Supplementary Information

Pd-Catalyzed Highly Regio-, Diastereo-, and Enantioselective Allylic Alkylation of α-Fluorophosphonate

Ying Huang,[b] Qing-Song Zhang,[a] Ping Fang,*[a] Tie-Gen Chen,[a] Jun Zhu[b] and Xue-Long Hou*[a]

[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

[b] State Key Laboratory of Physical Chemistry of Solid Surfaces Department of Chemistry, College of Chemistry and Chemical Engineering Xiamen University, Xiamen 361005, China.

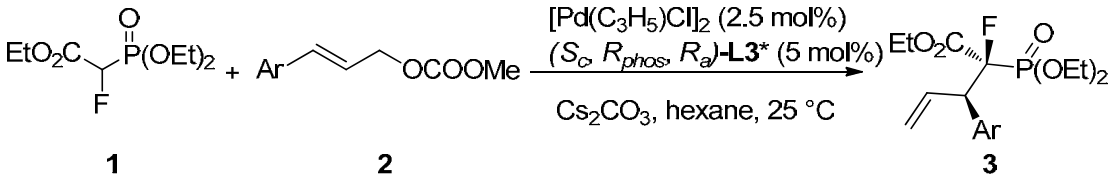
Contents **Page**

General Methods……. S2
General Experimental Procedure and Characterization of Products for Allylation……... S2
Experimental Procedure for Transformations of **3f**…… S9
Reference…… S13
Copies of ^{1}H and ^{13}C NMR Spectra of Products…… S14
Copies of 2D NMR Spectra of **6**…… S40
Copies of HPLC Spectra of Products……. S42

1. General Methods.

The reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified by using standard methods prior to use. Commercially available reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a NMR instrument operated at 300, 400, 600 MHz respectively. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or unresolved), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a NMR instrument operated at 75, 100 MHz respectively with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0 ppm). Infrared spectra were recorded from thin films of pure samples. MS and HRMS were measured in EI or ESI mode and the mass analyzer of the HRMS was TOF. Thin layer chromatography was performed on pre-coated glass back plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. Enantiomer ratios were determined by chiral HPLC analysis in comparison with authentic racemic materials. α-fluorophosphonate **1** is commercially available. (S_c, R_{phos}, R_a)-**L3*** was synthesized using our previously reported procedures.[1] **2** were prepared according to the literature procedures.[2]

2. Experimental Procedure and Characterization of Products for Allylation

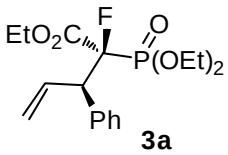


1 **2** **3**

General Experimental Procedure for Allylation

In a 20 mL flame-dried Schlenk tube were placed $[Pd(C_3H_5)Cl]_2$ (1.8 mg, 0.005 mmol) and ligand (S_c, R_{phos}, R_a)-**L3*** (6.9 mg, 0.010 mmol) under argon, Anhydrous hexane (2.0 mL) was added, and then the mixture was magnetically stirred at 25 °C for 30 min.

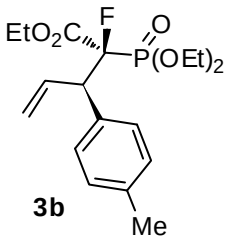
In a separated flame-dried Schlenk tube, **1** (96.6 mg, 0.4 mmol), anhydrous hexane (2.0 mL), Cs_2CO_3 (113.2 mg, 0.48 mmol) and allylic carbonate **2** (0.2 mmol) were added, then the in-situ generated catalyst was added to the solution, finally anhydrous hexane (2.0 mL) was added. The resulted mixture was stirred for 16 hours, then filtered and concentrated in vacuo to afford a crude oil. Purification with preparative TLC (PE : EA = 1 : 1) furnished the product.



3a

(*2R*,*3R*)-ethyl 2-(diethoxyphosphoryl)-2-fluoro-3-phenylpent-4-enoate

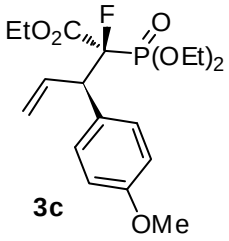
53.8 mg, 78% yield; b/l > 20:1; dr > 20:1; 99% ee; $[\alpha]_D^{27}$ -26.4 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.07 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 3.39-3.50 (m, 1H), 3.74-3.84 (m, 1H), 3.95-4.08 (m, 2H), 4.17-4.29 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 5.15-5.28 (m, 2H), 6.12-6.21 (m, 1H), 7.25-7.36 (m, 3H), 7.43-7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.08 (dd, *J* = 7.1, 6.0 Hz), 53.50 (dd, *J* = 17.8, 2.2 Hz), 62.4, 63.6 (d, *J* = 7.0 Hz), 98.5 (dd, *J* = 206.4, 161.4 Hz), 118.7, 127.5, 128.3, 129.7 (d, *J* = 2.3 Hz), 134.2 (dd, *J* = 12.6, 5.2 Hz), 137.2 (d, *J* = 3.4 Hz), 166.6 (dd, *J* = 23.0, 4.1 Hz); ^{19}F NMR (376 MHz): δ -184.5 (dd, *J* = 78.2, 34.2 Hz); ^{31}P NMR (162 MHz): δ 10.8 (d, *J* = 78.2 Hz); HRMS (ESI+) calcd for $C_{17}H_{25}FO_5P$ $[M+H]^+$: 359.1425; Found: 359.1418; IR (film): 2982 (s), 1761 (s), 1736 (s), 1261 (s), 1235 (s), 1097 (s), 1017 (s), 796 (s), 734 (w), 701 (s) cm^{-1}; HPLC: (Chiralpak OJ-H, hexane/2-propanol = 96/4, Flow rate = 0.5 mL/min, 214 nm) t_R = 19.46 min, 39.61 min.



3b

(*2R*,*3R*)-ethyl 2-(diethoxyphosphoryl)-2-fluoro-3-(p-tolyl)pent-4-enoate

51.4 mg, 69% yield; b/l = 14:1; dr = 17:1; 98% ee; $[\alpha]_D^{27}$ -34.9 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 3.46-3.57 (m, 1H), 3.78-3.88 (m, 1H), 3.95-4.09 (m, 2H), 4.20 (ddd, *J* = 2.0, 9.2, 34.8 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 5.15-5.20 (m, 2H), 6.10-6.20 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.1 (t, *J* = 5.6 Hz), 21.0, 53.2 (dd, *J* = 17.8, 2.2 Hz), 62.4, 63.6 (t, *J* = 7.0 Hz), 98.5 (dd, *J* = 205.6, 161.0 Hz), 118.4, 128.9, 129.5 (d, *J* = 2.6 Hz), 134.1 (d, *J* = 3.0 Hz), 134.4 (dd, *J* = 12.7, 5.2 Hz), 137.1, 166.6 (dd, *J* = 23.0, 4.1 Hz); ^{19}F NMR (376 MHz): δ -186.9 (dd, *J* = 79.3, 34.6 Hz); ^{31}P NMR (162 MHz): δ 11.5 (d, *J* = 78.9 Hz); HRMS (ESI+) calcd for $C_{18}H_{27}FO_5P$ $[M+H]^+$: 373.1575; Found: 373.1575; IR (film): 2982 (s), 1761 (s), 1736 (s), 1260 (s), 1233 (s), 1096 (s), 1017 (s), 975 (s), 795 (w), 750 (w) cm^{-1}; HPLC: (supercritical fluid chromatography (SFC) IC, hexane/2-propanol = 90/10, Flow rate = 1.5 mL/min, 214 nm) t_R = 30.22 min, 36.58 min.

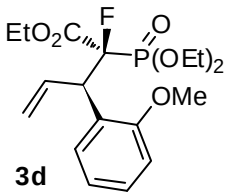


3c

(*2R,3R*)-ethyl 2-(diethoxyphosphoryl)-2-fluoro-3-(4-methoxyphenyl)pent-4-enoate

58.3 mg, 75% yield; b/l = 7:1; dr > 20:1; 92%ee; $[\alpha]_D^{27}$ -27.1 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.07 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 3.45-3.55 (m, 1H), 3.74-3.86 (m, 4H), 3.94-4.07 (m, 2H), 4.12-4.24 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 5.10-5.16 (m, 2H), 6.05-6.15 (m, 1H), 6.85(d, *J* = 8.8 Hz, 2H), 7.33(d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.12 (dd, *J* = 7.8, 6.0 Hz), 52.7 (dd, *J* = 17.9, 2.2 Hz), 55.2, 62.4, 63.62 (dd, *J* = 9.3, 7.1 Hz), 98.5 (dd, *J* = 205.2, 161.3 Hz), 113.6, 118.3, 129.24 (d, *J* = 2.6 Hz), 130.78 (d, *J* = 2.2 Hz), 134.45 (dd, *J* = 13.0, 5.6 Hz), 158.9, 166.6 (dd, *J* = 23.5, 4.5 Hz); ^{19}F NMR (376 MHz): δ -187.2 (dd, *J* = 78.2, 34.6 Hz); ^{31}P NMR (162 MHz): δ 11.7 (d, *J* = 78.9 Hz); HRMS (ESI+) calcd for $C_{18}H_{27}FO_6P$ $[M+H]^+$: 389.1532; Found: 389.1524; IR (film):

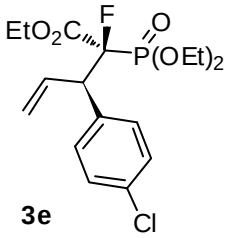
2963 (s), 1260 (s), 1092 (s), 1019 (s), 798 (s); HPLC: (supercritical fluid chromatography (SFC) IC, hexane/2-propanol = 80/20, Flow rate = 1.5 mL/min, 214 nm) t_R = 9.64 min, 10.34 min.



3d

(*2R,3R*)-ethyl 2-(diethoxyphosphoryl)-2-fluoro-3-(2-methoxyphenyl)pent-4-enoate

58.3 mg, 75% yield; b/l = 7:1; dr > 20:1; 97% ee; $[\alpha]_D^{27}$ -15.7 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.14 (t, *J* = 7.2 Hz, 6H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.61-3.76 (m, 1H), 3.80-4.06 (m, 6H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.92 (ddd, *J* = 2.1, 9.0, 36 Hz 1H), 5.07-5.18 (m, 2H), 5.98 -6.11 (m, 1H), 6.82-6.95 (m, 2H), 7.19-7.26 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 16.16 (dd, *J* = 8.6, 6.3 Hz), 44.2 (d, *J* = 17.7 Hz), 55.7, 62.4, 63.6 (dd, *J* = 13.1, 6.8 Hz), 76.6, 99.0 (dd, *J* = 204.8, 163.1 Hz), 110.8, 118.3, 120.3, 125.8, 128.4, 130.47 (d, *J* = 6.3 Hz), 134.57 (dd, *J* = 12.5, 5.1 Hz), 156.8, 166.9 (dd, *J* = 23.4, 4.1 Hz); ^{19}F NMR (376 MHz): δ -182.9 (dd, *J* = 82.7, 35.2 Hz); ^{31}P NMR (162 MHz): δ 11.2 (m); HRMS (ESI+) calcd for $C_{18}H_{27}FO_6P$ $[M+H]^+$: 389.1531; Found: 389.1524; IR (film): 2981 (s), 2936 (s), 1760 (s), 1736 (s), 1736 (s), 1493 (s), 1258 (s), 1093 (s), 1017 (s), 976 (s), 793 (s), 754 (s) cm^{-1}; HPLC: (supercritical fluid chromatography (SFC) AD, hexane/2-propanol = 95/5, Flow rate = 1.5 mL/min, 214 nm) t_R = 12.24 min, 14.62 min.

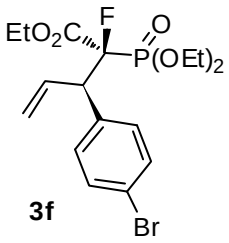


3e

(*2R,3R*)-ethyl 3-(4-chlorophenyl)-2-(diethoxyphosphoryl)-2-fluoropent-4-enoate

66.8 mg, 85% yield; b/l = 10:1; dr > 20:1; 97% ee; $[\alpha]_D^{27}$ -42.9 (*c* 1.00, $CHCl_3$); ^1H

NMR (400 MHz, $CDCl_3$): δ 1.04 (t, J = 7.2 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H), 3.51-3.62 (m, 1H), 3.75-3.85 (m, 1H), 3.87-4.04 (m, 2H), 4.14 (ddd, J = 2.0, 9.2, 34 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 5.09-5.14 (m, 2H), 5.98-6.08 (m, 1H), 7.21-7.31(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.06 (dd, J = 5.5, 4.1 Hz), 52.8 (dd, J = 17.8, 1.9 Hz), 62.5, 63.78 (dd, J = 7.4, 2.6 Hz), 98.2 (dd, J = 205.9. 161.3 Hz), 119.1, 128.3, 131.09 (d, J = 2.3 Hz), 133.4, 133.74 (dd, J = 12.7, 5.2 Hz), 135.7 (d, J = 2.6 Hz), 166.3 (dd, J = 22.7, 4.1 Hz); ^{19}F NMR (376 MHz): δ -187.3 (dd, J = 78.6, 34.6 Hz); ^{31}P NMR (162 MHz): δ 11.8 (d, J = 78.7 Hz); HRMS (ESI+) calcd for $C_{17}H_{24}ClFO_5P$ $[M+H]^+$: 393.104; Found: 393.1028; IR (film): 2983 (s), 1761 (s), 1736 (s), 1492 (s), 1261 (s), 1233 (s), 1091 (s), 1013 (s), 976 (s), 794 (s), 749 (s) cm^{-1}; HPLC: (supercritical fluid chromatography (SFC) OD-H, hexane/2-propanol = 98/2, Flow rate = 1.5 mL/min, 214 nm) t_R = 11.90 min, 13.40 min.

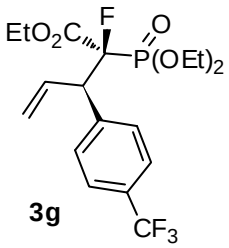


3f

(*2R*,*3R*)-ethyl 3-(4-bromophenyl)-2-(diethoxyphosphoryl)-2-fluoropent-4-enoate

74.3 mg, 85% yield; b/l = 10:1; dr = 20:1; 98% ee; $[\alpha]_D^{27}$ -38.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 3.57-3.68 (m, 1H), 3.81-3.91 (m, 1H), 3.94-4.08 (m, 2H), 4.13-4.24 (ddd, J = 2.4, 9.6, 34.4 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 5.15-5.19 (m, 2H), 6.04-6.13 (m, 1H), 7.28-7.31 (m, 2H), 7.43-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.1 (dd, J = 5.6, 4.1 Hz), 52.9 (dd, J = 17.8, 1.8 Hz), 62.5, 63.8 (dd, J = 7.4, 3.0 Hz), 98.2 (dd, J = 206.0, 161.0 Hz), 119.2, 121.6, 131.3, 131.45 (d, J = 2.6 Hz), 133.67 (dd, J = 12.3, 4.9 Hz), 136.22 (dd, J = 3.0, 0.7 Hz), 166.35 (dd, J = 22.7, 4.1 Hz); ^{19}F NMR (376 MHz): δ -187.3 (dd, J = 78.6, 34.2 Hz); ^{31}P NMR (162 MHz): δ 11.8 (d, J = 78.9 Hz); HRMS (ESI+) calcd for $C_{17}H_{24}BrFO_5P$ $[M+H]^+$: 437.0535; Found: 437.0523; IR (film): 2982 (s), 1760 (s), 1736 (s), 1488(s), 1261 (s), 1233 (s), 1096(s), 1009 (s), 976 (s), 794 (s), 748 (s) cm^{-1}; HPLC: (supercritical fluid

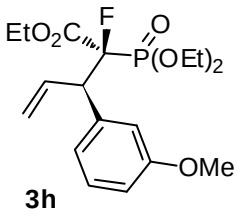
chromatography (SFC) OD-H, hexane/2-propanol = 97/3, Flow rate = 1.5 mL/min, 214 nm) t_R = 9.44 min, 10.28 min.



3g

(*2R,3R*)-ethyl 2-(diethoxyphosphoryl)-2-fluoro-3-(4-(trifluoromethyl)phenyl)pent -4-enoate

61.4 mg, 72% yield; b/l = 10:1; dr > 20:1; 90% ee; $[\alpha]_D^{28}$ -27.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 3.56-3.66 (m, 1H), 3.79-3.86 (m, 1H), 3.87-4.09 (m, 2H), 4.23-4.37 (m, 3H), 5.18-5.23 (m, 2H), 6.08-6.17 (m, 1H), 7.53-7.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.0 (d, *J* = 6.1 Hz), 53.2 (dd, *J* = 17.4, 1.5 Hz), 62.6, 63.85 (dd, *J* = 11.4, 7.6 Hz), 98.1 (dd, *J* = 206.5, 161.0 Hz), 119.6, 119.9-128.1 (q, *J* = 270.3 Hz), 125.1 (q, *J* = 7.6, 3.8 Hz), 129.2-130.2 (q, *J* = 31.9 Hz), 130.1 (d, *J* = 3.1 Hz), 133.4 (dd, *J* = 12.2, 5.3 Hz), 141.3, 166.3 (dd, *J* = 22.7, 4.5 Hz); ^{19}F NMR (376 MHz): δ -187.3 (dd, *J* = 78.6, 33.8 Hz), -62.6; ^{31}P NMR (162 MHz): δ 11.2 (d, *J* = 78.1 Hz); HRMS (ESI+) calcd for $C_{18}H_{24}F_4O_5P$ $[M+H]^+$: 427.1305; Found: 427.1292; IR (film): 2985 (s), 1761 (s), 1737 (s), 1325 (s), 1262 (s), 1235 (s), 1163 (s), 1122 (s), 1067 (s), 1016 (w), 977 (s), 845 (s), 797 (w), 751 (s), 727 (s) cm^{-1}; HPLC: (supercritical fluid chromatography (SFC) IC, hexane/2-propanol = 95/5, Flow rate = 1.5 mL/min, 214 nm) t_R = 12.54 min, 14.22 min.

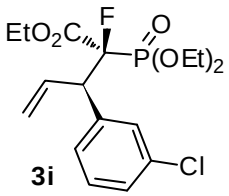


3h

(*2R,3R*)-ethyl 2-(diethoxyphosphoryl)-2-fluoro-3-(3-methoxyphenyl)pent-4-enoate

52.8 mg, 68% yield; b/l = 10:1; dr > 20:1; 96% ee; $[\alpha]_D^{27}$ -29.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.31 (t,

J = 7.2 Hz, 3H), 3.41-3.52 (m, 1H), 3.72-3.82 (m, 4H), 3.91-4.04 (m, 2H), 4.10-4.18 (m, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 5.10-5.17 (m, 2H), 6.05-6.15 (m, 1H), 6.76-6.99 (m, 3H), 7.17-7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.06 (dd, *J* = 7.4, 6.0 Hz), 53.5 (dd, *J* = 17.9, 2.3 Hz), 55.1, 62.4, 63.6 (d, *J* = 6.7 Hz), 98.4 (dd, *J* = 206.3, 161.4 Hz), 113.1, 115.17 (d, *J* = 2.6 Hz), 118.7, 122.05 (d, *J* = 2.2 Hz), 129.2, 134.1 (dd, *J* = 12.6, 5.2 Hz), 138.5 (dd, *J* = 2.6, 0.7 Hz), 159.3, 166.5 (dd, *J* = 23.0, 4.0 Hz); ^{19}F NMR (376 MHz): δ -184.1 (dd, *J* = 78.6, 34.6 Hz); ^{31}P NMR (162 MHz): δ 11.5 (d, *J* = 78.1 Hz); HRMS (ESI+) calcd for $C_{18}H_{27}FO_6P$ $[M+H]^+$: 389.1531; Found: 389.1524; IR (film): 2937 (s), 1760 (s), 1736 (s), 1259 (s), 1159 (s), 1094 (s), 1017 (s), 976 (s), 859 (s), 796 (s), 702 (s) cm^{-1}; HPLC: (supercritical fluid chromatography (SFC) IC, hexane/2-propanol = 80/20, Flow rate = 1.5 mL/min, 214 nm) t_R = 9.55 min, 17.37 min.

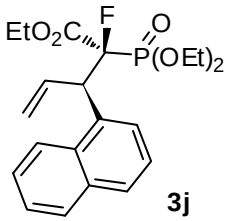


3i

(*2R*,*3R*)-ethyl 3-(3-chlorophenyl)-2-(diethoxyphosphoryl)-2-fluoropent-4-enoate

60.5 mg, 77% yield; b/l = 10:1; dr = 16:1; 96% ee; $[\alpha]_D^{27}$ -22.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 3.52-3.63 (m, 1H), 3.77-3.87 (m, 1H), 3.89-4.02 (m, 2H), 4.07-4.18 (m, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 5.10-5.15 (m, 2H), 5.98-6.08 (m, 1H), 7.18-7.24 (m, 3H), 7.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 16.1 (t, *J* = 6.4 Hz), 53.1 (dd, *J* = 17.8, 2.2 Hz), 62.6, 63.8 (t, *J* = 8.1 Hz), 98.2 (dd, *J* = 206.4, 161.4 Hz), 119.3, 127.6, 128.0 (d, *J* = 2.2 Hz), 129.4, 129.7 (d, *J* = 2.9 Hz), 133.5 (dd, *J* = 11.9, 5.2 Hz), 133.9, 139.15 (dd, *J* = 3.0, 1.1 Hz), 166.3 (dd, *J* = 22.7, 3.7 Hz); ^{19}F NMR (376 MHz): δ -184.7 (dd, *J* = 78.6, 33.8 Hz); ^{31}P NMR (162 MHz): δ 10.5 (d, *J* = 78.9 Hz); HRMS (ESI+) calcd for $C_{17}H_{24}ClFO_5P$ $[M+H]^+$: 393.1037; Found: 393.1028; IR (film): 2983 (s), 1761 (s), 1736 (s), 1261 (s), 1235 (s), 1095(s), 1016 (w), 976 (s), 792 (w), 752 (w), 699 (s) cm^{-1}; HPLC: (supercritical fluid chromatography (SFC) IC, hexane/2-propanol

= 90/10, Flow rate = 1.5 mL/min, 214 nm) t_R = 19.19 min, 24.78 min.



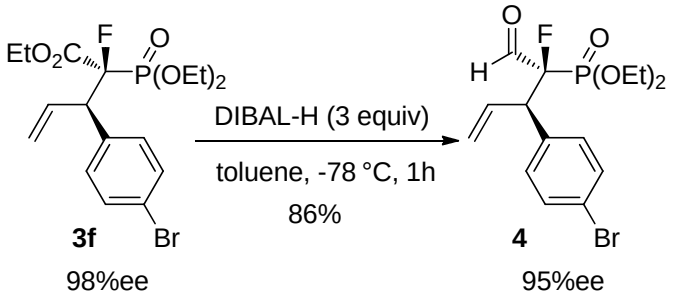
3j

(*2R,3R*)-ethyl 2-(diethoxyphosphoryl)-2-fluoro-3-(naphthalen-1-yl)pent-4-enoate

66.2 mg, 81% yield; b/l = 16:1; dr > 20:1; 95% ee; $[\alpha]_D^{28}$ -48.8 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 3.29-3.40 (m, 1H), 3.65-3.75 (m, 1H), 3.90-4.05 (m, 2H), 4.32-4.47 (m, 3H), 5.17-5.29 (m, 2H), 6.20-6.30 (m, 1H), 7.42-7.48 (m, 2H), 7.54-7.57 (m, 1H), 7.77-7.83 (m, 3H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 15.9 (t, *J* = 6.4 Hz), 53.6 (dd, *J* = 17.9, 2.2 Hz), 62.5, 63.6 (t, *J* = 8.6 Hz), 98.5 (dd, *J* = 206.0, 161.4 Hz), 118.9, 125.88, 125.92, 127.4, 127.47 (d, *J* = 3.0 Hz), 127.7, 127.9, 128.8 (d, *J* = 1.8 Hz), 132.6, 133.2, 134.2 (dd, *J* = 12.7, 5.2 Hz), 134.6 (dd, *J* = 0.8, 2.6 Hz), 166.6 (dd, *J* = 23.1, 4.5 Hz); ^{19}F NMR (376 MHz): δ -186.5 (dd, *J* = 78.2, 34.6 Hz); ^{31}P NMR (162 MHz): δ 11.5 (d, *J* = 78.1 Hz); HRMS (ESI+) calcd for $C_{21}H_{27}FO_5P$ $[M+H]^+$: 409.1581; Found: 409.1575; IR (film): 2982 (s), 1759 (s), 1735 (s), 1260 (s), 1235 (s), 1161 (s), 1096 (s), 1016 (s), 975 (s), 858 (s), 792 (s), 751 (s) cm^{-1}; HPLC: (Chiralpak IF, hexane/2-propanol = 80/20, Flow rate = 0.5 mL/min, 214 nm) t_R = 26.29 min, 32.71 min.

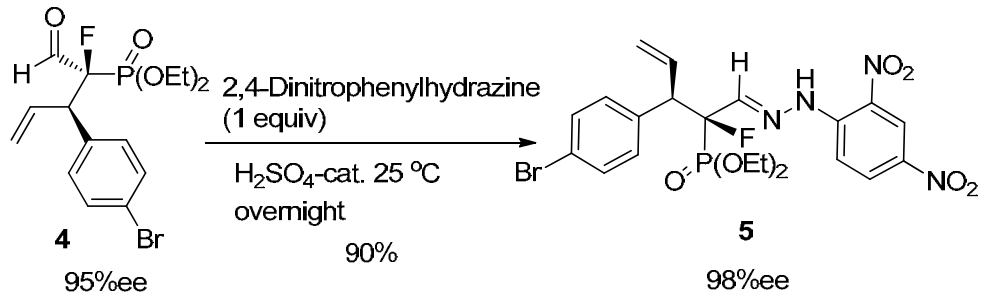
3. Experimental Procedure for Transformations of 3f

Reduction of 3f to (*2R,3R*) Diethyl 3-(4-bromophenyl)-2-fluoro-1–oxopent -4-en-2-yl phosphonate (4).



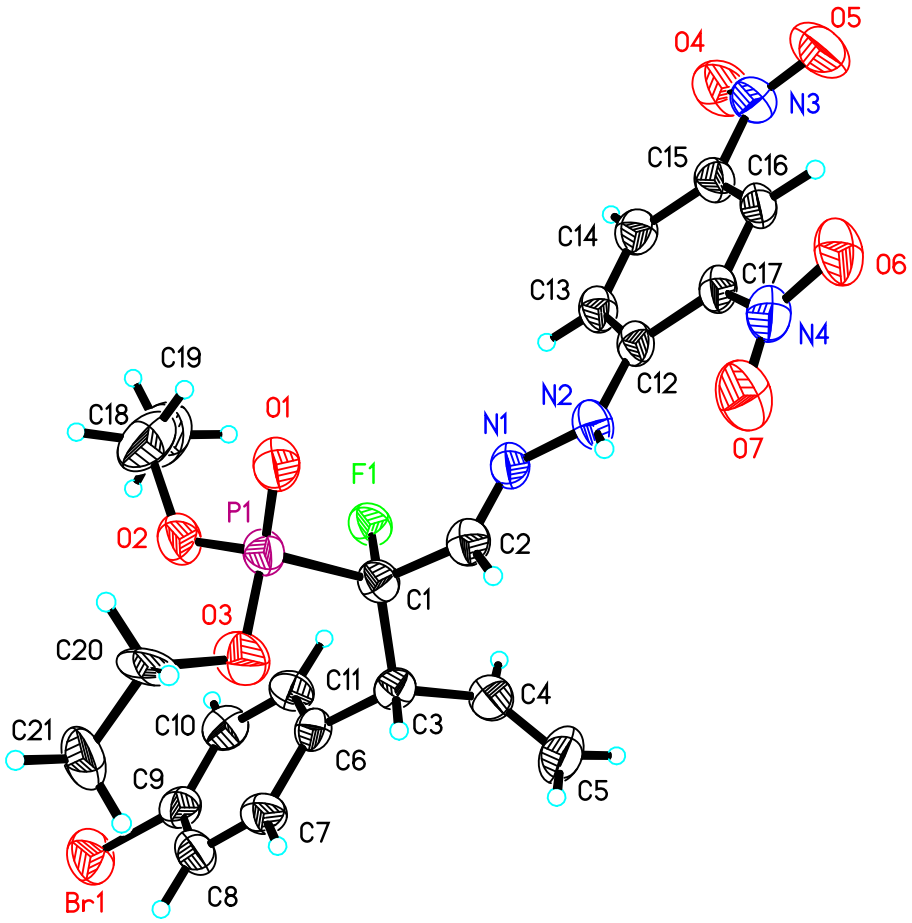
In a 50 mL flame-dried round-bottomed flask, DIBAL-H (2.25 mL, 1.0 M in toluene, 2.25 mmol) was added slowly to a solution of **3f** (327.0 mg, 0.748 mmol) in toluene (20 mL) at -78 °C. The mixture was stirred for 1h at -78 °C, then quenched with NH_4Cl (aq.) and organic materials were extracted with ethyl acetate (20 mL x 3). The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. The solvent was concentrated under reduced pressure by an aspirator and the residue was purified by the column chromatography (SiO_2) with hexane and ethyl acetate (1:1) as eluent to give aldehyde **4** as a pale yellow oil (252.9 mg, 86% yield, 95% ee). $[\alpha]_D^{25}$ -48.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 3.55–3.66 (m, 1H), 3.76 –3.83 (m, 1H), 3.86–4.04 (m, 2H), 4.16 (ddd, *J* = 33.2, 8.8, 2.2 Hz, 1H), 5.07–5.15 (m, 2H), 5.88-6.00 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 9.61 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1 (dd, *J* = 5.7, 4.1 Hz), 51.8 (dd, *J* = 17.8, 1.6 Hz), 63.9 (dd, *J* = 23.4, 7.7 Hz), 101.7 (dd, *J* = 200.2, 157.4 Hz), 120.1, 121.7, 131.2 (d, *J* = 2.0 Hz), 131.5, 133.0 (dd, *J* = 11.3, 6.1 Hz), 136.0 (d, *J* = 4.5 Hz), 195.4 (dd, *J* = 30.6, 3.2 Hz); ^{19}F NMR (376 MHz): δ -194.3 (ddd, *J* = 78.6, 33.1, 8.6 Hz); ^{31}P NMR (162 MHz): δ 10.4 (d, *J* = 78.2 Hz); HRMS (MALDI/DHB) calcd for $C_{15}H_{19}BrFO_4PNa$ $[M+Na]^+$: 415.0092; Found: 415.0081; IR (film): 3341 (w), 2982 (s), 1738 (s), 1488 (s), 1260 (s), 1098 (m), 1010 (m), 980 (m), 830 (m), 793 (m), 742 (s), 701 (s), 633 (m) cm^{-1}; HPLC: (supercritical fluid chromatography (SFC) AD-H, hexane/2-propanol = 95/5, Flow rate = 1.5 mL/min, 214 nm) t_R = 10.62 min, 17.01 min.

Synthesis of (*2R,3R*) diethyl (*E*)-3-(4-bromophenyl)-1-(2-(2,4-dinitrophenyl) hydrazono)-2-fluropent-4-en-2-yl)phosphonate (5).

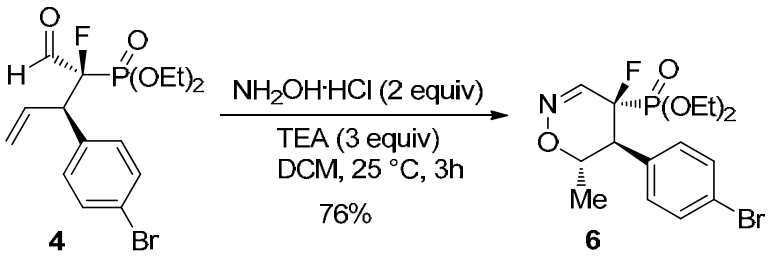


In a Schlenk tube were placed 2,4-dinitrophenylhydrazine (51.5 mg, 0.26 mmol) and aldehyde **4** (101.9 mg, 0.26 mmol), methanol (3.0 mL) and a half drops of H_2SO_4 (con.) were added, and then the mixture was magnetically stirred at 25 ℃ overnight. After finished, quenched with water, adjusted the pH value to 7 with NaOAc (10%, aq.). Extracted with chloroform. The combined extracts were dried over anhydrous Na_2SO_4. The solvent was concentrated under reduced pressure by an aspirator and the residue was purified by recrystallized with EA/hexane to give the hydrozone **5** (134.2 mg, 90% yield, 98% ee). $[\alpha]_D^{27}$ -81.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (dt, *J* = 10.8, 6.8 Hz, 6H), 3.72-3.83 (m, 1H), 3.90-4.16 (m, 3H), 4.24 (ddd, *J* = 30.4, 9.2, 3.6 Hz, 1H), 5.15-5.26 (m, 1H), 6.11-6.20 (m, 1H), 7.26-7.28 (m, 2H), 7.46-7.49 (m, 2H), 7.57 (dd, *J* = 13.2, 3.6 Hz, 1H), 7.96 (d, *J* = 9.6 Hz, 1H), 8.37 (dd, *J* = 9.6, 2.8 Hz, 1H), 9.14 (d, *J* = 2.4 Hz, 1H), 11.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1 (d, *J* = 5.4 Hz), 53.4 (d, *J* = 18.1 Hz), 63.7 (dd, *J* = 15.4, 7.3 Hz), 97.0 (dd, *J* = 194.3, 169.0 Hz), 116.6, 119.9, 121.4, 123.0, 129.6, 130.0, 131.2, 131.3, 133.9 (t, *J* = 7.2 Hz), 136.74 (d, *J* = 4.6 Hz), 138.6, 144.6, 145.2 (d, *J* = 25.3 Hz). ^{19}F NMR (376 MHz): δ -185.07 (ddd, *J* = 83.1, 30.1, 13.2 Hz); ^{31}P NMR (162 MHz): δ 12.4 (d, *J* = 82.7 Hz); HRMS (MALDI/DHB) calcd for $C_{21}H_{23}BrFO_7N_4PNa$ $[M+Na]^+$: 595.0383; Found: 595.0364; IR (film): 3708 (m), 3635 (m), 3295 (s), 3083 (w), 2931 (m), 2850 (w), 1613 (s), 1588 (s), 1488 (s), 1425 (s), 1325 (s), 1242 (s), 1139 (s), 1100 (s), 1011 (s), 869 (s), 791 (s), 742 (s), 628 (s) cm^{-1}; HPLC: (Chiralpak AD-H, hexane/2-propanol = 70/30, Flow rate = 0.7 mL/min, 214 nm) t_R = 16.62 min, 50.02 min.

ORTEP diagram of X-ray diffraction structure of **5**



Synthesis of (*4R,5S,6S*) Diethyl 5-(4-bromophenyl)-4-fluoro-6-methyl -5,6-dihydro-4H-1,2-oxazin-4-yl phosphonate (6).



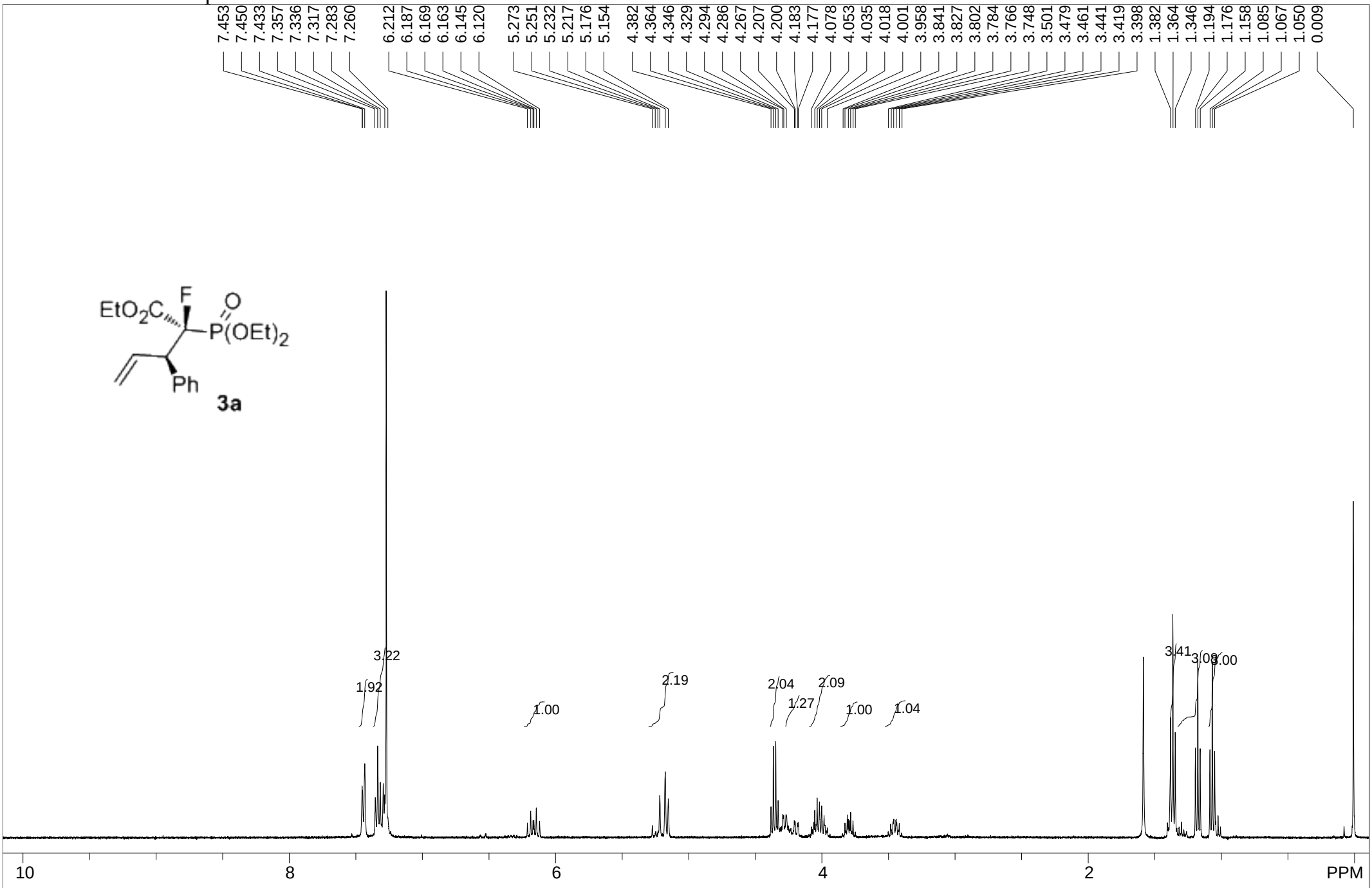
In a Schlenk tube were placed $NH_2OH{\cdot}HCl$ (13.8 mg, 0.20 mmol) and aldehyde **4** (39.2 mg, 0.10 mmol), DCM (1.0 mL) was added, and then TEA (43 uL, 0.30 mmol)

was added. The mixture was magnetically stirred at 25 ℃ for 3h. After finished, quenched with water, extracted with DCM. The combined extracts were dried over anhydrous Na_2SO_4. The solvent was concentrated under reduced pressure by an aspirator and the residue was purified with preparative TLC (PE : EA = 1 : 5) to give the **6** (30.9 mg, 76% yield, dr > 20:1, 98% ee). $[\alpha]_D^{25}$ -96.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12–1.18 (m, 6H), 1.39 (d, *J* = 6.8 Hz, 3H), 3.66 (dt, *J* = 23.6, 8.9 Hz, 1H), 3.91–4.03 (m, 4H), 4.25-4.34 (m, 1H), 6.97 (s, 1H), 7.17 (d, *J* = 16.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.9 (d, *J* = 2.4 Hz), 16.2 (t, *J* = 5.3 Hz), 53.1 (dd, *J* = 19.7, 1.6 Hz), 64.1 (t, *J* = 6.1 Hz), 73.8 (d, *J* = 8.1 Hz), 95.4 (t, *J* = 195.7 Hz), 122.7, 127.7 (dd, *J* = 15.4, 7.3 Hz), 131.2 (d, *J* = 1.6 Hz), 131.67, 131.69, 131.72; ^{19}F NMR (376 MHz): δ -163.4 (m); ^{31}P NMR (162 MHz): δ 12.5 (d, *J* = 107.2 Hz); HRMS (EI+) calcd for $C_{15}H_{20}BrFO_4NP$ $[M]^+$: 407.0297; Found: 407.0301; IR (film): 2980 (m), 2867 (s), 1553 (s), 1489 (s), 1310 (m), 1257 (s), 1050 (s), 1010 (s), 943 (s), 787 (s), 744 (s), 662 (s) cm^{-1}; HPLC: (Chiralpak AD-H, hexane/2-propanol = 70/30, Flow rate = 0.7 mL/min, 214 nm) t_R = 10.39 min, 12.09 min.

4. Reference

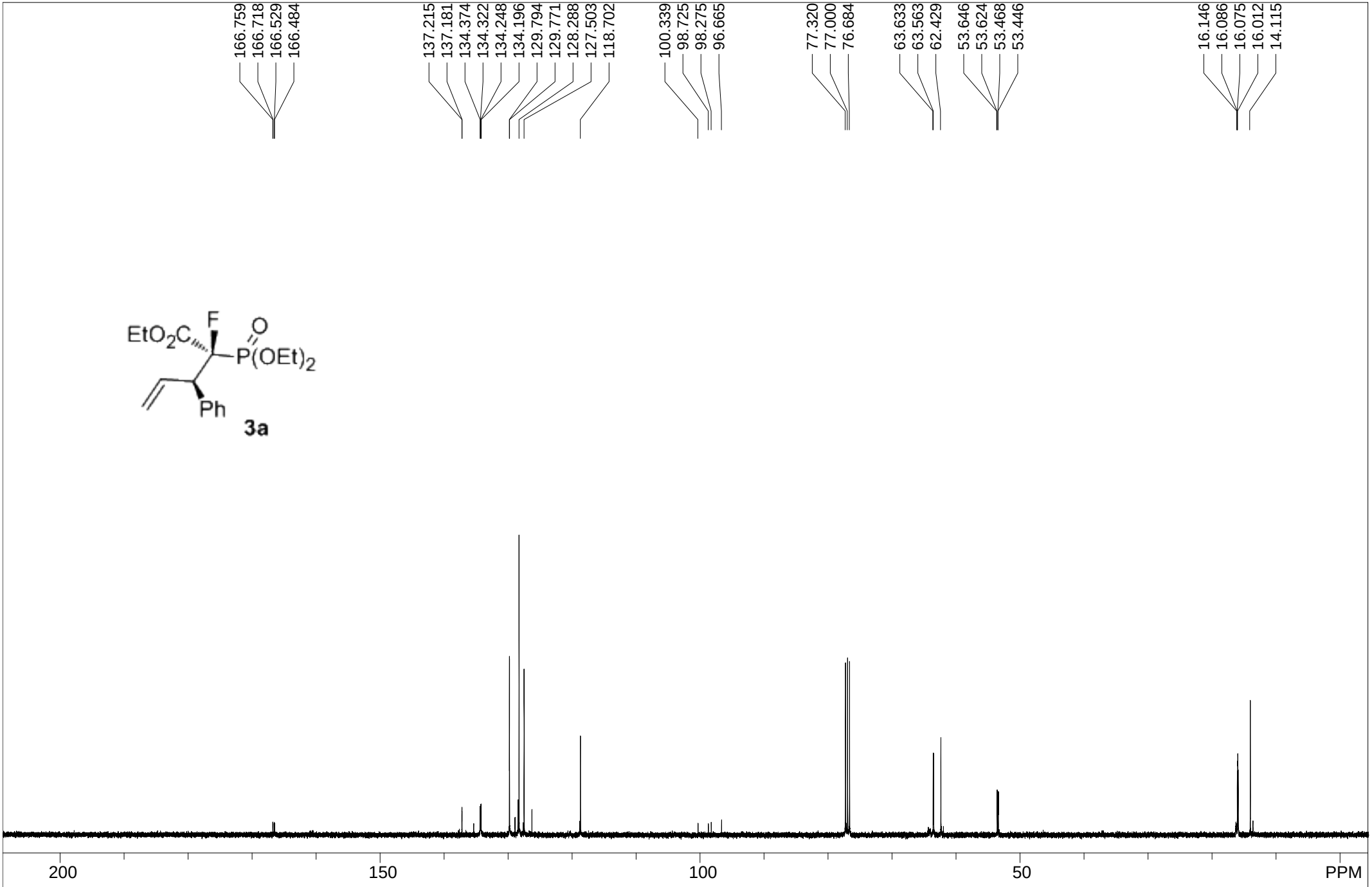
1. S.-L. You, X.-Z. Zhu, Y.-M. Luo, X.-L. Hou and L.-X. Dai, *J. Am. Chem. Soc.*, 2001, **123**, 7471.
2. J. Lehmann and G. C. Lloyd-Jones, *Tetrahedron*, 1995, **51**, 8863.

1H and 13C NMR Spectra of Products



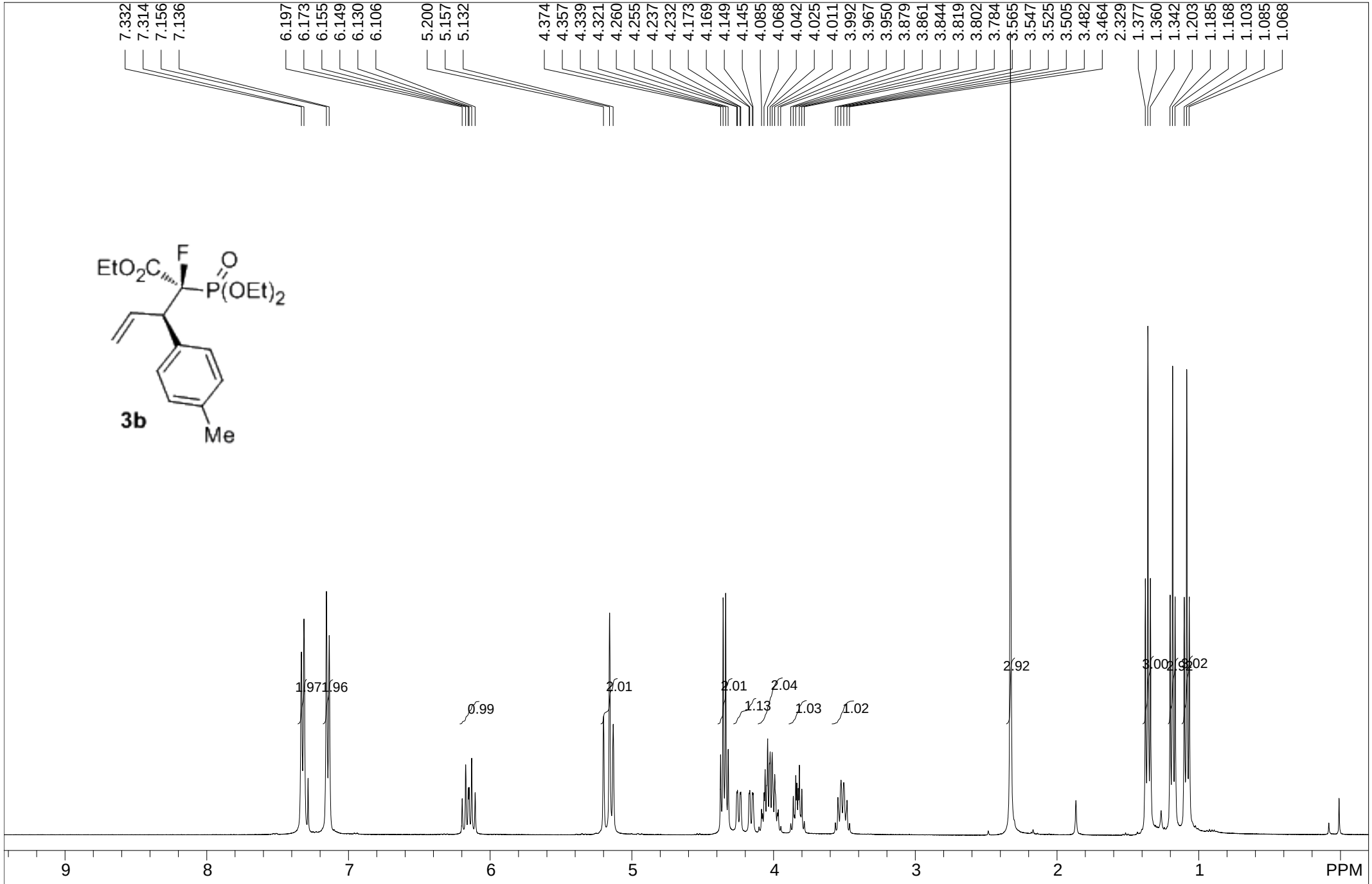
;blank line USER: -- DATE: Dec 28 2013

F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2802.9		PTS1d: 21552 , 32768
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 12	LB: 0.0	Nuts - $hy-2-67-h.fid



Std carbon;blank line USER: -- DATE: Dec 28 2013

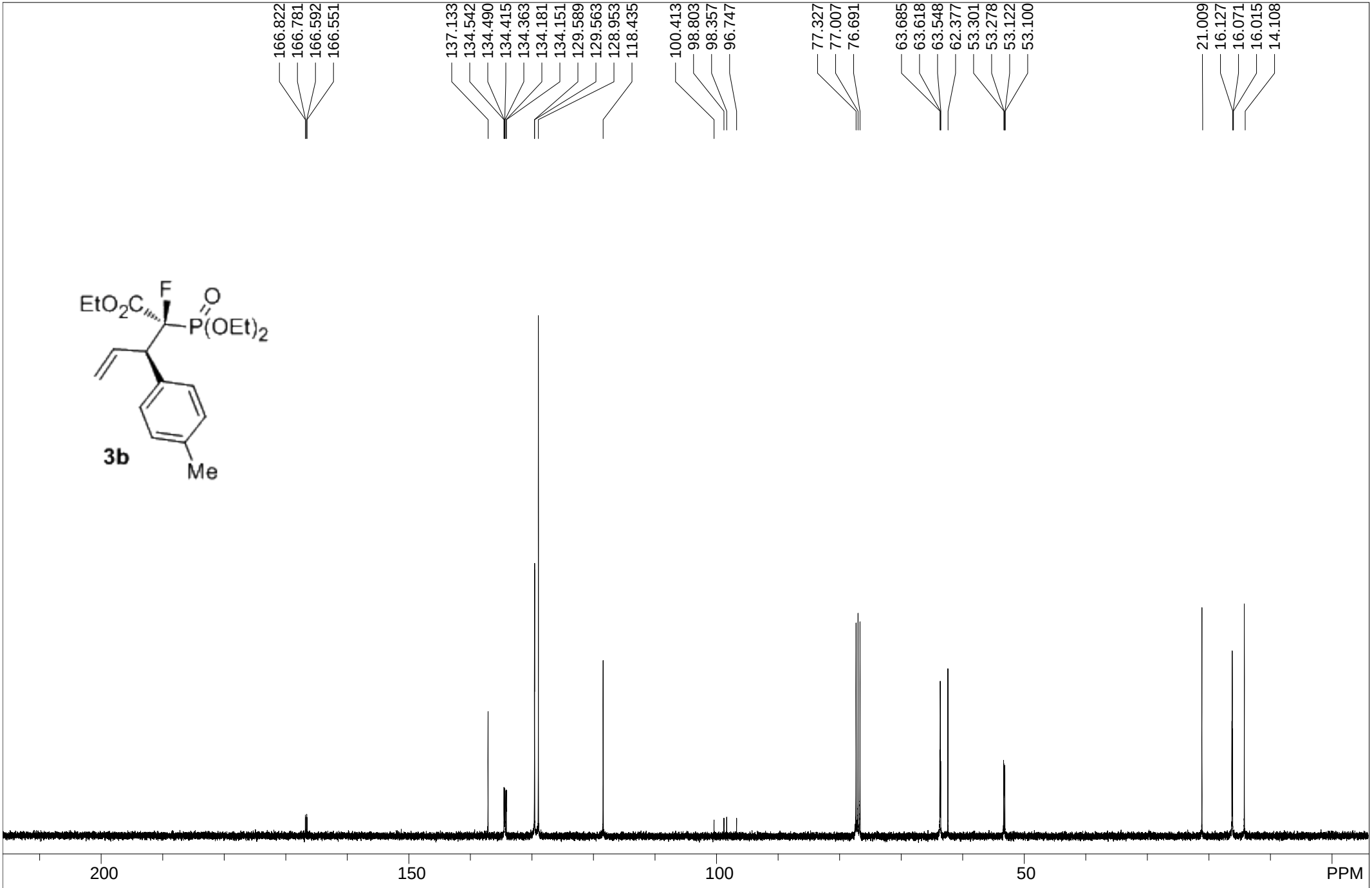
F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10558.6		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 1176	LB: 0.2		Nuts - $hy-2-67-c.fid



;blank line

USER: -- DATE: Dec 22 2013

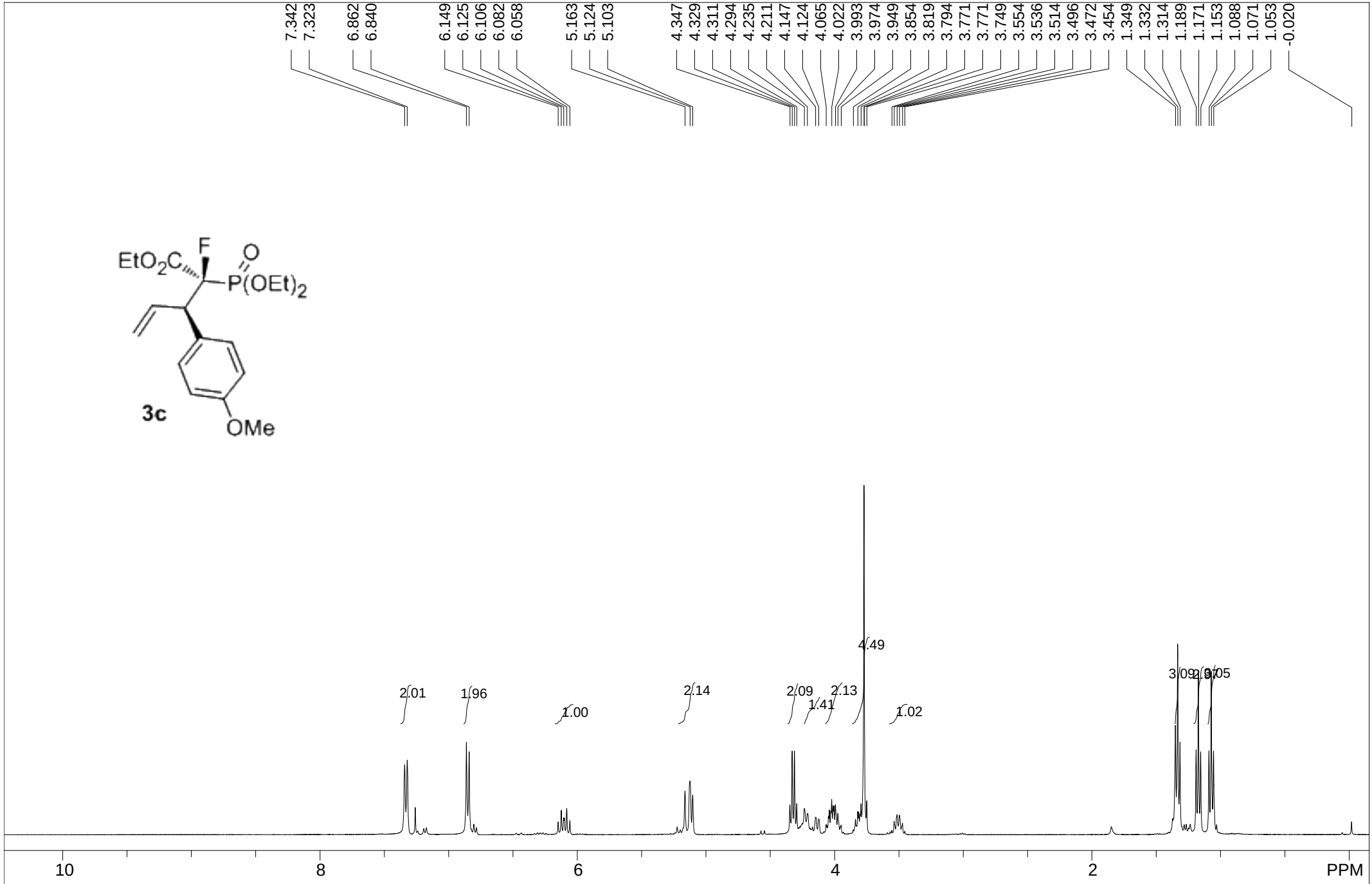
F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2808.4		PTS1d: 21552 , 32768	
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 12	LB: 0.0		Nuts - $hy-2-86-3-h.fid



Std carbon;blank line

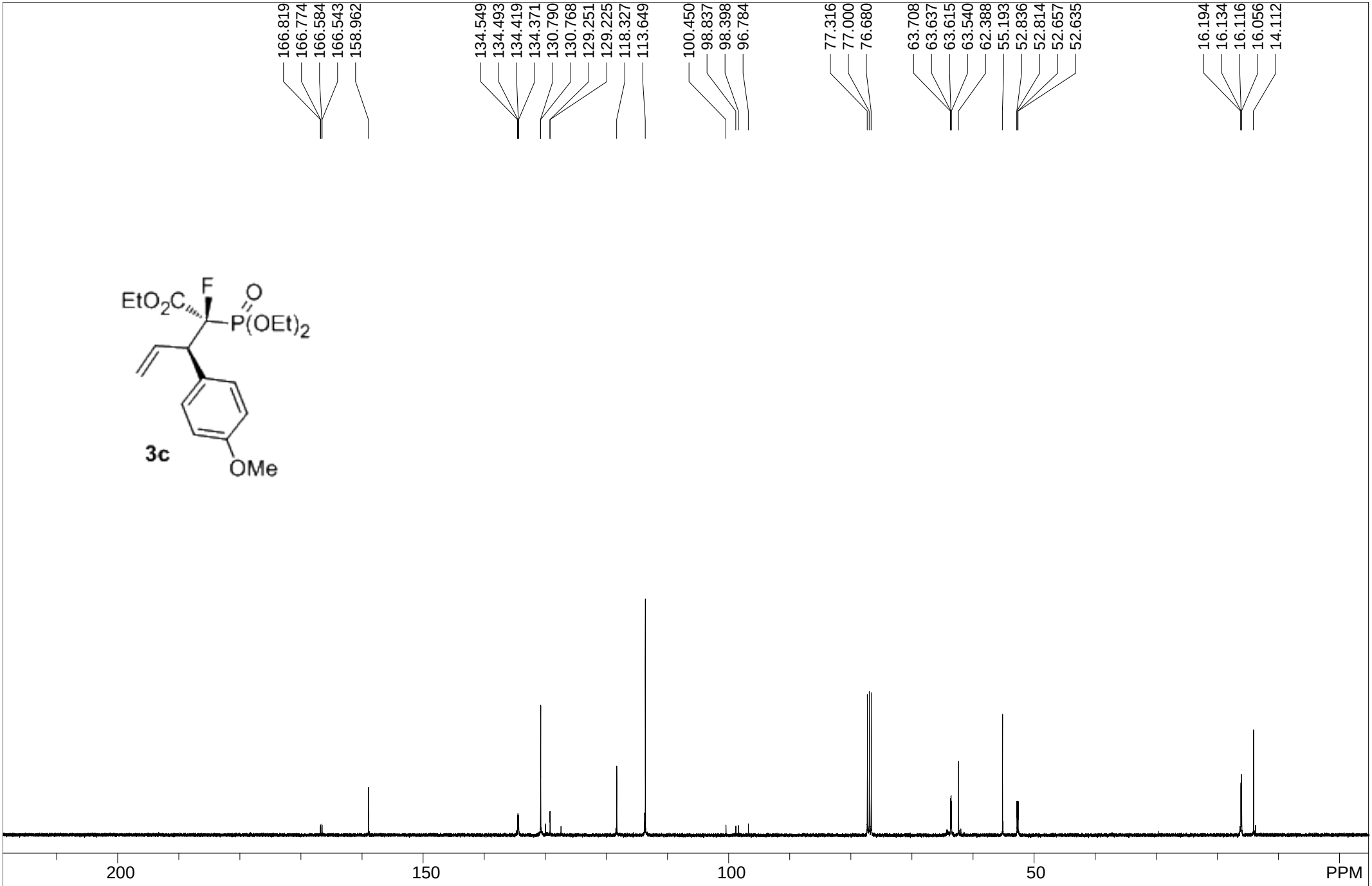
USER: -- DATE: Dec 22 2013

F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10560.1		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 1204	LB: 0.2		Nuts - $hy-2-86-3-c.fid



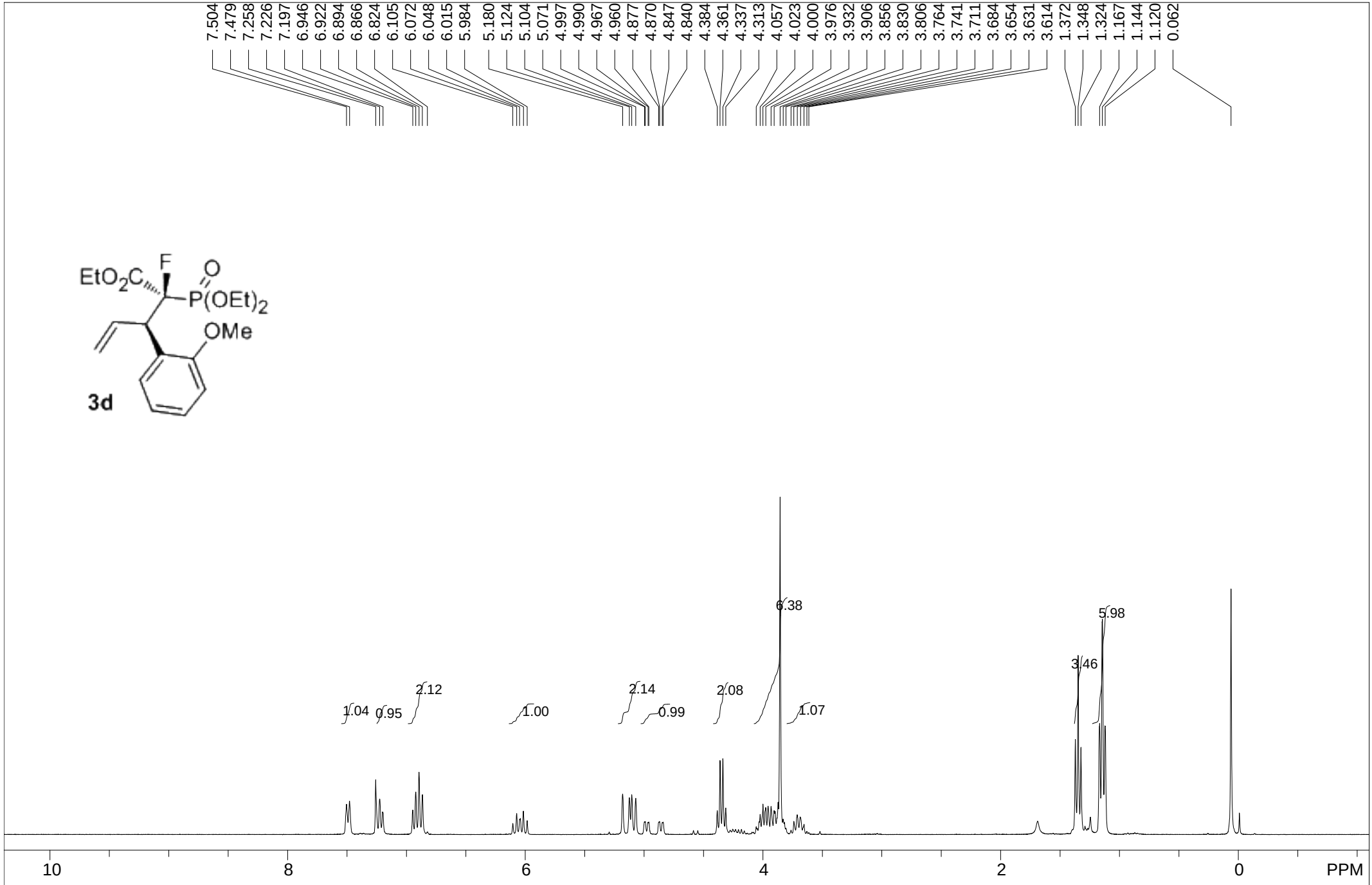
;blank line USER: -- DATE: Dec 27 2013

F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2798.2		PTS1d: 21552 , 32768
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 24	LB: 0.0	Nuts - $hy-2-92-5-h.fid



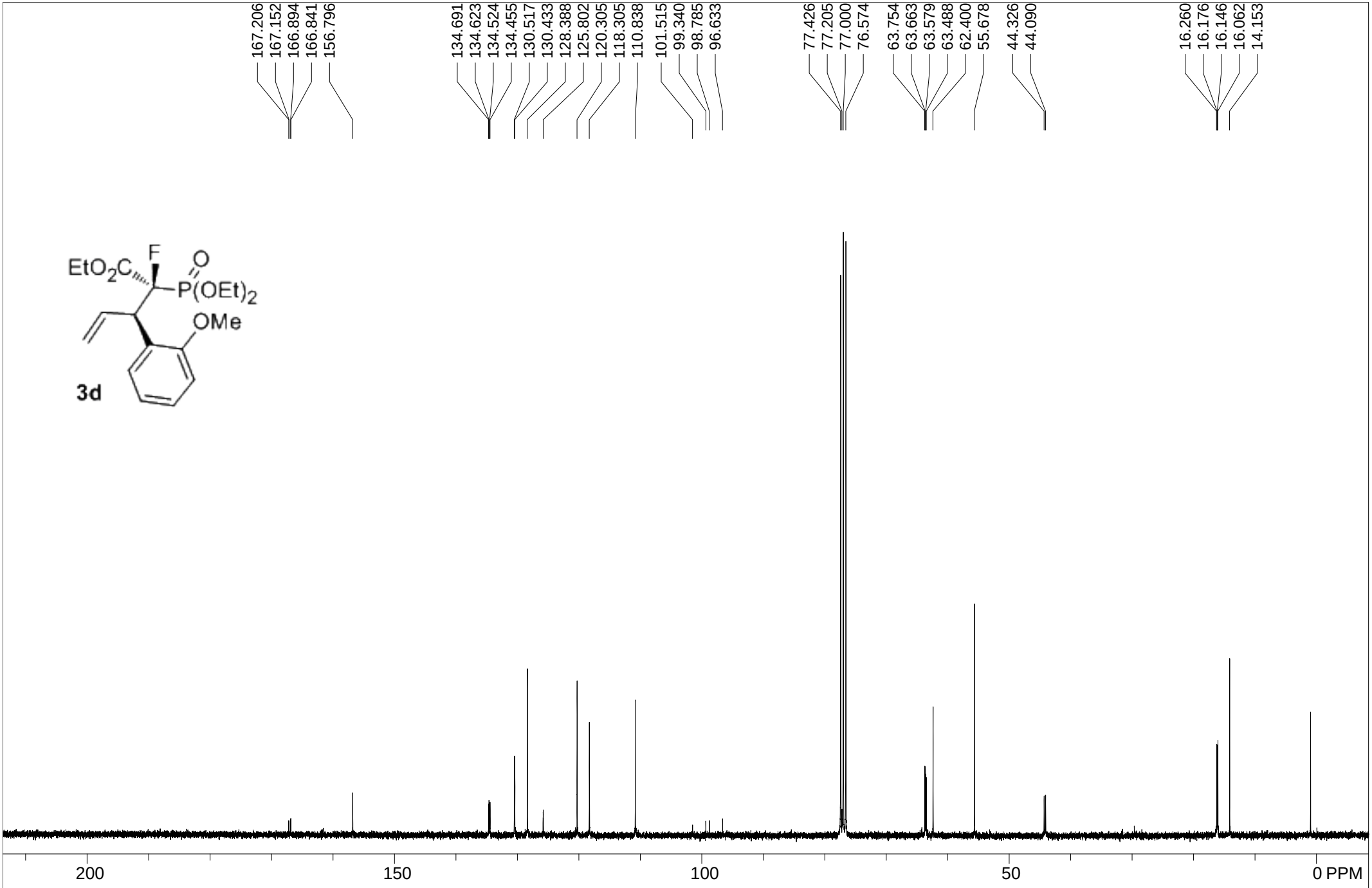
Std carbon;blank line USER: -- DATE: Dec 27 2013

F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10557.9		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 2260	LB: 0.2		Nuts - $hy-2-92-5-c.fid



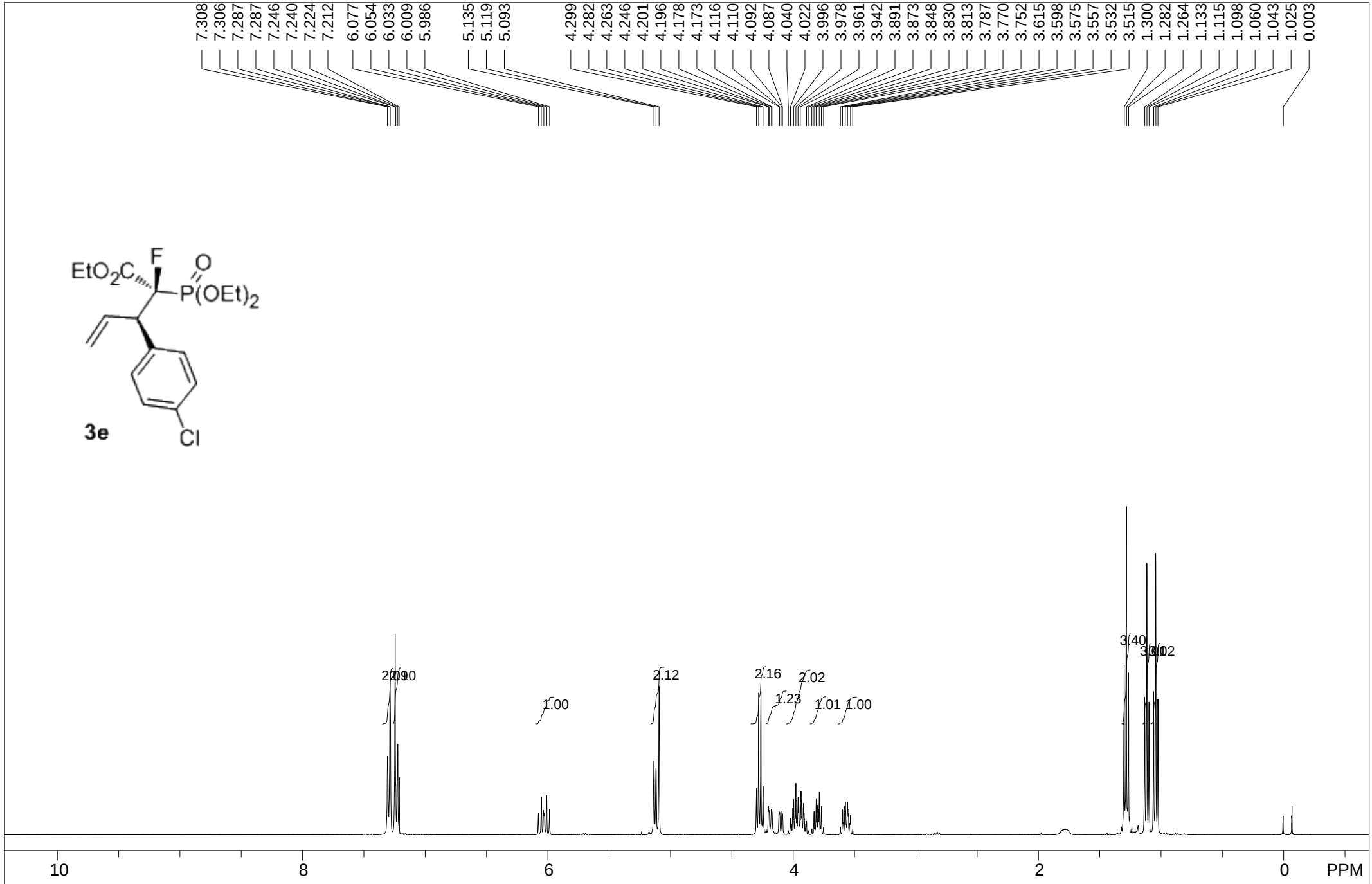
STANDARD 1H OBSERVE;blank line USER: -- DATE: Dec 26 2013

F1: 300.029	F2: 300.028	SW1: 5495		OF1: 2036.7		PTS1d: 10975 , 16384	
EX: s2pul		PW: 4.2 us	PD: 1.0 sec	NA: 12	LB: 0.0		Nuts - $hy-2-88-5-h-2.fid



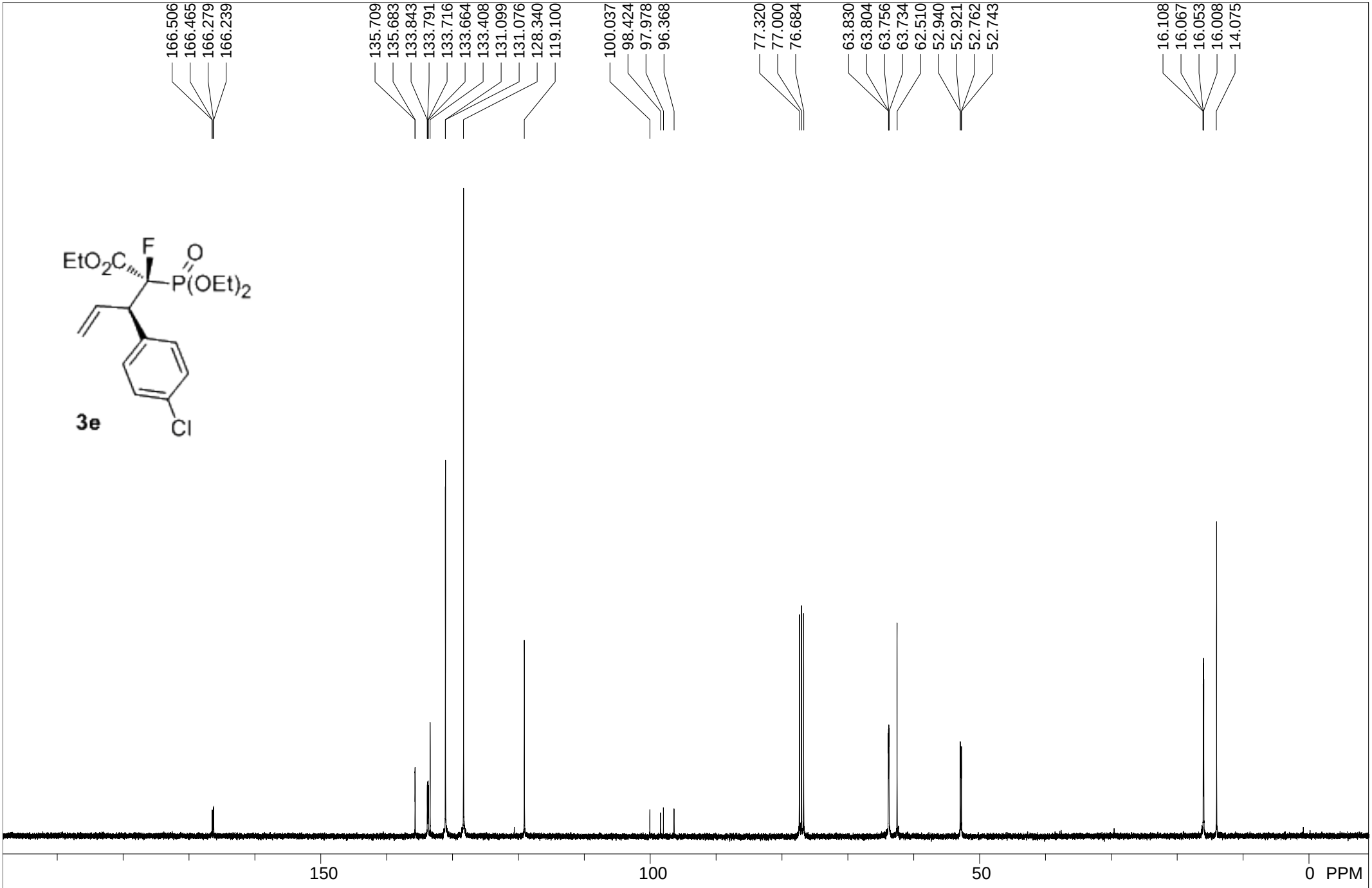
13C OBSERVE;blank line USER: -- DATE: Dec 26 2013

F1: 75.450	F2: 300.028	SW1: 18797		OF1: 7751.1		PTS1d: 30075 , 32768
EX: s2pul		PW: 4.6 us	PD: 1.0 sec	NA: 13276	LB: 0.2	Nuts - $hy-2-88-C.fid



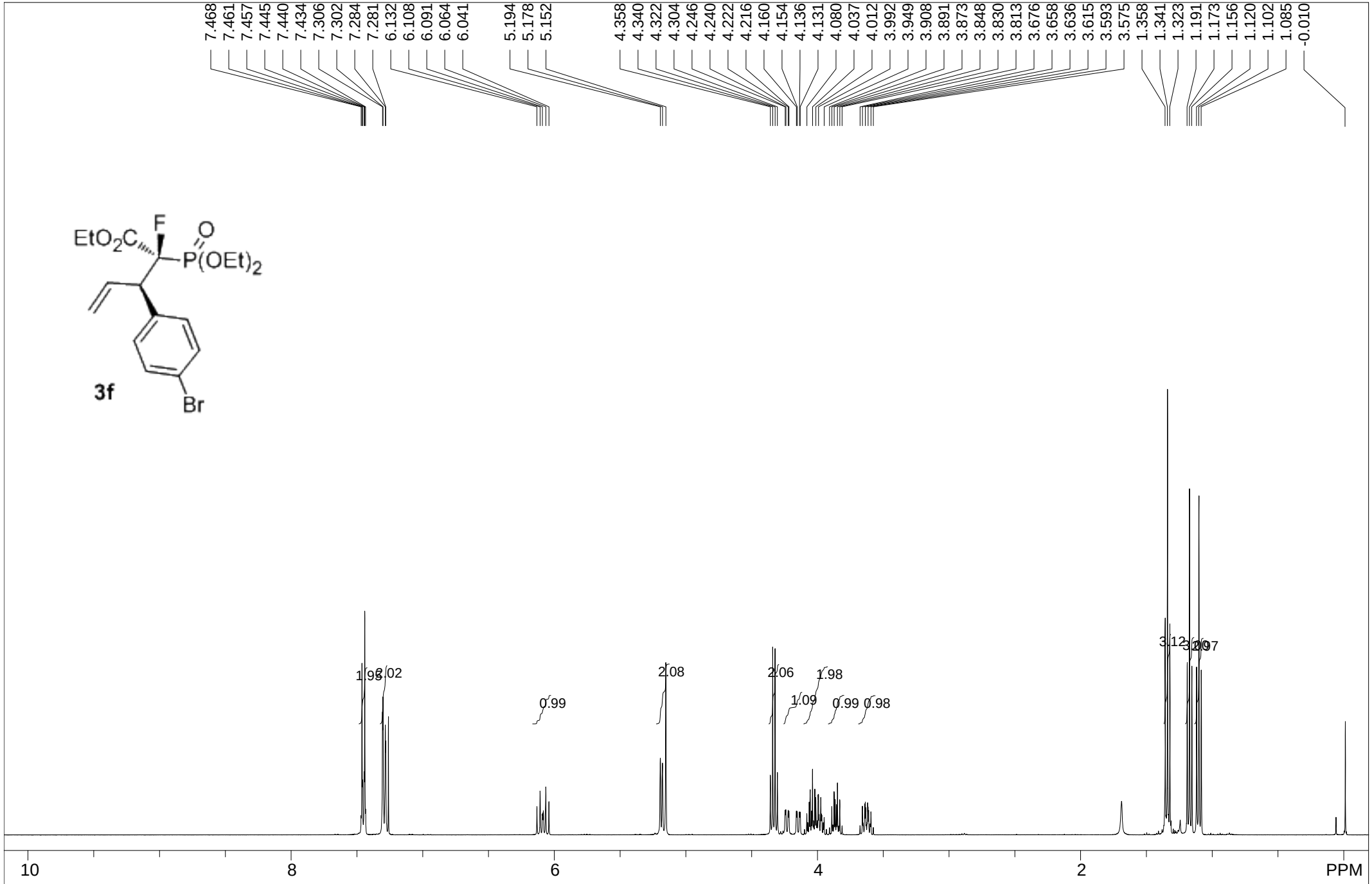
;blank line USER: -- DATE: Dec 15 2013

F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2779.4		PTS1d: 21552 , 32768
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 16	LB: 0.0	Nuts - $hy-2-73-3-h.fid



Std carbon;blank line USER: -- DATE: Dec 17 2013

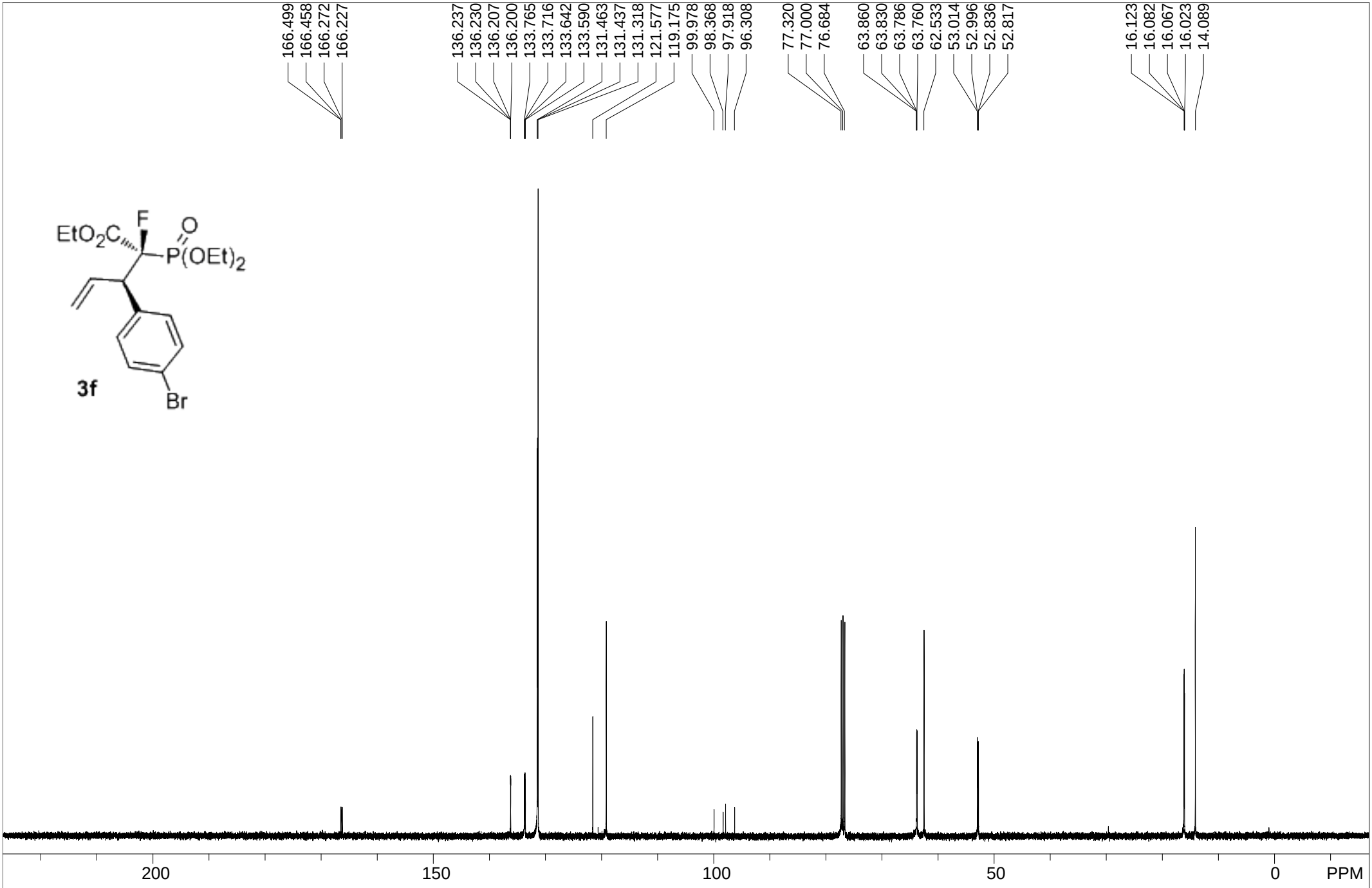
F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10557.1		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 2000	LB: 0.2		Nuts - $hy-2-73-3-c.fid



;blank line

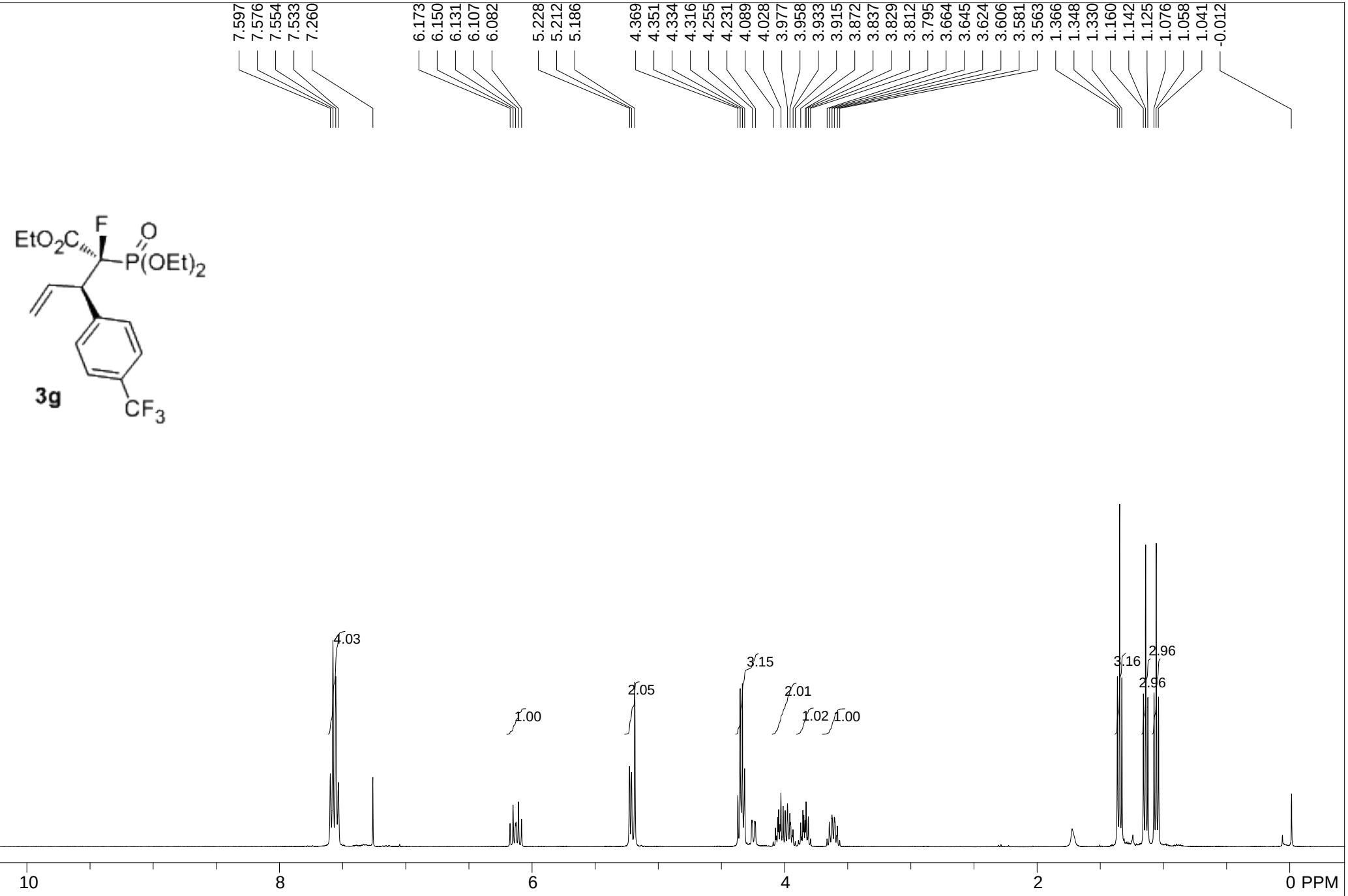
USER: -- DATE: Dec 15 2013

F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2798.6		PTS1d: 21552 , 32768	
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 20	LB: 0.0		Nuts - $hy-2-74-3-h.fid



Std carbon;blank line USER: -- DATE: Dec 18 2013

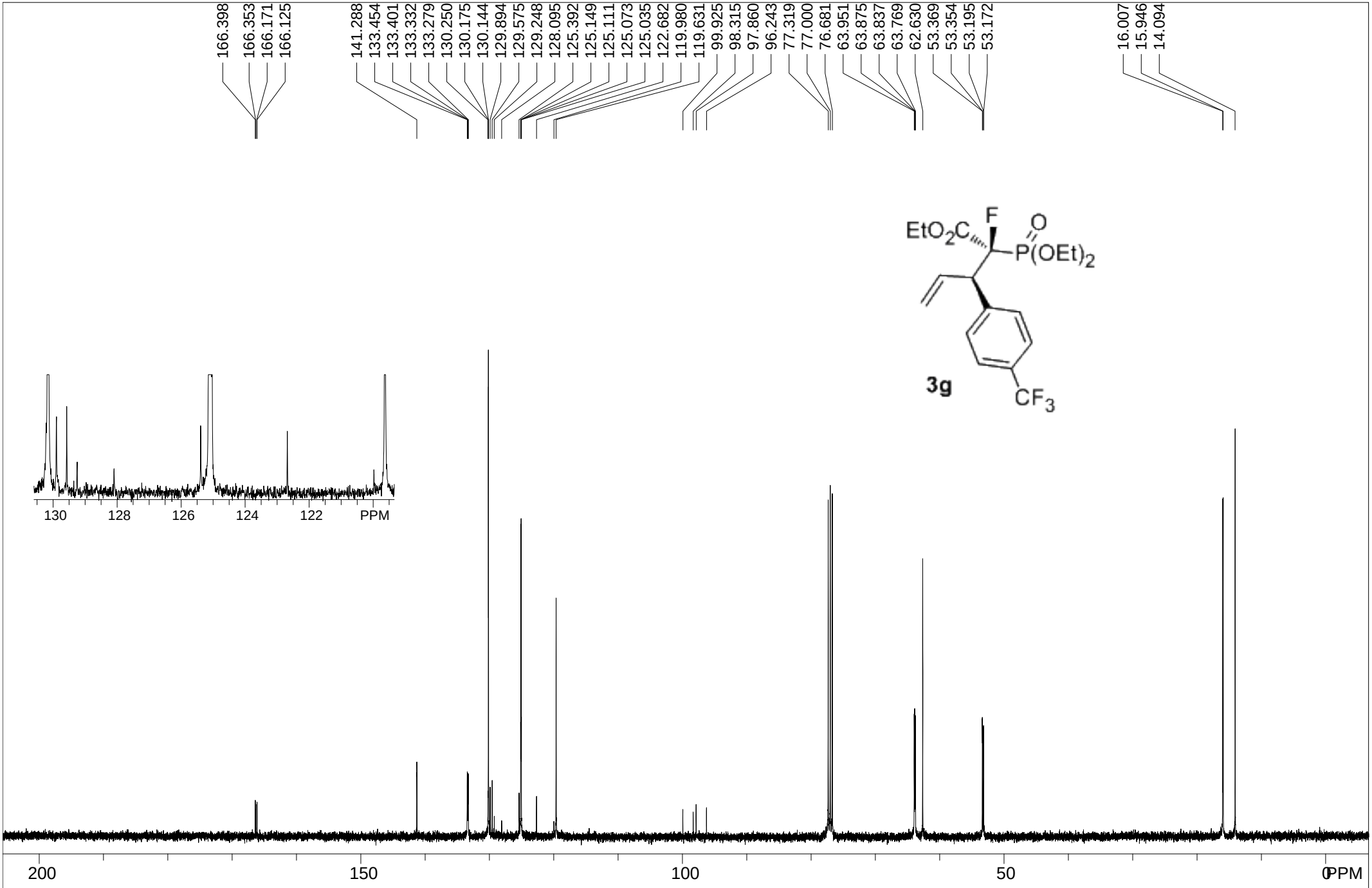
F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10557.9		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 2120	LB: 0.2		Nuts - $hy-2-74-3-c.fid



;blank line

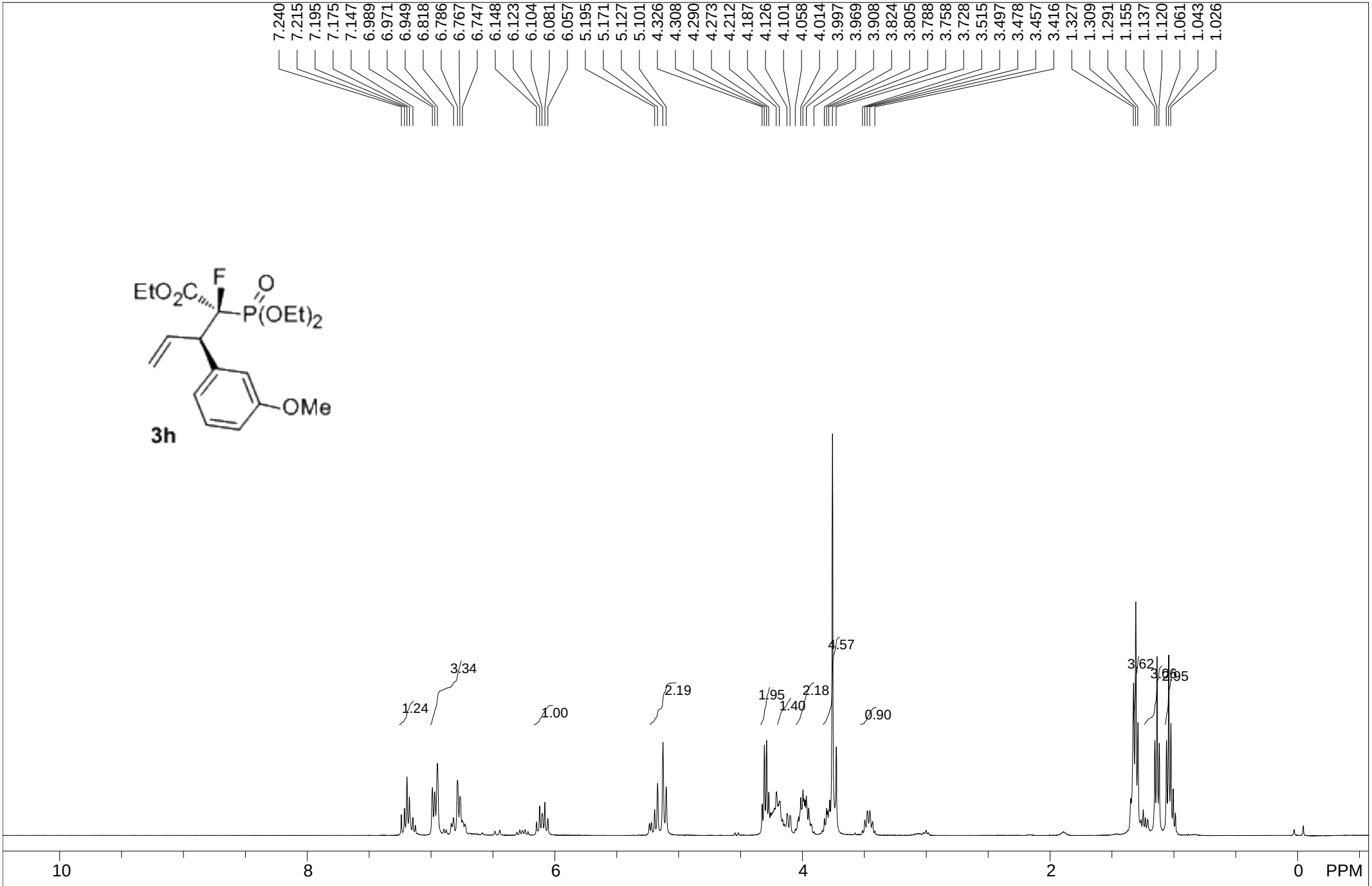
USER: -- DATE: Dec 15 2013

F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2798.4		PTS1d: 21552 , 32768	
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 16	LB: 0.0		Nuts - $hy-2-72-3-h.fid



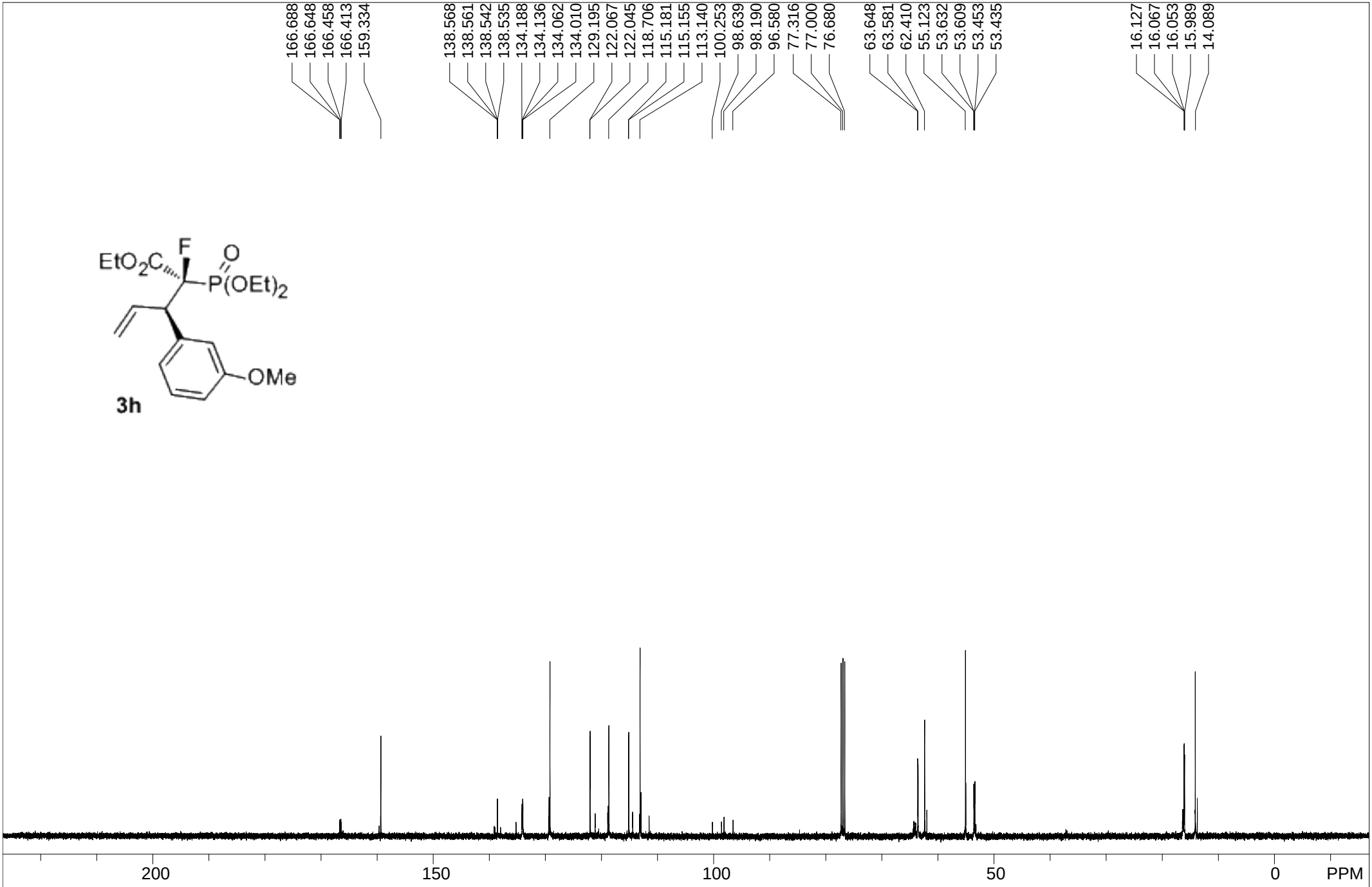
sw-2-10-2-2-HHCOSY USER: -- DATE: Dec 16 2013

F1: 100.521	F2: 399.722	SW1: 25000		OF1: 11052.4		PTS1d: 32768 , 32768	
EX: s2pul		PW: 7.2 us	PD: 1.0 sec	NA: 2156	LB: 0.2		Nuts - $hy-2-72-3-c-2.fid



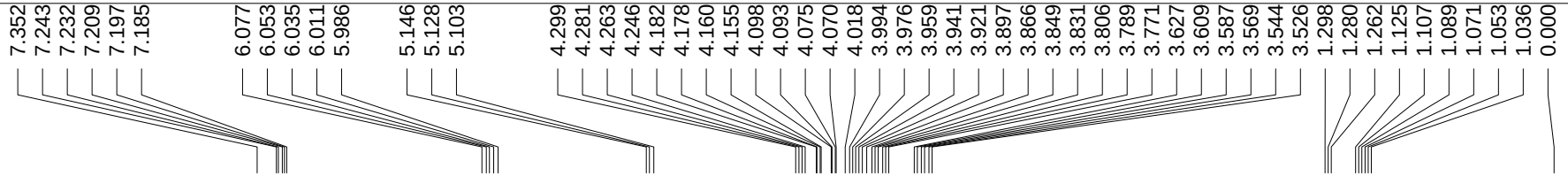
Std proton;blank line0v USER: -- DATE: Dec 28 2013

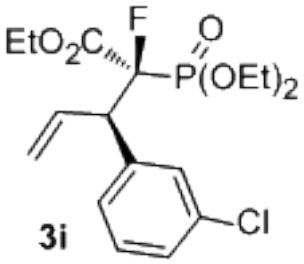
F1: 400.032	F2: 100.597	SW1: 7225		OF1: 2800.0		PTS1d: 21676 , 32768	
EX: s2pul		PW: 10.4 us	PD: 1.0 sec	NA: 16	LB: 0.0		Nuts - $hy-2-93-5-h-2.fid



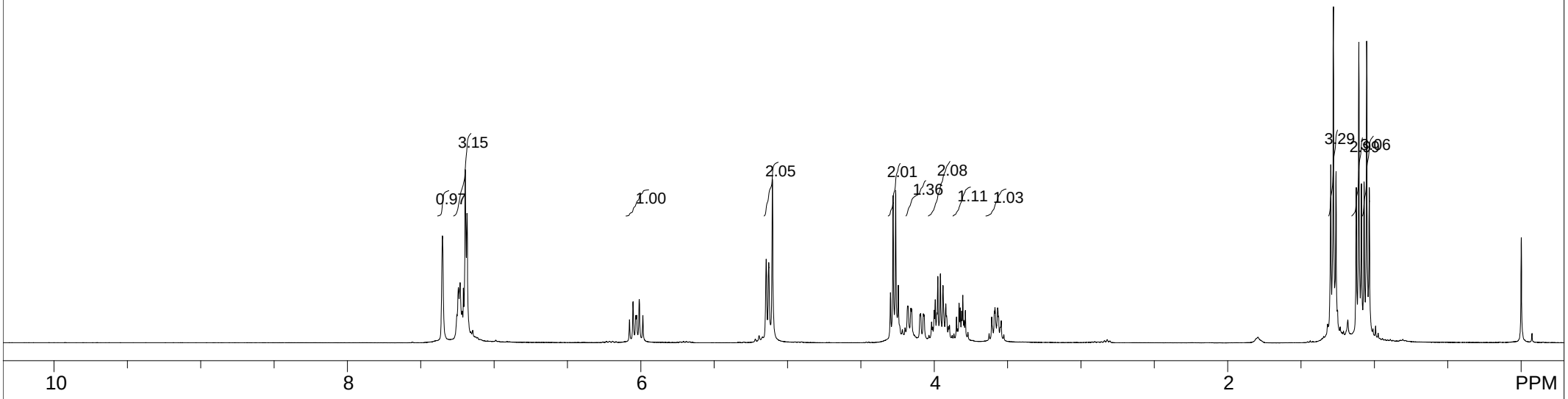
Std carbon;blank line USER: -- DATE: Dec 28 2013

F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10556.4		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 868	LB: 0.2		Nuts - $hy-2-93-5-c.fid



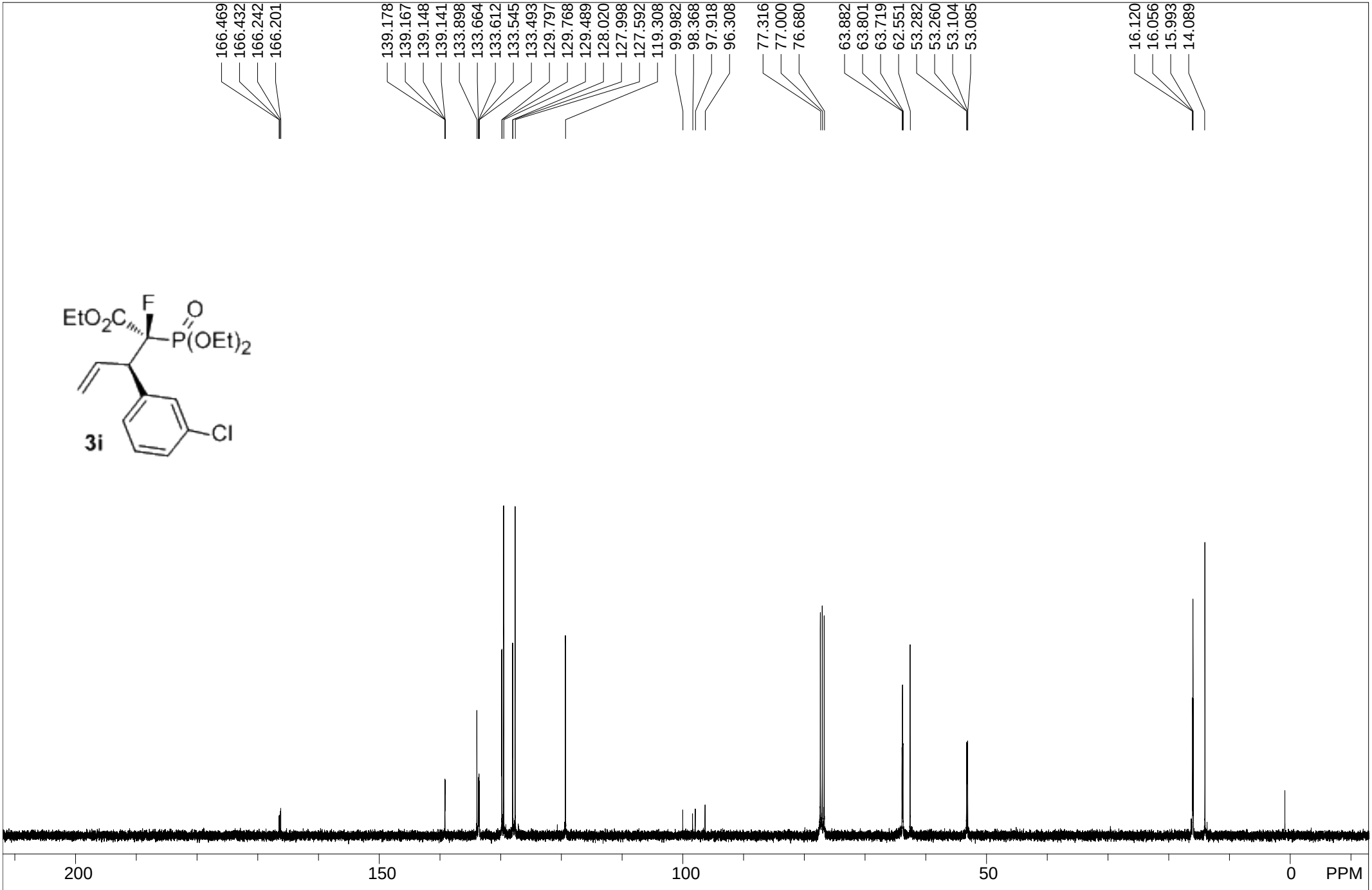


3i



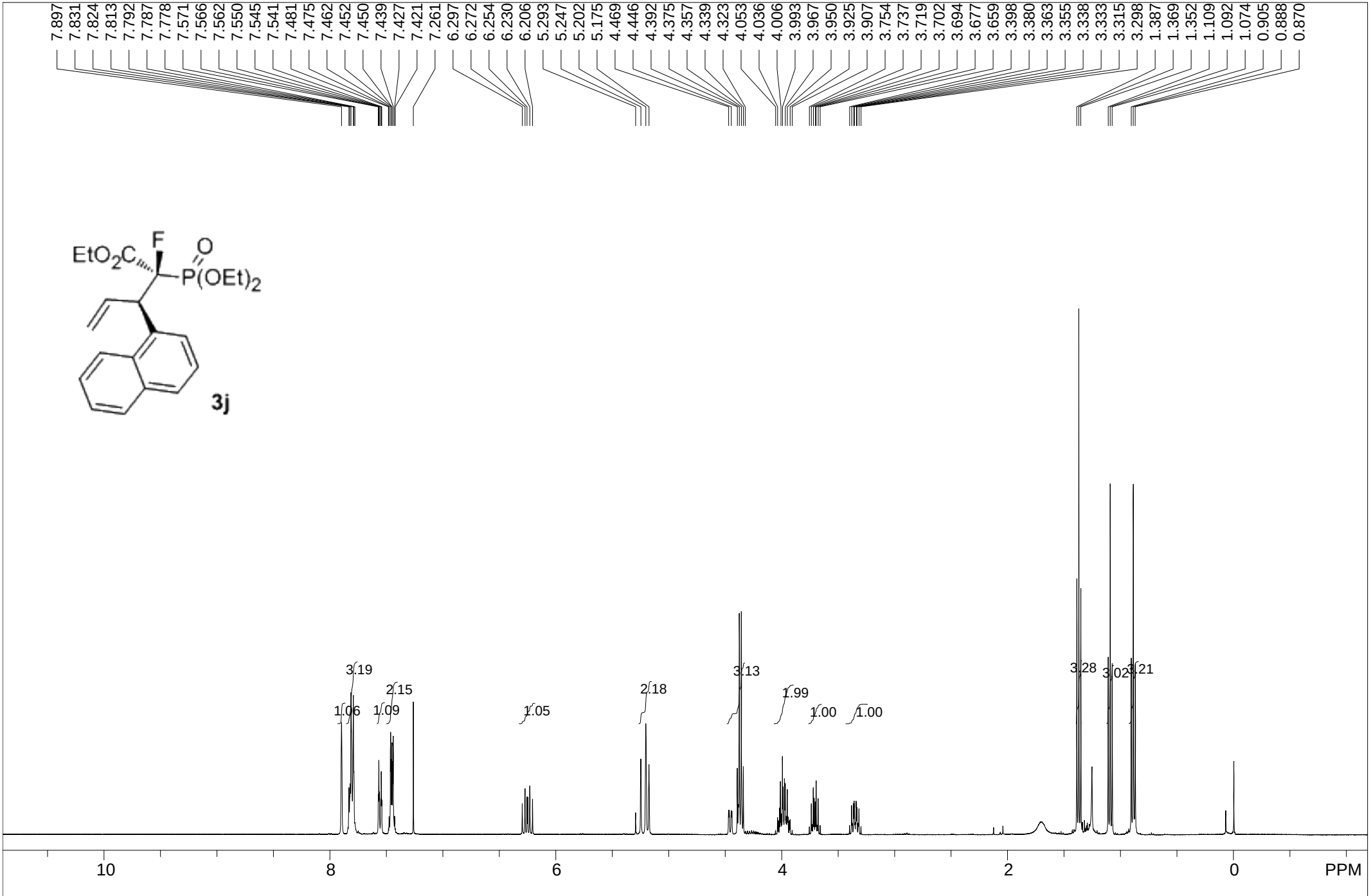
Std proton;blank line USER: -- DATE: Dec 20 2013

F1: 400.032	F2: 100.597	SW1: 7225		OF1: 2787.1		PTS1d: 21676 , 32768
EX: s2pul		PW: 10.4 us	PD: 1.0 sec	NA: 20	LB: 0.0	Nuts - $hy-2-81-4-h-2.fid



Std carbon;blank line USER: -- DATE: Dec 20 2013

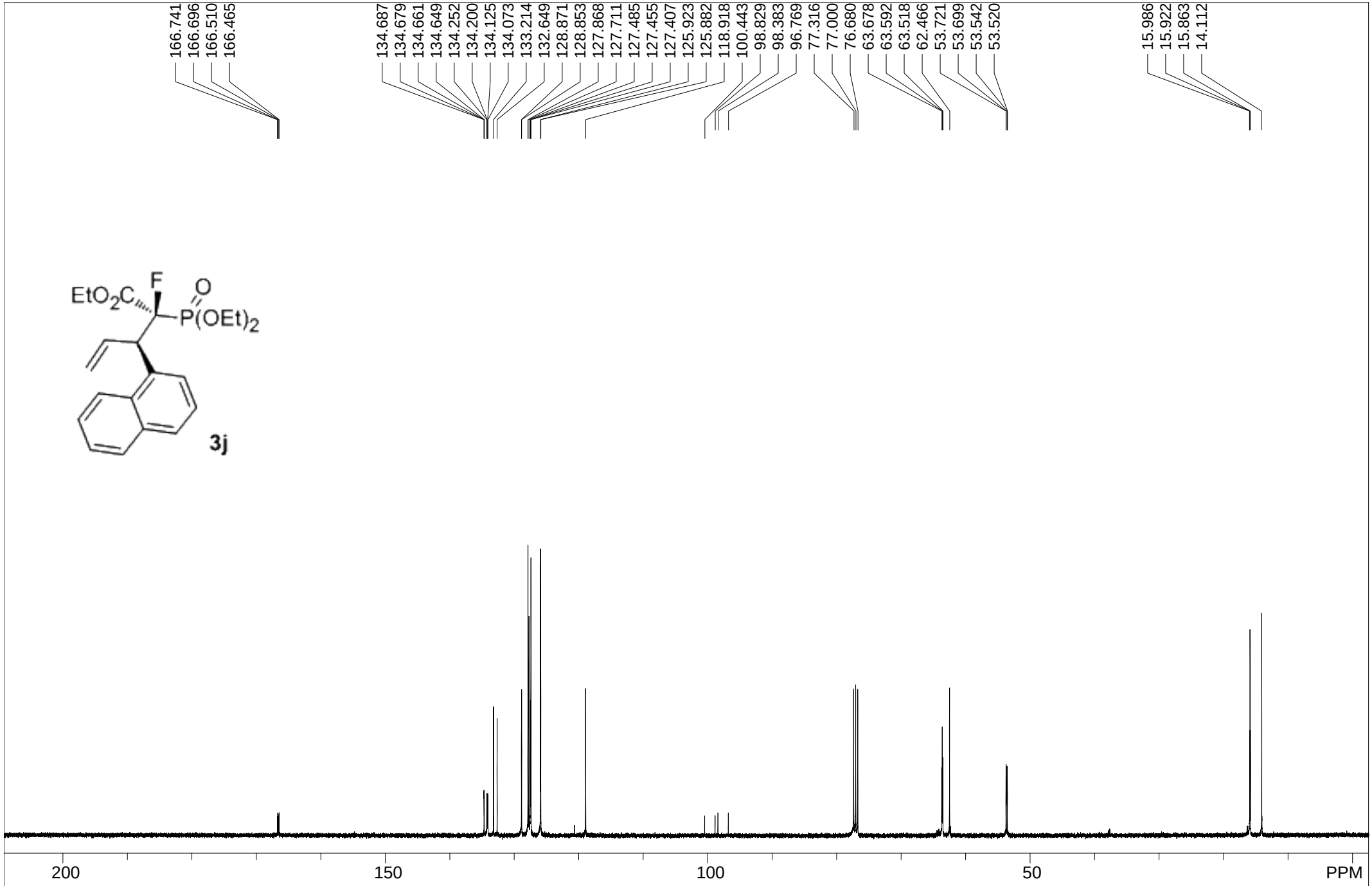
F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10557.9		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 1040	LB: 0.2		Nuts - $hy-2-81-4-c.fid



;blank line

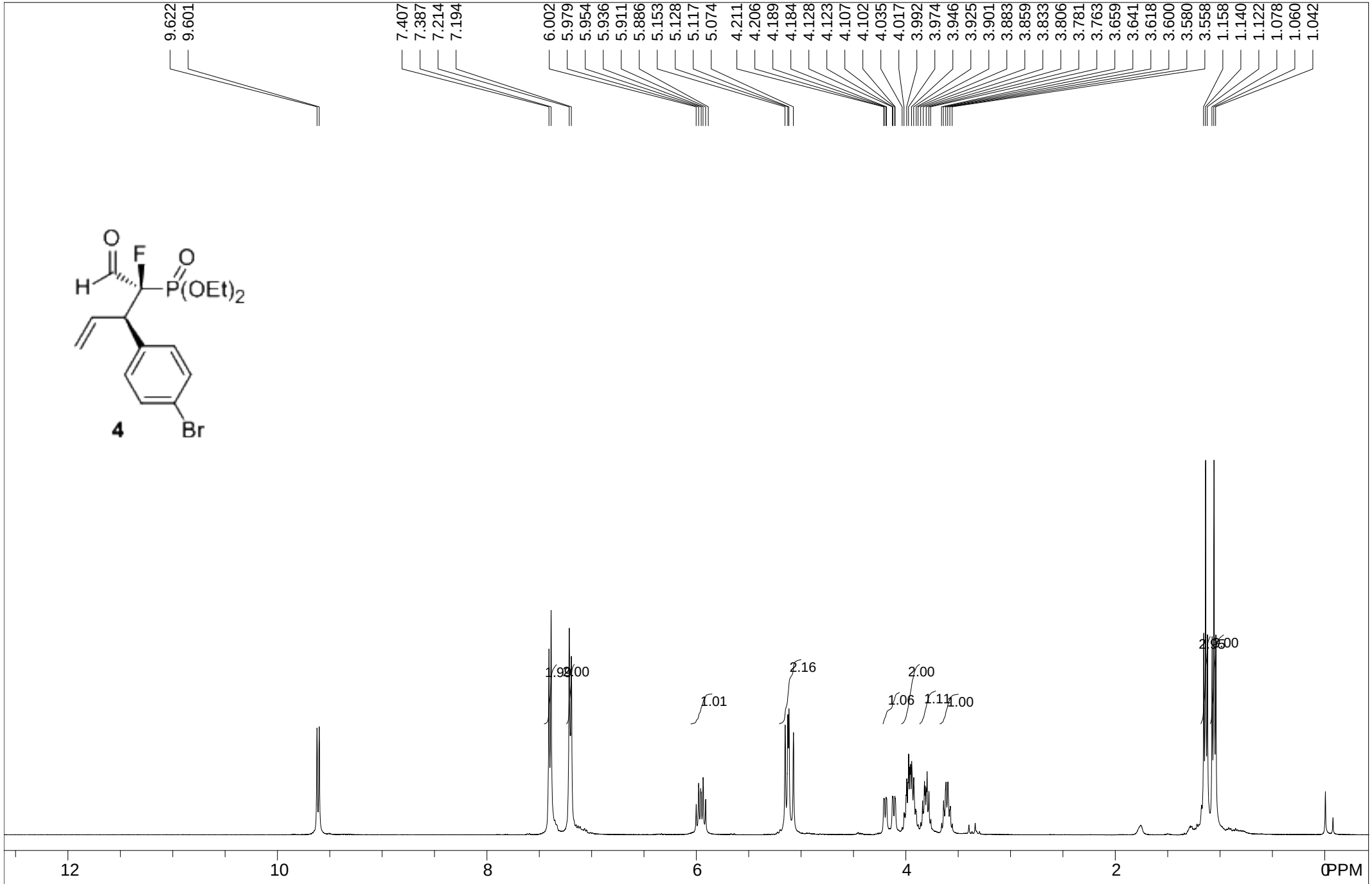
USER: -- DATE: Oct 14 2013

F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2799.0		PTS1d: 21552 , 32768	
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 4	LB: 0.0		Nuts - $hy-2-2-1-h.fid



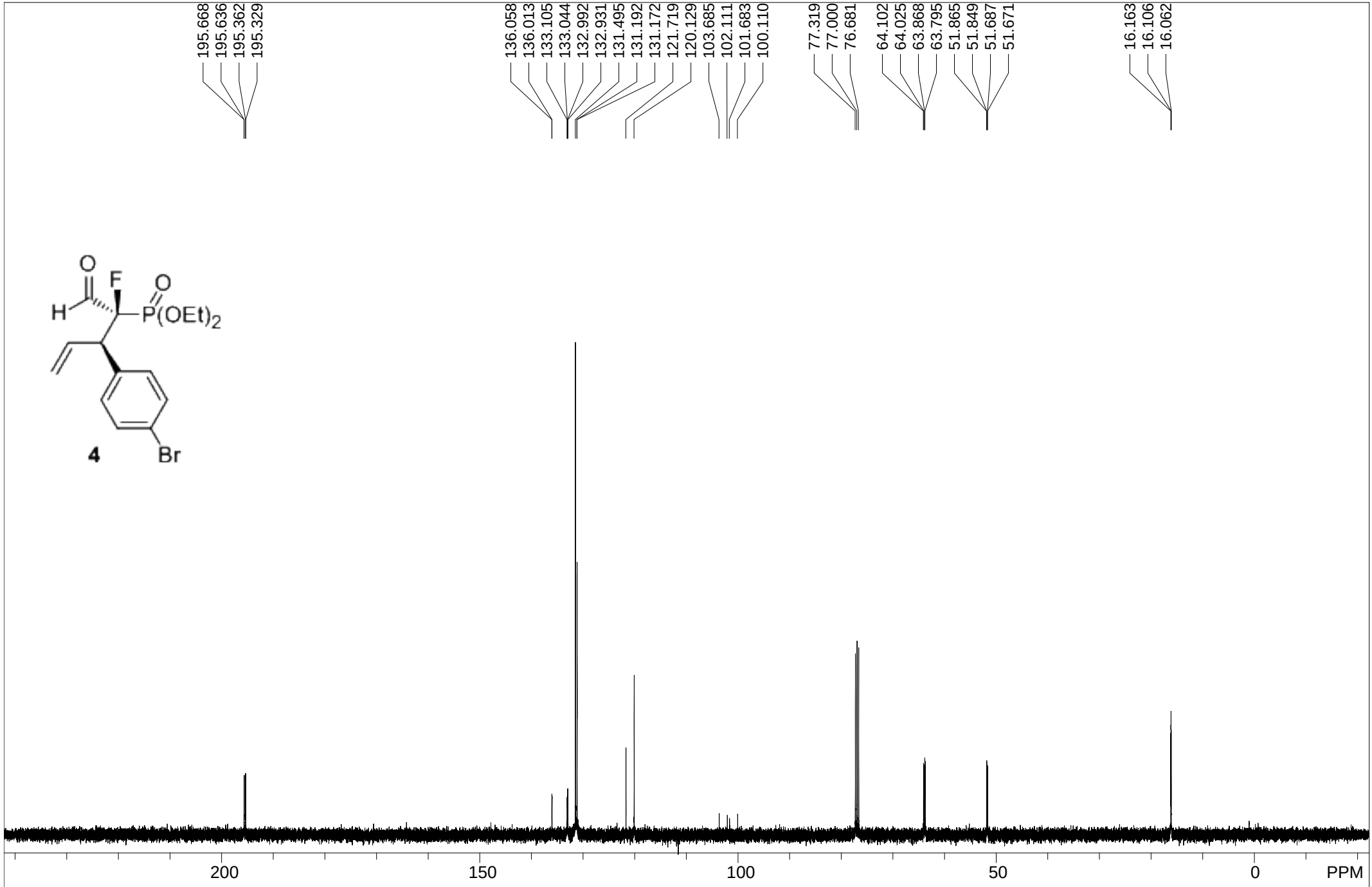
Std carbon;blank line USER: -- DATE: Dec 23 2013

F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10556.0		PTS1d: 36765 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 2104	LB: 0.2		Nuts - $hy-2-85-3-c.fid



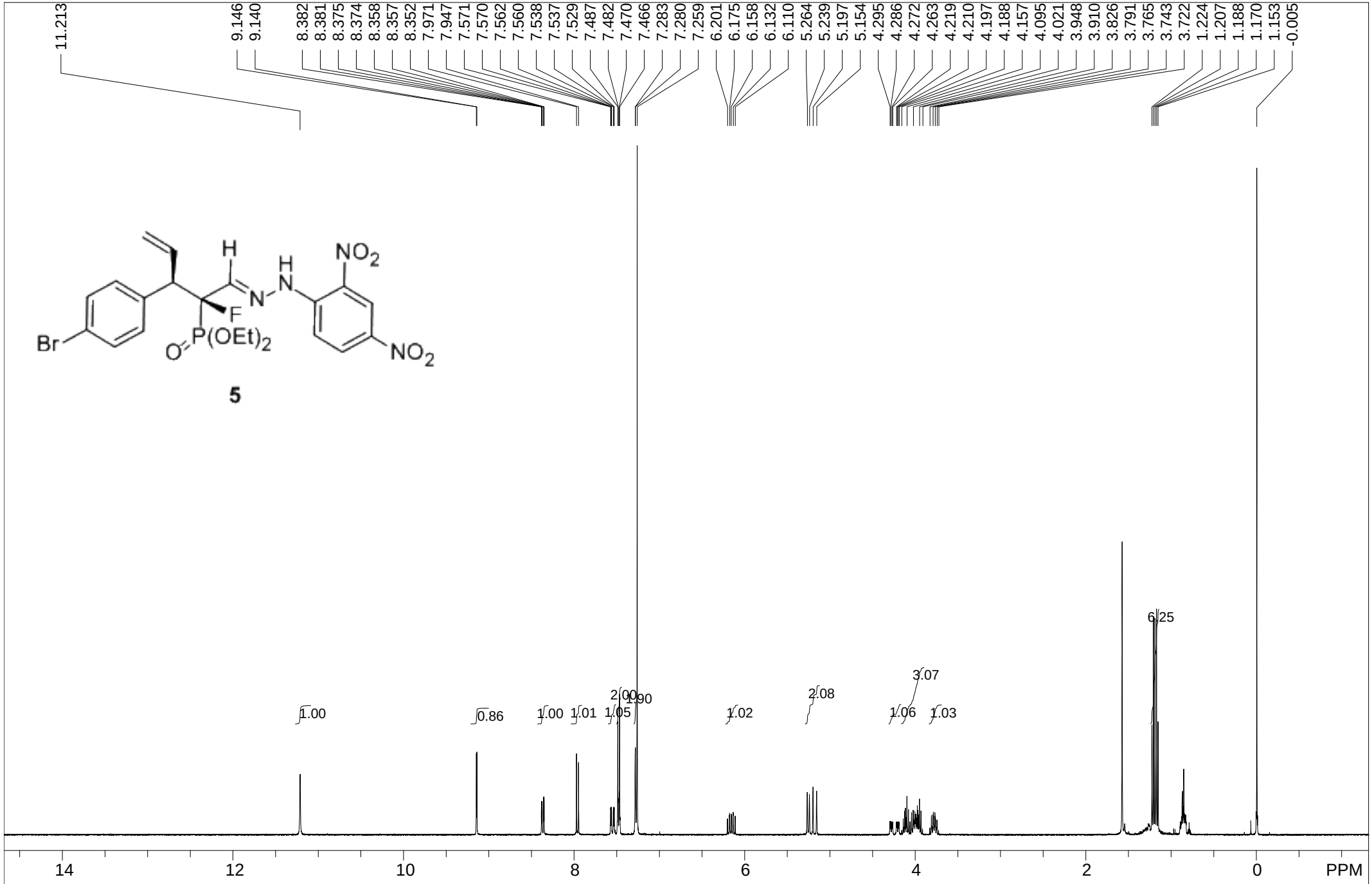
Std proton;blank line USER: -- DATE: Jan 14 2014

F1: 400.032	F2: 100.597	SW1: 7225		OF1: 2786.2		PTS1d: 21676 , 32768
EX: s2pul		PW: 10.4 us	PD: 1.0 sec	NA: 16	LB: 0.0	Nuts - $hy-2-115-2-h-2.fid



Std carbon;blank line USER: -- DATE: Jan 14 2014

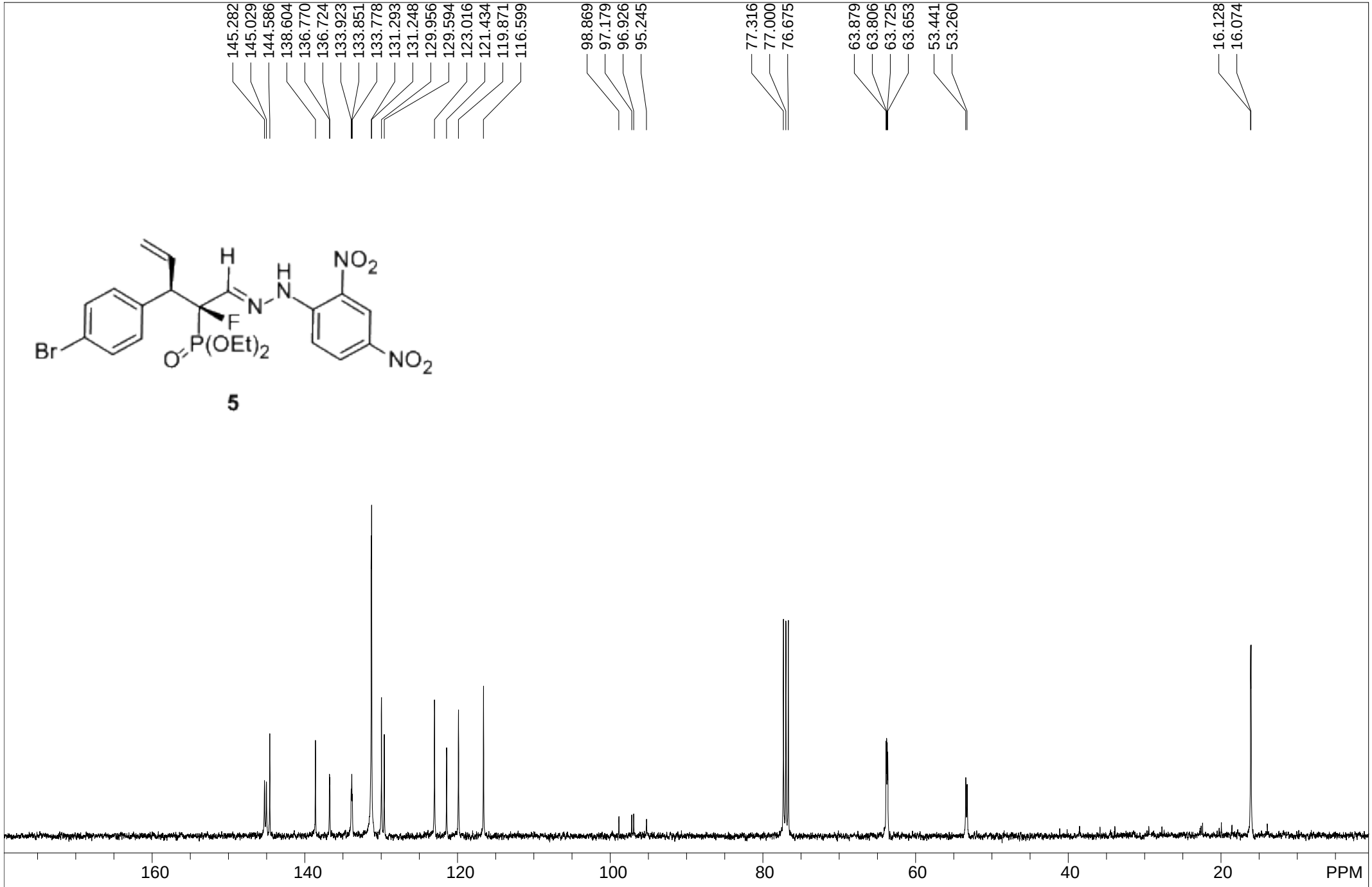
F1: 100.598	F2: 400.031	SW1: 26596		OF1: 11061.0		PTS1d: 39894 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 328	LB: 0.2		Nuts - $hy-2-115-2-c.fid



;blank line

USER: -- DATE: Jan 23 2014

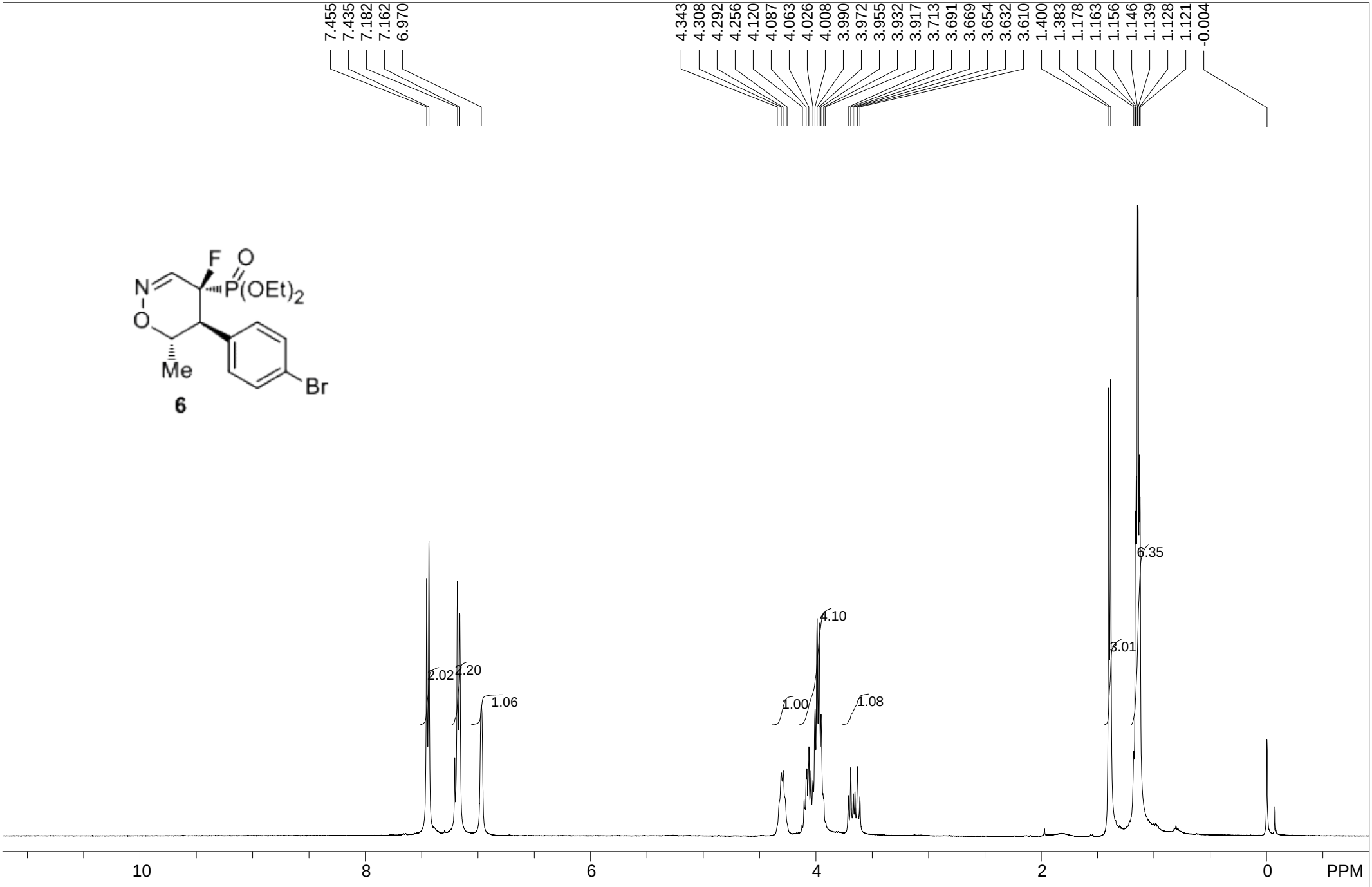
F1: 399.723	F2: 100.519	SW1: 7184		OF1: 2798.0		PTS1d: 21552 , 32768
EX: s2pul		PW: 7.8 us	PD: 1.0 sec	NA: 12	LB: 0.0	Nuts - $hy-2-122-s-h-3.fid



5

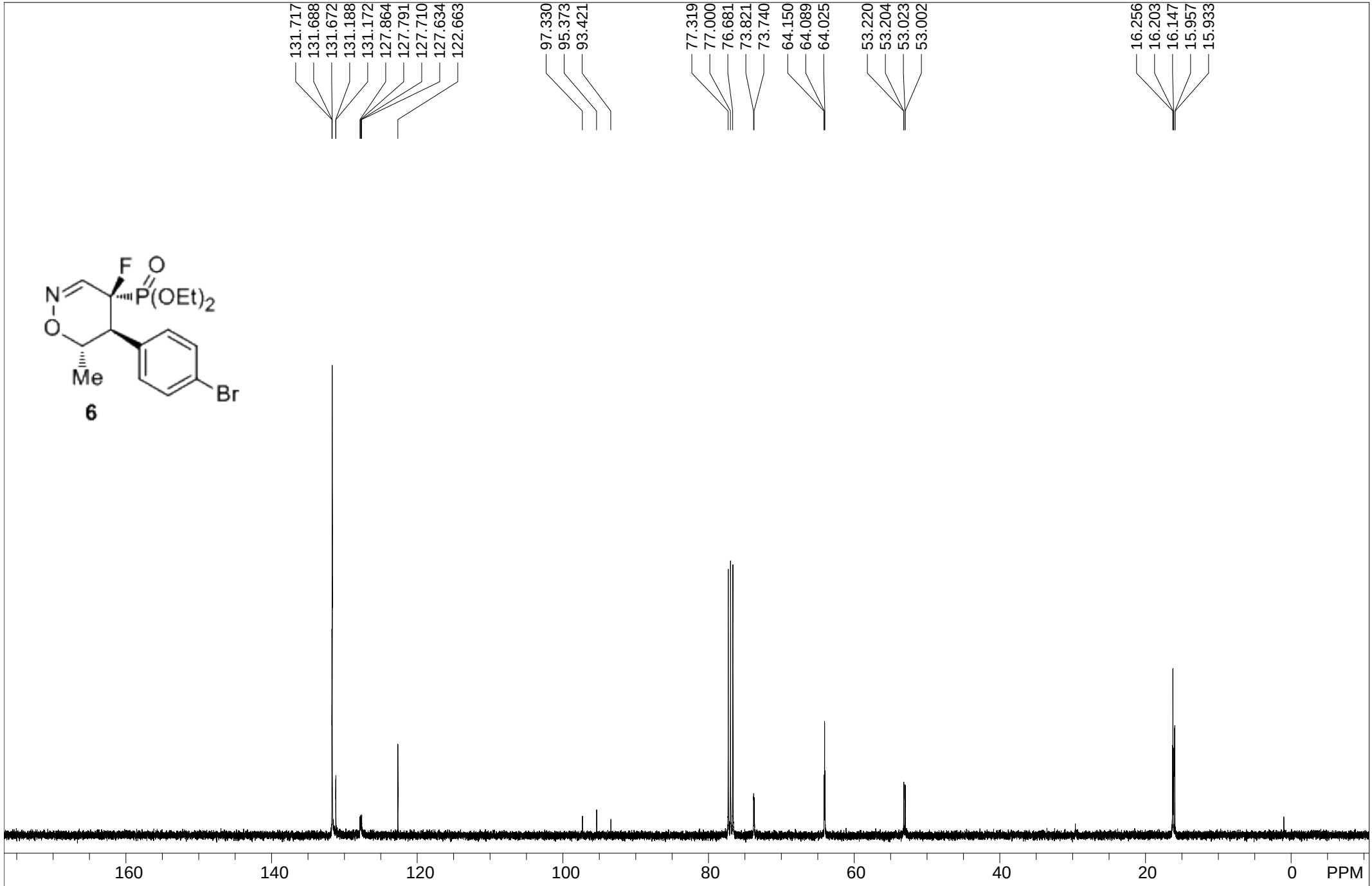
new experimentJre USER: -- DATE: Jan 22 2014

F1: 100.523	F2: 399.722	SW1: 29762		OF1: 13332.9		PTS1d: 32768 , 32768	
EX: s2pul		PW: 4.9 us	PD: 1.0 sec	NA: 500	LB: 2.0		Nuts - $hy-2-122-c.fid



Std proton;blank line USER: -- DATE: Jan 14 2014

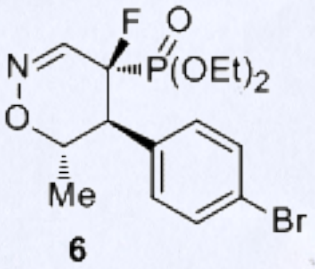
F1: 400.032	F2: 100.597	SW1: 7225		OF1: 2787.2		PTS1d: 21676 , 32768	
EX: s2pul		PW: 10.4 us	PD: 1.0 sec	NA: 12	LB: 0.0		Nuts - $hy-2-109-3-h-2.fid



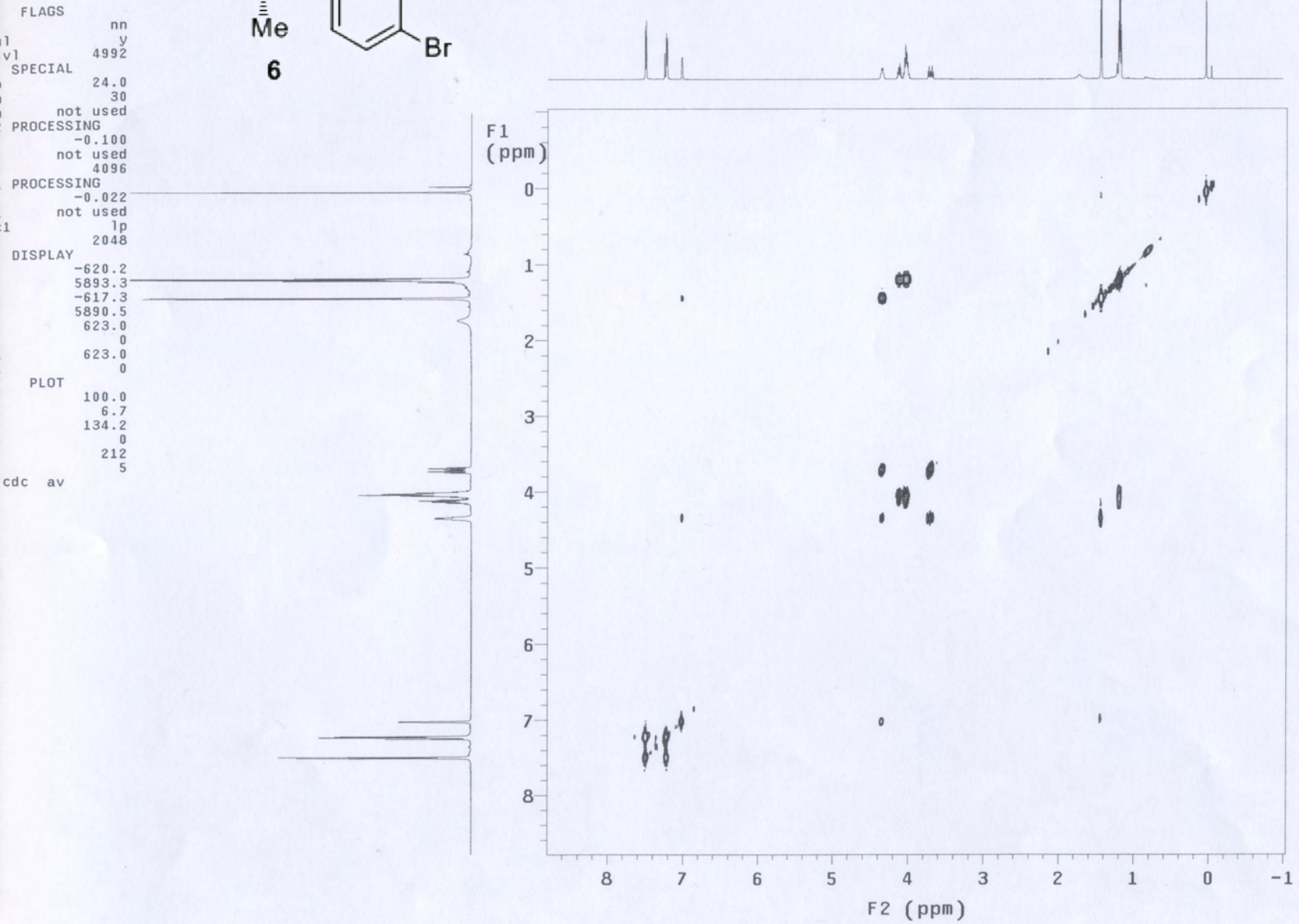
Std carbon;blank line USER: -- DATE: Jan 14 2014

F1: 100.598	F2: 400.031	SW1: 26596		OF1: 11061.0		PTS1d: 39894 , 65536	
EX: s2pul		PW: 9.5 us	PD: 1.0 sec	NA: 1328	LB: 0.2		Nuts - $hy-2-109-3-c.fid

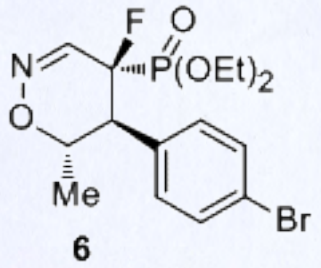
2D NMR Spectra of 6 H-H COSY



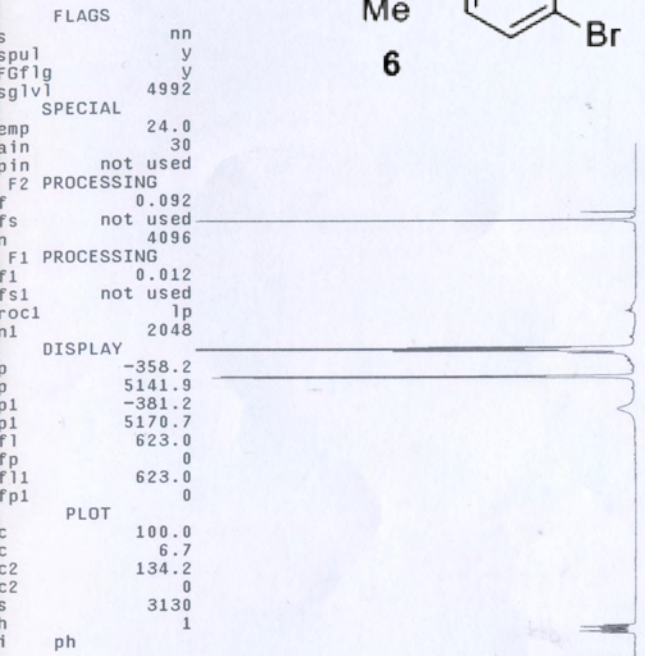
6

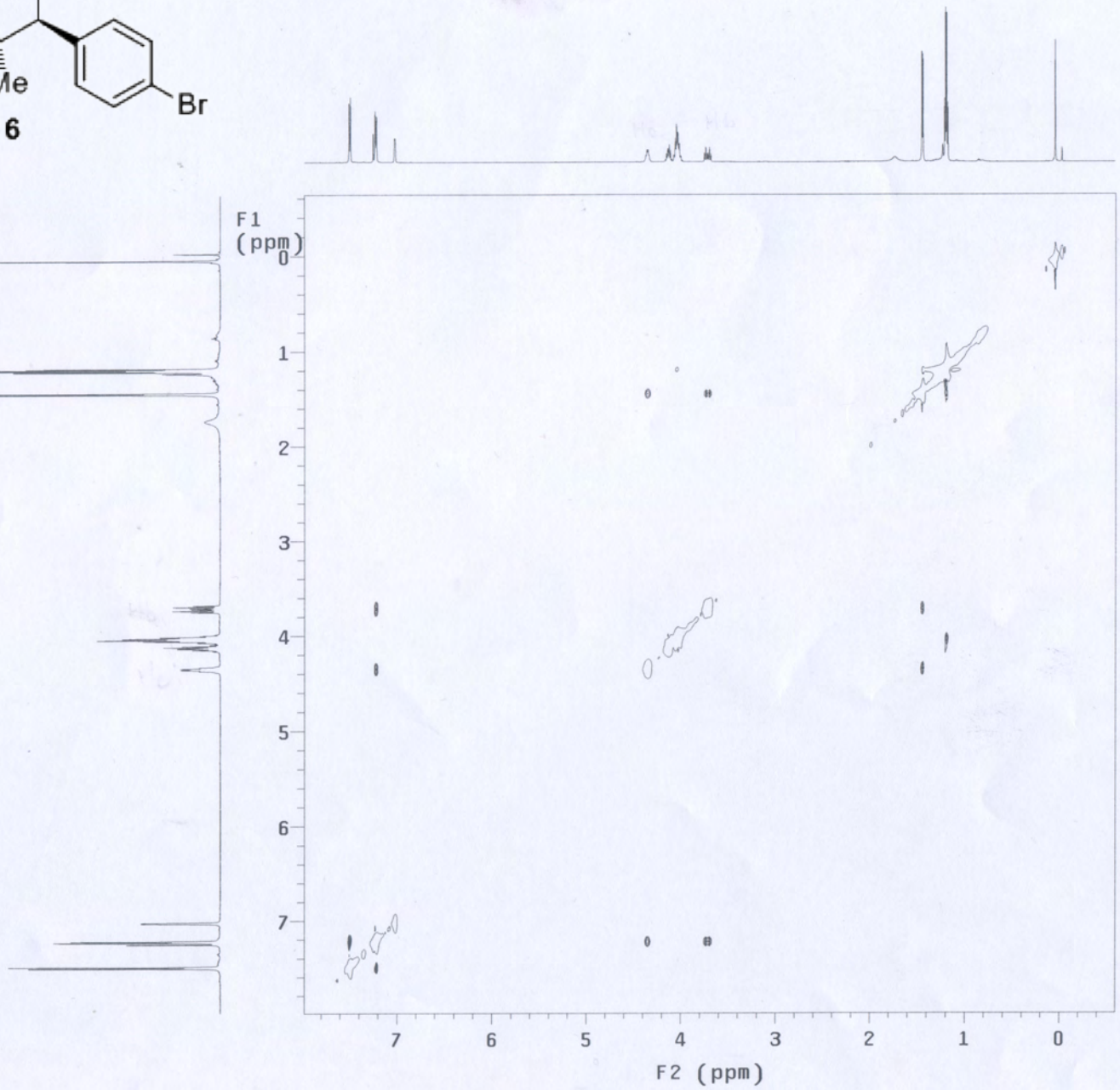


2D NMR Spectra of 6 H-H NOE



6





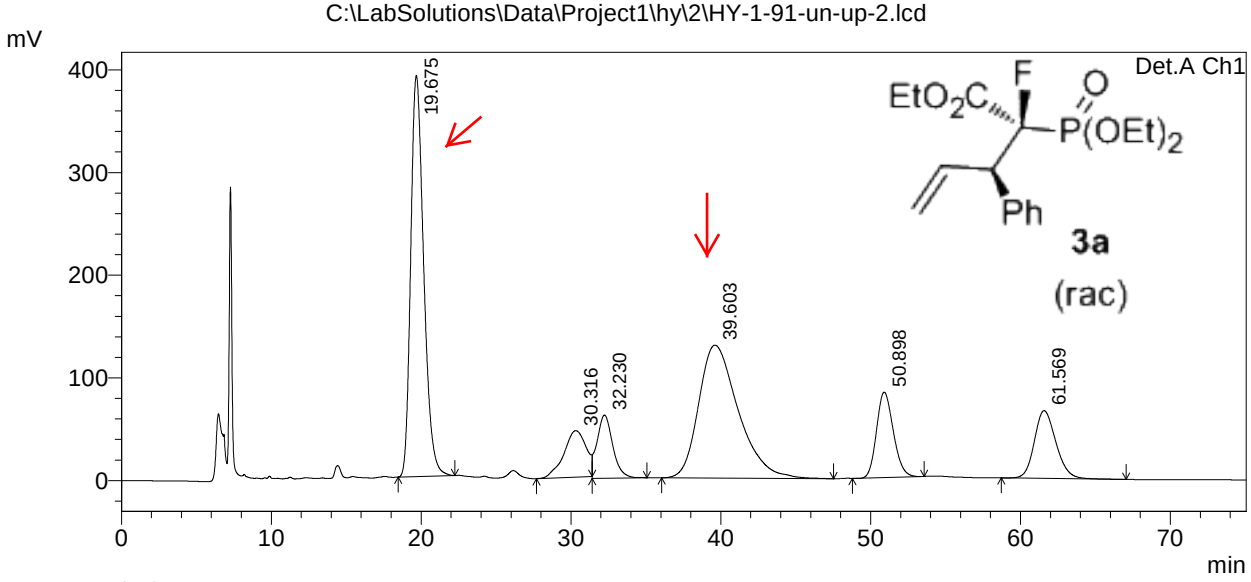
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\hy\2\HY-1-91-un-up-2.lcd

Acquired by	: Admin
Sample Name	: HY-1-91-un-up-2
method	:OJ-H, 96/4,0.5, 214
Injection Volume	: 2.5 uL
Data File Name	: HY-1-91-un-up-2.lcd
Method File Name	: 222.lcm
Report File Name	: 1.lcr
Data Acquired	: 2013-12-4 10:44:48
Data Processed	: 2013-12-4 13:26:07

<Chromatogram>

C:\LabSolutions\Data\Project1\hy\2\HY-1-91-un-up-2.lcd



1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

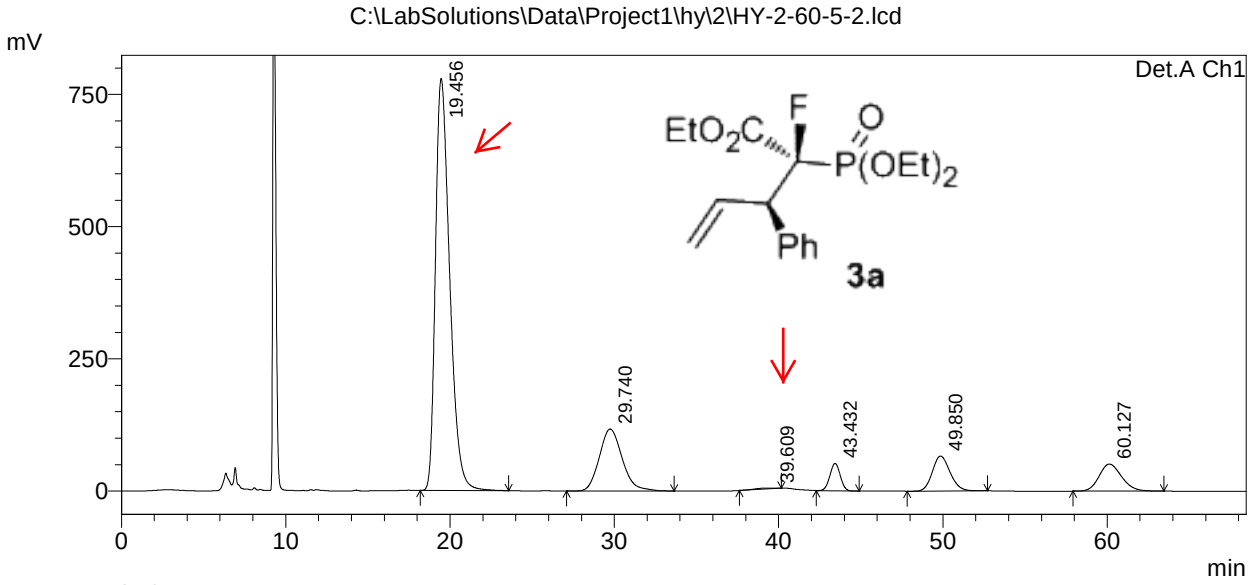
Peak#	Ret. Time	Area	Height	Area %
1	19.675	23453054	390655	33.741
2	30.316	4688468	45268	6.745
3	32.230	4453509	61419	6.407
4	39.603	23823641	129545	34.274
5	50.898	6464873	83148	9.301
6	61.569	6626190	66035	9.533
Total		69509736	776070	100.000

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\hy\2\HY-2-60-5-2.lcd

Acquired by	: Admin
Sample Name	: HY-2-60-5-2
method	:OJ-H, 96/4,0.5, 214
Injection Volume	: 2.5 uL
Data File Name	: HY-2-60-5-2.lcd
Method File Name	: 222.lcm
Report File Name	: 1.lcr
Data Acquired	: 2013-12-4 13:29:27
Data Processed	: 2013-12-4 18:31:15

<Chromatogram>



1 Det.A Ch1/214nm

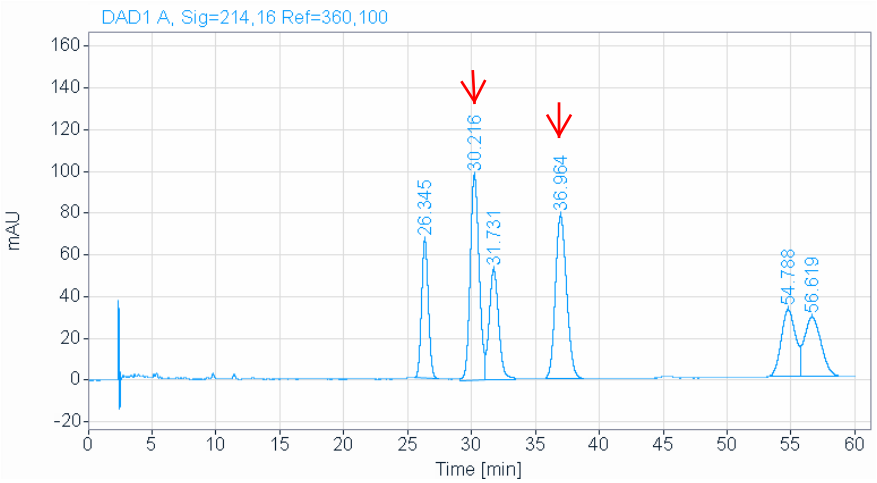
PeakTable

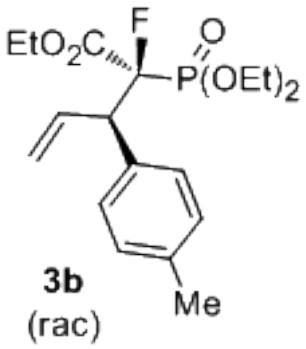
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %
1	19.456	46828892	779149	66.503
2	29.740	11319904	117067	16.076
3	39.609	148337	1176	0.211
4	43.432	2272324	51757	3.227
5	49.850	4956425	66113	7.039
6	60.127	4890371	51271	6.945
Total		70416253	1066534	100.000

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10225.D		
Sample name:	hy-2-10-rac-ic-9-1-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/11/2013 12:03:56 PM	Injection:	1 of 1





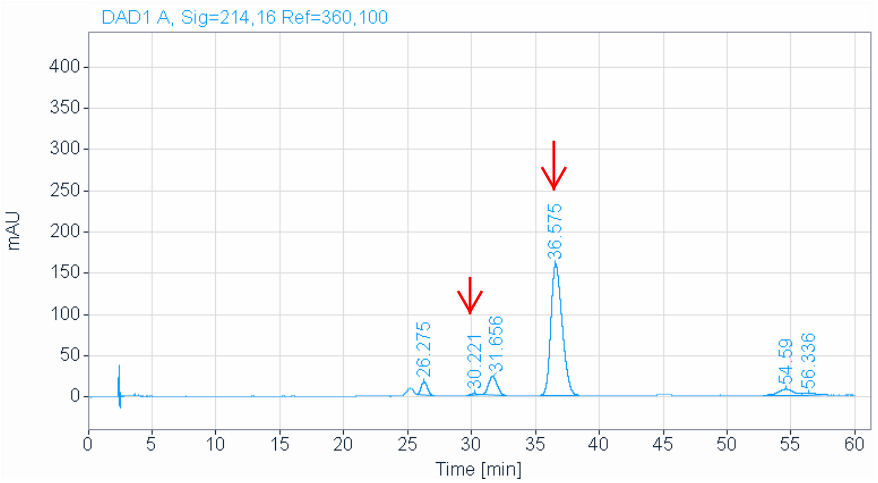
3b
(rac)

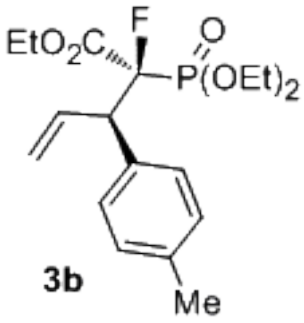
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
26.345	BB	0.4948	2440.4304	66.4037	12.3721
30.216	MF R	0.7957	4791.8770	98.3723	24.2932
31.731	FM R	0.8412	2732.7156	53.0204	13.8539
36.964	VB	0.7156	4752.0405	78.2386	24.0912
54.788	BV	0.9102	2461.7344	31.7292	12.4802
56.619	VB	1.0594	2546.3972	28.0948	12.9094
		Sum	19725.1951		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10226.D		
Sample name:	hy-2-4-ic-9-1-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/11/2013 1:09:24 PM	Injection:	1 of 1



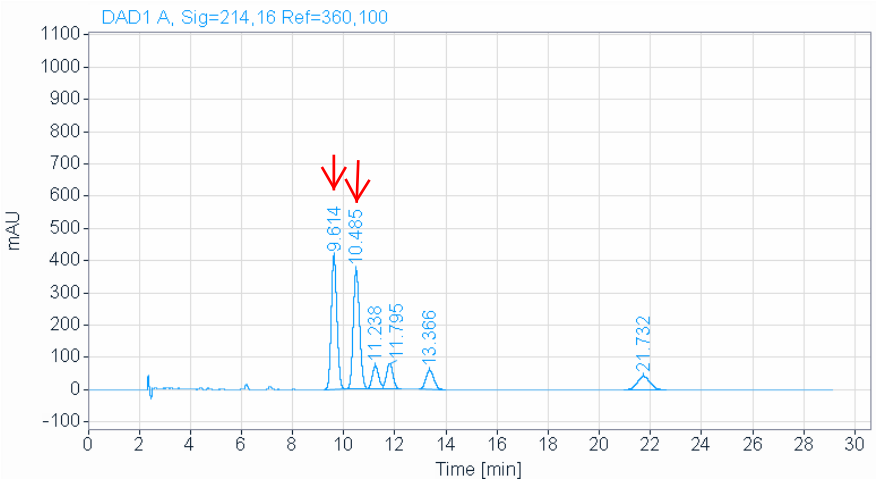


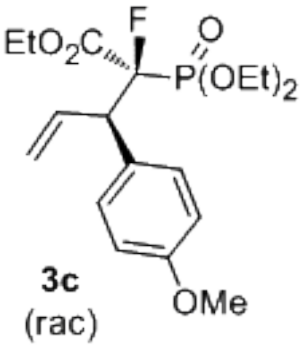
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
26.275	BB	0.4019	521.5670	15.3697	4.3066
30.221	BB	0.4276	73.7869	2.0419	0.6093
31.656	BB	0.5601	1066.6555	22.6210	8.8075
36.575	BB	0.7336	9715.6396	159.0625	80.2229
54.590	MF R	1.3672	596.7386	7.2743	4.9273
56.336	FM R	1.1825	136.4187	1.8411	1.1264
		Sum	12110.8063		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10235.D		
Sample name:	hy-2-12-rac-ic-8-2-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/12/2013 2:59:15 PM	Injection:	1 of 1





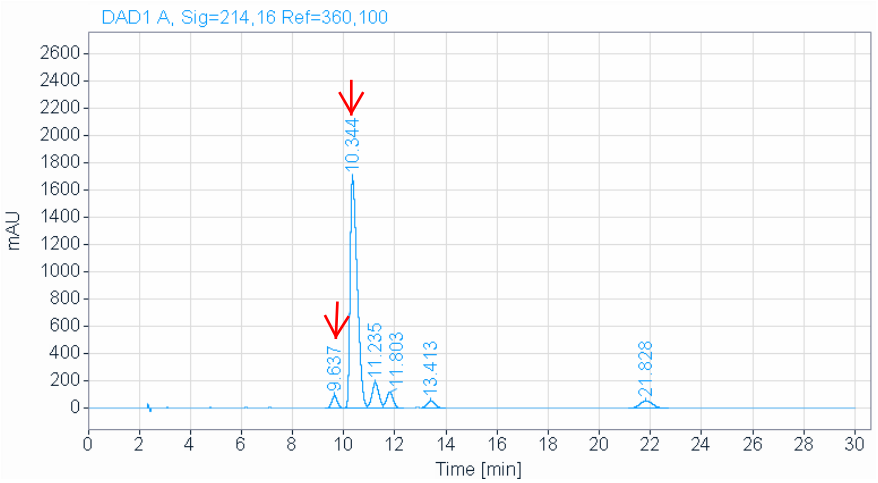
3c
(rac)

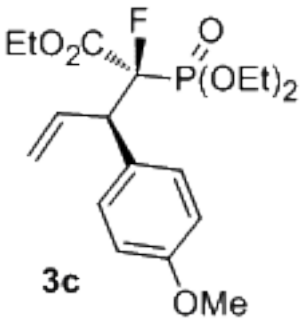
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.614	BB	0.2395	6436.0605	413.6351	35.6566
10.485	BB	0.2712	6370.3120	369.3106	35.2924
11.238	BV	0.2544	1208.7128	69.3421	6.6964
11.795	VB	0.2620	1383.5409	78.7376	7.6650
13.366	BB	0.2987	1248.2645	57.3964	6.9155
21.732	VB	0.4042	1403.2272	41.0130	7.7741
		Sum	18050.1179		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10237.D		
Sample name:	hy-2-25-ic-8-2-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/12/2013 4:11:12 PM	Injection:	1 of 1



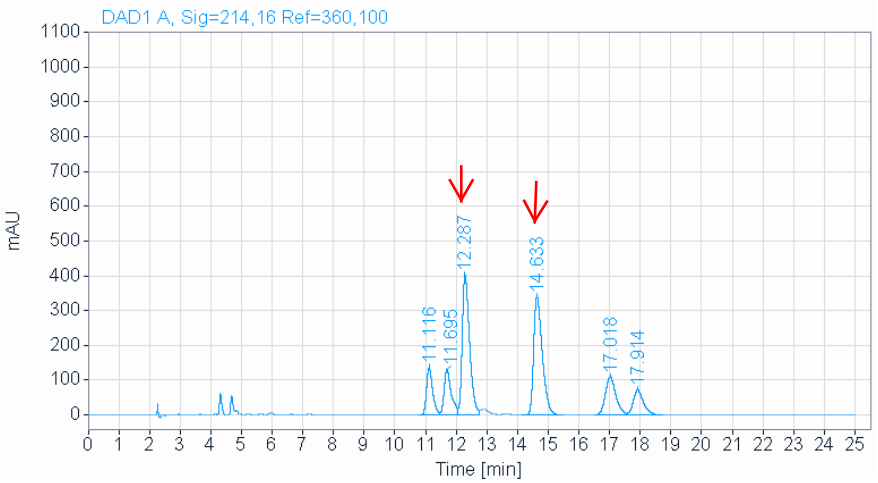


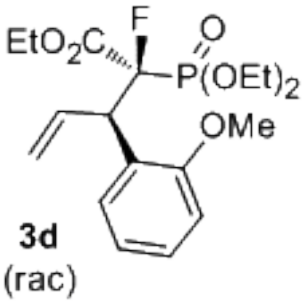
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.637	BB	0.2338	1386.2765	91.9913	3.2394
10.344	BV	0.2885	32687.9766	1691.5066	76.3850
11.235	VV	0.2925	3516.4031	186.0591	8.2171
11.803	VB	0.2745	2154.1702	119.4042	5.0338
13.413	VB	0.3168	1151.3828	51.9102	2.6905
21.828	BV	0.4098	1897.4990	54.8184	4.4341
		Sum	42793.7081		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10302.D		
Sample name:	hy-2-96-rac-ad-95-5-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/30/2013 2:59:48 PM	Injection:	1 of 1





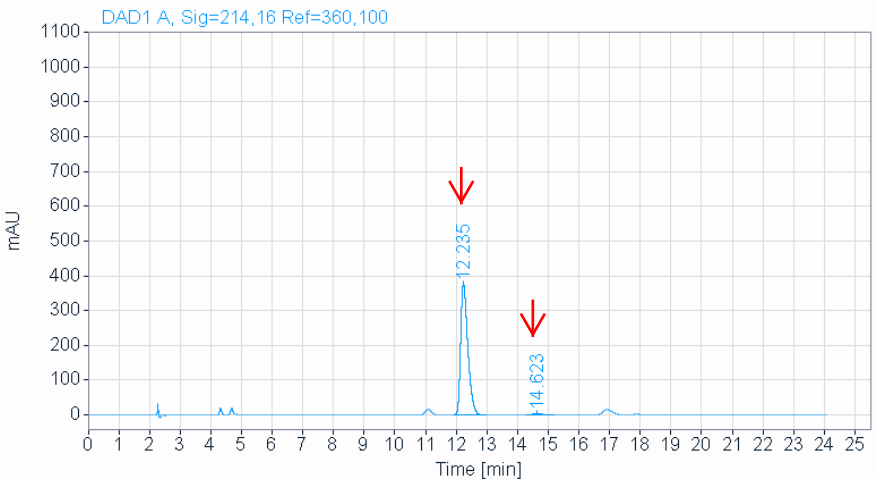
3d
(rac)

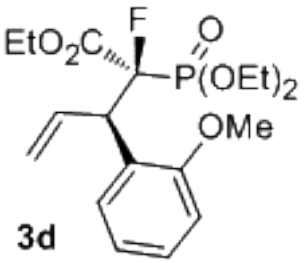
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
11.116	BV	0.2107	1878.6339	135.5589	8.7514
11.695	VV	0.2366	2089.0635	130.6407	9.7316
12.287	VV	0.2540	6650.4424	401.9446	30.9803
14.633	BB	0.2967	6625.1279	339.3983	30.8624
17.018	BV	0.3665	2580.2551	108.4767	12.0198
17.914	VB	0.3430	1643.1715	71.2724	7.6545
		Sum	21466.6943		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10304.D		
Sample name:	hy-2-75		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/30/2013 4:04:59 PM	Injection:	1 of 1





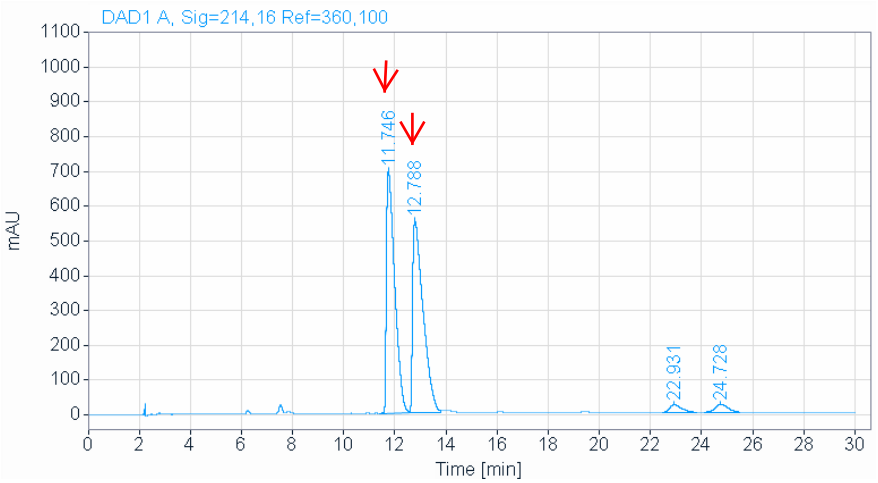
3d

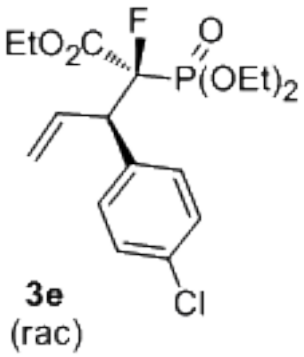
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.235	BB	0.2502	6139.6602	376.6262	98.5253
14.623	BB	0.2557	91.8972	4.6886	1.4747
		Sum	6231.5574		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10289.D		
Sample name:	hy-2-89-od-h-98-2-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/27/2013 8:36:26 AM	Injection:	1 of 1





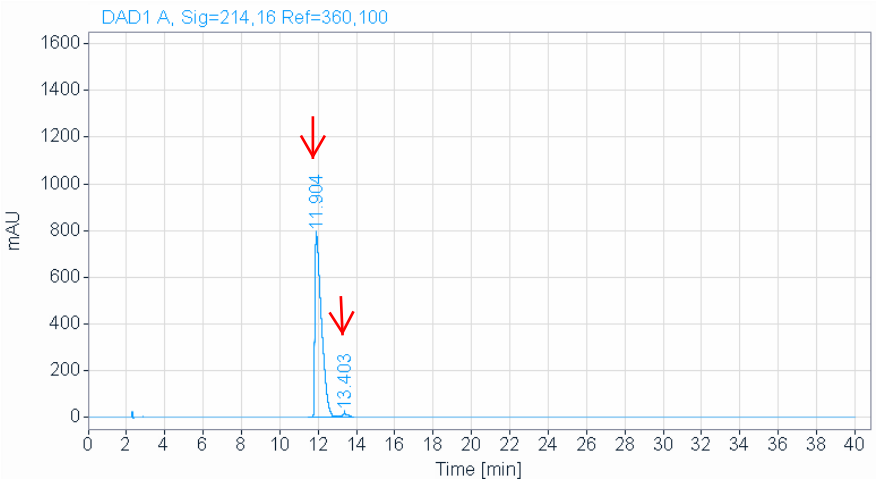
3e
(rac)

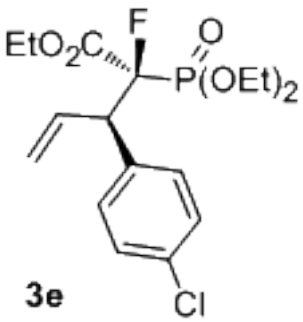
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
11.746	BV	0.3455	15736.1279	696.7659	47.4629
12.788	VV	0.4118	15893.6016	552.1722	47.9379
22.931	BB	0.3922	731.6619	22.1580	2.2068
24.728	VB	0.4214	793.1845	22.2771	2.3924
		Sum	33154.5759		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10291.D		
Sample name:	hy-2-24-2		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/27/2013 10:06:07 AM	Injection:	1 of 1





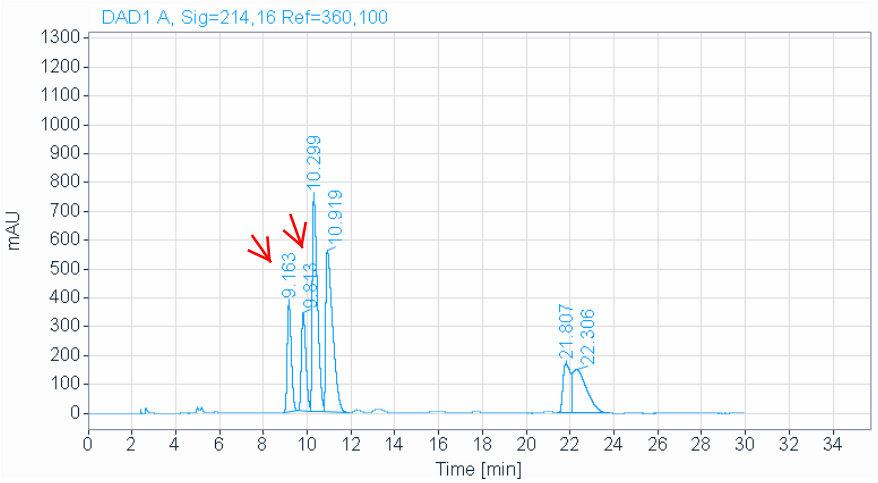
3e

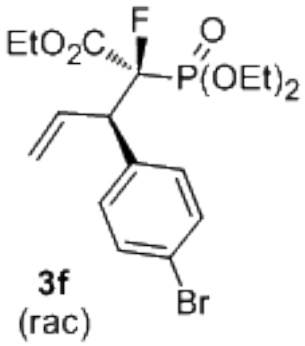
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
11.904	BV	0.3430	18828.5527	784.5944	98.4137
13.403	VV	0.2868	303.5002	12.9775	1.5863
		Sum	19132.0529		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10205.D		
Sample name:	hy-2-14-od-h-97-3-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/9/2013 3:18:59 PM	Injection:	1 of 1





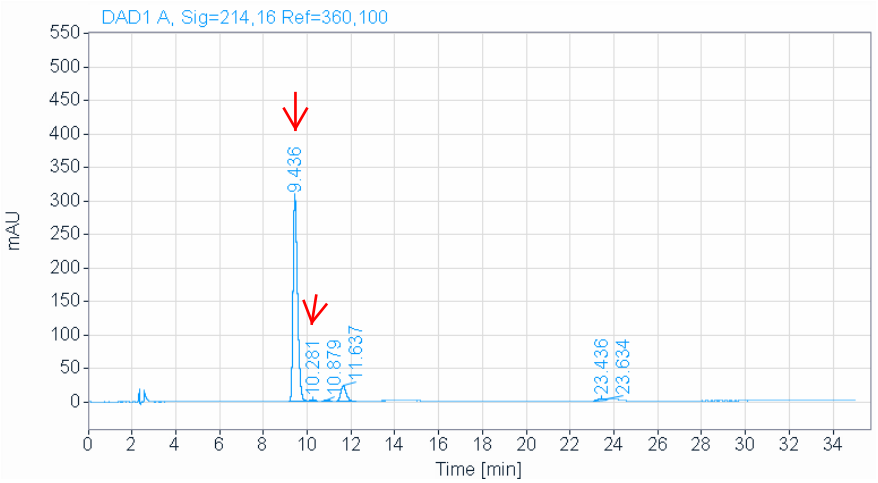
3f
(rac)

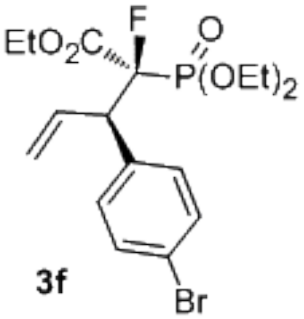
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.163	BB	0.1990	4876.9102	379.2871	10.8456
9.813	BV	0.2245	4823.8467	338.0752	10.7276
10.299	VV	0.2460	12141.2666	745.3655	27.0005
10.919	VB	0.3236	12298.7012	561.3129	27.3507
21.807	MF R	0.3989	4149.3589	171.1984	9.2276
22.306	FM R	0.7291	6676.6626	152.1576	14.8480
		Sum	44966.7461		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10211.D		
Sample name:	hy-2-32		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/10/2013 10:15:43 AM	Injection:	1 of 1



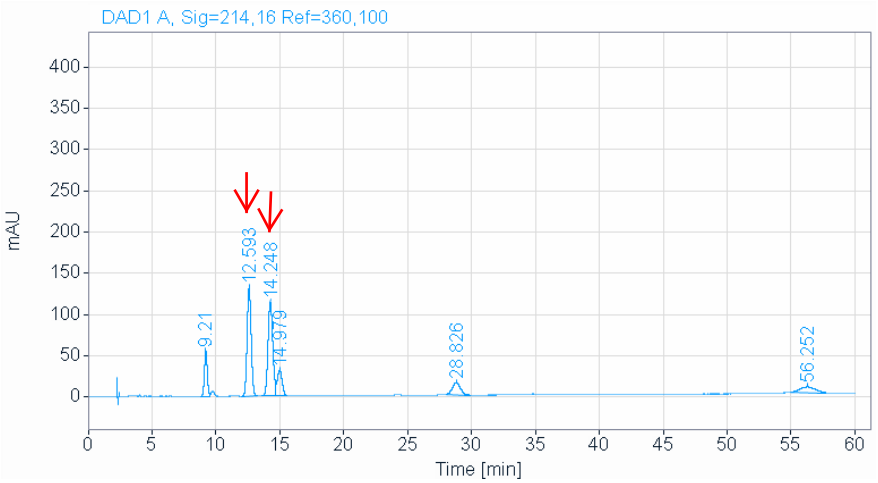


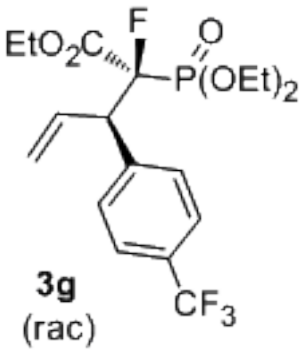
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.436	BV	0.2182	4309.9478	306.2605	89.1742
10.281	VB	0.1874	37.3772	2.4034	0.7733
10.879	BB	0.1808	28.3808	1.8621	0.5872
11.637	BB	0.2443	407.2950	23.3767	8.4271
23.436	BV	0.2298	43.9582	2.2815	0.9095
23.634	VV	0.0608	6.2173	1.3238	0.1286
		Sum	4833.1762		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10163.D		
Sample name:	wf-2-9-ic-95-5-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/2/2013 10:37:20 AM	Injection:	1 of 1





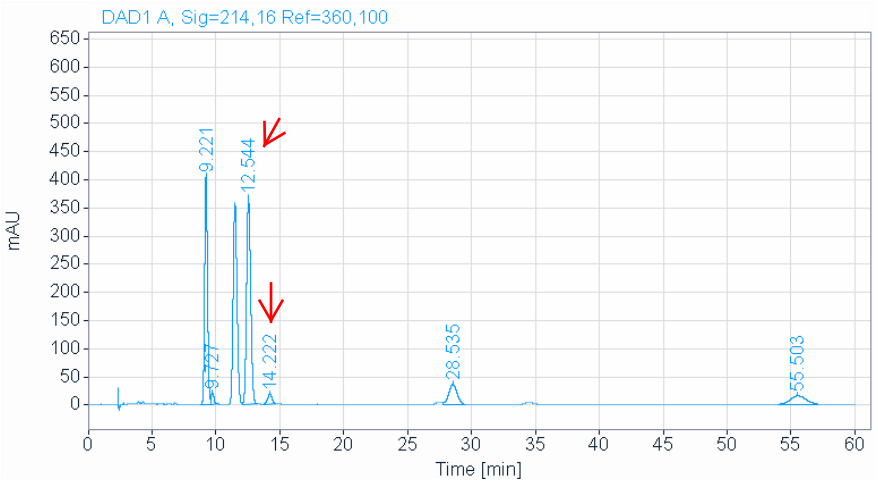
3g
(rac)

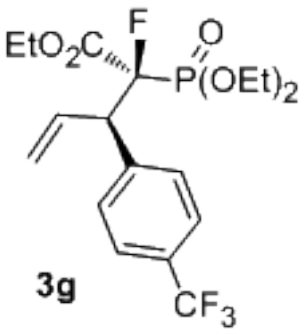
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.210	VV	0.2440	853.0151	54.0941	9.7519
12.593	BB	0.3471	2909.0464	130.9943	33.2569
14.248	BV	0.3955	2960.0449	113.7761	33.8400
14.979	VB	0.3302	829.3217	31.1920	9.4810
28.826	BB	0.5129	620.6021	14.3979	7.0949
56.252	BB	0.9720	575.1555	6.9247	6.5753
		Sum	8747.1856		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10165.D		
Sample name:	hy-2-3		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/2/2013 12:37:21 PM	Injection:	1 of 1



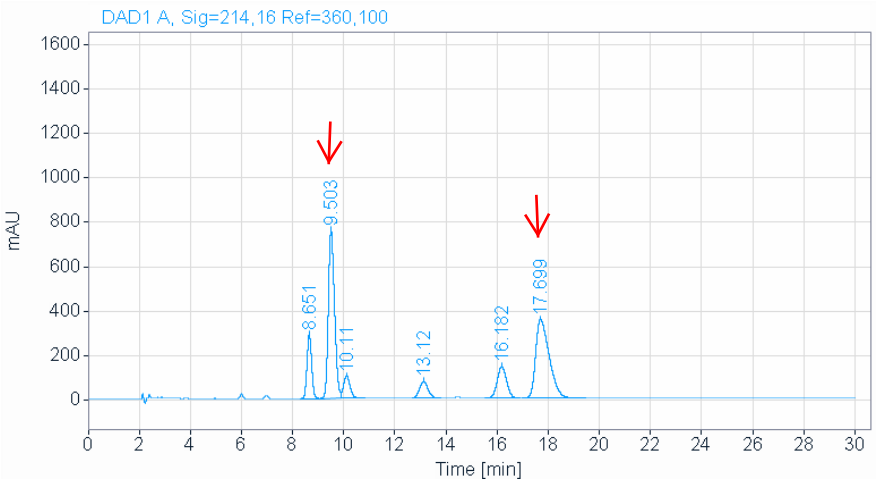


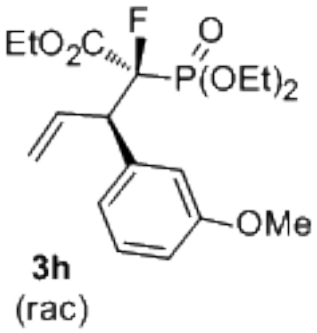
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.221	BV	0.2423	6304.4956	405.6434	34.7473
9.727	VB	0.2184	313.8568	20.4058	1.7298
12.544	VB	0.3542	8203.6992	366.4441	45.2147
14.222	BB	0.3093	431.2502	17.5095	2.3768
28.535	VB	0.5321	1615.8915	35.9006	8.9060
55.503	BB	0.9881	1274.6682	15.0958	7.0253
		Sum	18143.8616		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10238.D		
Sample name:	hy-2-15-rac-ic-8-2-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/13/2013 8:46:46 AM	Injection:	1 of 1





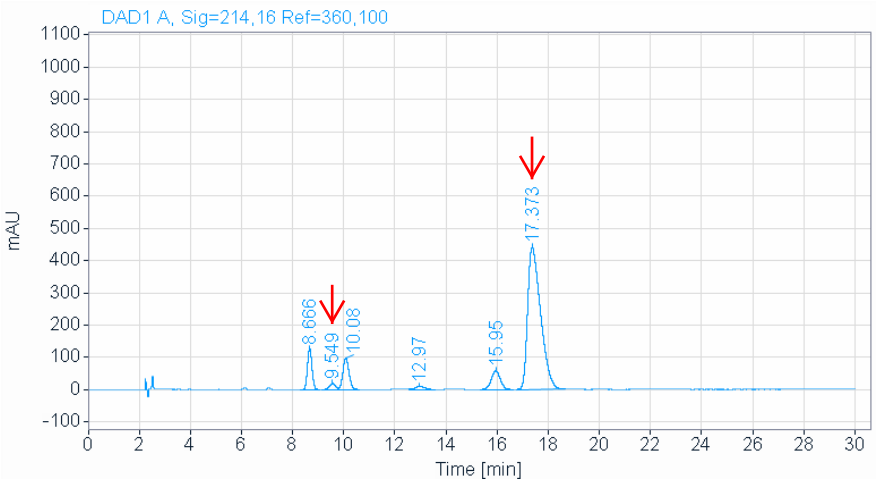
3h
(rac)

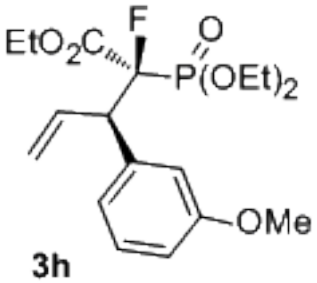
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.651	BB	0.1994	3632.3792	287.5131	9.9061
9.503	BV	0.2612	12763.4180	758.9139	34.8079
10.110	VB	0.2775	1832.7869	101.0882	4.9983
13.120	VB	0.3503	1782.5280	76.3682	4.8612
16.182	BB	0.3915	3649.3528	143.1284	9.9524
17.699	BB	0.5375	13007.6943	354.9834	35.4741
		Sum	36668.1591		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10240.D		
Sample name:	hy-2-26-ic-8-2-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/13/2013 10:01:38 AM	Injection:	1 of 1





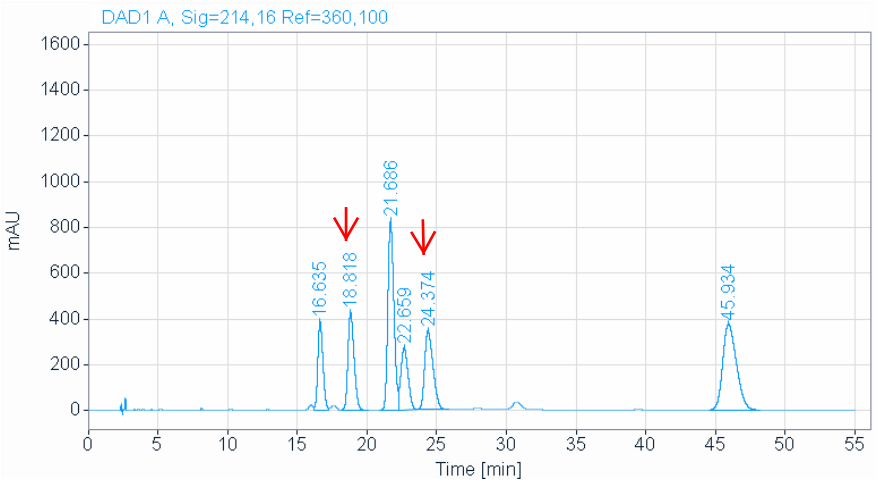
3h

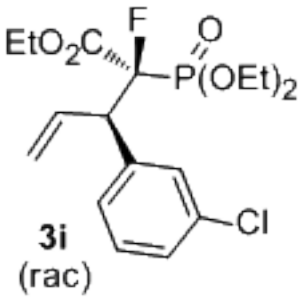
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.666	BB	0.1933	1570.0139	126.9617	7.6432
9.549	VV	0.2130	291.7448	18.4958	1.4203
10.080	VB	0.2526	1630.9989	98.2937	7.9401
12.970	BB	0.2775	235.6446	10.0904	1.1472
15.950	BB	0.3586	1403.1627	57.3232	6.8309
17.373	BB	0.5127	15409.8125	439.9107	75.0184
		Sum	20541.3774		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10231.D		
Sample name:	hy-2-52-rac-ic-9-1-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/12/2013 10:35:26 AM	Injection:	1 of 1





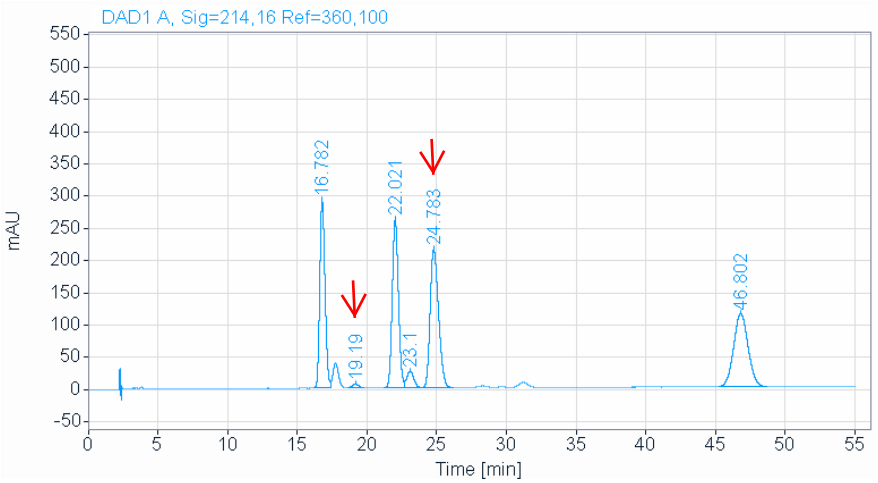
3i
(rac)

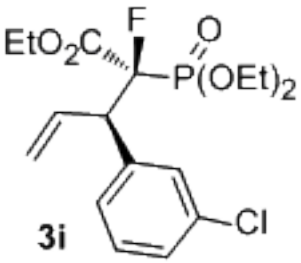
Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.635	VV	0.3924	9921.0986	386.6142	10.1612
18.818	BB	0.4644	13056.6973	426.2437	13.3727
21.686	BV	0.4703	24840.3203	824.8807	25.4415
22.659	VB	0.5532	9842.6426	271.3603	10.0808
24.374	BB	0.6160	14485.4697	344.9135	14.8360
45.934	BB	0.9754	25490.8516	373.9105	26.1078
		Sum	97637.0801		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10230.D		
Sample name:	hy-2-40		
Instrument:	SFC	Sample type:	Sample
Injection date:	12/12/2013 9:25:32 AM	Injection:	1 of 1





Signal: DAD1 A, Sig=214,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.782	BV	0.3967	7546.7305	289.9241	22.3654
19.190	BB	0.3424	157.4754	5.4613	0.4667
22.021	BV	0.4758	8065.7002	260.8410	23.9034
23.100	VB	0.4244	910.9361	25.7048	2.6996
24.783	BB	0.6218	8959.5049	214.7158	26.5523
46.802	BB	0.8419	8102.5420	113.6290	24.0126
		Sum	33742.8890		

HPLC REPORT

Sample Name:hy-5-3-rac-if-8-2-0.5-214...che

Date:2013-12-05

Time:08:43

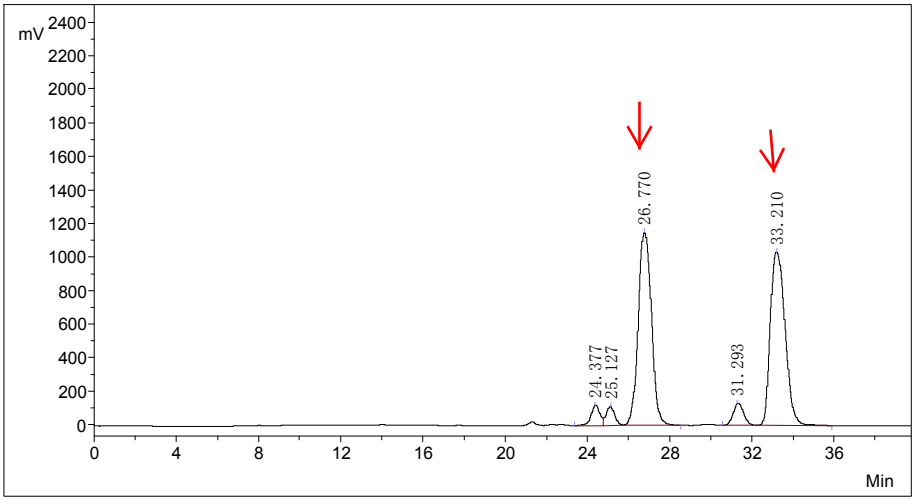
Method:

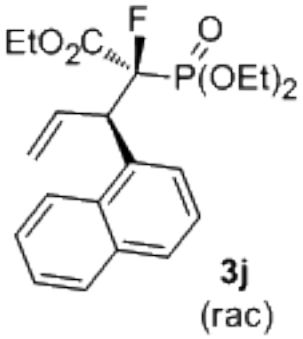
Column:

Flow Rate:

Wave Length:

Mobile Phase:





3j
(rac)

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	24.377	120936.1	3766396.7	3.2576
2	2	Unknown	25.127	113295.4	3339566.9	2.8885
3	3	Unknown	26.770	1150061.4	51663728.0	44.6849
4	4	Unknown	31.293	129736.0	4698075.9	4.0635
5	5	Unknown	33.210	1034530.7	52150041.0	45.1055
Total				2548559.7	115617808.4	100.0000

HPLC REPORT

Sample Name:hy-2-2...che

Date:2013-12-05

Time:09:24

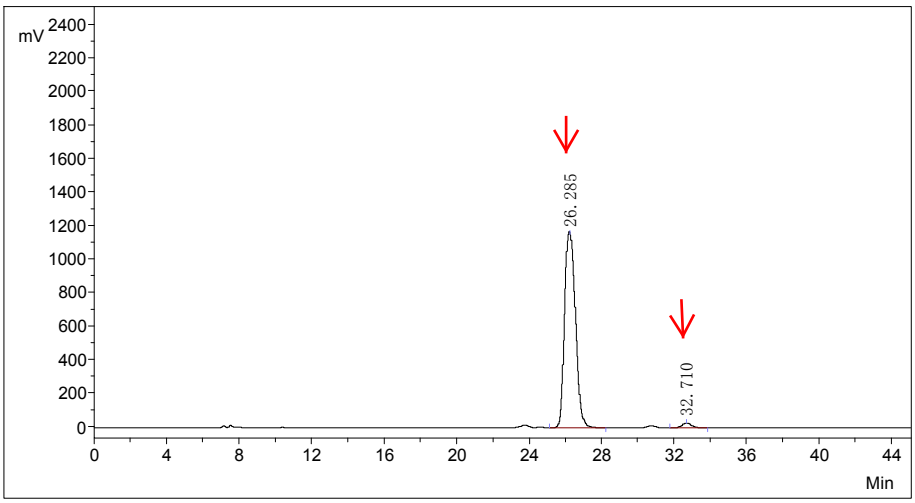
Method:

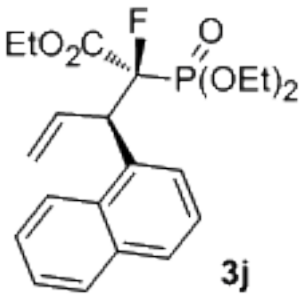
Column:

Flow Rate:

Wave Length:

Mobile Phase:



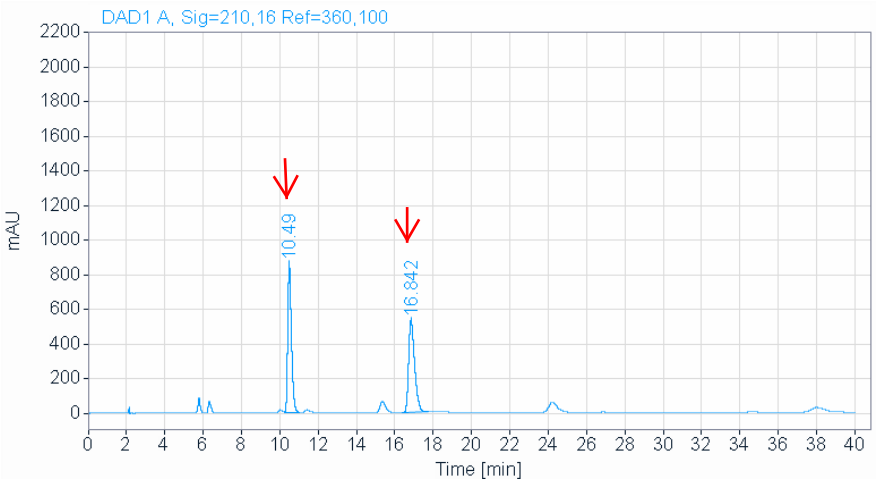


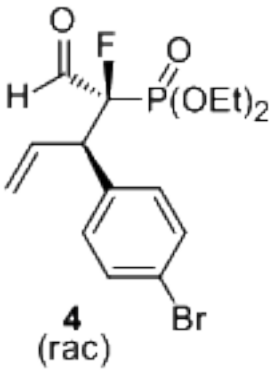
3j

No.	PeakNo	ID.Name	R.Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	26.285	1022869.9	49105750.1	97.6021
2	2	Unknown	32.710	30204.8	1206442.7	2.3979
Total				1053074.6	50312192.8	100.0000

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10354.D		
Sample name:	HY-CHO-RAC-AD-H-95-5-1.5-214		
Instrument:	SFC	Sample type:	Sample
Injection date:	1/16/2014 10:45:19 AM	Injection:	1 of 1





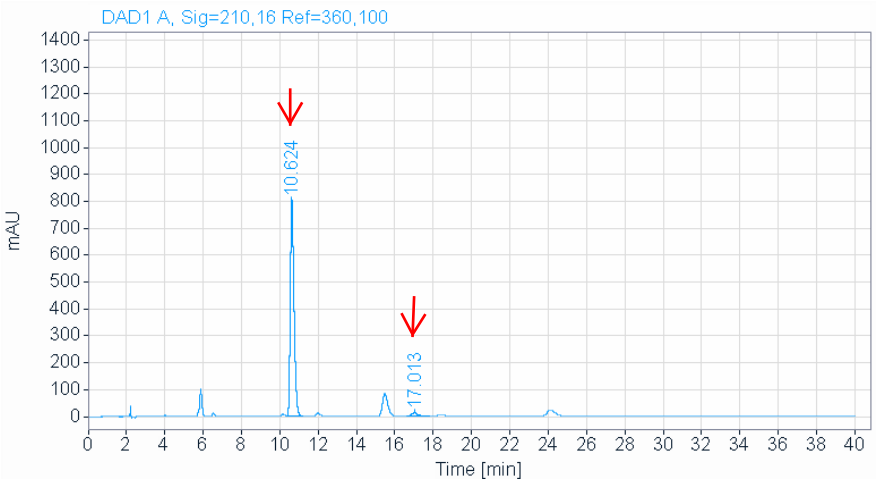
4
(rac)

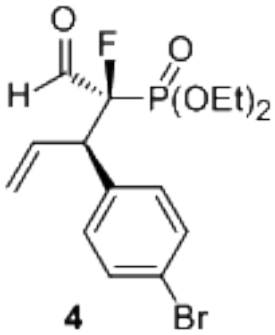
Signal: DAD1 A, Sig=210,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
10.490	VB	0.2025	11409.8643	855.8928	49.6610
16.842	BB	0.3340	11565.6318	531.1412	50.3390
		Sum	22975.4961		

Agilent Technologies

Data file:	C:\CHEM32\1\DATA\2013-10355.D		
Sample name:	HY-CHO		
Instrument:	SFC	Sample type:	Sample
Injection date:	1/16/2014 12:06:15 PM	Injection:	1 of 1





4

Signal: DAD1 A, Sig=210,16 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
10.624	VB	0.2031	10753.9766	803.6212	97.4567
17.013	BV	0.2933	280.6400	12.2034	2.5433
		Sum	11034.6166		

HPLC Report

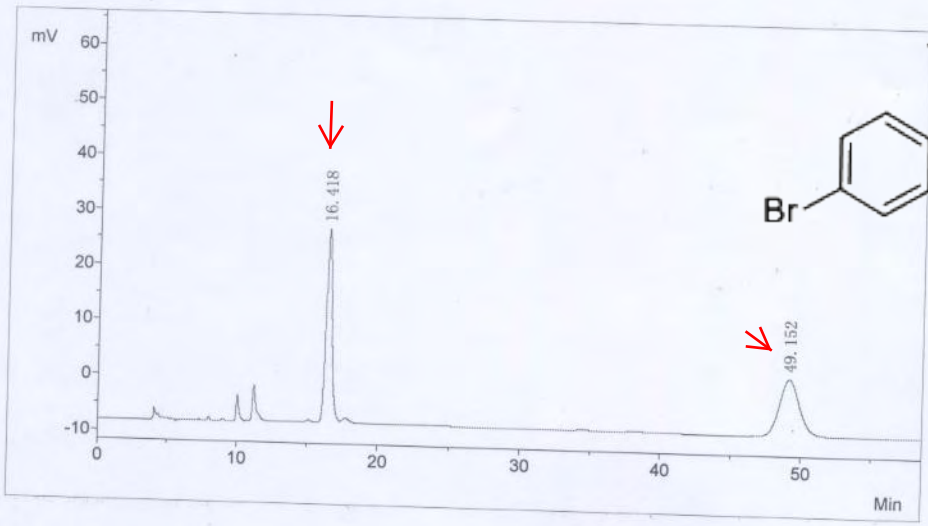
Sample Name:

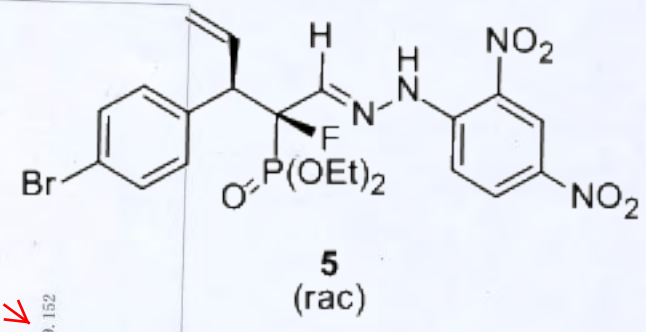
Operator:

Time:15:20

Data File:HY-NNH+- AD-H 73 214 0.7.che

Date:2014-01-16





5
(rac)

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		16.418	34889.8	999474.7	49.7412
2	2		49.152	10274.3	1009876.7	50.2588
Total				45164.1	2009351.4	100.0000

HPLC Report

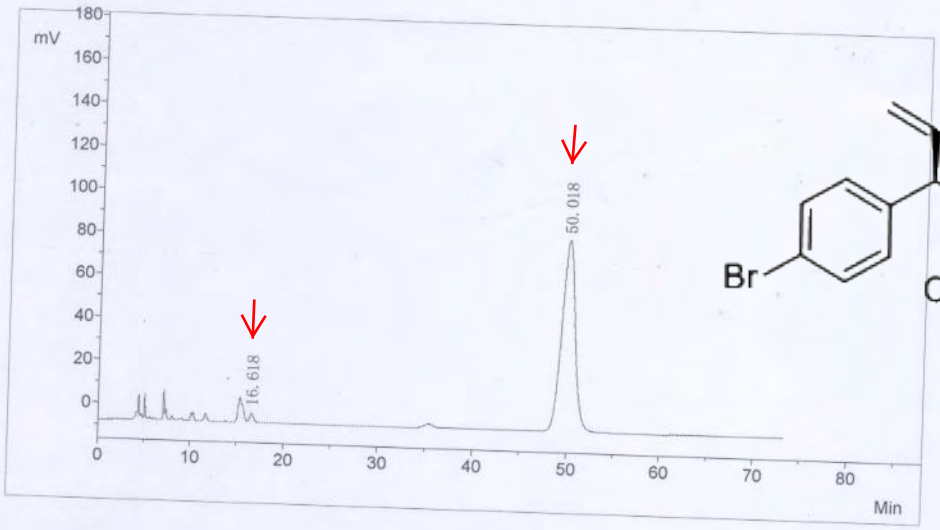
Sample Name:

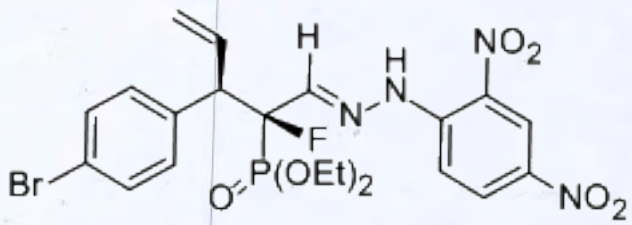
Operator:

Time:16:23

Data File:HY-NNH.che

Date:2014-01-16





5

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		16.618	3935.2	106572.2	1.1951
2	2		50.018	89078.6	8810642.9	98.8049
Total				93013.8	8917215.0	100.0000

HPLC Report

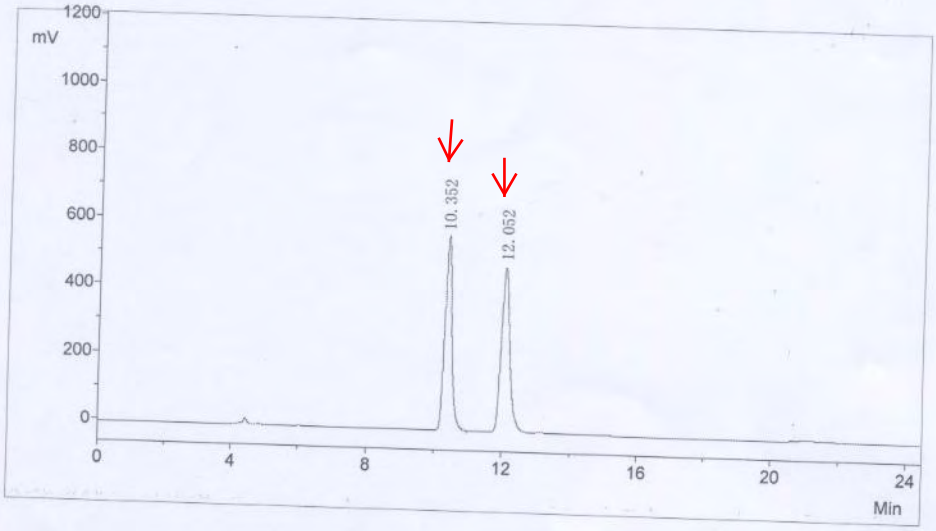
Sample Name:

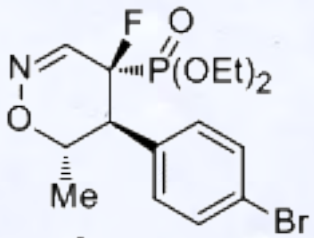
Operator:

Time:14:27

Data File:HY-CYCLE+- AD-H 73 214 0.7.che

Date:2014-01-16





6
(rac)

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10.352	569977.7	8391328.6	49.4710
2	2		12.052	485269.2	8570800.8	50.5290
Total				1055247.0	16962129.4	100.0000

HPLC Report

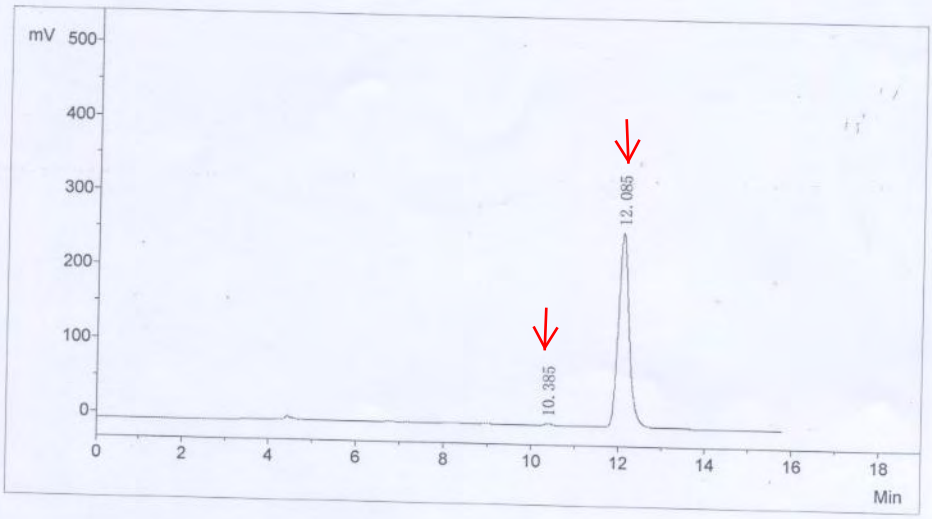
Sample Name:

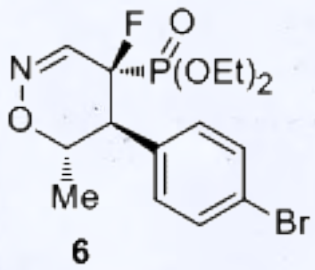
Operator:

Time:14:52

Data File:HY-CYCLE.che

Date:2014-01-16





6

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		10.385	2690.2	40305.0	0.8788
2	2		12.085	260891.0	4546080.3	99.1212
Total				263581.3	4586385.3	100.0000