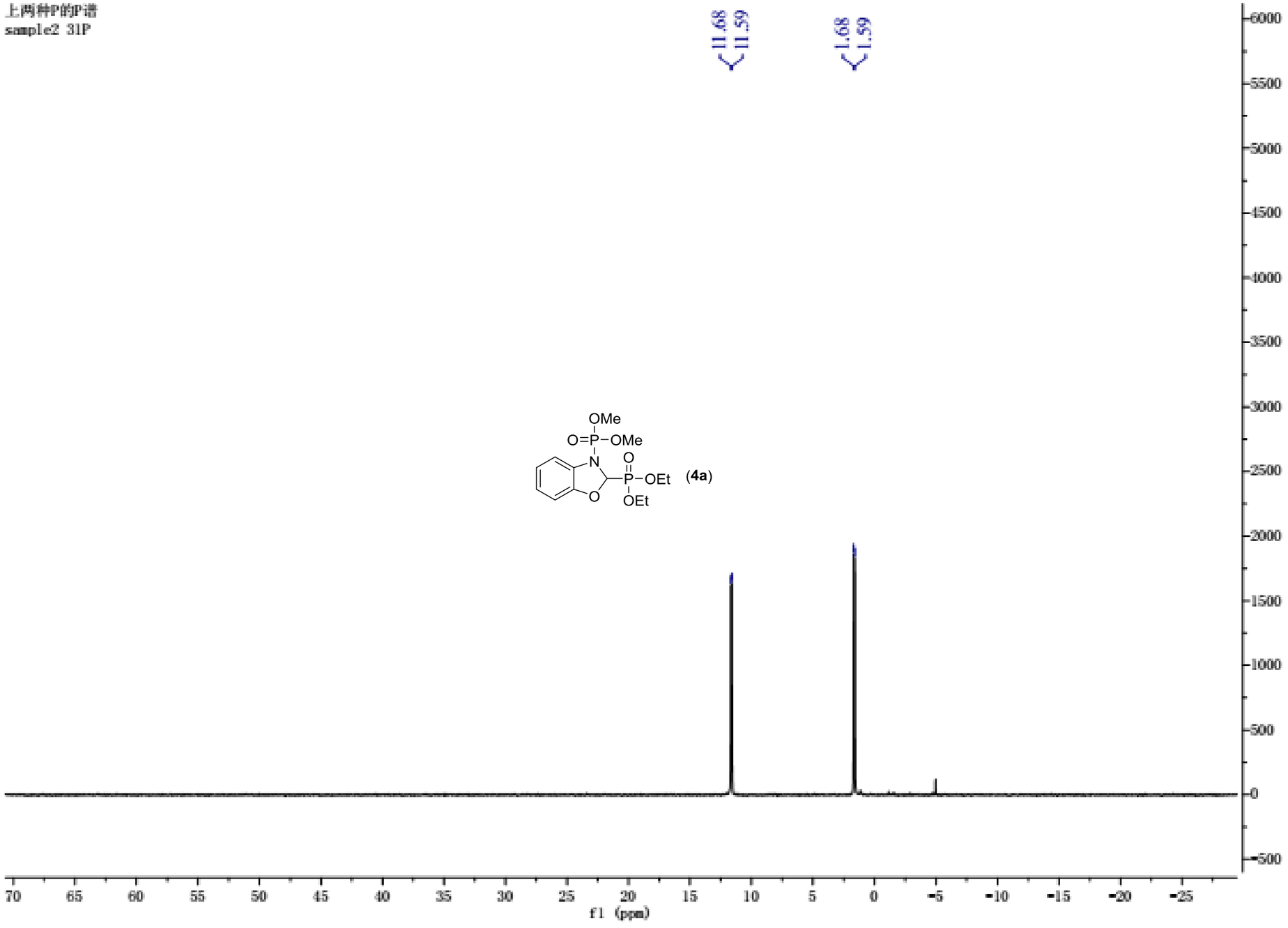
151.41
151.39
151.32
151.31
131.76
131.74
123.96
122.19
122.18
113.68
109.30
91.12
91.07
89.17
89.12
64.04
63.98
63.69
63.62
54.30
54.25
54.08
54.03
16.47
16.43
16.41
16.38

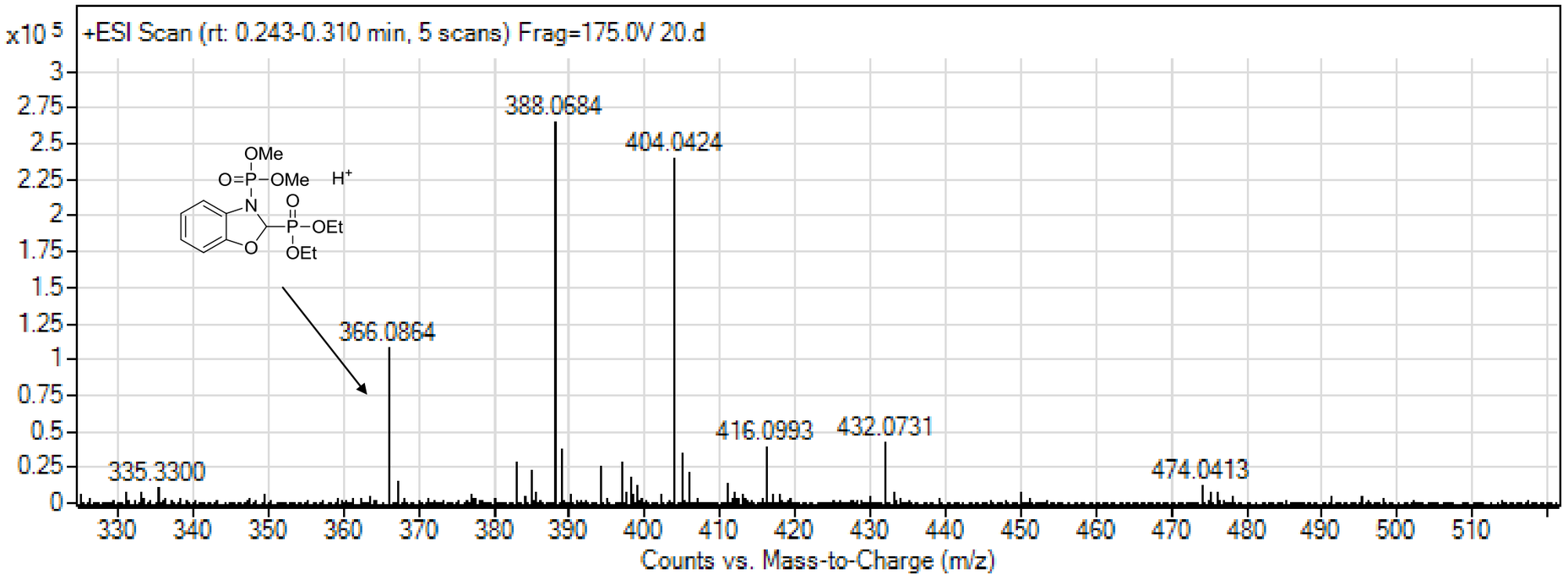


(**4a**)

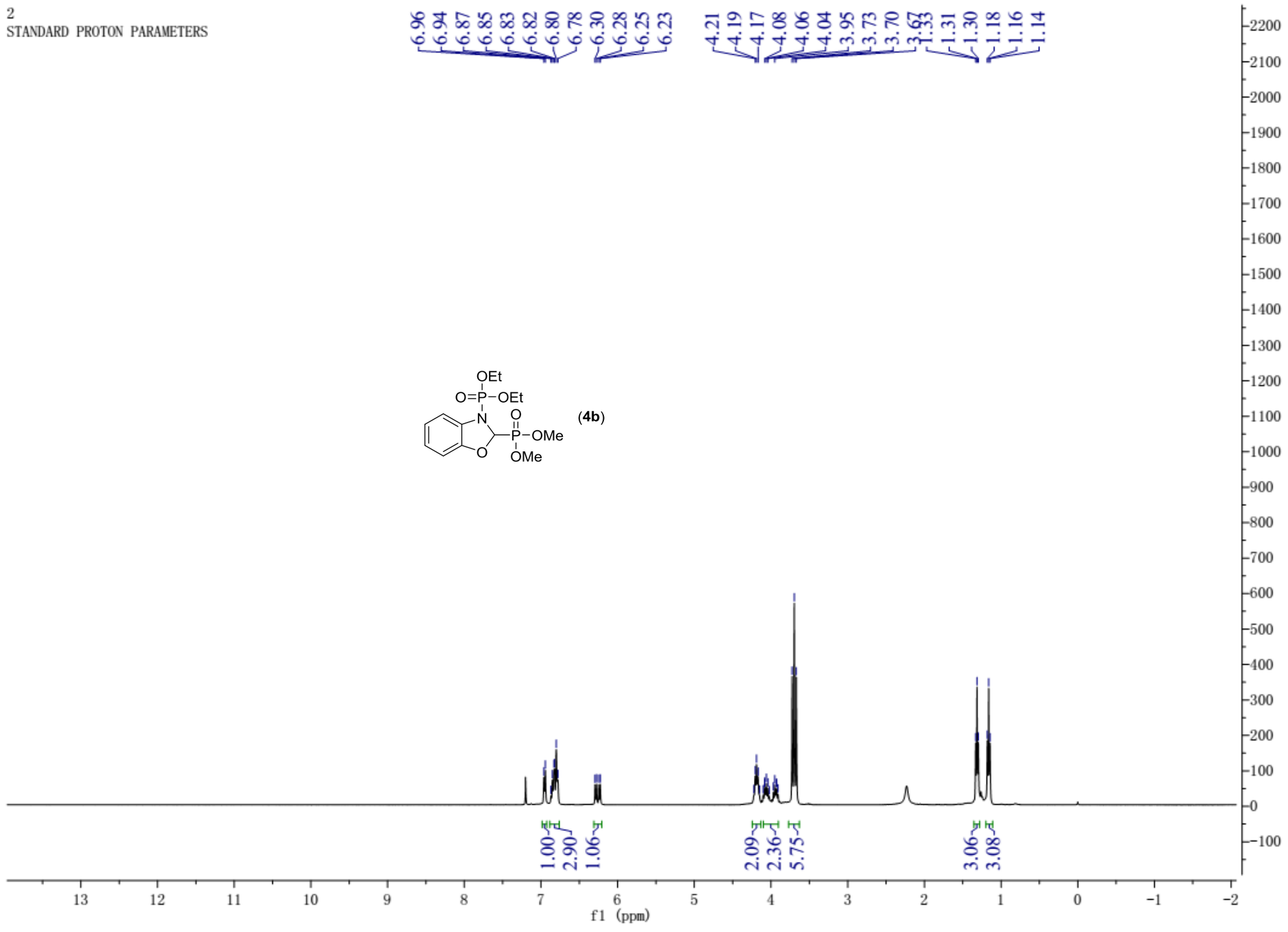


上两种P的P谱
sample2 31P

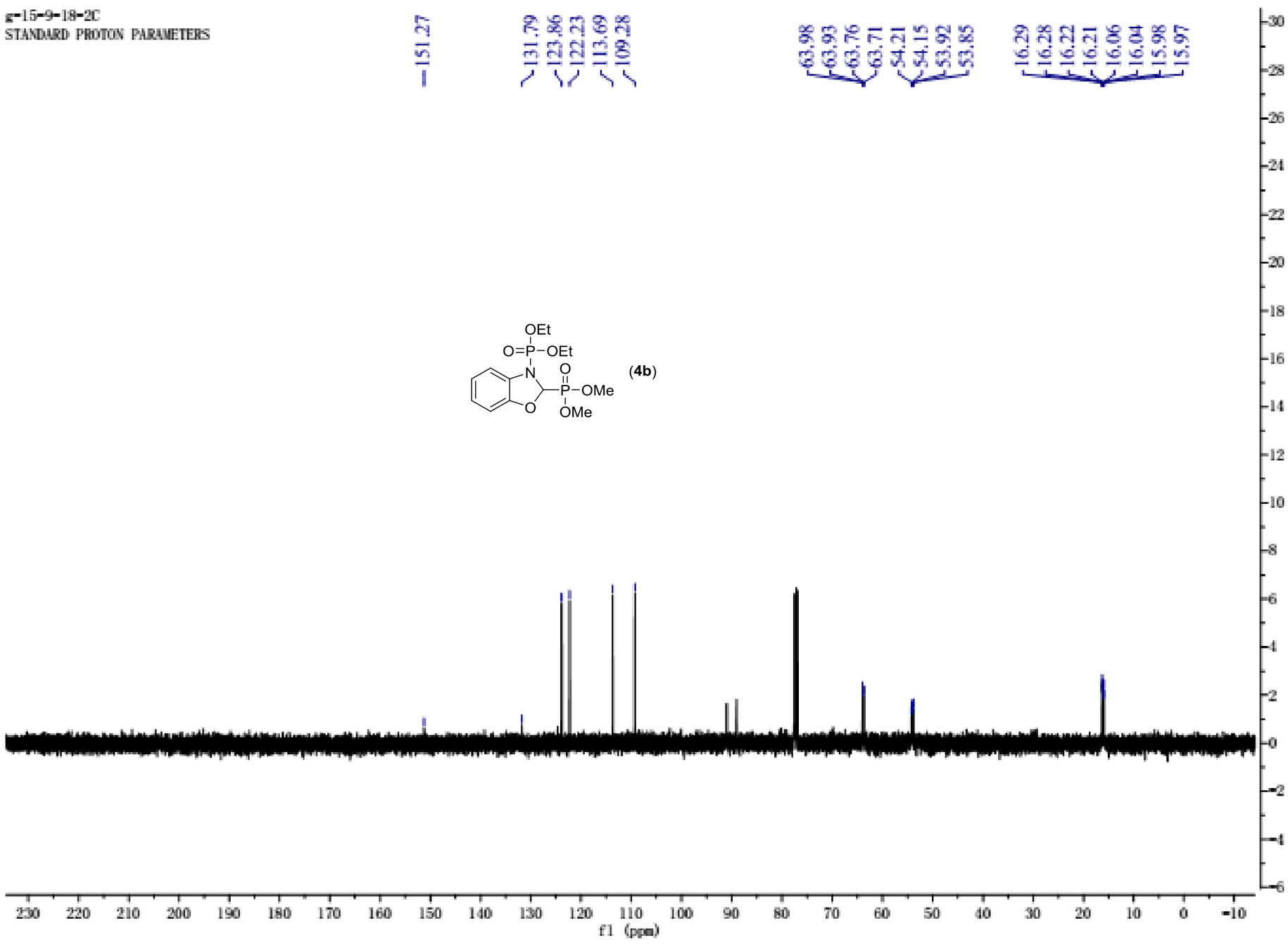



x10 5
+ESI Scan (rt: 0.243-0.310 min, 5 scans) Frag=175.0V 20.d
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
388.0684
404.0424
366.0864
416.0993
432.0731
335.3300
474.0413
OMe
O=P–OMe
H+
N
O
P–OEt
O
OEt
330
340
350
360
370
380
390
400
410
420
430
440
450
460
470
480
490
500
510
Counts vs. Mass-to-Charge (m/z)

2
STANDARD PROTON PARAMETERS

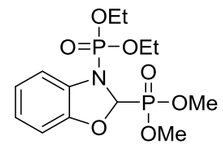


g-15-9-18-2C
STANDARD PROTON PARAMETERS



上两种P的P谱
sample7 31P

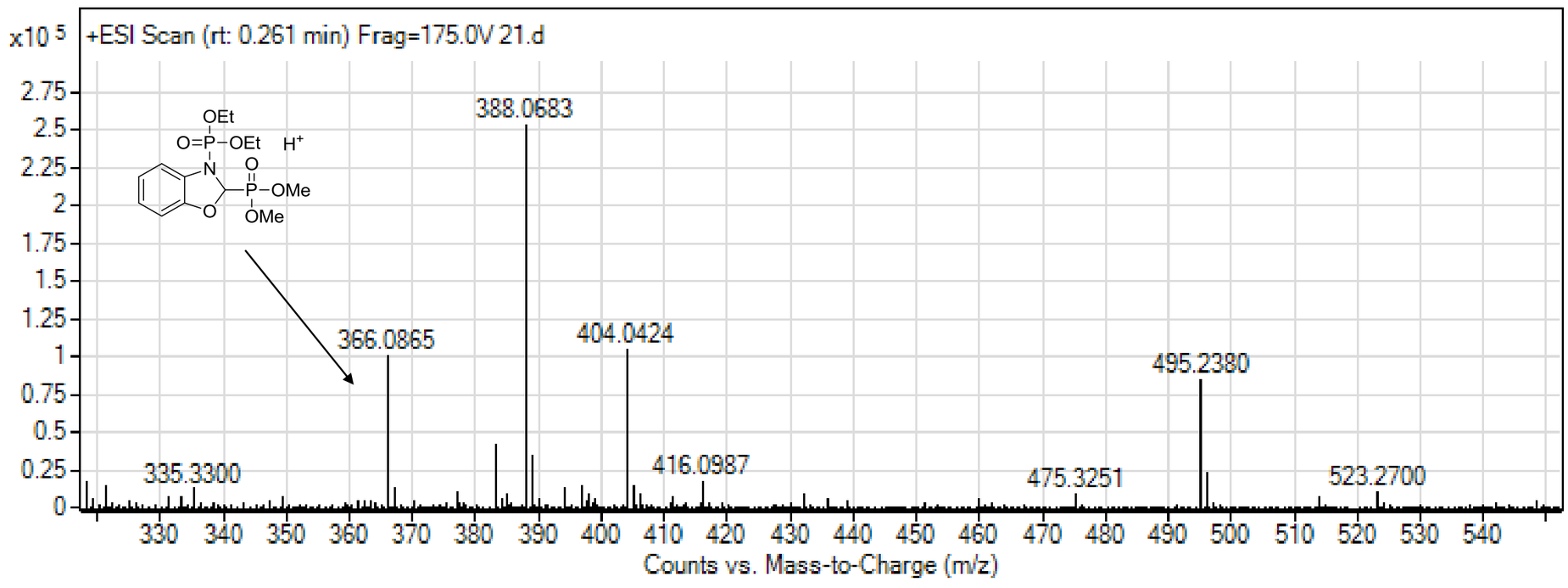
14.36
14.28
-1.28
-1.37



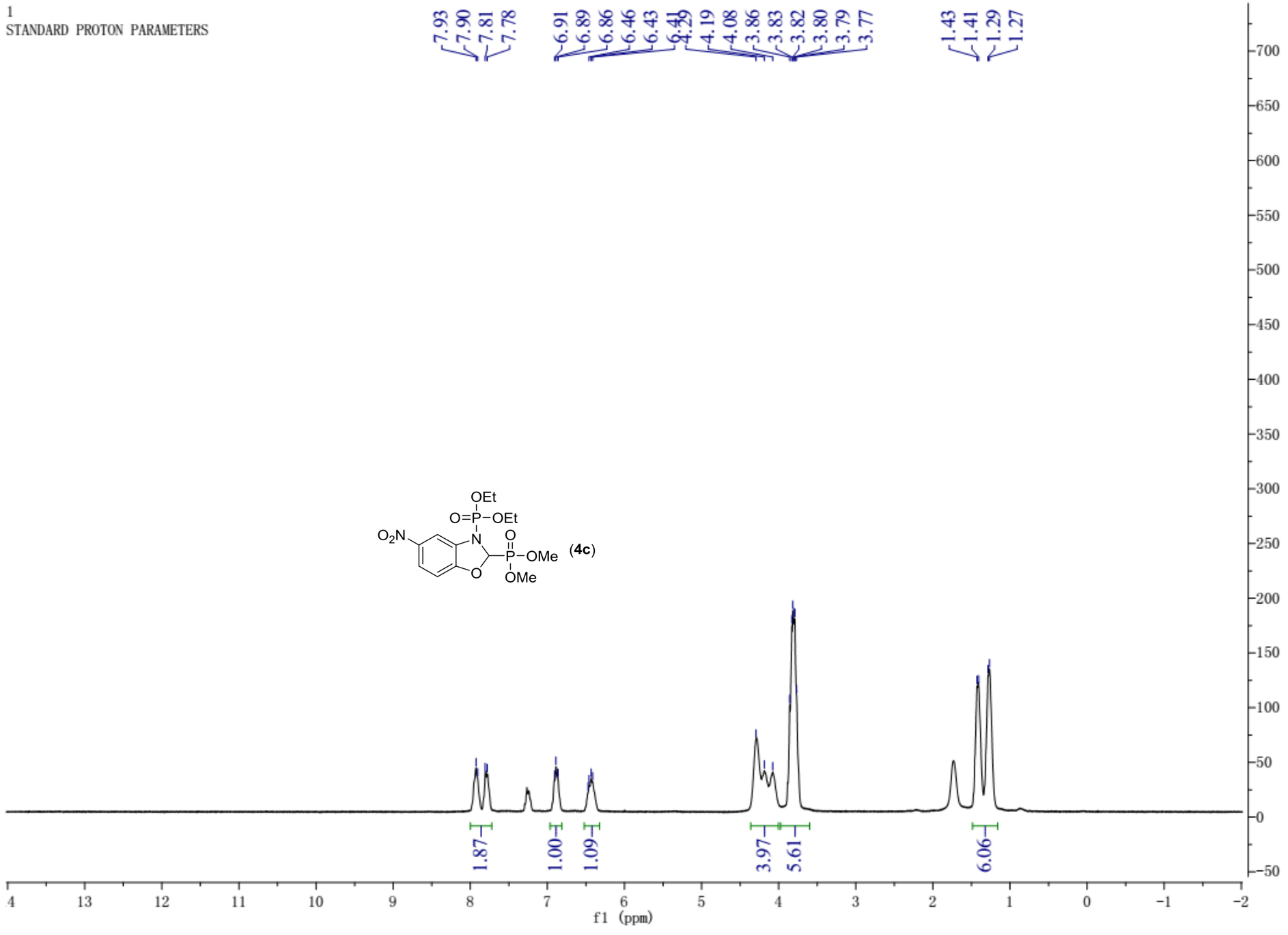
(**4b**)

14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

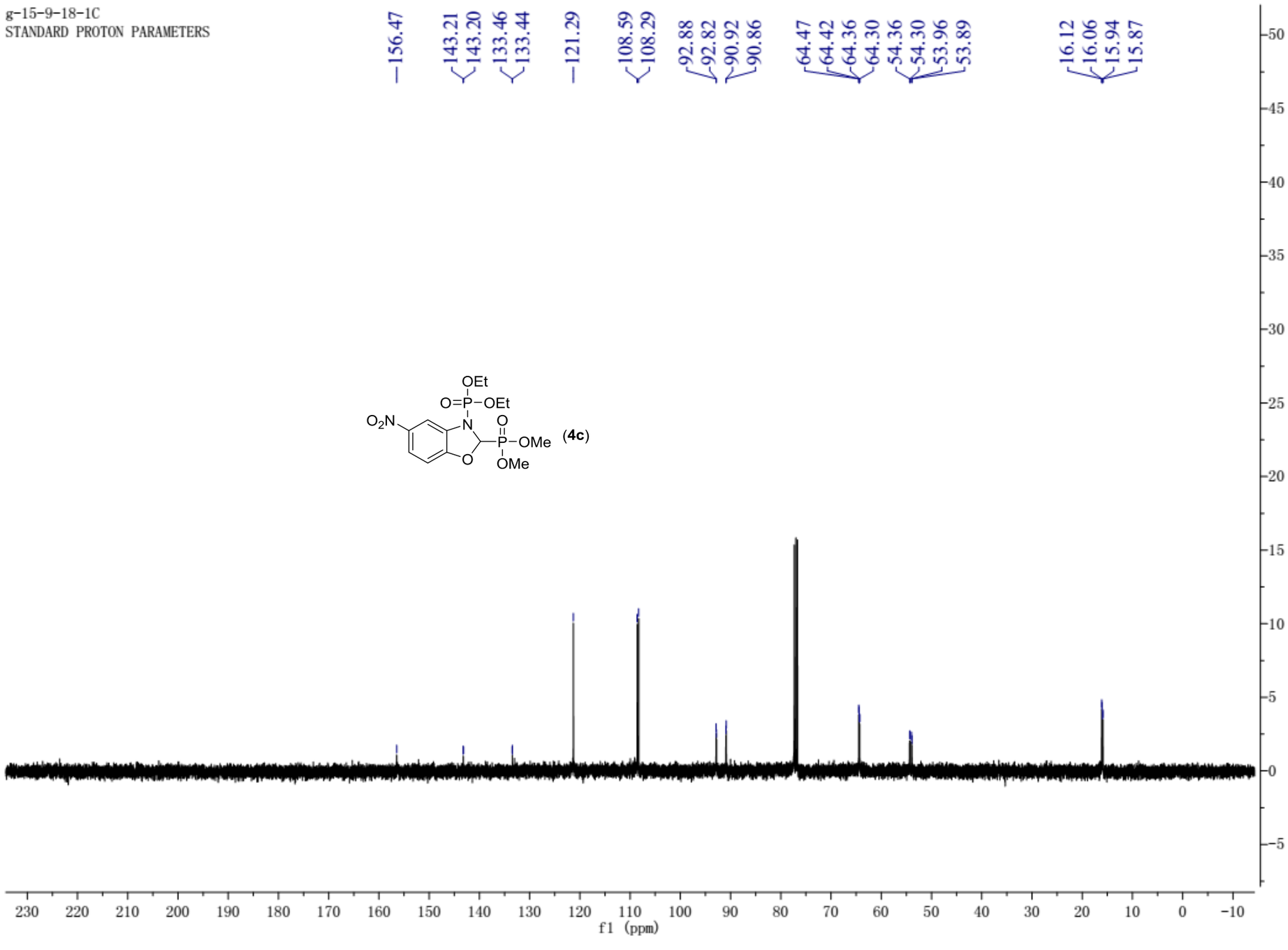
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)


x10 5
+ESI Scan (rt: 0.261 min) Frag=175.0V 21.d
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
OEt
O=P–OEt
H+
N
O
P–OMe
O
OMe
388.0683
366.0865
404.0424
495.2380
335.3300
416.0987
475.3251
523.2700
330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540
Counts vs. Mass-to-Charge (m/z)

1
STANDARD PROTON PARAMETERS

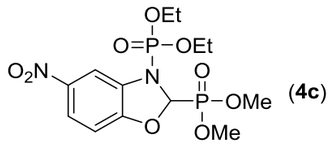


g-15-9-18-1C
STANDARD PROTON PARAMETERS



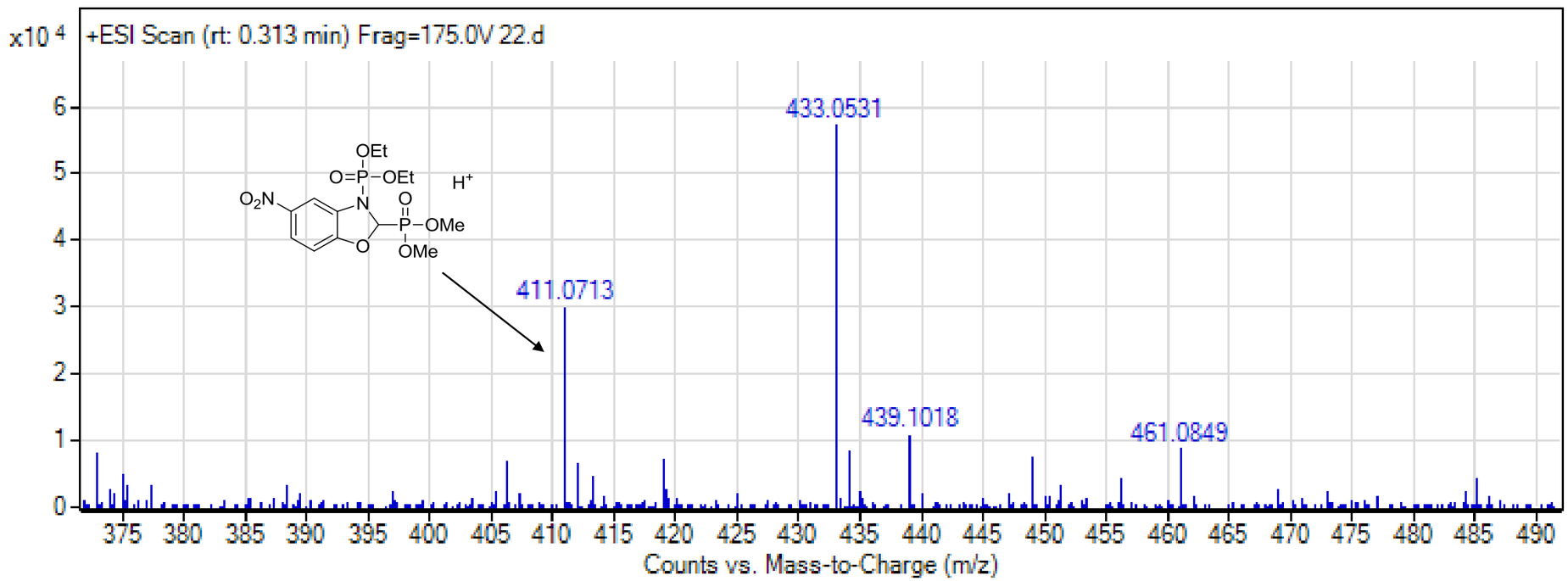
上两种P的P谱
sample6 31P

12.99
12.92
-2.83
-2.89

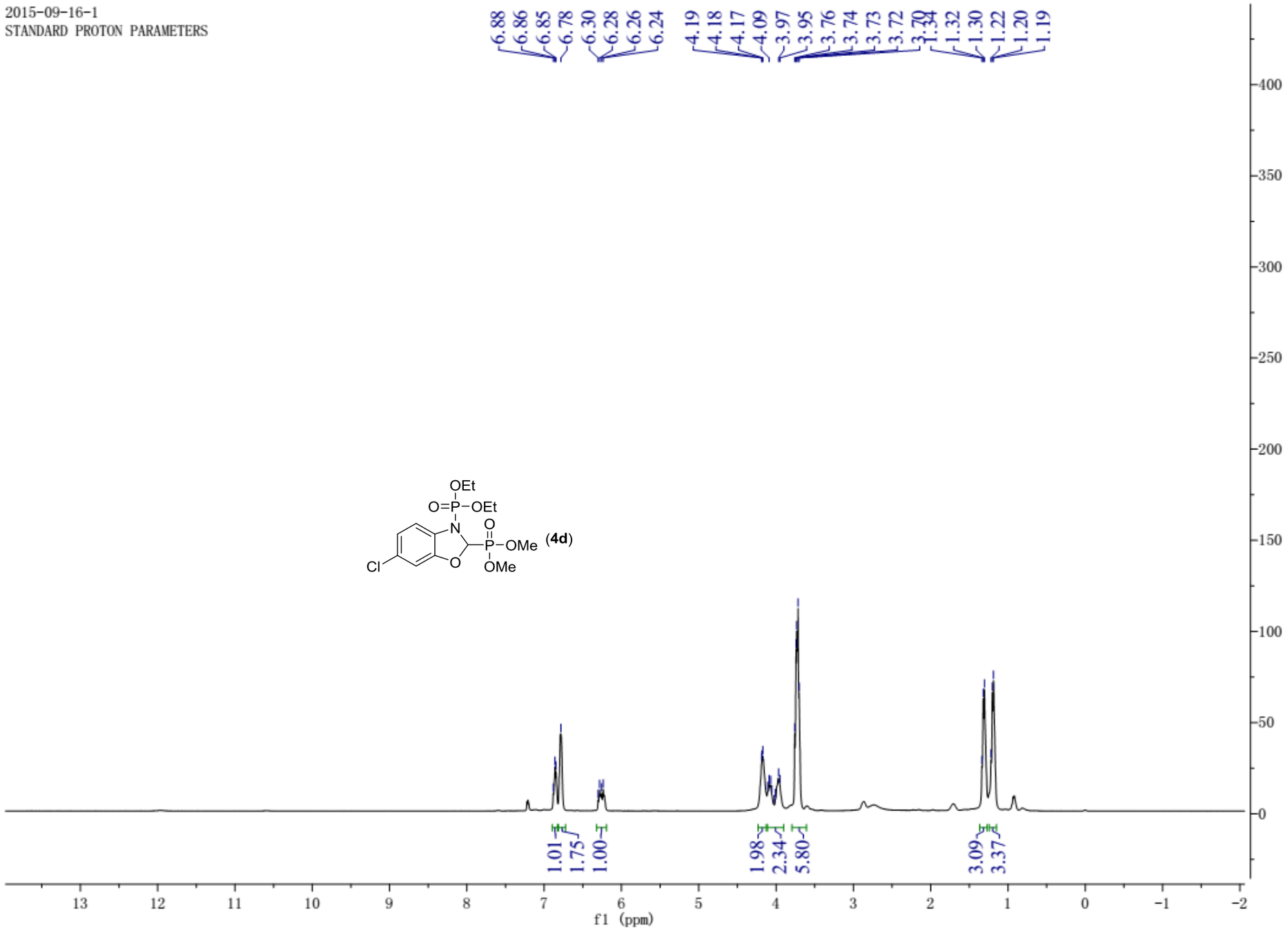


(**4c**)

f1 (ppm)

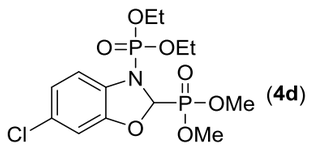

x10 4
+ESI Scan (rt: 0.313 min) Frag=175.0V 22.d
433.0531
411.0713
439.1018
461.0849
OEt
O=P–OEt
H+
O2N
N
O
P–OMe
OMe
6
5
4
3
2
1
0
375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490
Counts vs. Mass-to-Charge (m/z)

2015-09-16-1
STANDARD PROTON PARAMETERS



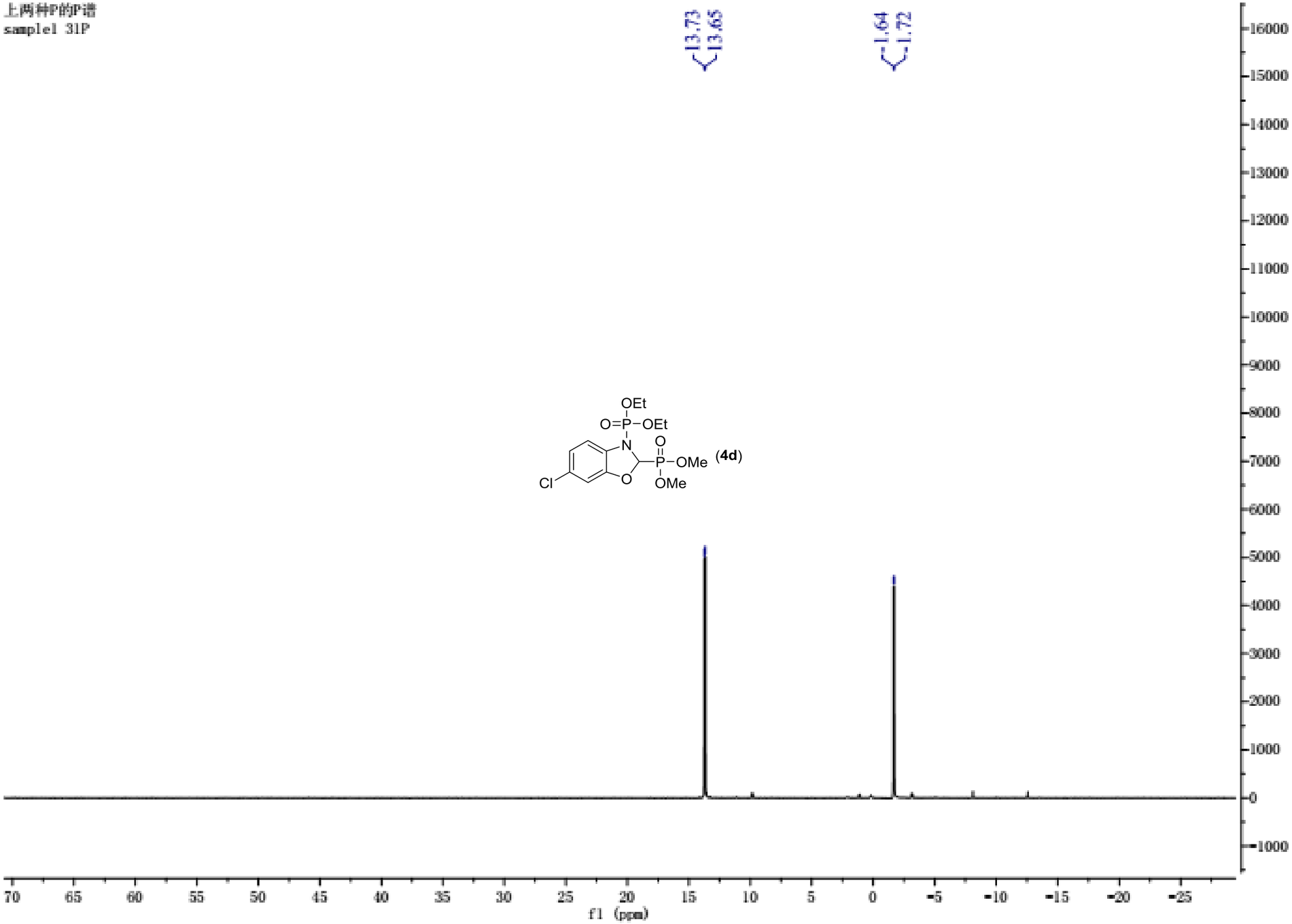
g-15-9-16-1-C13
STANDARD PROTON PARAMETERS

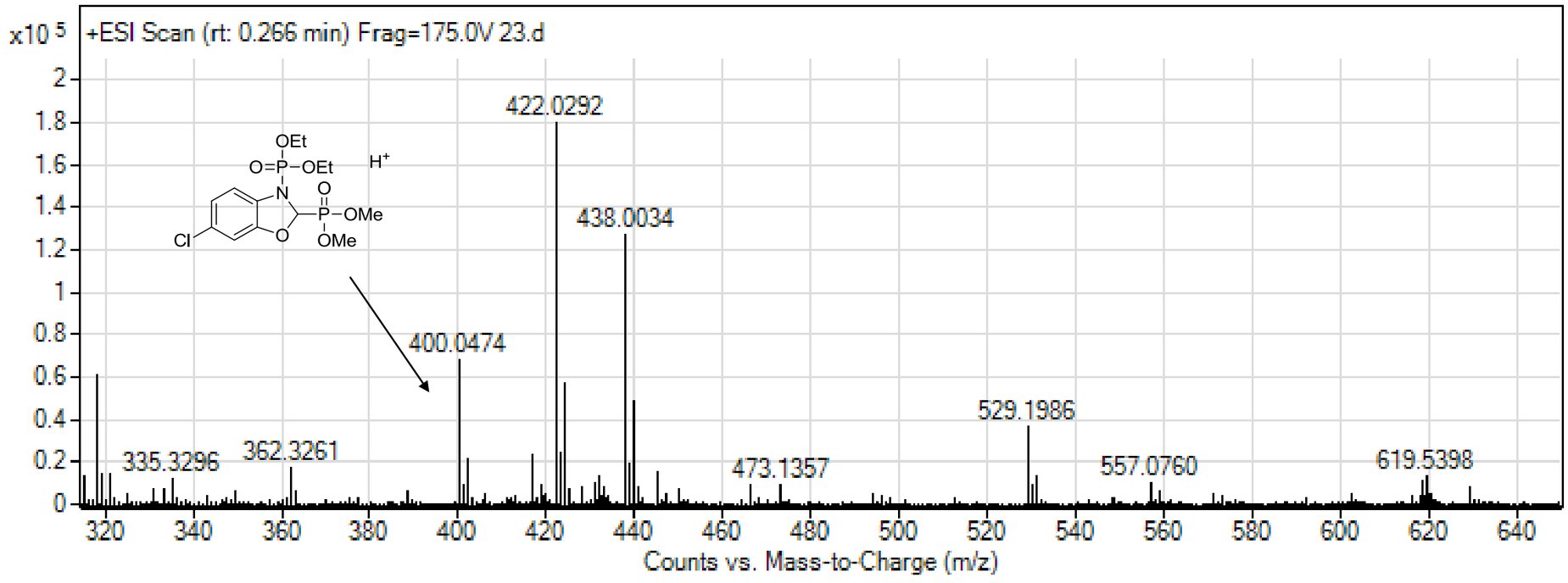
152.09
152.01
131.00
130.97
128.73
128.72
122.03
113.94
110.19
91.89
91.84
89.93
89.88
64.13
64.08
63.98
63.92
54.32
54.26
53.96
53.89
16.24
16.17
16.05
15.98

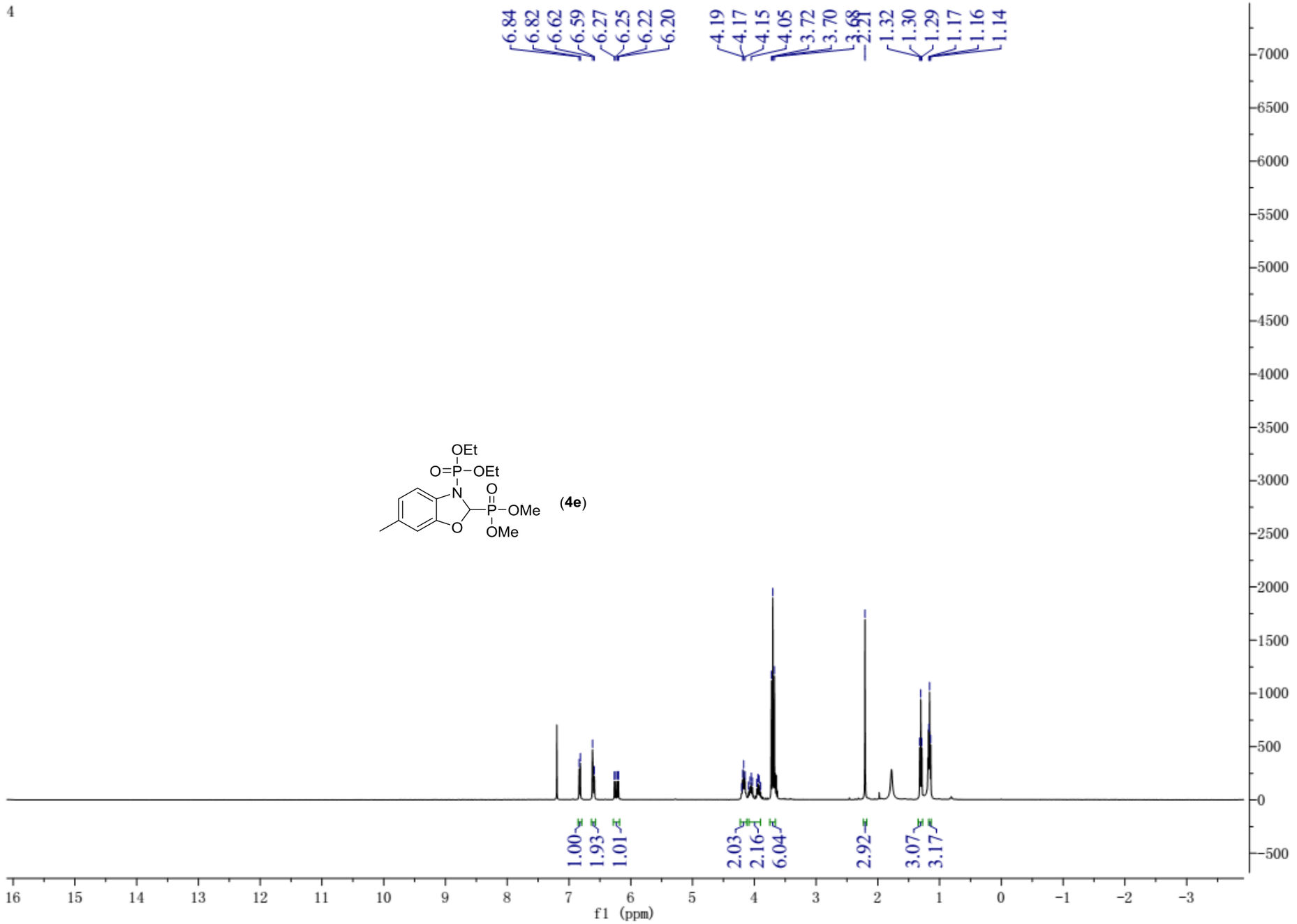


(**4d**)

上两种P的P谱
samplel 31P

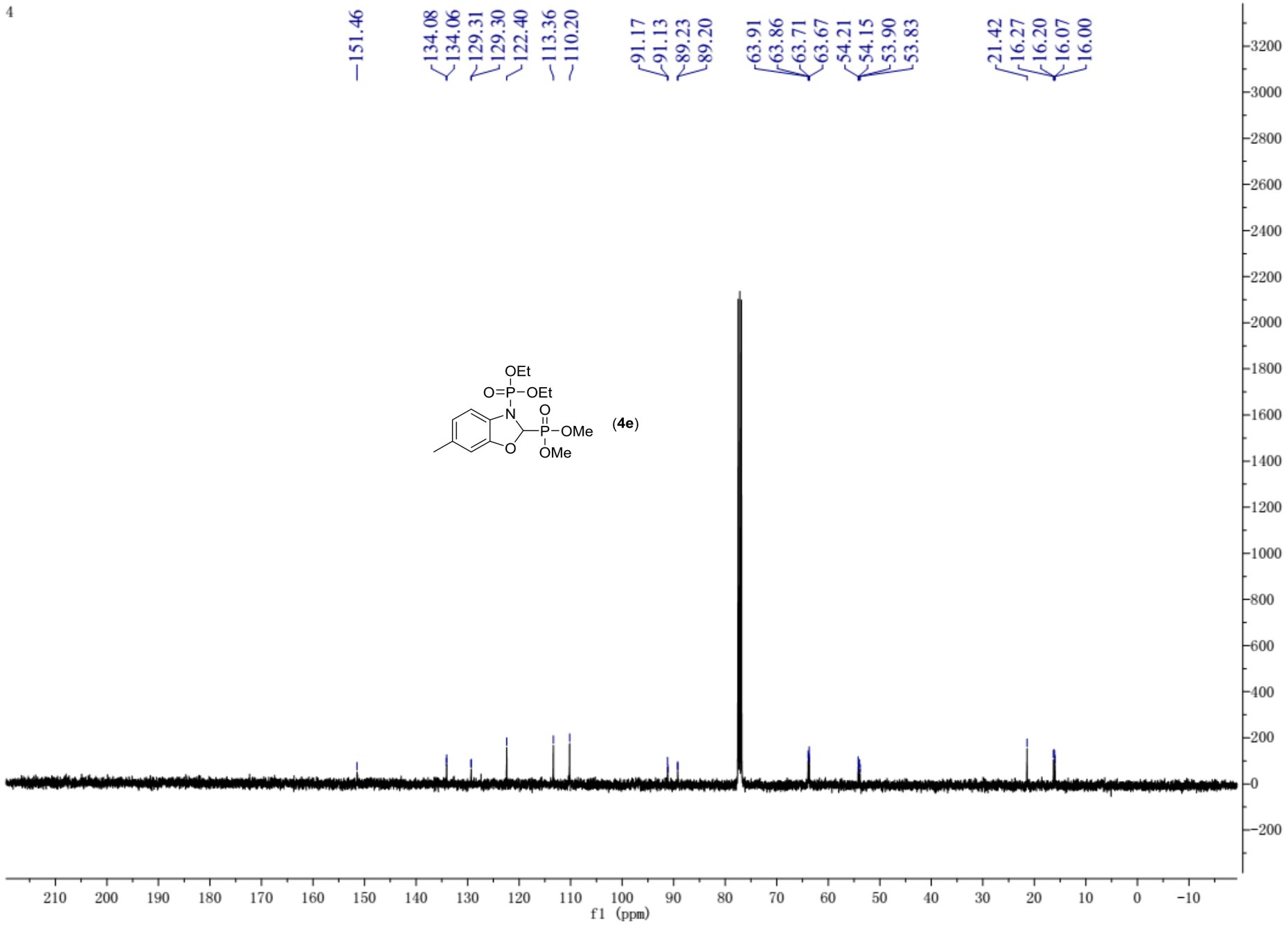



x10 5
+ESI Scan (rt: 0.266 min) Frag=175.0V 23.d
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
422.0292
438.0034
400.0474
529.1986
335.3296
362.3261
473.1357
557.0760
619.5398
OEt
O=P–OEt
H+
N
O
P–OMe
OMe
Cl
O
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
620
640
Counts vs. Mass-to-Charge (m/z)

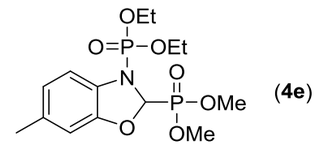

6.84
6.82
6.62
6.59
6.27
6.25
6.22
6.20
4.19
4.17
4.15
4.05
3.72
3.70
3.68
2.21
1.32
1.30
1.29
1.17
1.16
1.14
OEt
O=P–OEt
N
O
P–OMe
O
OMe
1.00
1.93
1.01
2.03
2.16
6.04
2.92
3.07
3.17
f1 (ppm)

(**4e**)

4


151.46
134.08
134.06
129.31
129.30
122.40
113.36
110.20
91.17
91.13
89.23
89.20
63.91
63.86
63.71
63.67
54.21
54.15
53.90
53.83
21.42
16.27
16.20
16.07
16.00
OEt
O=P−OEt
N
O
P−OMe
O
OMe
(4e)
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

13.91
13.77
1.47
1.61

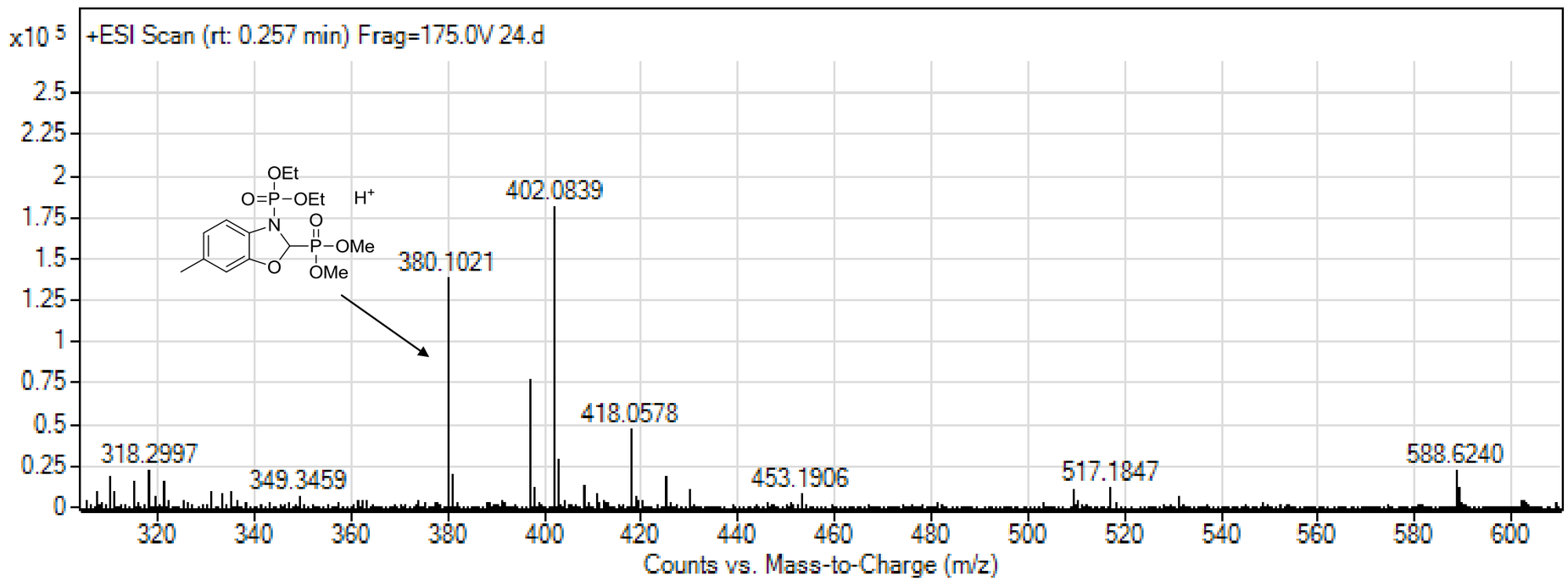


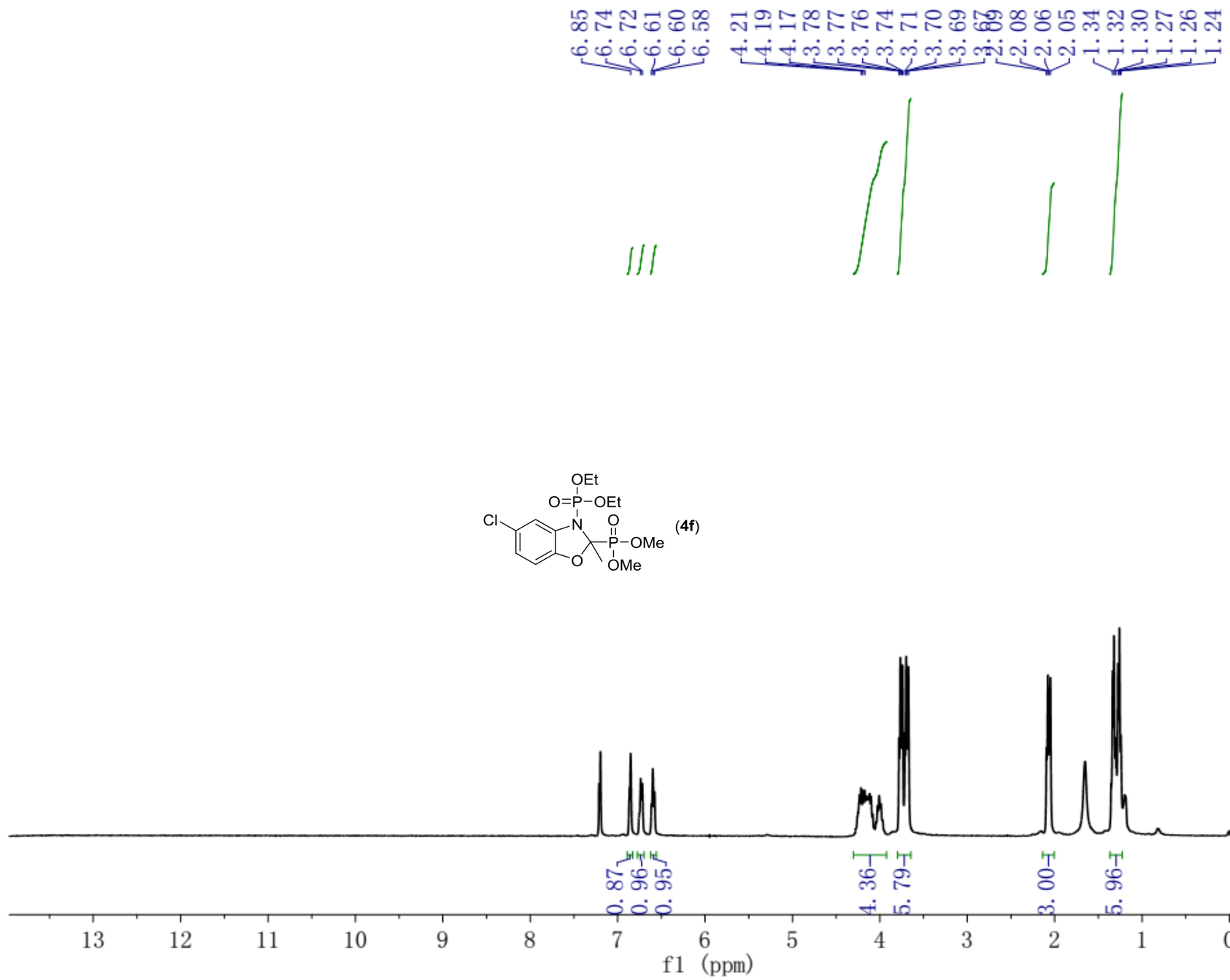
(**4e**)

400
350
300
250
200
150
100
50
0
-50

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

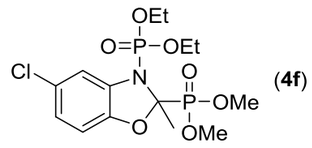
f1 (ppm)


x10 5
+ESI Scan (rt: 0.257 min) Frag=175.0V 24.d
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
OEt
O=P–OEt
H+
N
O
P–OMe
O
OMe
380.1021
402.0839
418.0578
318.2997
349.3459
453.1906
517.1847
588.6240
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
Counts vs. Mass-to-Charge (m/z)


6.85
6.74
6.72
6.61
6.60
6.58
4.21
4.19
4.17
3.78
3.77
3.76
3.74
3.71
3.70
3.69
3.67
2.08
2.06
2.05
1.34
1.32
1.30
1.27
1.26
1.24
OEt
O=P–OEt
Cl
N
O
O
P–OMe
OMe
(4f)
0.87
0.96
0.95
4.36
5.79
3.00
5.96
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

g-15-10-23-2-C13
STANDARD PROTON PARAMETERS

148.56
148.45
134.38
134.33
126.64
122.14
112.65
108.83
102.10
100.28
64.03
63.98
63.57
63.52
54.41
54.34
54.06
53.99
22.70
22.53
16.25
16.18
16.16
16.09

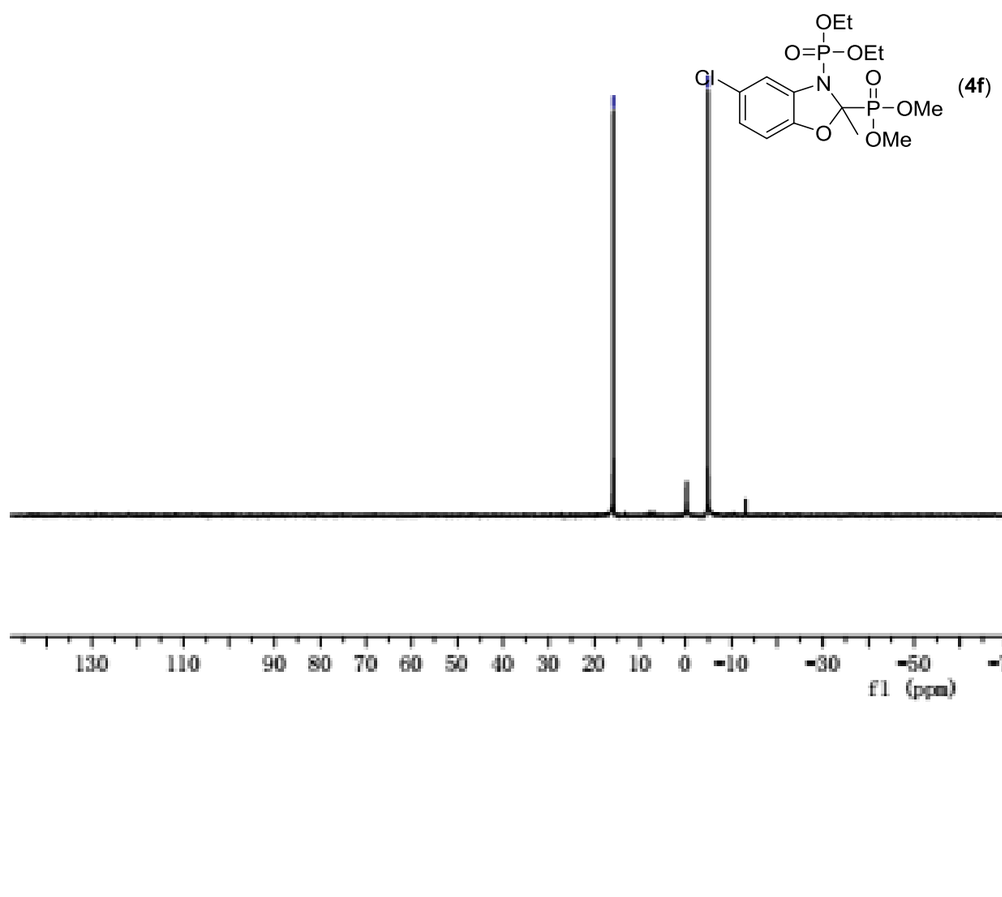


(**4f**)

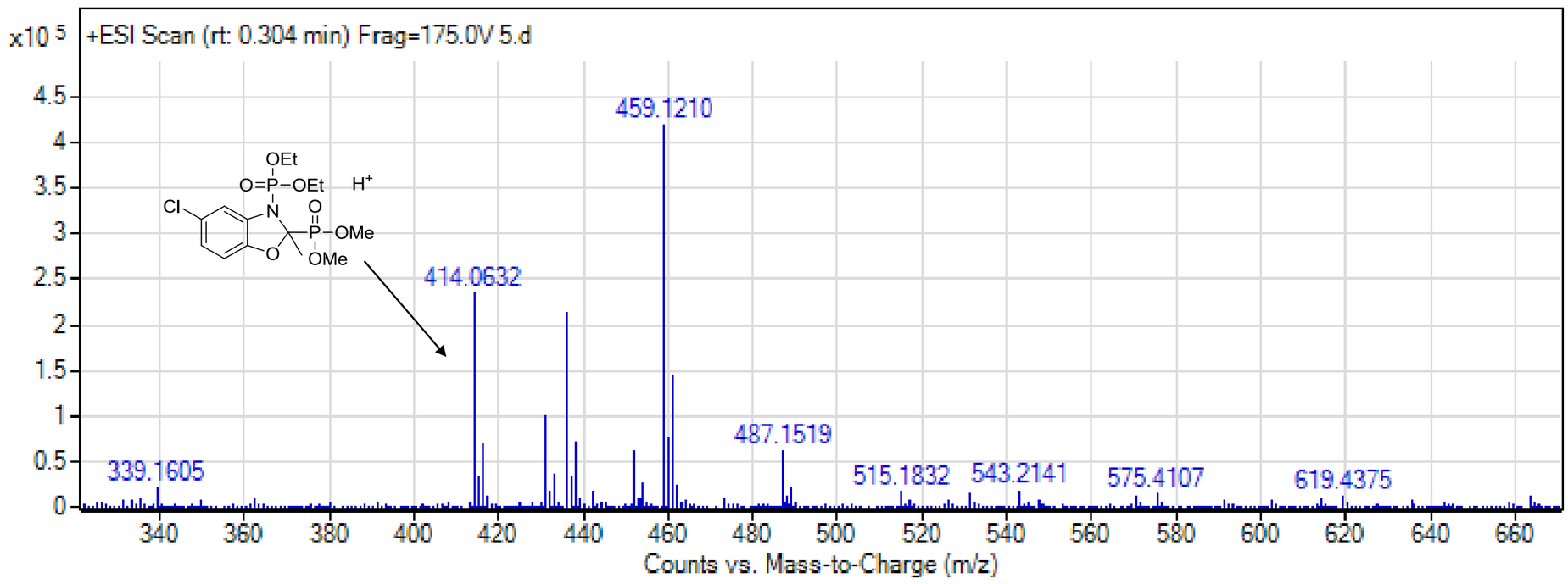
2

15.90

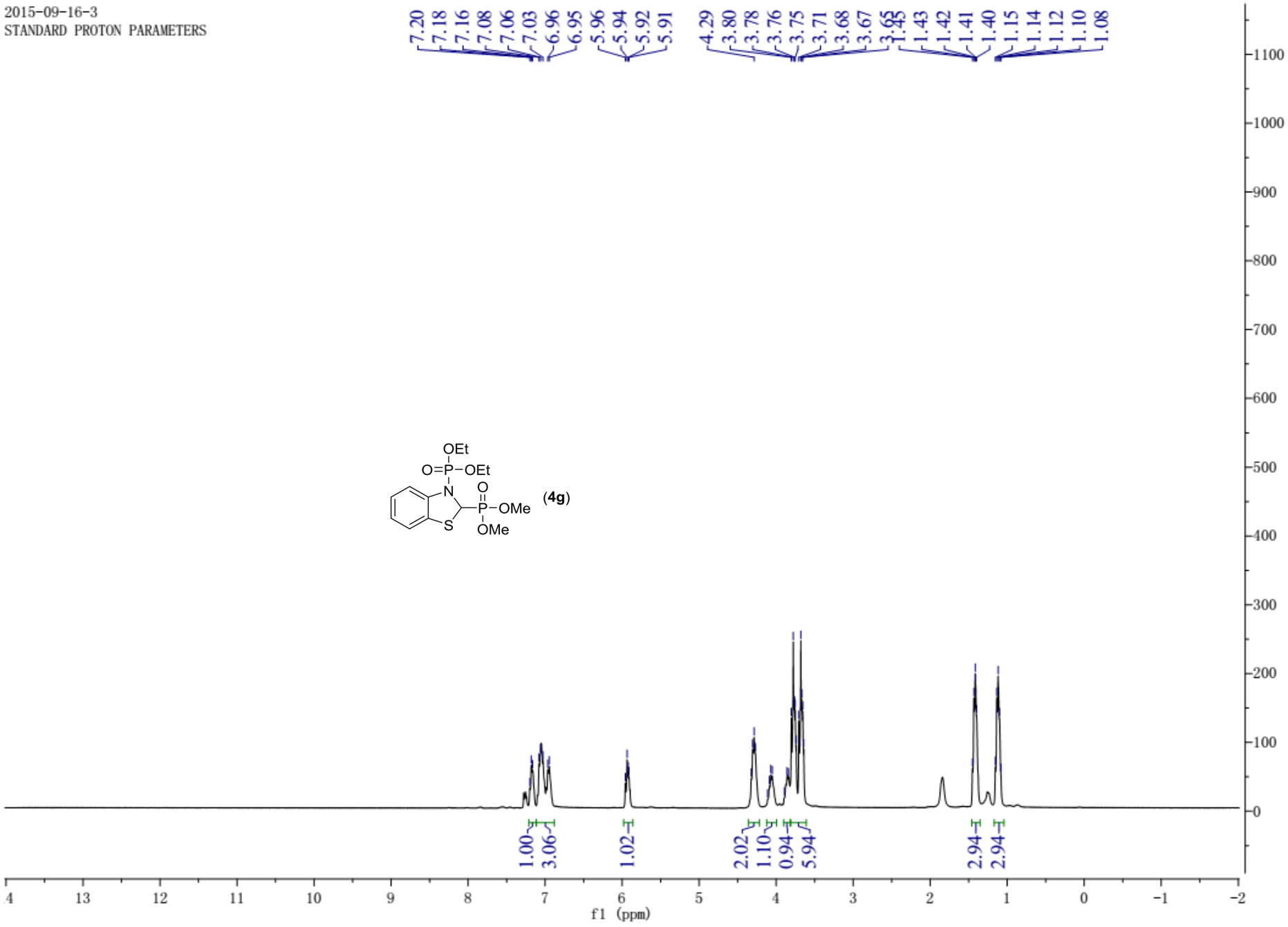
4.87


OEt
O=P–OEt
Cl
N
O
O
P–OMe
OMe
(4f)

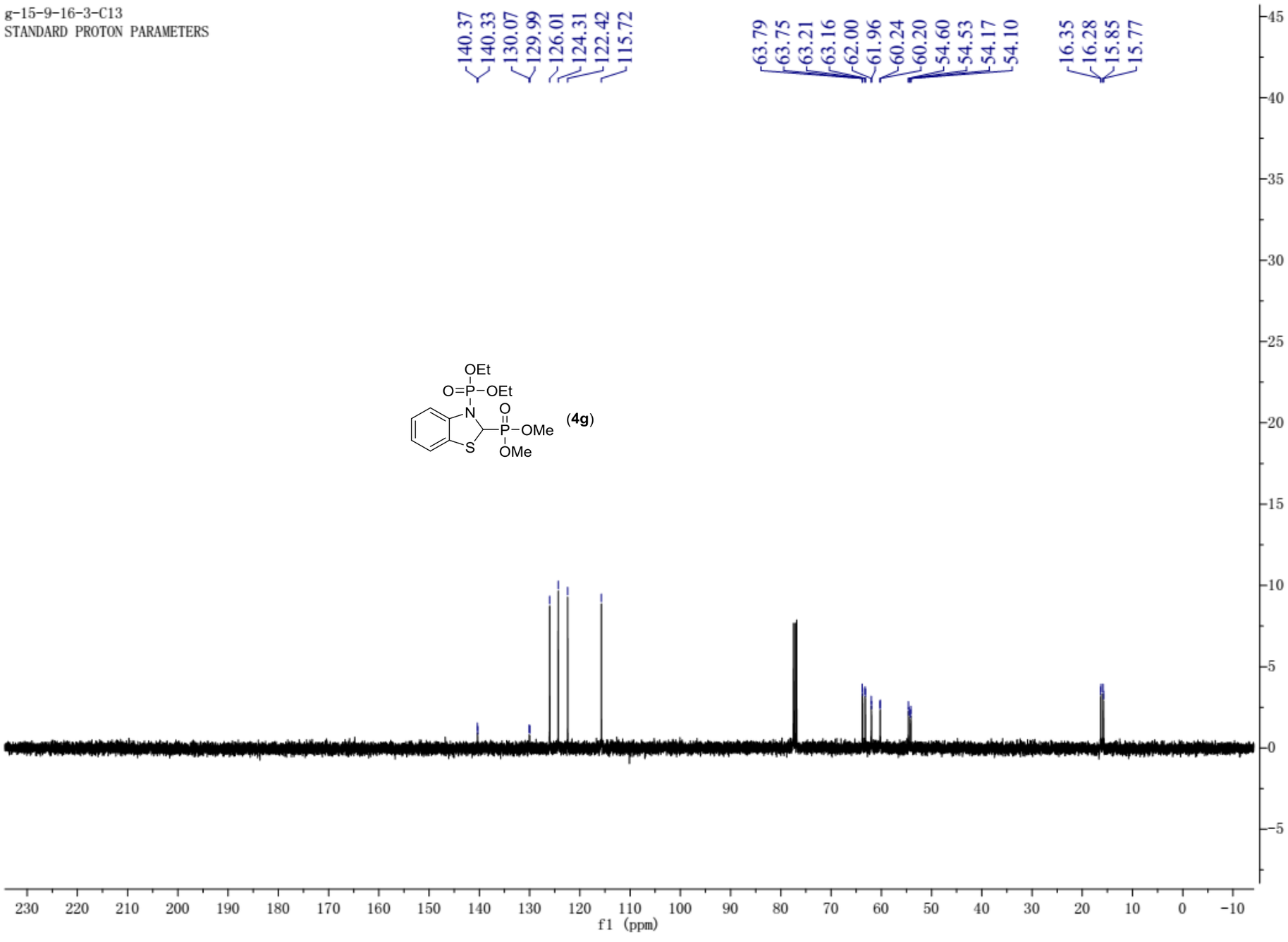
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)


x10 5
+ESI Scan (rt: 0.304 min) Frag=175.0V 5.d
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
459.1210
414.0632
487.1519
339.1605
515.1832
543.2141
575.4107
619.4375
340
360
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
Counts vs. Mass-to-Charge (m/z)
OEt
O=P–OEt
H+
Cl
N
O
P–OMe
O
OMe

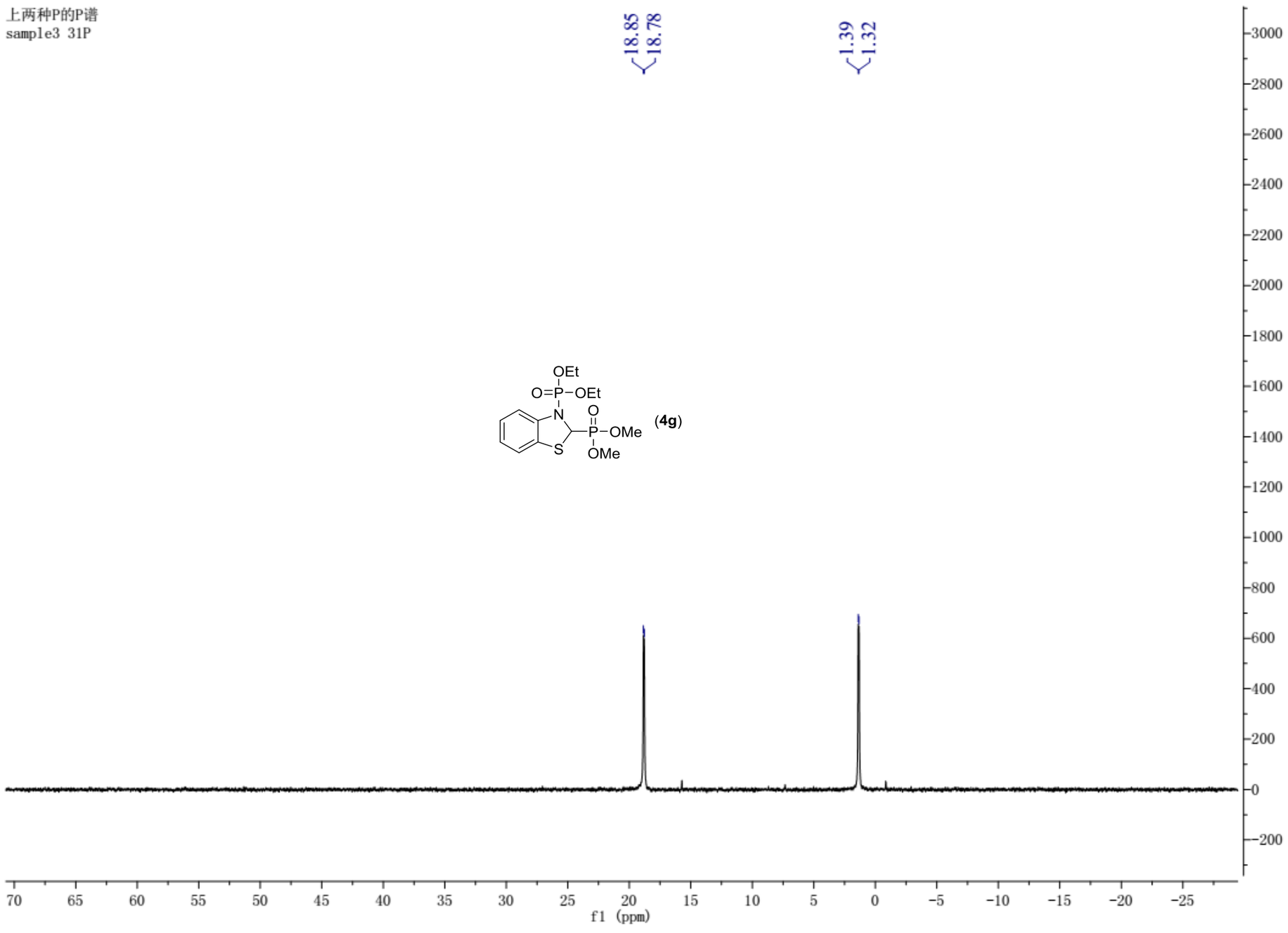
2015-09-16-3
STANDARD PROTON PARAMETERS

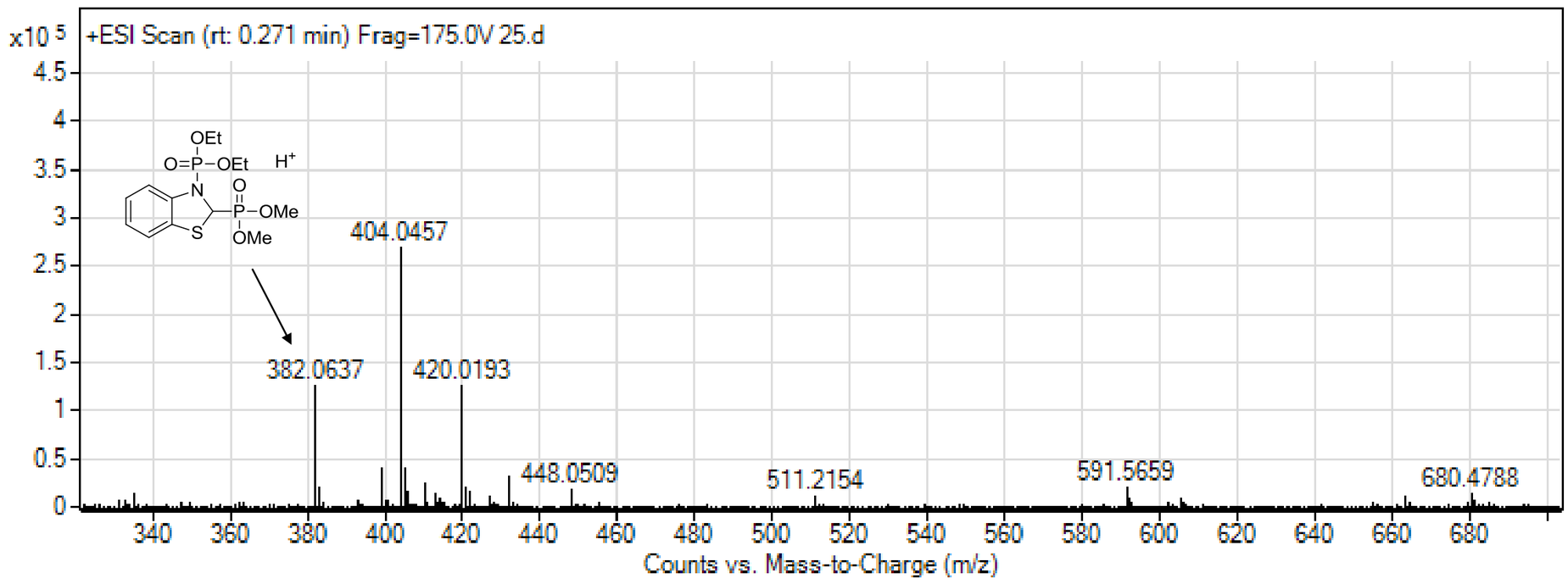


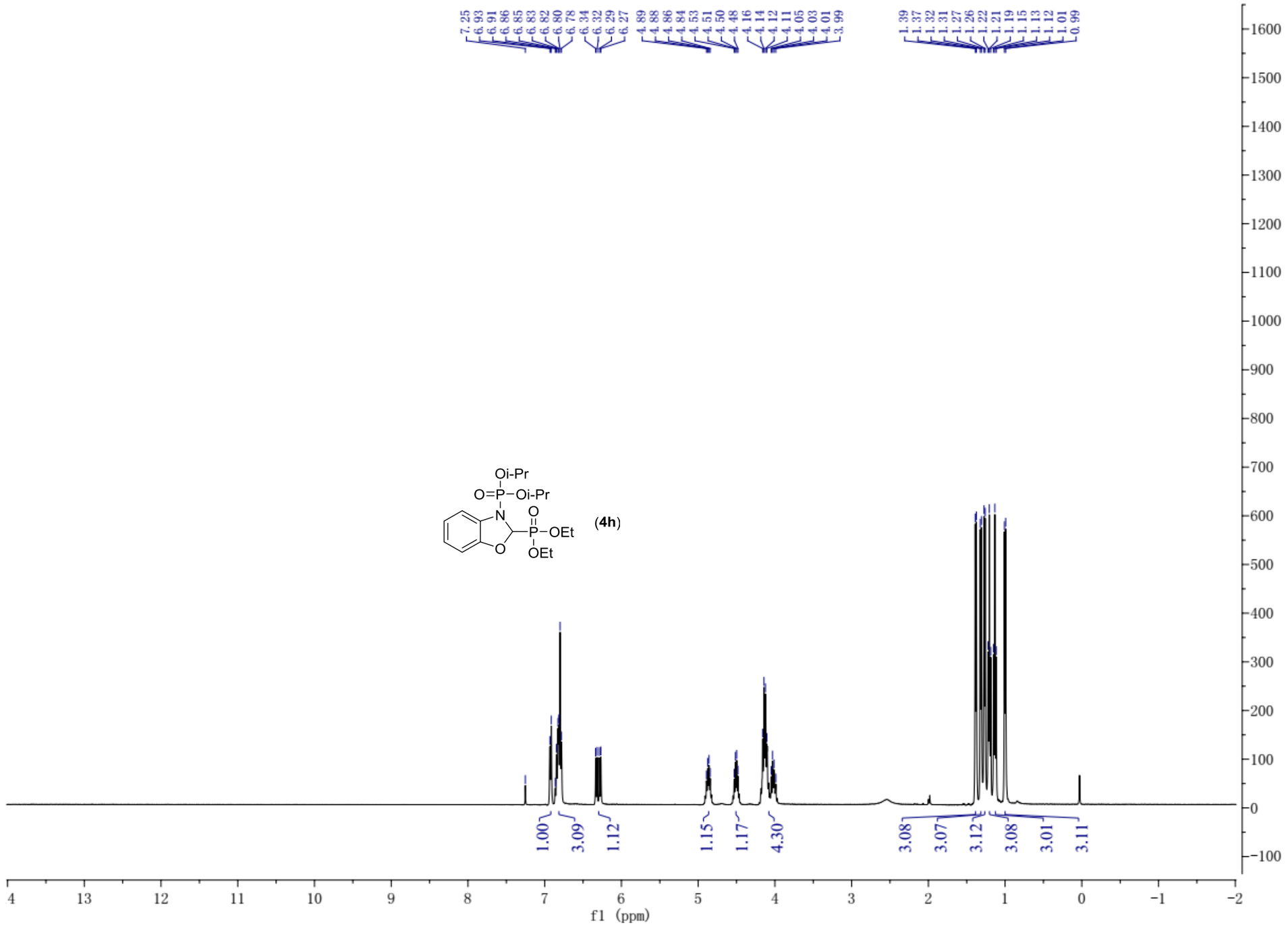
g-15-9-16-3-C13
STANDARD PROTON PARAMETERS

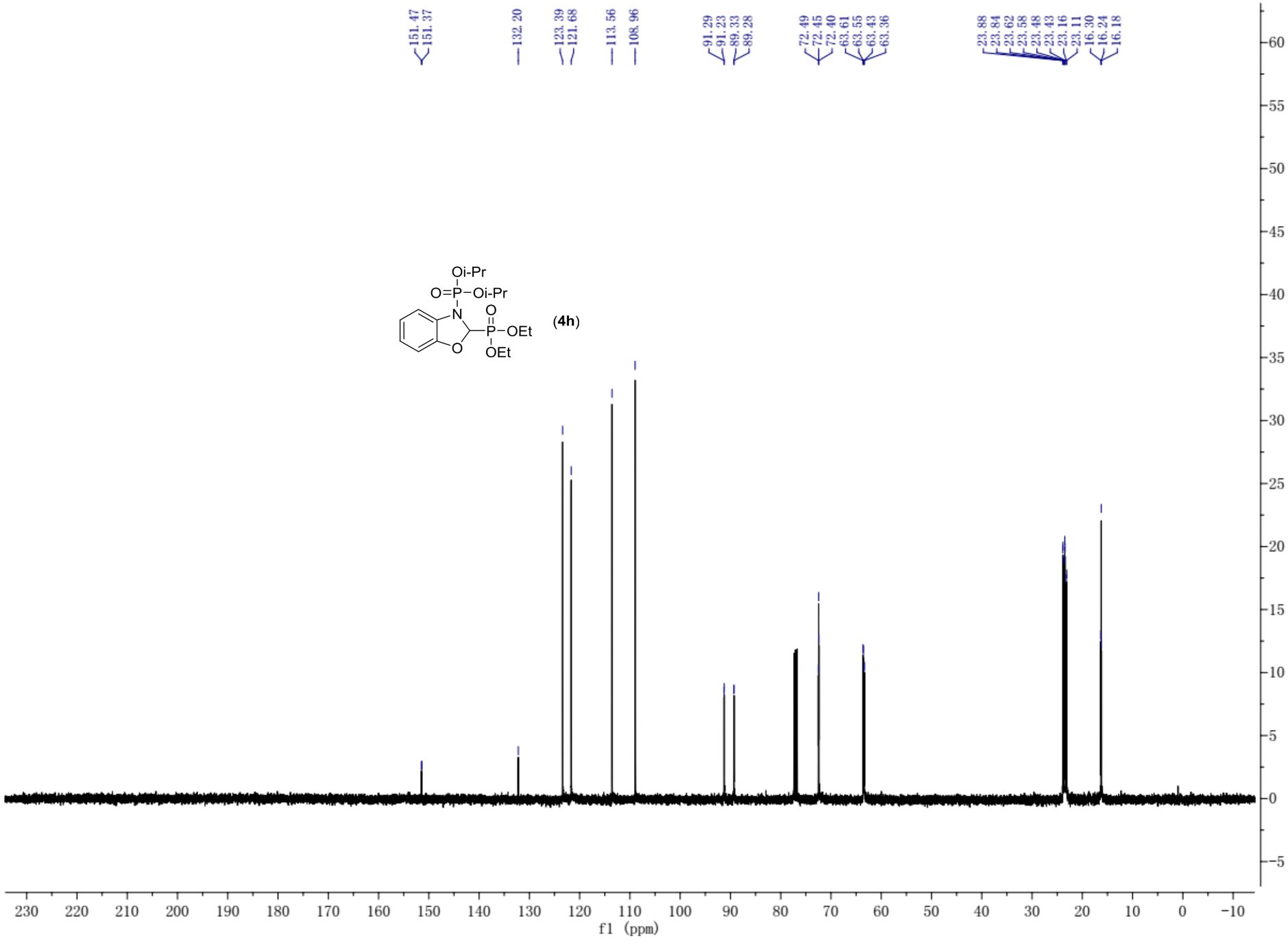


上两种P的P谱
sample3 31P




x10 5
+ESI Scan (rt: 0.271 min) Frag=175.0V 25.d
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
OEt
O=P–OEt
H+
N
O
P–OMe
S
OMe
404.0457
382.0637
420.0193
448.0509
511.2154
591.5659
680.4788
340
360
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
Counts vs. Mass-to-Charge (m/z)

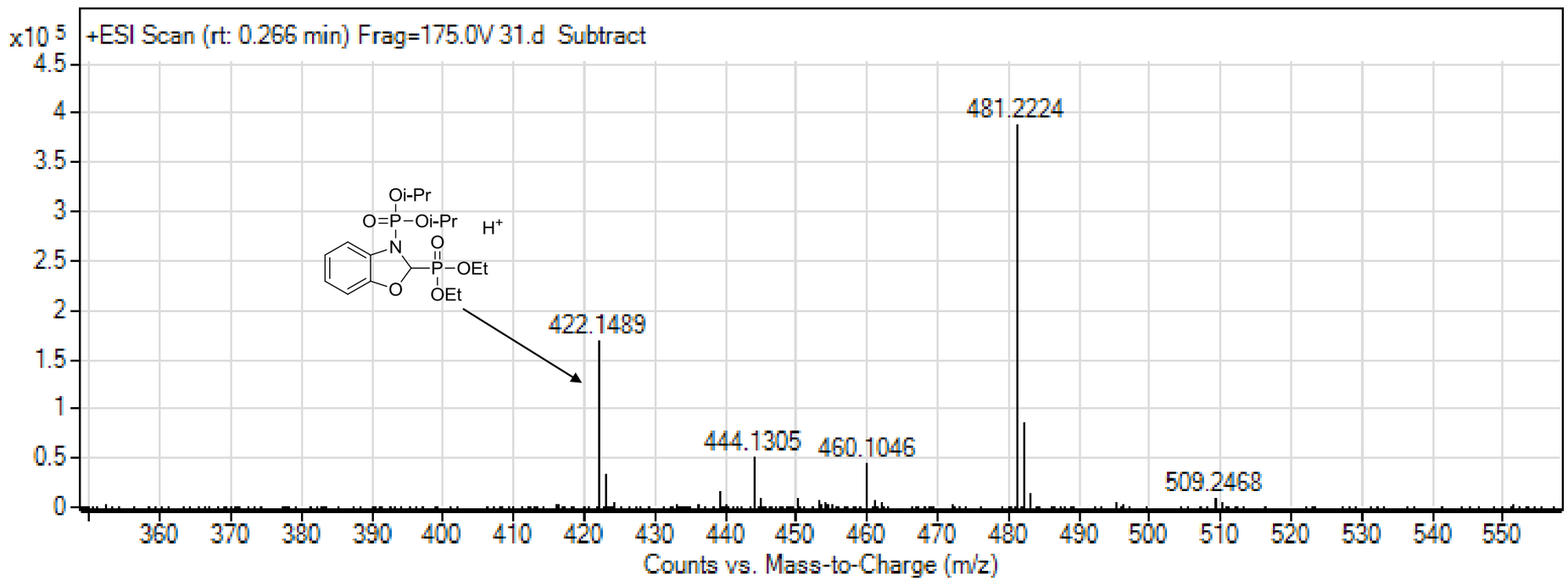

7.25
6.93
6.91
6.86
6.85
6.83
6.82
6.80
6.78
6.34
6.32
6.29
6.27
4.89
4.88
4.86
4.84
4.53
4.51
4.50
4.48
4.16
4.14
4.12
4.11
4.05
4.03
4.01
3.99
1.39
1.37
1.32
1.31
1.27
1.26
1.22
1.21
1.19
1.15
1.13
1.12
1.01
0.99
Oi-Pr
O=P–Oi-Pr
N
O
P–OEt
OEt
(4h)
1.00
3.09
1.12
1.15
1.17
4.30
3.08
3.07
3.12
3.08
3.01
3.11
f1 (ppm)

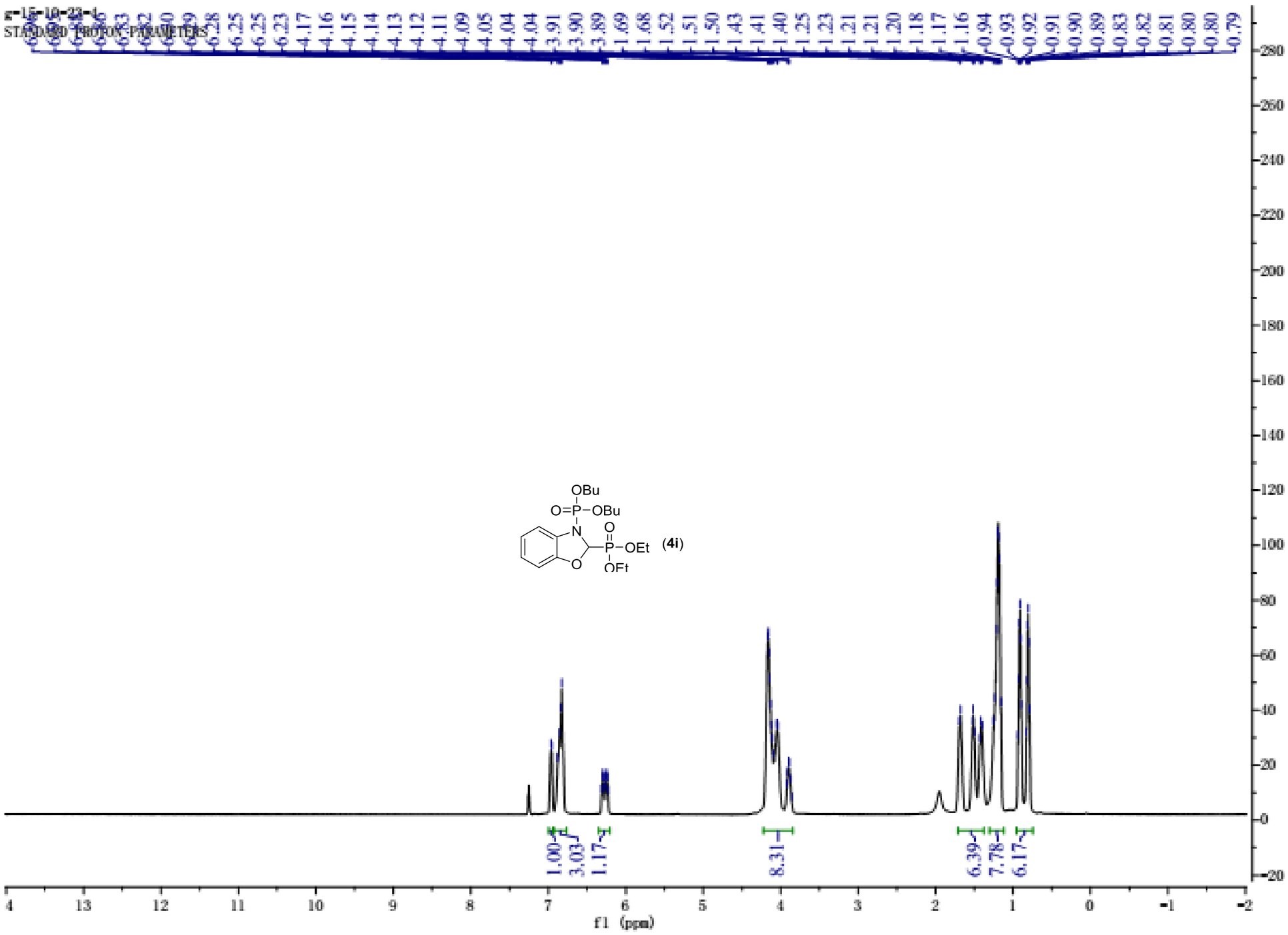

151.47
151.37
132.20
123.39
121.68
113.56
108.96
91.29
91.23
89.33
89.28
72.49
72.45
72.40
63.61
63.55
63.43
63.36
23.88
23.84
23.62
23.58
23.48
23.43
23.16
23.11
16.30
16.24
16.18
Oi-Pr
O=P−Oi-Pr
N
O
P−OEt
O
OEt
O
(4h)
f1 (ppm)

1

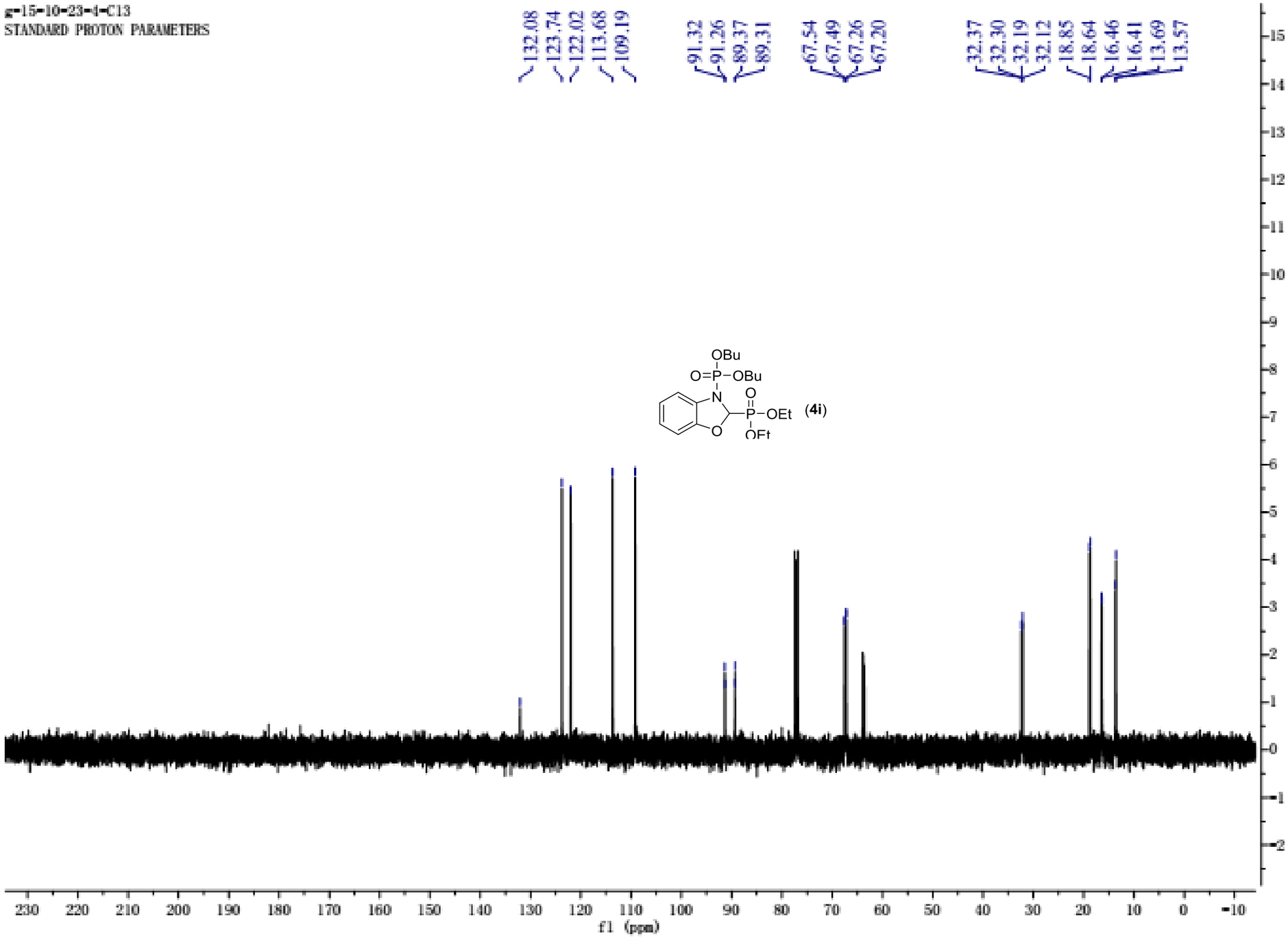
11.30
11.17
-3.95
-4.08

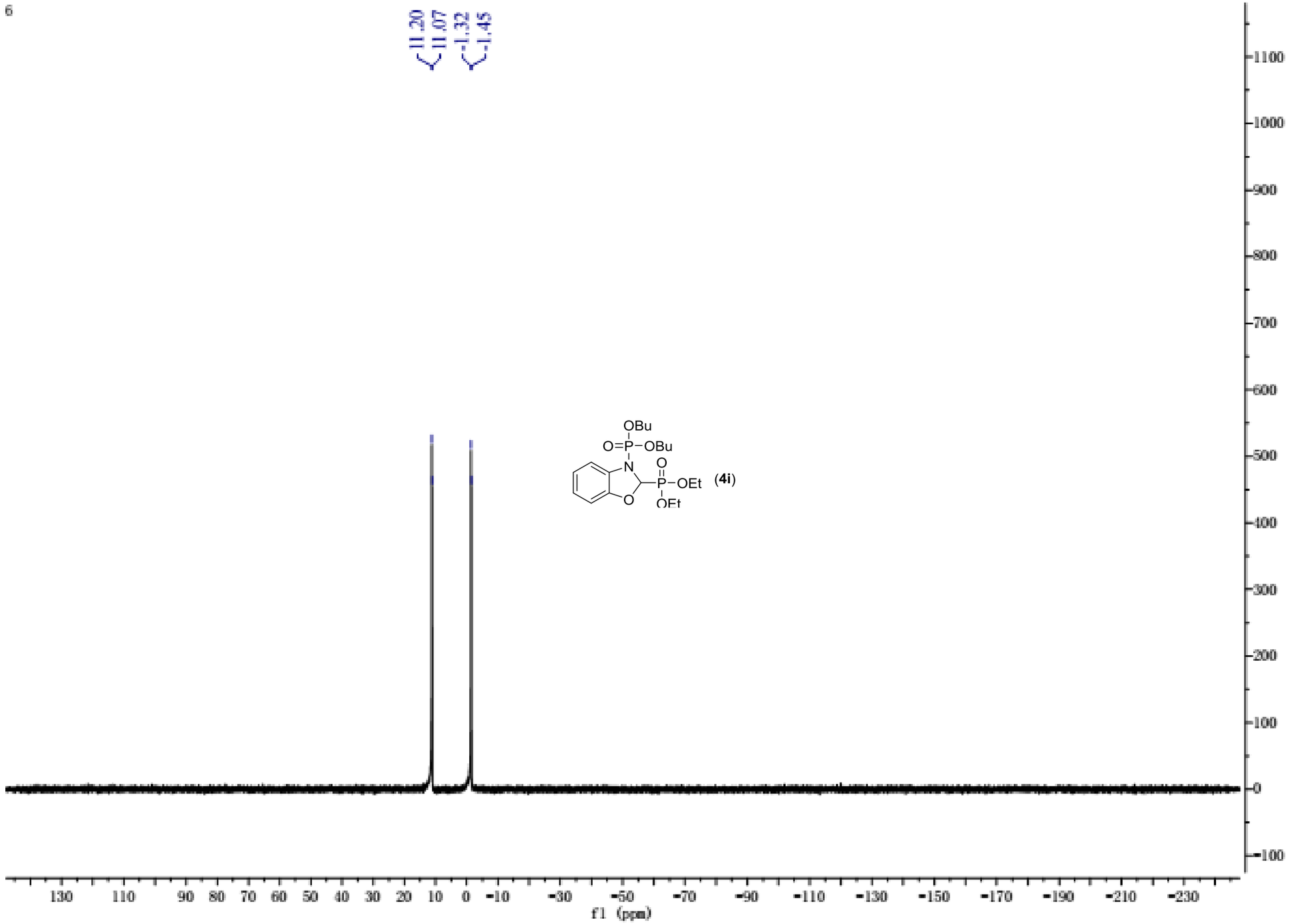
(**4h**)

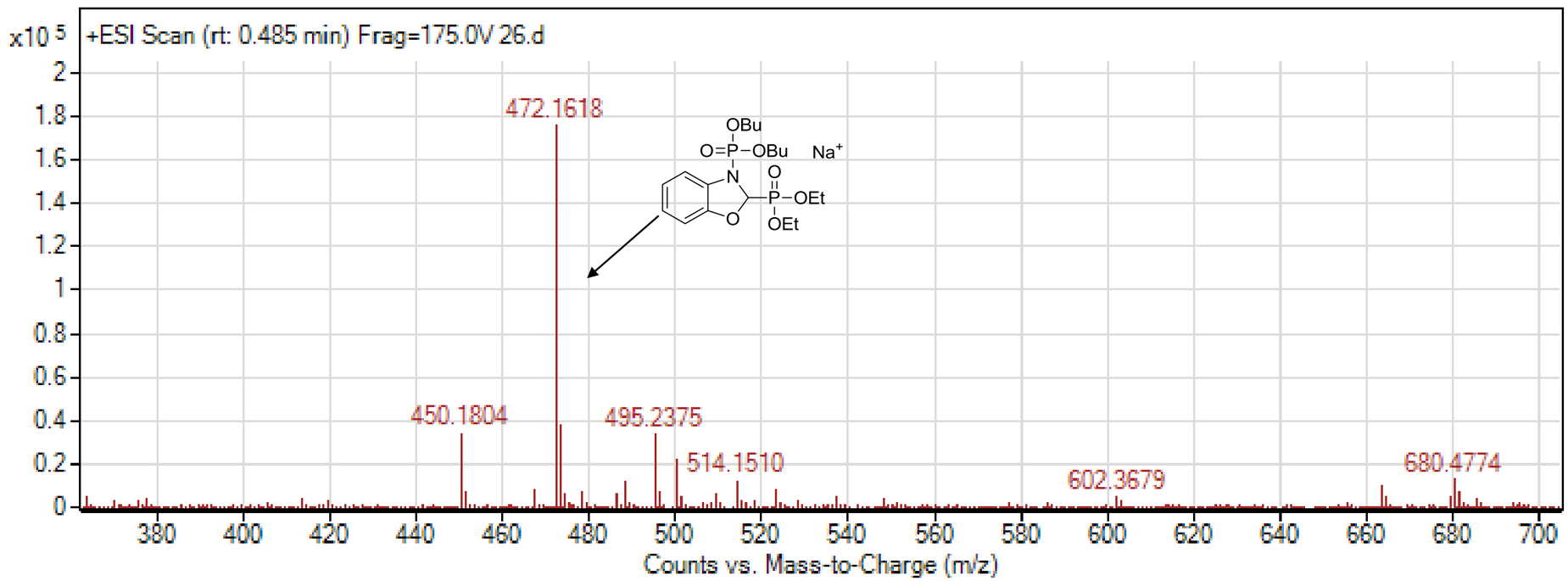

x10 5
+ESI Scan (rt: 0.266 min) Frag=175.0V 31.d Subtract
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
481.2224
422.1489
444.1305
460.1046
509.2468
Oi-Pr
O=P–Oi-Pr
H+
N
O
O
P–OEt
OEt
360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550
Counts vs. Mass-to-Charge (m/z)


OBu
O=P–OBu
N
O
P–OEt
OEt
O
(4i)
1.00
3.03
1.17
8.31
6.39
7.78
6.17
f1 (ppm)

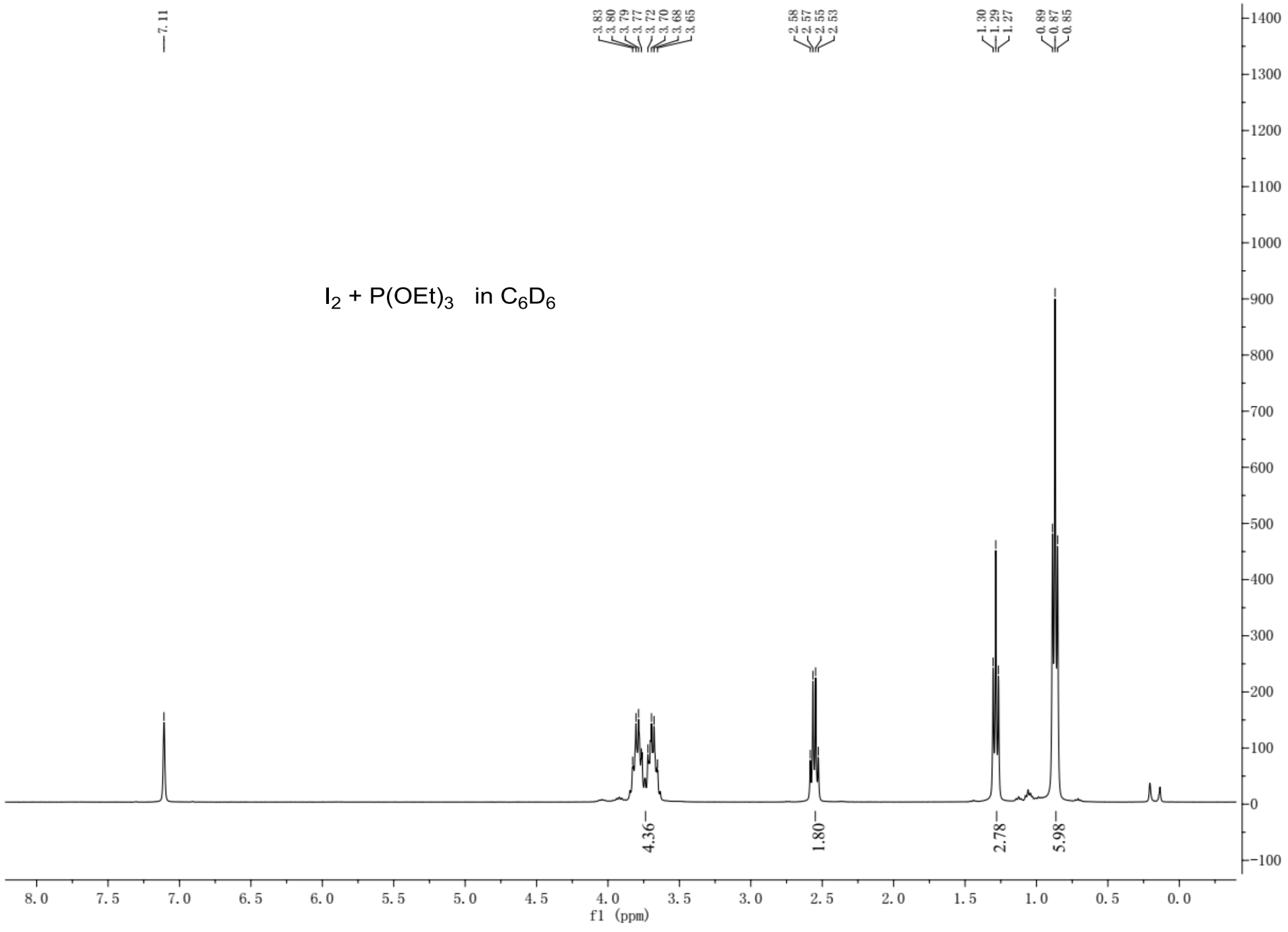
g-15-10-23-4-C13
STANDARD PROTON PARAMETERS

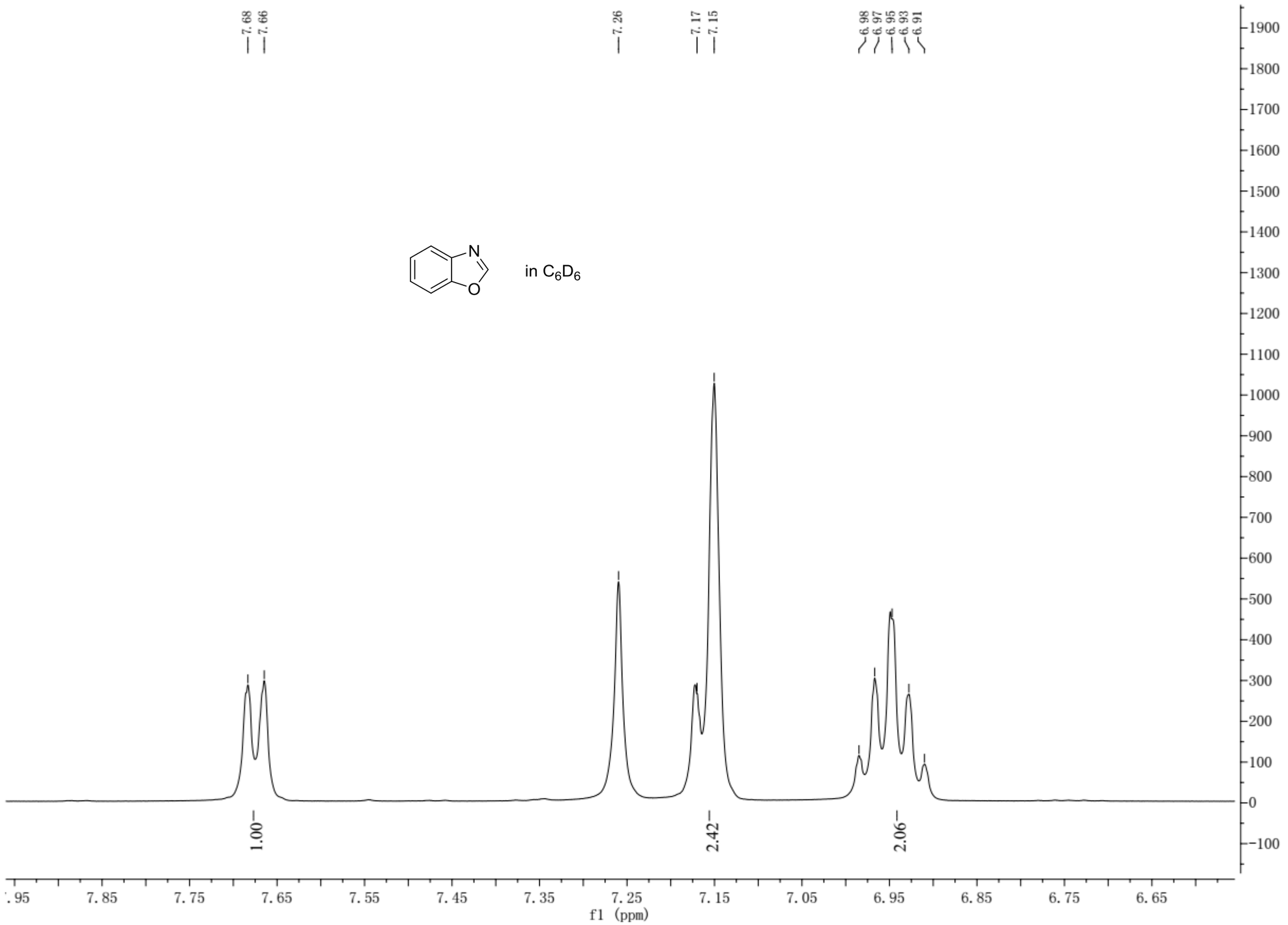


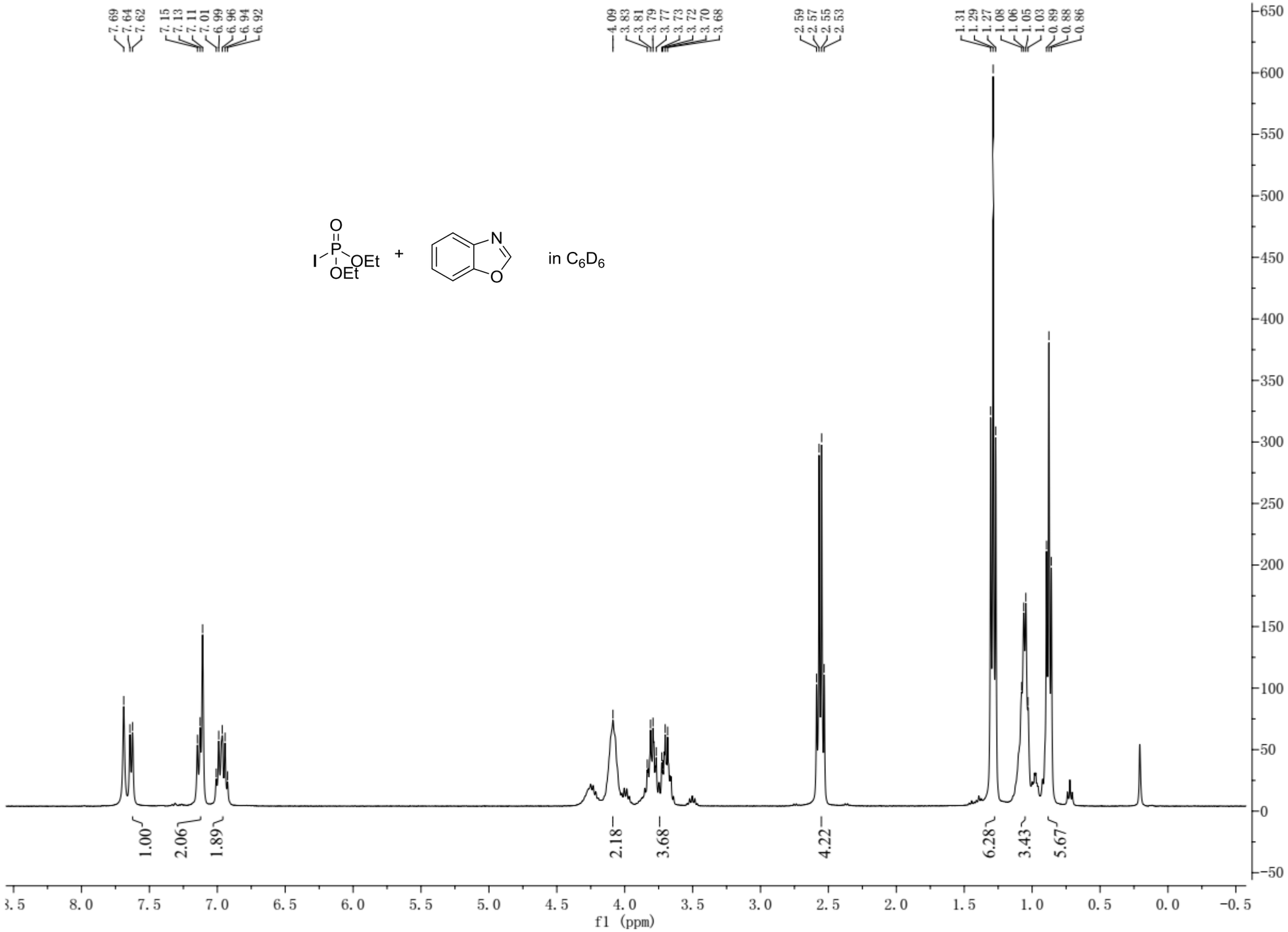

11.20
11.07
-1.32
-1.45
OBu
O=P−OBu
N
O
O
P−OEt
OEt
(4i)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

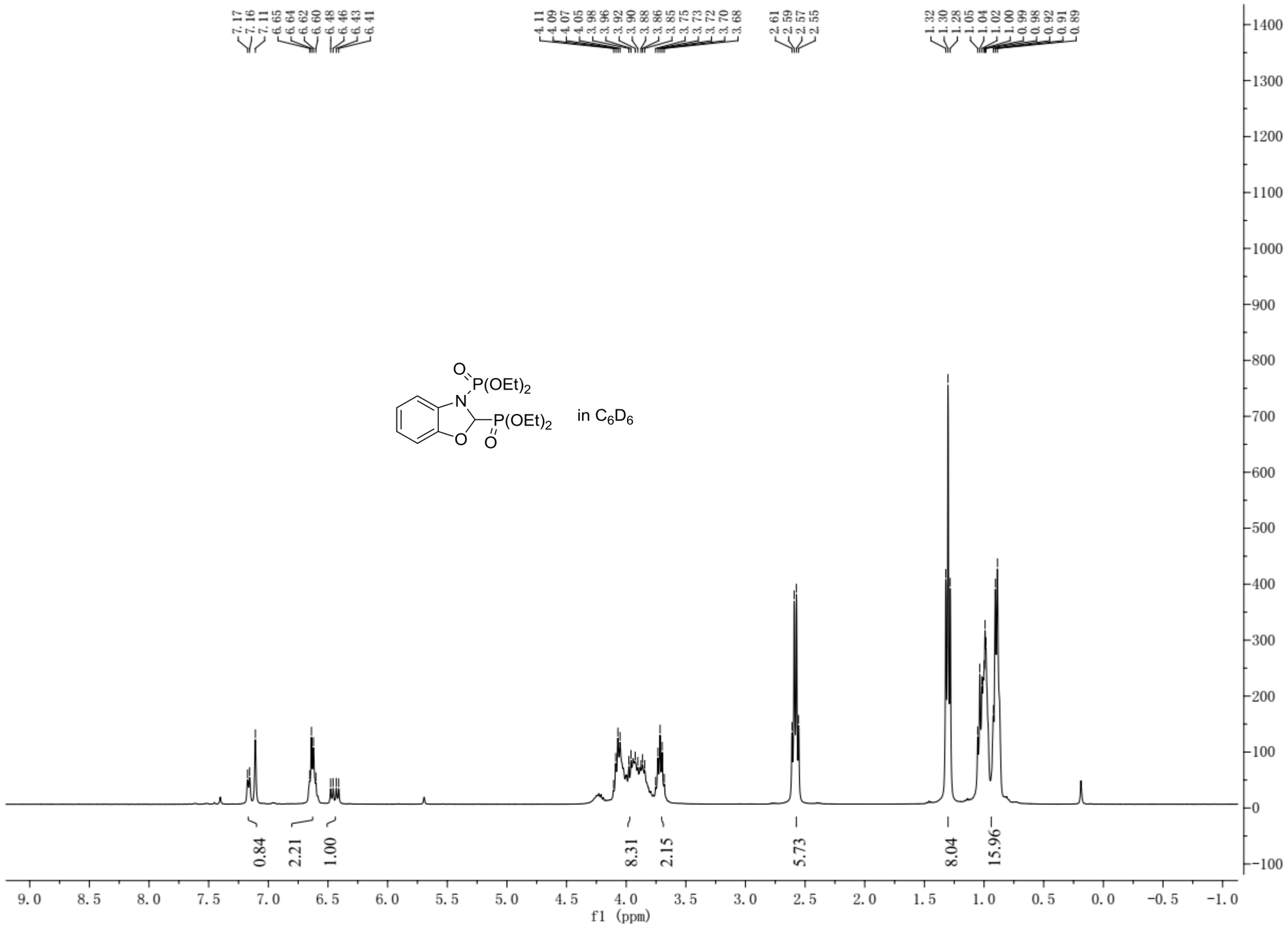

x10 5
+ESI Scan (rt: 0.485 min) Frag=175.0V 26.d
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
472.1618
450.1804
495.2375
514.1510
602.3679
680.4774
OBu
O=P–OBu
Na+
N
O
P–OEt
O
OEt
380
400
420
440
460
480
500
520
540
560
580
600
620
640
660
680
700
Counts vs. Mass-to-Charge (m/z)

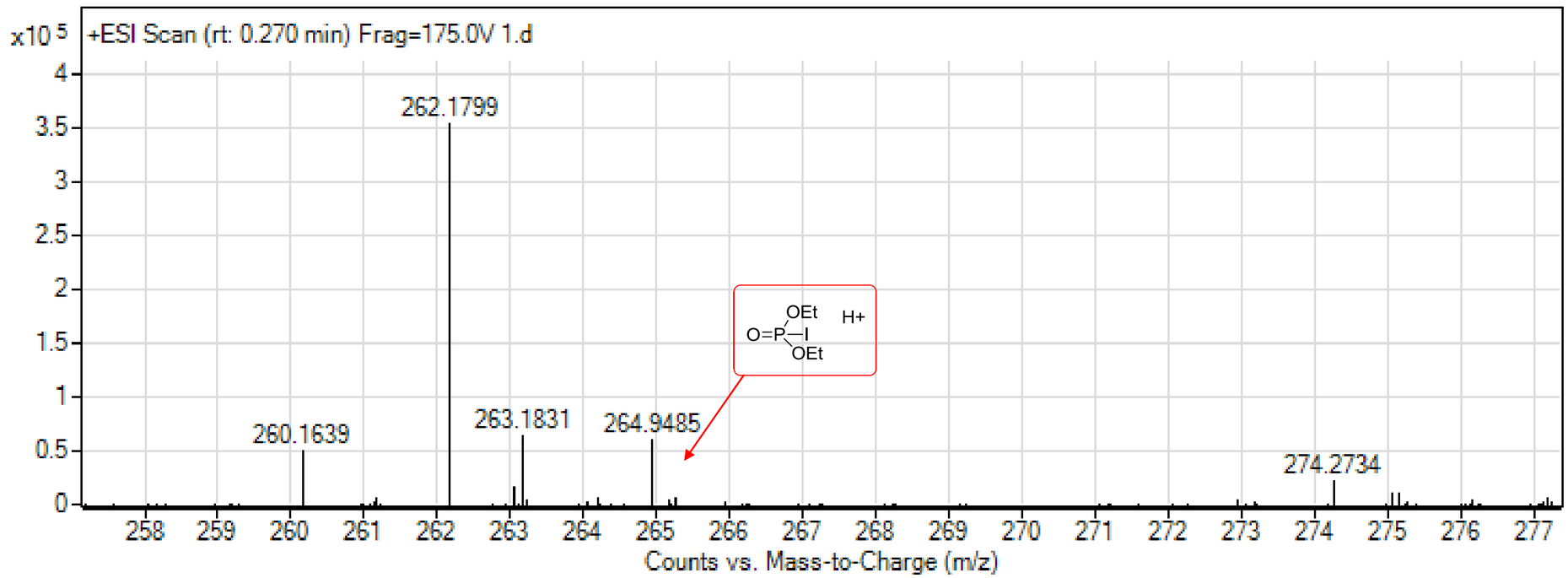
$I_2 + P(OEt)_3$ in C_6D_6

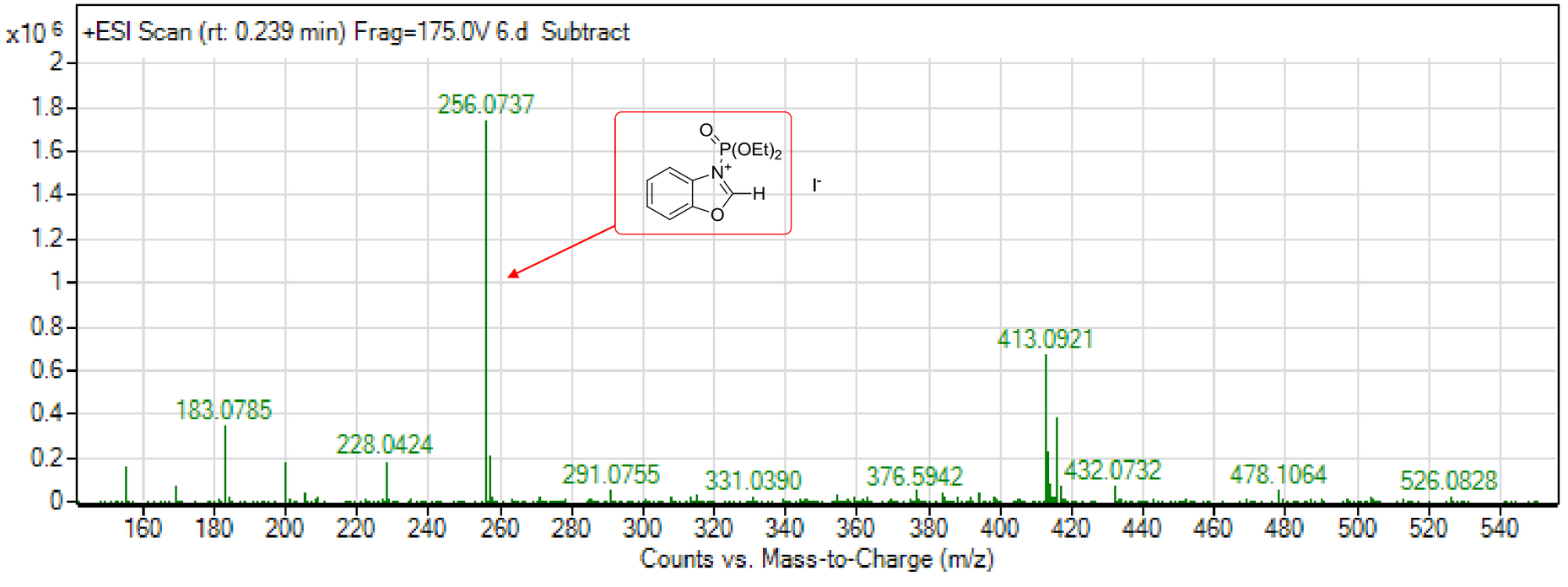



7.68
7.66
7.26
7.17
7.15
6.98
6.97
6.95
6.93
6.91
in C_6D_6
1.00
2.42
2.06
f1 (ppm)


7.69
7.64
7.62
7.15
7.13
7.11
7.01
6.99
6.96
6.94
6.92
4.09
3.83
3.81
3.79
3.77
3.73
3.72
3.70
3.68
2.59
2.57
2.55
2.53
1.31
1.29
1.27
1.08
1.06
1.05
1.03
0.89
0.88
0.86
O
P
I
OEt
OEt
+
N
O
in C6D6
1.00
2.06
1.89
2.18
3.68
4.22
6.28
3.43
5.67
f1 (ppm)


7.17
7.16
7.11
6.65
6.64
6.62
6.60
6.48
6.46
6.43
6.41
4.11
4.09
4.07
4.05
3.98
3.96
3.92
3.90
3.88
3.86
3.85
3.75
3.73
3.72
3.70
3.68
2.61
2.59
2.57
2.55
1.32
1.30
1.28
1.05
1.04
1.02
1.00
0.99
0.98
0.92
0.91
0.89
O
P(OEt)2
N
O
P(OEt)2
O
in C6D6
0.84
2.21
1.00
8.31
2.15
5.73
8.04
15.96
f1 (ppm)


x10 5
+ESI Scan (rt: 0.270 min) Frag=175.0V 1.d
262.1799
260.1639
263.1831
264.9485
274.2734
OEt
O=P—I
OEt
H+
Counts vs. Mass-to-Charge (m/z)


x10 6
+ESI Scan (rt: 0.239 min) Frag=175.0V 6.d Subtract
256.0737
P(OEt)2
N+
H
O
I-
413.0921
183.0785
228.0424
291.0755
331.0390
376.5942
432.0732
478.1064
526.0828
Counts vs. Mass-to-Charge (m/z)