Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Metal-free C(aryl)–P bond cleavage: Experimental and computational studies of the Michael addition/aryl migration of triarylphosphines to alkenyl esters

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Contents

1. General Information

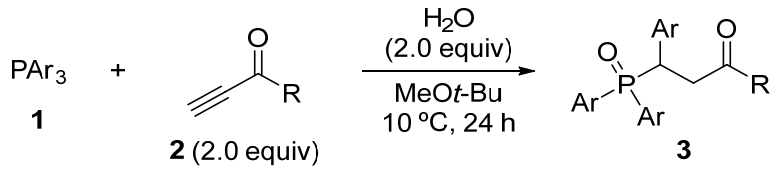
^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with JEOL JMN ECS400 FT NMR, JMN ECS600 FT NMR, or Bruker AVANCE II (^{1}H-NMR 400, 600 or 700 MHz, ^{13}C-NMR 101, 151 or 175 MHz, ^{31}P-NMR 243 MHz.). ^{1}H NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift of tetramethylsilane (TMS) at 0.0 ppm, integration, multiplets (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra are reported in ppm relative to the central line of triplet for $CDCl_3$ at 77.0 ppm. ^{31}P NMR spectra are reported in ppm relative to singlet for H_3PO_4 at 0.0 ppm.

ESI mass spectra of the newly synthesized compounds were obtained by using JMS-T100LC (JEOL).

Methyl- and ethyl propiolate (**2a** and **2b**), tri(*p*-tolyl)-, tri(*o*-tolyl) phosphine (**1a** and **1k**), methyl vinyl ketone (**5**) were purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. Triphenylphosphine (**1b**) and phosphorus trichloride were purchased from KISHIDA CHEMICAL CO., LTD. Tri(*p*-methoxyphenyl)phosphine (**1c**) and tri[*p*-(trifluoromethyl)phenyl]phosphine (**1f**) were purchased from WAKO PURE CHEMICAL INDUSTRIES CO., LTD. Tri(*m*-tolyl)phosphine (**1g**) was purchased from KANTO CHEMICAL CO., INC. Methyldiphenylphosphine (**1n**), diphenylpropylphosphine (**1o**) and ethyl buta-2,3-dienoate (**4**) were purchased from SIGMA-ALDRICH CO. LLC. Other starting materials were synthesized according to reported procedures (**1d**[1], **1e**[2], **1h**[3], **1i**[4], **1j**[5], **1l**,[6] **1m**[7], **2c**[8], **2d**[9], **2e**[10], **2f**[11], **2g**[12], **2h**[13], **2i**[14]). The other simple chemicals and solvents were purchased from commercial suppliers and used without further purification. Unless otherwise noted, all reactions were performed with dry solvents in flame-burned flask under an atmosphere of N_2 gas using standard vacuum-line techniques. rt = 23-25 ℃.

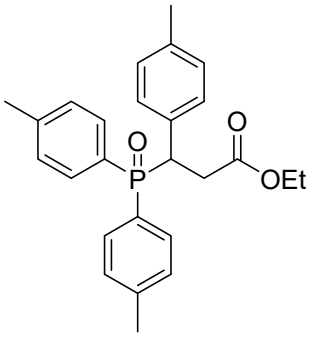
2. Experimental procedure

2-1. General procedure for the synthesis of rearranged product **3**



Under a nitrogen atmosphere, to a mixture of triarylphosphine **1** (0.1 mmol) and water (0.2 mmol) in MeO*t*-Bu (0.5 mL), alkyne **2** (0.1 mmol) was added at 10 ℃ and resulting mixture was stirred for 24 h. After the reaction, crude mixture was filtrated through silica gel to remove remaining phosphine and concentrated under the reduced pressure. The mixture was purified by silica gel chromatography (EtOAc:hexane = 1:4) or preparative thin-layer chromatography (EtOAc:hexane = 3:7, 5 runs) to give the desired product **3**.

Ethyl 3-(di-*p*-tolylphosphoryl)-3-(*p*-tolyl)propanoate (**3aa**):


3aa

White solid, m.p. 161-162 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, $J_{H\text{-}P}$ = 10.5 Hz, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 7.30-7.37 (m, 4H), 7.14 (dd, J = 8.2, 2.3 Hz, 2H), 7.07 (dd, J = 8.2, 2.3 Hz, 2H), 6.98 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 4.00 (ddd, $J_{H\text{-}P}$ = 8.3, $J_{H\text{-}H}$ = 11.3, 3.0 Hz, 1H), 3.87-3.95 (m, 2H), 3.02 (ddd, $J_{H\text{-}P}$ = 6.4 Hz, $J_{H\text{-}H}$ = 16.5, 11.3 Hz, 1H), 2.86 (ddd, $J_{H\text{-}P}$ = 9.0 Hz, $J_{H\text{-}H}$ = 16.5, 3.0 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 1.04 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H).

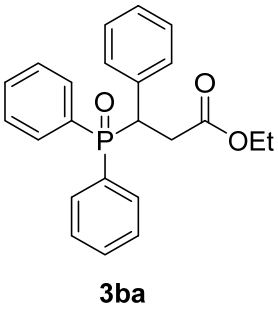
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5 (d, $J_{C\text{-}P}$ = 17.3 Hz), 142.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 136.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.63 (d, $J_{C\text{-}P}$ = 97.8 Hz), 131.56 (d, $J_{C\text{-}P}$ = 100.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.53, 129.48 (d, $J_{C\text{-}P}$ = 14.4 Hz), 128.9, 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.8, 60.6, 42.5 (d, $J_{C\text{-}P}$ = 68.1 Hz), 35.0, 21.54, 21.45, 21.0, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.3.

IR (KBr) ν 3033, 2924, 2858, 1737, 1602, 1514, 1403, 1175, 654, 550 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{29}O_3PNa$ ($[M+Na]^+$): 443.1747, found 443.1744.

Ethyl 3-(diphenylphosphoryl)-3-phenylpropanoate (**3ba**):


3ba

White solid, m.p. 183-184 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.97 (m, 2H), 7.53 -7.59 (m, 3H), 7.44-7.47 (m, 2H), 7.35 (t, $J_{H\text{-}H}$ = 7.2 Hz, 1H) 7.24-7.27 (m, 4H), 7.14-7.18 (m, 3H), 4.08 (ddd, $J_{H\text{-}P}$ = 8.0, $J_{H\text{-}H}$ = 11.2, 3.2 Hz, 1H), 3.91 (q, $J_{H\text{-}H}$ = 7.2 Hz, 2H), 3.10 (ddd, $J_{H\text{-}P}$ = 6.4 Hz, $J_{H\text{-}H}$ = 16.5, 11.2 Hz, 1H), 2.89 (ddd, $J_{H\text{-}P}$ = 9.6 Hz, $J_{H\text{-}H}$ = 16.5, 3.2 Hz, 1H), 1.03 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H).

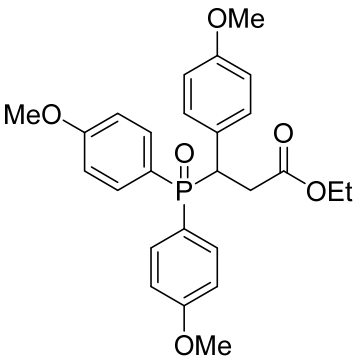
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3 (d, $J_{C\text{-}P}$ = 15.9 Hz), 135.0 (d, $J_{C\text{-}P}$ = 5.9 Hz), 132.0, 131.5, 131.4 (d, $J_{C\text{-}P}$ = 8.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 101.2 Hz), 131.1 (d, $J_{C\text{-}P}$ = 95.4 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.7 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.2, 128.1 (d, $J_{C\text{-}P}$ = 11.6 Hz), 127.2, 60.8, 42.9 (d, $J_{C\text{-}P}$ = 67.9 Hz), 34.9, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.3.

IR (KBr) ν 3052, 2978, 2923, 2852, 1735, 1438, 1179, 707, 537, 502 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{23}H_{23}O_3PNa$ ([M+Na]$^+$): 401.1277, found 401.1276.

Ethyl 3-(bis(4-methoxyphenyl)phosphoryl)-3-(4-methoxyphenyl)propanoate (**3ca**):



3ca

Yellowish white solid, m.p. 128-129 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, $J_{H\text{-}P}$ = 10.5 Hz, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 7.34 (dd, $J_{H\text{-}P}$ = 10.5 Hz, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 7.16 (dd, $J_{H\text{-}H}$ = 8.7, 2.3 Hz, 2H), 7.02 (dd, $J_{H\text{-}H}$ = 8.7, 2.3 Hz, 2H), 6.77 (dd, $J_{H\text{-}H}$ = 8.7, 2.3 Hz, 2H), 6.73 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 3.90-3.96 (m, 3H), 3.86 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 2.99 (ddd, $J_{H\text{-}P}$ = 6.4 Hz, $J_{H\text{-}H}$ = 16.5, 11.2 Hz, 1H), 2.86 (ddd, $J_{H\text{-}P}$ = 8.7 Hz, $J_{H\text{-}H}$ = 16.5, 3.7 Hz, 1H), 1.05 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H).

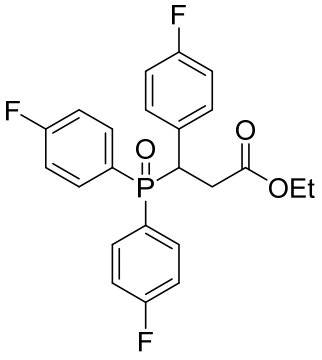
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6 (d, $J_{C\text{-}P}$ = 17.3 Hz), 162.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 162.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 158.6 (d, $J_{C\text{-}P}$ = 1.9 Hz), 133.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 4.8 Hz), 127.3 (d, $J_{C\text{-}P}$ = 4.8 Hz), 123.0 (d, $J_{C\text{-}P}$ = 106.4 Hz), 122.5 (d, $J_{C\text{-}P}$ = 101.6 Hz), 114.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 113.7, 113.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 60.6, 55.3, 55.2, 55.1, 42.5 (d, $J_{C\text{-}P}$ = 70.0 Hz), 35.1, 14.0.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.4.

IR (KBr) *v* 3044, 2930, 2837, 1735, 1600, 1509, 1255, 1035 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{29}O_6PNa$ ([M+Na]$^+$): 491.1594, found 491.1591.

Ethyl 3-(bis(4-fluorophenyl)phosphoryl)-3-(4-fluorophenyl)propanoate (**3da**):



3da

White solid, m.p. 138-139 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92-7.96 (m, 2H), 7.41-7.45 (m, 2H), 7.23-7.27 (m, 4H), 6.98 (dd, J = 8.3, 8.3 Hz, 2H), 6.90 (dd, J = 8.3, 8.3 Hz, 2H), 3.99-4.03 (m, 1H), 3.94 (q, $J_{H\text{-}H}$ = 6.9 Hz, 2H), 3.03 (ddd, $J_{H\text{-}P}$ = 6.0 Hz, $J_{H\text{-}H}$ = 16.5, 11.0 Hz, 1H), 2.83 (ddd, $J_{H\text{-}P}$ = 9.3 Hz, $J_{H\text{-}H}$ = 16.5, 3.4 Hz, 1H), 1.06 (t, $J_{H\text{-}H}$ = 6.9 Hz, 3H).

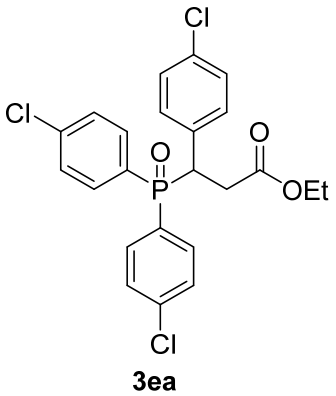
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0 (d, $J_{C\text{-}P}$ = 17.3 Hz), 165.2 (dd, $J_{C\text{-}F}$ = 254.3 Hz, $J_{C\text{-}P}$ = 2.9 Hz), 164.8 (dd, $J_{C\text{-}F}$ = 254.3 Hz, $J_{C\text{-}P}$ = 2.9 Hz), 162.1 (d, $J_{C\text{-}F}$ = 245.6 Hz), 133.8 (dd, $J_{C\text{-}F}$ = 8.7 Hz, $J_{C\text{-}P}$ = 10.1 Hz), 133.3 (dd, $J_{C\text{-}F}$ = 8.7 Hz, $J_{C\text{-}P}$ = 10.1 Hz), 131.2 (dd, $J_{C\text{-}F}$ = 8.7 Hz, $J_{C\text{-}P}$ = 5.8 Hz), 130.5, 126.9 (d, $J_{C\text{-}P}$ = 106.9 Hz), 126.5 (d, $J_{C\text{-}P}$ = 98.3 Hz), 116.5 (dd, $J_{C\text{-}F}$ = 20.9 Hz, $J_{C\text{-}P}$ = 13.0 Hz), 115.7 (dd, $J_{C\text{-}F}$ = 20.2 Hz, $J_{C\text{-}P}$ = 13.0 Hz), 115.4 (d, $J_{C\text{-}P}$ = 20.2 Hz), 61.0, 42.3 (d, $J_{C\text{-}P}$ = 70.8 Hz), 34.9, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 31.2.

IR (KBr) *v* 3073, 2979, 2923, 1729, 1592, 1510, 13107, 1161, 921, 834 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{23}H_{20}F_3NaO_3P$ ([M+Na]$^+$): 455.1000, found 455.0994.

Ethyl 3-(bis(4-chlorophenyl)phosphoryl)-3-(4-chlorophenyl)propanoate (**3ea**):



3ea

White solid, m.p. 159-160 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (dd, $J_{H\text{-}P}$ = 10.1 Hz, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 7.54 (dd, $J_{H\text{-}P}$ = 2.1 Hz, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.38 (dd, $J_{H\text{-}P}$ = 11.0 Hz, $J_{H\text{-}H}$ = 8.9 Hz, 2H), 7.28 (dd, $J_{H\text{-}P}$ = 2.4 Hz, $J_{H\text{-}H}$ = 8.6 Hz, 2H), 7.17-7.23 (m, 4H), 4.00 (ddd, $J_{H\text{-}P}$ = 10.8 Hz, $J_{H\text{-}H}$ = 7.7, 2.8 Hz, 1H), 3.94 (qd, $J_{H\text{-}P}$ = 1.9 Hz, $J_{H\text{-}H}$ = 7.1, Hz, 2H), 3.00 (ddd, $J_{H\text{-}P}$ = 16.7 Hz, $J_{H\text{-}H}$ = 10.8, 6.2 Hz, 1H), 2.81 (ddd, $J_{H\text{-}P}$ = 16.6 Hz, $J_{H\text{-}H}$ = 9.5, 3.4 Hz, 1H), 1.06 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H).

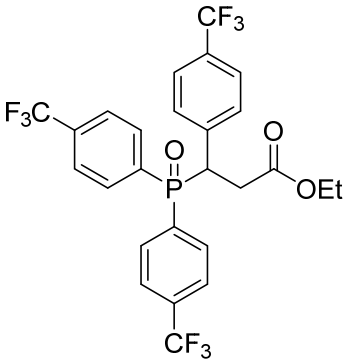
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8 (d, $J_{C\text{-}P}$ = 16.3 Hz), 139.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 138.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.2 (d, $J_{C\text{-}P}$ = 5.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.9 (d, $J_{C\text{-}P}$ = 5.8 Hz), 129.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.2 (d, $J_{C\text{-}P}$ = 101.6 Hz), 129.0 (d, $J_{C\text{-}P}$ = 95.9 Hz), 128.8 (d, $J_{C\text{-}P}$ = 15.3 Hz), 128.7, 61.1, 42.1 (d, $J_{C\text{-}P}$ = 69.0 Hz), 34.8, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 31.8.

IR (KBr) ν 3056, 2983, 2922, 1738, 1583, 1491, 1393, 1176, 1096 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{23}H_{20}Cl_3NaO_3P$ ($[M+Na]^+$): 503.0108, found 503.0106.

Ethyl 3-(bis(4-(trifluoromethyl)phenyl)phosphoryl)-3-(4-(trifluoromethyl)phenyl)propanoate (**3fa**):



3fa

White solid, m.p. 186-187 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, $J_{H\text{-}P}$ = 10.3 Hz, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.85 (dd, $J_{H\text{-}H}$ = 8.2, 1.8 Hz, 2H), 7.62-7.67 (m, 2H), 7.58 (dd, $J_{H\text{-}H}$ = 8.2, 2.3 Hz, 2H), 7.44-7.49 (m, 4H), 4.22 (ddd, $J_{H\text{-}P}$ = 7.1 Hz, $J_{H\text{-}H}$ = 10.7, 3.7 Hz, 1H), 3.94 (q, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 3.10 (ddd, $J_{H\text{-}P}$ = 6.4 Hz, $J_{H\text{-}H}$ = 16.9, 10.7 Hz, 1H), 2.86 (ddd, $J_{H\text{-}P}$ = 10.1 Hz, $J_{H\text{-}H}$ = 16.9, 3.7 Hz, 1H), 1.06 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H).

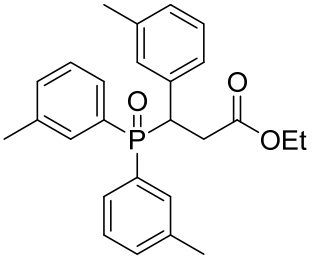
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.5 (d, $J_{C\text{-}P}$ = 15.9 Hz), 138.6 (d, $J_{C\text{-}P}$ = 5.8 Hz), 134.64 (d, $J_{C\text{-}P}$ = 98.3 Hz), 134.58 (d, $J_{C\text{-}P}$ = 92.5 Hz), 134.4 (q, $J_{C\text{-}F}$ = 31.8 Hz), 133.9 (q, $J_{C\text{-}F}$ = 34.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.7 Hz), 130.01 (q, $J_{C\text{-}F}$ = 30.3 Hz), 129.99 (d, $J_{C\text{-}P}$ = 5.8 Hz), 126.0-126.1 (m), 125.5, 125.3-125.4 (m), 123.8 (q, $J_{C\text{-}F}$ = 271.7 Hz), 123.3 (q, $J_{C\text{-}F}$ = 271.7 Hz), 123.2 (q, $J_{C\text{-}F}$ = 273.1 Hz), 61.3, 42.3 (d, $J_{C\text{-}P}$ = 67.9 Hz), 34.7, 13.8.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.9.

IR (KBr) ν 3067, 2990, 2914, 1734, 1401, 1325, 1072, 1019, 837, 713 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{20}F_9NaO_3P$ ($[M+Na]^+$): 605.0899, found 605.0898.

Ethyl 3-(di-*m*-tolylphosphoryl)-3-(*m*-tolyl)propanoate (**3ga**):



3ga

White solid, m.p. 133-134 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, $J_{H\text{-}P}$ = 11.5 Hz, 1H), 7.65-7.69 (m, 1H), 7.41 (ddd, 7.5, 7.5, 3.4 Hz, 1H), 7.36 (d, $J_{H\text{-}H}$ = 7.3 Hz, 1H), 7.21-7.26 (m, 2H), 7.14-7.17 (m, 2H), 7.03-7.09 (m, 3H), 6.95-6.97 (m, 1H), 4.01 (ddd, $J_{H\text{-}P}$ = 11.4 Hz, $J_{H\text{-}H}$ = 11.4, 3.4 Hz, 1H), 3.93 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H), 3.07 (ddd, $J_{H\text{-}P}$ = 6.1 Hz, $J_{H\text{-}H}$ = 16.5, 11.4 Hz, 1H), 2.87 (ddd, $J_{H\text{-}P}$ = 9.1 Hz, $J_{H\text{-}H}$ = 16.5, 3.4 Hz, 1H), 2.42 (s, 3H), 2.2 (s, 6H), 2.21

(s, 3H), 1.04 (t, J_{H-H} = 7.1 Hz, 3H).

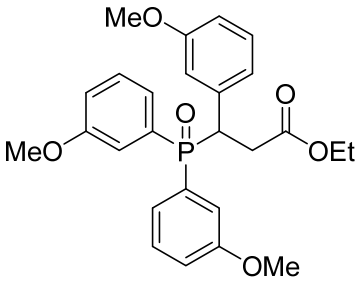
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4 (d, J_{C-P} = 17.3 Hz), 138.7 (d, J_{C-P} = 11.5 Hz), 137.8 (d, J_{C-P} = 11.5 Hz), 137.6 (d, J_{C-P} = 1.9 Hz), 135.0 (d, J_{C-P} = 4.8 Hz), 132.7 (d, J_{C-P} = 1.9 Hz), 132.2, 132.1 (d, J_{C-P} = 7.7 Hz), 131.9 (d, J_{C-P} = 7.7 Hz), 131.1 (d, J_{C-P} = 102.6 Hz), 131.0 (d, J_{C-P} = 99.7 Hz), 130.5 (d, J_{C-P} = 5.8 Hz), 128.6 (d, J_{C-P} = 12.5 Hz), 128.2 (d, J_{C-P} = 8.6 Hz), 127.98, 127.94 (d, J_{C-P} = 12.5 Hz), 127.91, 127.78 (d, J_{C-P} = 12.5 Hz), 126.8 (d, J_{C-P} = 5.8 Hz), 60.7, 42.9 (d, J_{C-P} = 67.1 Hz), 34.7, 21.5, 21.3, 21.2, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 32.8.

IR (KBr) ν 3051, 2981, 2918, 1739, 1211, 863, 788, 703 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{29}NaO_3P$ ($[M+Na]^+$): 443.1747, found 443.1747.

Ethyl 3-(bis(3-methoxyphenyl)phosphoryl)-3-(3-methoxyphenyl)propanoate (**3ha**):



3ha

White solid, m.p. 101-102 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, J_{H-P} = 12.0 Hz, J_{H-H} = 2.4 Hz, 1H), 7.45-7.48 (m, 2H), 7.19 (ddd, J_{H-P} = 4.2 Hz, J_{H-H} = 7.9, 7.9 Hz, 1H), 7.09-7.12 (m, 2H), 7.02 (dd, J_{H-P} = 11.3 Hz, J_{H-H} = 7.6 Hz, 1H), 6.93-6.96 (m, 1H), 6.90 (dd, J_{H-H} = 8.3, 2.1 Hz, 1H), 6.87 (d, J_{H-H} = 6.9 Hz, 1H), 6.82 (d, J_{H-H} = 1.4 Hz, 1H), 6.72 (dd, J_{H-H} = 8.3, 1.4 Hz, 1H), 4.01 (ddd, J_{H-P} = 8.0 Hz, J_{H-H} = 11.2, 3.4 Hz, 1H), 3.94 (dq, J_{H-H} = 7.2, 1.4 Hz, 2H), 3.86 (s, 3H), 3.69 (s, 3H), 3.64 (s, 3H), 3.08 (ddd, J_{H-P} = 6.2 Hz, J_{H-H} = 16.5, 11.2 Hz, 1H), 2.88 (ddd, J_{H-P} = 9.6 Hz, J_{H-H} = 16.5, 3.4 Hz, 1H), 1.06 (t, 7.2 Hz, 3H).

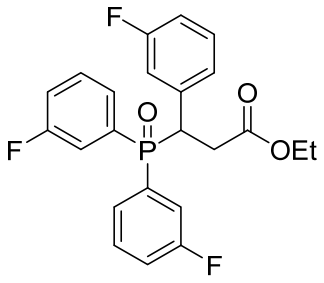
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3 (d, J_{C-P} = 17.3 Hz), 159.8 (d, J_{C-P} = 13.0 Hz), 159.3, 159.1 (d, J_{C-P} = 14.5 Hz), 136.5 (d, J_{C-P} = 5.8 Hz), 132.5 (d, J_{C-P} = 99.7 Hz), 132.2 (d, J_{C-P} = 95.4 Hz), 130.0 (d, J_{C-P} = 14.5 Hz), 129.22 (d, J_{C-P} = 15.9 Hz), 129.16, 123.1 (d, J_{C-P} = 8.7 Hz), 123.0 (d, J_{C-P} = 8.7 Hz), 122.2 (d, J_{C-P} = 5.8 Hz), 118.5, 118.2, 116.3 (d, J_{C-P} = 8.7 Hz), 115.7 (d, J_{C-P} = 10.1 Hz), 114.7 (d, J_{C-P} = 4.3 Hz), 113.5, 60.8, 55.5, 55.2, 55.1, 43.0 (d, J_{C-P} = 67.9 Hz), 34.8, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 32.8.

IR (KBr) ν 3060, 3042, 2959, 2838, 1739, 1601 ,1577, 1241, 1173, 1046, 1035, 700 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{29}NaO_6P$ ($[M+Na]^+$): 491.1594, found 491.1593.

Ethyl 3-(bis(3-fluorophenyl)phosphoryl)-3-(3-fluorophenyl)propanoate (**3ia**):



3ia

White solid, m.p. 148-149 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70-7.73 (m, 1H), 7.65-7.68 (m, 1H), 7.56-7.59 (m, 1H), 7.26-7.32 (m, 3H), 7.15-7.22 (m, 2H), 7.08-7.10 (m, 2H), 7.04 (dd, J = 10.0 Hz, 1.7 Hz, 1H), 6.88 (dd, J = 8.3,8.3 Hz, 1H), 4.05 (ddd, J_{H-P} = 7.6 Hz, J_{H-H} = 11.0, 3.4 Hz, 1H), 3.96 (q, J_{H-H} = 6.9 Hz, 2H), 3.07 (ddd, J_{H-P} = 6.2 Hz, J_{H-H} = 16.7, 11.0 Hz, 1H), 2.85 (ddd, J_{H-P} = 9.4 Hz, J_{H-H} = 16.7, 3.4 Hz, 1H), 1.07 (t, 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7 (d, J_{C-P} = 17.3 Hz), 162.8 (dd, J_{C-F} = 252.2 Hz, J_{C-P} = 15.9 Hz), 162.5 (d, J_{C-F} = 247.1 Hz), 161.3 (dd, J_{C-F} = 251.4 Hz, J_{C-P} = 15.9 Hz), 137.0 (dd, J_{C-F} = 7.2, J_{C-P} = 5.8 Hz), 133.2 (dd, J_{C-F} = 4.3 Hz, J_{C-P} = 100.4 Hz), 133.2 (dd, J_{C-F} = 4.3 Hz, J_{C-P} = 94.6 Hz), 131.1 (dd, J_{C-F} = 7.2 Hz, J_{C-P} = 13.0 Hz), 130.3 (dd, J_{C-F} = 7.2 Hz, J_{C-P} = 13.7 Hz), 129.9 (d, J_{C-F} = 7.2 Hz), 126.7 (dd, J_{C-F} = 2.9 Hz, J_{C-P} = 8.7 Hz), 126.5 (dd, J_{C-F} = 2.9

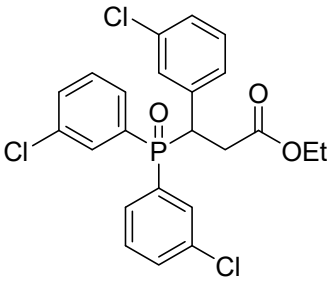
Hz, J_{C-P} = 8.7 Hz), 125.4 (dd, J_{C-F} = 2.9 Hz, J_{C-P} = 5.8 Hz), 119.7 (dd, J_{C-F} = 18.8 Hz), 119.2 (d, J_{C-F} = 21.7 Hz), 118.4 (dd, J_{C-F} = 23.1 Hz, J_{C-P} = 8.7 Hz), 117.9 (dd, J_{C-F} = 22.4 Hz, J_{C-P} = 8.7 Hz), 116.6 (dd, J_{C-F} = 21.7 Hz, J_{C-P} = 5.8 Hz), 114.64 (d, J_{C-F} = 20.2 Hz), 61.1, 42.5 (d, J_{C-P} = 69.4 Hz), 34.7, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 31.1.

IR (KBr) ν 3058, 3029, 2984, 1739, 1584, 1479, 1423, 1227, 898, 696 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{23}H_{20}F_3NaO_3P$ ($[M+Na]^+$): 455.0994, found 455.0992.

Ethyl 3-(bis(3-chlorophenyl)phosphoryl)-3-(3-chlorophenyl)propanoate (**3ja**):



3ja

White solid, m.p. 112-113 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J_{H-P} = 11.0 Hz, 1H), 7.77-7.80 (m, 1H), 7.56-7.59 (m, 1H), 7.52 (ddd, J_{H-P} = 3.4 Hz, J_{H-H} = 7.9, 7.9 Hz, 1H), 7.45 (d, J_{H-P} = 11.0 Hz, 1H), 7.34-7.39 (m, 2H), 7.25-7.28 (m, 2H), 7.14-7.22 (m, 3H), 4.02 (ddd, J_{H-P} = 7.6 Hz, J_{H-H} = 11.0, 3.4 Hz, 1H), 3.96 (q, J_{H-H} = 6.9 Hz, 2H), 3.05 (ddd, J_{H-P} = 6.9 Hz, J_{H-H} = 16.8, 11.0 Hz, 1H), 2.85 (ddd, J_{H-P} = 9.6 Hz, J_{H-H} = 16.8, 3.4 Hz, 1H), 1.08 (t, J_{H-H} = 6.9 Hz, 3H).

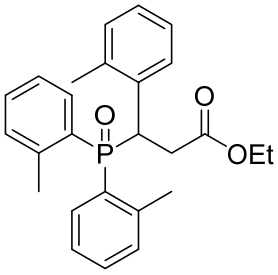
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7 (d, J_{C-P} = 17.3 Hz), 136.5 (d, J_{C-P} = 5.8 Hz), 135.7 (d, J_{C-P} = 14.5 Hz), 135.0 (d, J_{C-P} = 14.5 Hz), 134.3 (d, J_{C-P} = 2.9 Hz), 132.7 (d, J_{C-P} = 98.3 Hz), 132.7, 132.68 (d, J_{C-P} = 92.5 Hz), 132.2 (d, J_{C-P} = 2.9 Hz), 131.3 (d, J_{C-P} = 8.7 Hz), 130.9 (d, J_{C-P} = 10.1 Hz), 130.5 (d, J_{C-P} = 11.6 Hz), 129.8 (d, J_{C-P} = 10.1 Hz), 129.7 (2C), 129.0 (d, J_{C-P} = 8.7 Hz), 128.8 (d, J_{C-P} = 8.7 Hz), 127.9, 127.7 (d, J_{C-P} = 5.8 Hz), 61.1, 42.4 (d, J_{C-P} = 67.9 Hz), 34.6, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.35.

IR (KBr) ν 3060, 2981, 2923, 1733, 1567, 1470, 1405, 1183, 693 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{23}H_{20}Cl_3NaO_3P$ ($[M+Na]^+$): 503.0113, found 503.0107.

Ethyl 3-(di-o-tolylphosphoryl)-3-(o-tolyl)propanoate (**3ka**):



3ka

White solid, m.p. 134-135 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.91 (m, 2H), 7.45 (d, J_{H-H} = 7.6, 7.6 Hz, 1H), 7.37-7.40 (m, 1H), 7.15-7.26 (m, 4H), 7.05 (d, J_{H-H} = 7.6, 7.6 Hz, 1H), 6.90-6.98 (m, 3H), 4.52-4.58 (m, 1H), 3.96 (q, J_{H-H} = 7.3 Hz, 2H), 3.20-3.24 (m, 2H), 2.38 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H) 1.06 (t, J_{H-H} = 7.3 Hz, 3H).

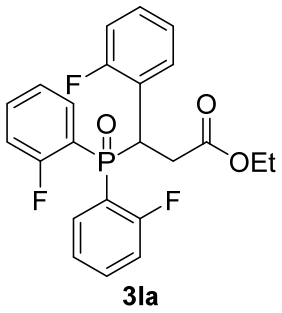
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8 (d, J_{C-P} = 16.3 Hz), 143.4 (d, J_{C-P} = 7.7 Hz), 143.2 (d, J_{C-P} = 7.7 Hz), 136.8 (d, J_{C-P} = 5.8 Hz), 134.3 (d, J_{C-P} = 3.8 Hz), 132.6 (d, J_{C-P} = 9.6 Hz), 131.9 (d, J_{C-P} = 12.5 Hz), 131.7 (d, J_{C-P} = 1.9 Hz), 131.4 (d, J_{C-P} = 10.5 Hz), 131.3 (d, J_{C-P} = 2.9 Hz), 131.19 (d, J_{C-P} = 101.6 Hz), 131.16 (d, J_{C-P} = 10.5 Hz), 131.08 (d, J_{C-P} = 103.5 Hz), 130.0, 129.7 (d, J_{C-P} = 3.8 Hz), 127.0, 126.1, 125.5 (d, J_{C-P} = 11.5 Hz), 124.9 (d, J_{C-P} = 12.5 Hz), 60.8, 36.6, 36.3 (d, J_{C-P} = 69.0 Hz), 21.5 (d, J_{C-P} = 4.8 Hz), 20.8 (d, J_{C-P} = 2.9 Hz), 19.5, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 37.2.

IR (KBr) ν 3052, 2984, 2953, 2926, 1731, 1252, 1188, 1139, 1031 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{29}NaO_3P$ ($[M+Na]^+$): 443.1747, found 443.1747.

Ethyl 3-(bis(2-fluorophenyl)phosphoryl)-3-(2-fluorophenyl)propanoate (**3la**):



3la

Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-8.01 (m, 1H), 7.69 (dddd, J = 7.8, 7.8, 2.3, 2.3 Hz, 1H), 7.55-7.64 (m, 2H), 7.34-7.40 (m, 1H), 7.32 (dd, J = 7.8, 7.8 Hz, 1H), 7.02-7.20 (m, 4H), 6.91 (ddd, J = 8.9, 8.9, 6.0 Hz, 1H), 6.81 (dd, J = 8.9, 8.9 Hz, 1H), 4.93-4.99 (m, 1H), 3.94-4.03 (m, 2H), 3.21 (ddd, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 16.4, 10.6 Hz, 1H), 3.03 (ddd, $J_{H\text{-}P}$ = 8.9 Hz, $J_{H\text{-}H}$ = 16.4, 3.7 Hz, 1H), 1.08 (t, 7.1 Hz, 3H).

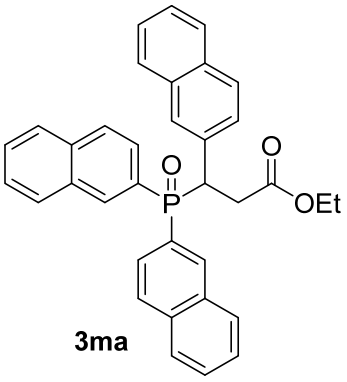
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 (d, $J_{C\text{-}P}$ = 19.2 Hz), 162.40 (dd, $J_{C\text{-}F}$ = 256.3 Hz, $J_{C\text{-}P}$ = 5.8 Hz), 162.36 (dd, $J_{C\text{-}F}$ = 248.7 Hz, $J_{C\text{-}P}$ = 5.8 Hz), 160.8 (dd, $J_{C\text{-}F}$ = 247.3 Hz, $J_{C\text{-}P}$ = 6.7 Hz), 134.9 (dd, $J_{C\text{-}F}$ = 1.9 Hz, $J_{C\text{-}P}$ = 8.6 Hz), 134.53, 134.51 (dd, $J_{C\text{-}F}$ = 1.9 Hz, $J_{C\text{-}P}$ = 8.6 Hz), 133.8 (dd, $J_{C\text{-}F}$ = 3.8 Hz, $J_{C\text{-}P}$ = 3.8 Hz), 130.6 (dd, $J_{C\text{-}F}$ = 3.8 Hz, $J_{C\text{-}P}$ = 3.8 Hz), 129.0 (dd, $J_{C\text{-}F}$ = 2.9 Hz, $J_{C\text{-}P}$ = 8.6 Hz), 125.0 (dd, $J_{C\text{-}F}$ = 2.9 Hz, $J_{C\text{-}P}$ = 10.0 Hz), 124.2, 124.1 (dd, $J_{C\text{-}F}$ = 2.9 Hz, $J_{C\text{-}P}$ = 12.0 Hz), 122.4 (dd, $J_{C\text{-}F}$ = 14.4 Hz, $J_{C\text{-}P}$ = 5.6 Hz), 119.2 (dd, $J_{C\text{-}F}$ = 19.2 Hz, $J_{C\text{-}P}$ = 94.9 Hz), 119.0 (dd, $J_{C\text{-}F}$ = 18.2 Hz, $J_{C\text{-}P}$ = 101.6 Hz), 116.5 (dd, $J_{C\text{-}F}$ = 23.0 Hz, $J_{C\text{-}P}$ = 5.8 Hz), 115.6 (dd, $J_{C\text{-}F}$ = 22.0 Hz, $J_{C\text{-}P}$ = 5.8 Hz), 115.0 (dd, $J_{C\text{-}F}$ = 23.0 Hz, $J_{C\text{-}P}$ = 1.9 Hz), 60.9, 34.9 (d, $J_{C\text{-}P}$ = 71.9 Hz), 34.5, 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 27.6.

IR (KBr) ν 2957, 2921, 2850, 1736, 1603, 1474, 1442, 1212, 760 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{23}H_{20}F_3NaO_3P$ ($[M+Na]^+$): 455.0994, found 455.0994.

Ethyl 3-(di(naphthalen-2-yl)phosphoryl)-3-(naphthalen-2-yl)propanoate (**3ma**):



3ma

White solid, m.p. 193-194 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, $J_{H\text{-}P}$ = 13.1 Hz, 1H), 8.16 (d, $J_{H\text{-}P}$ = 13.8 Hz, 1H), 7.99-8.01 (m, 2H), 7.95 (dd, J = 8.6, 8.6 Hz, 1H), 7.91 (d, $J_{H\text{-}H}$ = 8.3 Hz, 1H), 7.88 (s, 1H), 7.55-7.71 (m, 9H), 7.50 (d, $J_{H\text{-}H}$ = 8.9 Hz, 1H), 7.47 (dd, $J_{H\text{-}H}$ = 7.2, 7.2 Hz, 1H), 7.38-7.42 (m, 3H), 4.50 (ddd, $J_{H\text{-}P}$ = 7.9 Hz, $J_{H\text{-}H}$ = 11.0, 3.4 Hz, 1H), 3.84 (q, $J_{H\text{-}H}$ = 6.9 Hz, 2H), 3.26 (ddd, $J_{H\text{-}P}$ = 6.2 Hz, $J_{H\text{-}H}$ = 16.5, 11.0 Hz, 1H), 3.05 (ddd, $J_{H\text{-}P}$ = 9.6 Hz, $J_{H\text{-}H}$ = 16.5, 3.4 Hz, 1H), 0.95 (t, 6.9 Hz, 3H).

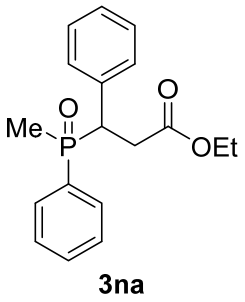
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3 (d, $J_{C\text{-}P}$ = 17.3 Hz), 134.7, 134.4, 133.8 (d, $J_{C\text{-}P}$ = 8.7 Hz), 133.4 (d, $J_{C\text{-}P}$ = 8.7 Hz), 133.2, 132.9 (d, $J_{C\text{-}P}$ =5.8 Hz), 132.7 (d, $J_{C\text{-}P}$ = 13.0 Hz), 132.51, 132.2 (d, $J_{C\text{-}P}$ = 13.0 Hz), 129.0, 128.85 (d, $J_{C\text{-}P}$ = 7.2 Hz), 128.77, 128.74 ($J_{C\text{-}P}$ = 10.1 Hz), 128.5 ($J_{C\text{-}P}$ = 93.9 Hz), 128.349, 128.345 ($J_{C\text{-}P}$ = 108.4 Hz), 128.0 (2C), 127.92 ($J_{C\text{-}P}$ = 4.3 Hz), 127.89 ($J_{C\text{-}P}$ = 7.2 Hz), 127.8, 127.7 (d, $J_{C\text{-}P}$ = 4.3 Hz), 127.6, 127.5, 127.1, 126.6, 125.9, 125.8 (2C), 125.7, 60.8, 42.8 (d, $J_{C\text{-}P}$ = 69.4 Hz), 35.3, 13.8.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.4.

IR (KBr) ν 3055, 2981, 2920, 1738, 1506, 1214, 1176, 746, 477 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{35}H_{29}NaO_3P$ ($[M+Na]^+$): 551.1747, found 551.1744.

Ethyl 3-(methyl(phenyl)phosphoryl)-3-phenylpropanoate (**3na**):



3na

White solid, m.p. 126-127 ℃ and 136-137 ℃ for each diastereomer.

Low polar diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.77 (m, 2H), 7.49-7.59 (m, 3H), 7.27-7.40 (m, 5H), 3.87 (q, $J_{H\text{-}H}$ = 6.9 Hz, 2H), 3.57 (ddd, $J_{H\text{-}P}$ = 8.9 Hz, $J_{H\text{-}H}$ = 11.0, 4.1 Hz, 1H), 3.00 (ddd, $J_{H\text{-}P}$ = 7.8 Hz, $J_{H\text{-}H}$ = 16.5, 11.0 Hz, 1H), 2.76 (ddd, $J_{H\text{-}P}$ = 8.9 Hz, $J_{H\text{-}H}$ = 11.0, 4.1 Hz, 1H), 1.45 (d, $J_{H\text{-}P}$ = 12.4 Hz, 3H), 1.01 (t, 6.9 Hz, 3H).

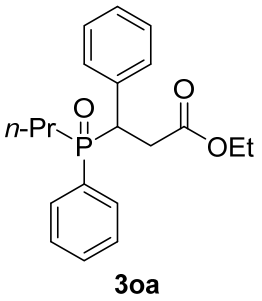
13C NMR (101 MHz, $CDCl_3$) δ 171.2, 135.7 (d, $J_{C\text{-}P}$ = 4.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 93.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 1.9 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.2 (d, $J_{C\text{-}P}$ = 5.8 Hz), 128.8, 128.7 (d, $J_{C\text{-}P}$ = 8.6 Hz), 127.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 60.7, 44.8 (d, $J_{C\text{-}P}$ = 66.1 Hz), 34.0, 14.4 (d, $J_{C\text{-}P}$ = 71.9 Hz), 13.9.

^{31}P NMR (243 MHz, $CDCl_3$) δ 38.4.

IR (KBr) ν 3048, 2983, 2905, 1731, 1428, 1224, 1173, 884, 700 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{18}H_{21}NaO_3P$ ($[M+Na]^+$): 339.1121, found 339.1119.

Ethyl 3-phenyl-3-(phenyl(propyl)phosphoryl)propanoate (**3oa**):



3oa

White solid, m.p. 52-53 ℃ and 103-104 ℃ for each diastereomer.

Low polar diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.77 (m, 2H), 7.49-7.58 (m, 3H), 7.41-7.43 (m, 2H), 7.36 (t, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.28-7.32 (m, 1H), 3.86 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H), 3.58 (ddd, $J_{H\text{-}P}$ = 7.8 Hz, $J_{H\text{-}H}$ = 11.3, 3.7 Hz, 1H), 3.00 (ddd, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 16.4, 11.3 Hz, 1H), 2.68 (ddd, $J_{H\text{-}P}$ = 8.6 Hz, $J_{H\text{-}H}$ = 16.4, 3.7 Hz, 1H), 1.60-1.69 (m, 2H), 1.31-1.46 (m, 1H), 1.10-1.28 (m, 1H), 1.00 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H), 0.79 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H).

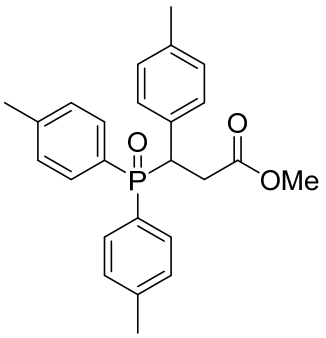
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.8 (d, $J_{C\text{-}P}$ = 15.9 Hz), 135.5 (d, $J_{C\text{-}P}$ = 4.3 Hz), 131.5 , 130.70 (d, $J_{C\text{-}P}$ = 88.1 Hz), 130.69 (d, $J_{C\text{-}P}$ = 8.7 Hz), 129.2 (d, $J_{C\text{-}P}$ = 5.8 Hz), 129.0 (d, $J_{C\text{-}P}$ = 5.8 Hz), 128.43, 128.42 (d, $J_{C\text{-}P}$ = 11.6 Hz), 60.3, 43.7 (d, $J_{C\text{-}P}$ = 63.6 Hz), 34.1, 29.5 (d, $J_{C\text{-}P}$ = 69.4 Hz), 15.2 (d, $J_{C\text{-}P}$ = 15.9 Hz), 14.6 (d, $J_{C\text{-}P}$ = 4.3 Hz), 13.7.

^{31}P NMR (243 MHz, $CDCl_3$): δ 41.5.

IR (KBr) ν 3061, 2957, 2924, 2871, 1730, 1226, 1171, 1110, 700, 535 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{20}H_{25}NaO_3P$ ($[M+Na]^+$): 367.1434, found 367.1431.

Methyl 3-(di-*p*-tolylphosphoryl)-3-(*p*-tolyl)propanoate (**3ab**):



3ab

White solid, m.p. 152-153 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, $J_{H\text{-}P}$ = 11.0 Hz, $J_{H\text{-}H}$ = 8.3 Hz, 2H), 7.31-7.36 (m, 4H), 7.16 (dd, J = 8.3, 2.1 Hz, 2H), 7.06 (dd, J = 7.9, 2.8 Hz 2H), 6.99 (d, $J_{H\text{-}H}$ = 7.6 Hz, 2H), 4.01 (ddd, $J_{H\text{-}P}$ = 8.6 Hz, $J_{H\text{-}H}$ = 11.3, 3.4 Hz, 1H), 3.47 (s, 3H), 3.05 (ddd, $J_{H\text{-}P}$ = 5.5 Hz, $J_{H\text{-}H}$ = 16.7, 11.3 Hz, 1H), 2.87 (ddd, $J_{H\text{-}P}$ = 9.6 Hz, $J_{H\text{-}H}$ = 16.7, 3.4 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0 (d, $J_{C\text{-}P}$ = 17.3 Hz), 142.3, 141.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 136.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 129.49 (d, $J_{C\text{-}P}$ = 15.9 Hz), 129.48, 129.0, 128.8 (d, $J_{C\text{-}P}$ = 13.0 Hz), 128.22 (d, $J_{C\text{-}P}$ = 105.5 Hz),

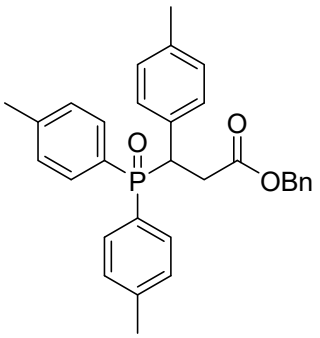
128.19 (d, $J_{C\text{-}P}$ = 95.4 Hz), 51.8, 42.4 (d, $J_{C\text{-}P}$ = 67.9 Hz), 34.9, 21.65, 21.5, 21.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.7.

IR (KBr) ν 3035, 2949, 2920, 2851, 1739, 1224, 1175, 547 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{25}H_{27}NaO_3P$ ($[M+Na]^+$): 429.1590, found 429.1589.

Benzyl 3-(di-*p*-tolylphosphoryl)-3-(*p*-tolyl)propanoate (**3ac**):



3ac

White solid, m.p. 164-165 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, $J_{H\text{-}P}$ = 10.5 Hz, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 7.22-7.36 (m, 7H), 7.11-7.14 (m, 2H), 7.04-7.07 (m, 4H), 6.96 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 4.90 (s, 2H), 4.01 (ddd, $J_{H\text{-}P}$ = 8.6 Hz, $J_{H\text{-}H}$ = 11.6, 3.2 Hz, 1H), 3.11 (ddd, $J_{H\text{-}P}$ = 6.0 Hz, $J_{H\text{-}H}$ = 16.6, 11.6 Hz, 1H), 2.91 (ddd, $J_{H\text{-}P}$ = 8.7 Hz, $J_{H\text{-}H}$ = 16.6, 3.2 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H).

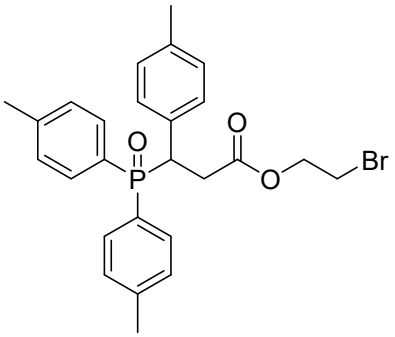
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4 (d, $J_{C\text{-}P}$ = 17.3 Hz), 142.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.8 (d, $J_{C\text{-}P}$ = 1.9 Hz), 136.7 (d, $J_{C\text{-}P}$ = 1.9 Hz), 135.5, 131.9 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.6, 129.5 (d, $J_{C\text{-}P}$ = 8.6 Hz), 129.0, 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.3, 128.20 (d, $J_{C\text{-}P}$ = 101.6 Hz), 128.18 (d, $J_{C\text{-}P}$ = 97.8 Hz), 128.0, 127.8, 66.47, 42.7 (d, $J_{C\text{-}P}$ = 68.1 Hz), 35.1, 21.5, 21.4, 21.1.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.4.

IR (KBr) ν 3035, 2919, 1720, 1454, 1249, 1175, 990, 808 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{31}H_{31}NaO_3P$ ($[M+Na]^+$): 505.1903, found 505.1900.

2-Bromoethyl 3-(di-*p*-tolylphosphoryl)-3-(*p*-tolyl)propanoate (**3ad**):



3ad

White solid, m.p. 187-188 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, $J_{H\text{-}P}$ = 10.7 Hz, $J_{H\text{-}H}$ = 7.9 Hz, 2H), 7.32-7.36 (m, 4H), 7.14 (dd, J = 7.9, 2.1 Hz, 2H), 7.07 (dd, J = 7.9, 2.1 Hz, 2H), 6.99 (d, $J_{H\text{-}H}$ = 8.3 Hz, 2H), 4.16 (t, $J_{H\text{-}H}$ = 5.5 Hz, 2H), 4.00 (ddd, $J_{H\text{-}P}$ = 8.3 Hz, $J_{H\text{-}H}$ = 11.5, 3.4 Hz, 1H), 3.24 (t, $J_{H\text{-}H}$ = 5.5 Hz, 2H), 3.07 (ddd, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 16.2, 11.5 Hz, 1H), 2.92 (ddd, $J_{H\text{-}P}$ = 8.9 Hz, $J_{H\text{-}H}$ = 16.2, 3.4 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H).

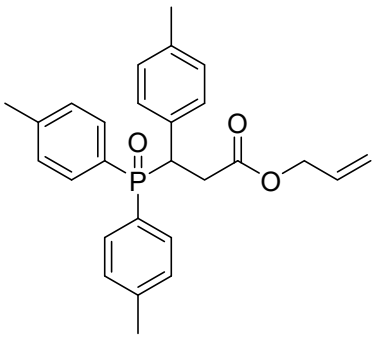
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0 (d, $J_{C\text{-}P}$ = 17.3 Hz), 142.4, 141.8, 136.8, 131.8 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 129.51 (d, $J_{C\text{-}P}$ = 14.5 Hz), 129.49, 129.0, 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.04 (d, $J_{C\text{-}P}$ = 96.8 Hz), 127.99 (d, $J_{C\text{-}P}$ = 101.2 Hz), 63.8, 42.6 (d, $J_{C\text{-}P}$ = 67.9 Hz), 34.9, 28.1, 21.54, 21.45, 21.0.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.3.

IR (KBr) ν 3033, 2923, 1743, 1600, 1515, 1174, 654, 549, 521 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{28}BrNaO_3P$ ($[M+Na]^+$): 521.0852, found 521.0850.

Allyl 3-(di-*p*-tolylphosphoryl)-3-(*p*-tolyl)propanoate (3ae):



3ae

White solid, m.p. 169-170 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, $J_{H\text{-}P}$ = 10.5 Hz, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 7.31-7.37 (m, 4H), 7.15 (dd, J = 8.2, 1.8 Hz, 2H), 7.07 (dd, J = 8.0, 2.8 Hz, 2H), 6.98 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 5.68 (ddt, $J_{H\text{-}H}$ = 16.5, 11.0, 5.5 Hz, 1H), 5.05-5.10 (m, 2H), 4.36 (d, $J_{H\text{-}H}$ = 5.5 Hz, 2H), 4.01 (ddd, $J_{H\text{-}P}$ = 8.7 Hz, $J_{H\text{-}H}$ = 11.3, 3.7 Hz, 1H), 3.08 (ddd, $J_{H\text{-}P}$ = 6.4 Hz, $J_{H\text{-}H}$ = 16.7, 11.0 Hz, 1H), 2.90 (ddd, $J_{H\text{-}P}$ = 9.2 Hz, $J_{H\text{-}H}$ = 16.7, 3.7 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H).

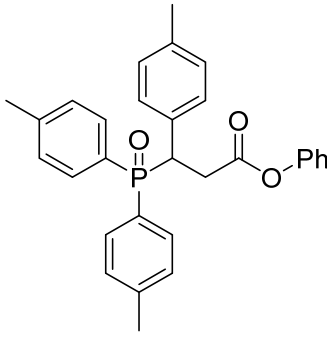
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2 (d, $J_{C\text{-}P}$ = 17.3 Hz), 142.3, 141.7, 136.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 4.3 Hz), 131.7, 131.3 (d, $J_{C\text{-}P}$ = 8.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.7 Hz), 129.53, 129.48 (d, $J_{C\text{-}P}$ = 7.2 Hz), 129.0, 128.8 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.21 (d, $J_{C\text{-}P}$ = 104.0 Hz), 128.18 (d, $J_{C\text{-}P}$ = 96.8 Hz), 117.9, 65.3, 42.5 (d, $J_{C\text{-}P}$ = 69.4 Hz), 35.0, 21.5, 21.4, 21.0.

^{31}P NMR (243 MHz, $CDCl_3$) 33.5.

IR (KBr) ν 3055, 3032, 2922, 1738, 1602, 1515, 1175, 930 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{27}H_{29}NaO_3P$ ($[M+Na]^+$): 455.1747, found 455.1743.

Phenyl 3-(di-*p*-tolylphosphoryl)-3-(*p*-tolyl)propanoate (**3af**):



3ae

White solid, m.p. 199-200 ℃.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (dd, $J_{H\text{-}P}$ = 11.0 Hz, $J_{H\text{-}H}$ = 8.3 Hz, 2H), 7.34-7.39 (m, 4H), 7.20-7.26 (m, 4H), 7.13 (t, J = 7.6 Hz, 1H), 7.09 (dd, J = 7.9, 2.1 Hz, 2H), 7.02 (d, $J_{H\text{-}H}$ = 7.6 Hz, 2H), 6.69-6.71 (m, 2H), 4.09 (ddd, $J_{H\text{-}P}$ = 8.6 Hz, $J_{H\text{-}H}$ = 11.0, 3.4 Hz, 1H), 3.29 (ddd, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 16.2, 11.0 Hz, 1H), 3.11 (ddd, $J_{H\text{-}P}$ = 8.3 Hz, $J_{H\text{-}H}$ = 16.2, 3.4 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H).

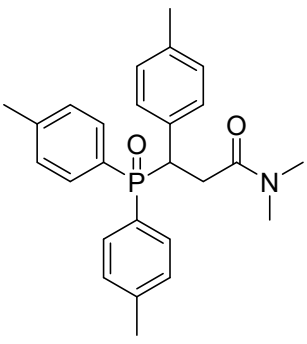
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2 (d, $J_{C\text{-}P}$ = 18.8 Hz), 150.4, 142.5, 141.9, 137.0, 131.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.7 Hz), 129.64, 129.59 (d, $J_{C\text{-}P}$ = 8.7 Hz), 129.2, 129.1, 128.9 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.0 (d, $J_{C\text{-}P}$ = 98.3 Hz), 127.9 (d, $J_{C\text{-}P}$ = 102.6 Hz), 125.7, 121.3, 42.8 (d, $J_{C\text{-}P}$ = 67.9 Hz), 35.2, 21.6, 21.5, 21.1.

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.3.

IR (KBr) ν 3016, 2921, 2852, 1748, 1349, 1217, 1197, 806 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{30}H_{29}NaO_3P$ ($[M+Na]^+$): 491.1747, found 491.1744.

3-(di-*p*-tolylphosphoryl)-*N*,*N*-dimethyl-3-(*p*-tolyl)propanamide (**3ag**):



3ag

Reddish white solid, m.p. 221-222 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, $J_{H\text{-}P}$ = 10.3 Hz, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 7.25-7.34 (m, 6H), 7.02 (dd, $J_{H\text{-}H}$ = 8.0, 2.1 Hz, 2H), 6.97 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 4.29 (ddd, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 10.0, 3.2 Hz, 1H), 3.16 (ddd, $J_{H\text{-}P}$ = 5.5 Hz, $J_{H\text{-}H}$ = 16.0, 10.0 Hz, 1H), 2.80 (s, 3H), 2.69-2.77 (m, 1H), 2.75 (s, 3H), 2.40 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1 (d, $J_{C\text{-}P}$ = 14.4 Hz), 142.1 (d, $J_{C\text{-}P}$ = 1.9 Hz),

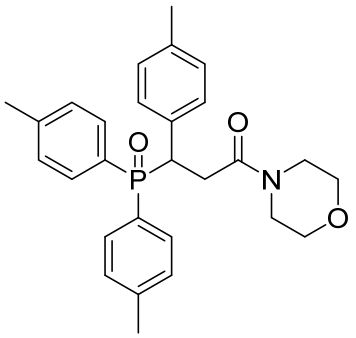
141.4 (d, $J_{C\text{-}P}$ = 1.9 Hz), 136.3 (d, $J_{C\text{-}P}$ = 1.9 Hz), 133.2 (d, $J_{C\text{-}P}$ = 4.8 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 129.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.94 (d, $J_{C\text{-}P}$ = 101.6 Hz), 128.9, 128.74 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.68 (d, $J_{C\text{-}P}$ = 96.8 Hz), 41.9(d, $J_{C\text{-}P}$ = 70.0 Hz), 37.1, 35.6, 33.8, 21.5, 21.4, 21.0.

^{31}P NMR (243 MHz, $CDCl_3$) δ 34.9.

IR (KBr) *v* 3020, 2919, 2897, 1655, 1649, 1509, 1398, 1175, 656, 548 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{30}NNaO_2P$ ([M+Na]$^+$): 442.1906, found 442.1904.

3-(di-*p*-tolylphosphoryl)-1-morpholino-3-(*p*-tolyl)propan-1-one (**3ah**):



3ah

Reddish white solid, m.p. 186-187 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, $J_{H\text{-}P}$ = 10.5 Hz, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.30-7.35 (m, 4H), 7.26 (dd, $J_{H\text{-}H}$ = 7.8, 1.8 Hz, 2H), 7.03 (dd, $J_{H\text{-}H}$ = 7.8, 2.3 Hz, 2H), 6.99 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 4.23 (ddd, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 10.3, 3.2 Hz, 1H), 3.27-3.54 (m, 7H), 3.12-3.20 (m, 2H), 2.70 (ddd, $J_{H\text{-}P}$ = 10.1 Hz, $J_{H\text{-}H}$ = 15.6, 3.2 Hz, 1H), 2.40 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H).

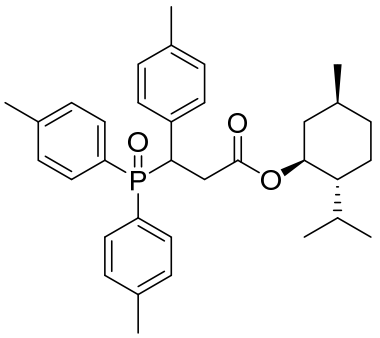
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (d, $J_{C\text{-}P}$ = 14.4 Hz), 142.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 136.6 (d, $J_{C\text{-}P}$ = 1.9 Hz), 132.9 (d, $J_{C\text{-}P}$ = 4.8 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.6, 129.5 (d, $J_{C\text{-}P}$ = 3.8 Hz), 129.0, 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 102.6 Hz), 128.5 (d, $J_{C\text{-}P}$ = 97.8 Hz), 66.6, 66.3, 46.0, 42.17 (d, $J_{C\text{-}P}$ = 69.0 Hz), 42.13, 33.0, 21.5, 21.4, 21.0.

^{31}P NMR (243 MHz, $CDCl_3$) δ 34.5.

IR (KBr) *v* 3018, 2922, 2852, 1627, 1604, 1466, 1434, 1175, 1115, 657 cm^{-1}.

HRMS (ESI) *m*/*z* calcd for $C_{28}H_{32}NNaO_3P$ ([M+Na]$^+$): 484.2012, found 484.2010.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 3-(di-*p*-tolylphosphoryl)-3-(*p*-tolyl)propanoate (**3ai**):



3ai

White solid, m.p. 149-150 ℃.

The peaks of each diastereomer are overlapping:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.81 (m, 2H), 7.31-7.39 (m, 4H), 7.06-7.14 (m, 4H), 6.96-6.98 (m, 2H), 4.41-4.50 (m, 1H), 3.95-4.02 (m, 1H), 2.97-3.06 (m, 1H), 2.76-2.88 (m, 1H), 2.41 (s, 3H), 2.28-2.29 (m, 3H), 2.24 (s, 3H), 2.04 (br, 1H), 1.08-1.60 (m, 6H), 0.69-0.96 (m, 7H), 0.63-0.65 (m, 1H), 0.54-0.60 (m, 2H), 0.34-0.35 (m, 1H).

13C NMR (151 MHz, $CDCl_3$) δ 171.1-171.3 (1C), 142.2, 141.7-141.8 (1C), 136.6 (1C), 131.7-131.8 (1C), 131.1-131.4 (2C), 129.4-129.6 (2C), 128.76-128.84 (2C), 127.7-128.7 (2C), 74.5 (1C), 46.6 (1C), 42.7-43.2 (1C), 40.3-40.6 (1C), 35.5 (1C), 35.1 (1C), 34.0-34.1 (1C), 31.1-31.2 (1C), 25.6-25.8 (1C), 23.1 (1C), 21.8-21.9 (1C), 21.46-21.54 (1C), 21.00-21.04 (1C), 20.5-20.7 (1C), 15.9-16.0 (1C).

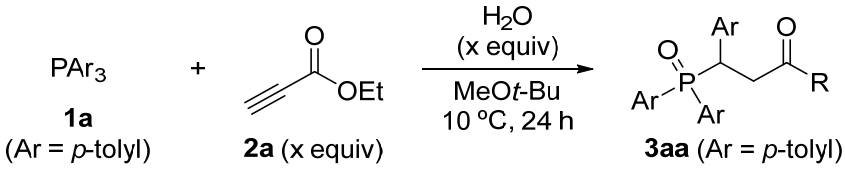
^{31}P NMR (243 MHz, $CDCl_3$) δ 33.4.

IR (KBr) *v* 3033, 2955, 2922, 2868, 1729, 1603, 1514, 1175, 805.

HRMS (ESI) *m*/*z* calcd for $C_{34}H_{43}NaO_3P$ ([M+Na]$^+$): 553.2842, found 553.2838.

3. Optimization of reaction conditions

3-1. Optimization of molar ratio



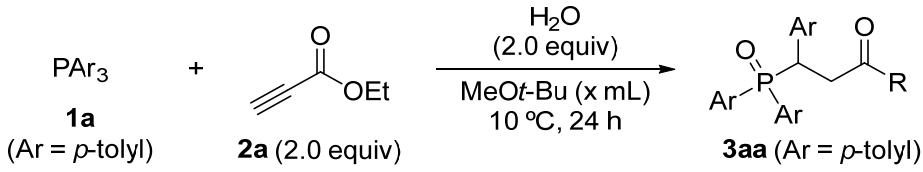
Under a nitrogen atmosphere, to a mixture of tri(*p*-tolyl)phosphine **1a** (0.1 mmol, 1.0 equiv) and water (x equiv) in MeO*t*-Bu (0.5 mL), alkyne **2a** (x equiv) was added at 10 ℃. The resulting mixture was stirred for 24 h, then filtrated through silica gel to remove remaining phosphine and concentrated under the reduced pressure. The yield of desired product **3aa** was determined *via* ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S1. Optimization of molar ratio

entry	**2a** (equiv)	H_2O (equiv)	yield (%)
1	1.1	1.1	77
2	1.5	1.5	91
3[a]	2.0	2.0	98 (94)[a]

[a]Same to entry 7 in **Table 1**. [b]Isolated yield.

3-2. Optimization of the amount of the solvent



Under a nitrogen atmosphere, to a mixture of tri(*p*-tolyl)phosphine **1a** (0.1 mmol, 1.0 equiv) and water (0.2 mmol, 2.0 equiv) in MeO*t*-Bu (x mL), alkyne **2a** (0.2 mmol, 2.0 equiv) was added at 10 ℃. The resulting mixture was stirred for 24 h, then filtrated through silica gel to remove remaining phosphine and concentrated under the reduced pressure. The yield of desired product **3aa** was determined *via* ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. Optimization of the amount of the solvent

entry	MeO*t*-Bu (mL)	yield (%)
1	2.0	95
2	1.0	93
3[a]	0.5	98 (94)[b]
4	0.2	88
5	0.1	88

[a]Same to entry 7 in **Table 1**. [b]Isolated yield.

4. Computational studies

All calculations were performed with the Caussian 09 (Rev E.01) program.[15] Geometries were fully optimized at B3LYP theory[16a,16b] with 6-31G(d) basis set[17] and characterized by frequency calculation. The reaction pathway was traced by intrinsic reaction coordinate (IRC) method from the located transition states.

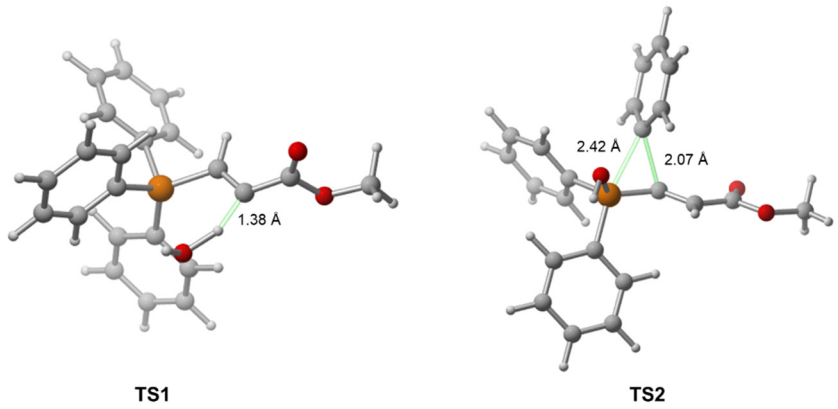


Figure S1. 3D drawing of transition states. The bond formation/dissociation is shown in light green, and the atom distances are indicated in Å.[18]

intA			
C	-1.22553100	0.09166400	-1.10832800
H	-1.09111400	0.17681400	-2.19547400
C	-2.33742700	-0.05616500	-0.37142800
C	-3.65346500	-0.22025600	-0.92919900
O	-4.13609900	-1.29649500	-1.26670800
O	-4.38398800	0.94257800	-0.92656900
C	-5.74600900	0.79186400	-1.33305700
H	-6.28147700	0.10164700	-0.67332300
H	-6.18469200	1.79020300	-1.27040200
H	-5.81647400	0.41325800	-2.35783600
P	0.29070000	0.02038000	-0.17002800
C	0.46598200	-1.56872700	0.71206500
C	-0.41212800	-2.62533200	0.43092600
C	1.48422000	-1.74142500	1.66363900
C	-0.25475100	-3.84771900	1.08582600
H	-1.22995600	-2.47804100	-0.26644800
C	1.63687900	-2.96742000	2.30959900
H	2.14966200	-0.91857800	1.91051600
C	0.76816100	-4.02214400	2.01901300
H	-0.94185100	-4.66076400	0.86980000
H	2.42547800	-3.09470300	3.04608000
H	0.88317400	-4.97518500	2.52837800
C	1.70517400	0.20353500	-1.31136800
C	2.69121500	-0.78032500	-1.46798400
C	1.74169000	1.35124000	-2.12321700
C	3.70528800	-0.61231200	-2.41275000
H	2.66766000	-1.67728100	-0.85792000
C	2.75599600	1.51323100	-3.06509400
H	0.97906000	2.11817600	-2.01722300
C	3.73989900	0.53206500	-3.21000100
H	4.46598000	-1.37968400	-2.52594100
H	2.77624000	2.40354000	-3.68723800
H	4.52926400	0.65867800	-3.94583500
C	0.44013400	1.34775500	1.08045900
C	-0.69886800	1.72234900	1.81123400
C	1.67130200	1.97129500	1.33512800
C	-0.59761800	2.71527900	2.78470200
H	-1.64763400	1.23653800	1.59157100
C	1.76191900	2.96123200	2.31490200
H	2.55455600	1.69759100	0.76576300
C	0.62896500	3.33318400	3.04006900
H	-1.48199100	3.00728900	3.34420500
H	2.71679700	3.44338200	2.50588200
H	0.70134500	4.10554700	3.80125300

intB			
C	1.12292900	-1.06549000	-0.38070700
H	0.95156900	-2.06730100	-0.79226400
C	2.29905900	-0.44320300	-0.19371200
H	2.56696900	1.30662500	0.56207600
C	3.53426400	-1.06854300	-0.63343800
O	4.00557700	-0.94901600	-1.75659800
O	4.18722600	-1.71827600	0.37530700
C	5.48492200	-2.21455800	0.03047200
H	6.14205800	-1.40194000	-0.29365500
H	5.87394200	-2.67618000	0.94009800
H	5.42476500	-2.95465000	-0.77369200
P	-0.40668800	-0.18816700	-0.04294600
C	-1.75970900	-1.20810600	-0.72745200
C	-1.77688100	-2.58540800	-0.44362300
C	-2.75702500	-0.66416900	-1.54888700
C	-2.78089900	-3.39794700	-0.96902800
H	-1.00974100	-3.02444400	0.18778400
C	-3.75838600	-1.48277800	-2.07286400
H	-2.74923700	0.39450800	-1.78620300
C	-3.77235600	-2.84781000	-1.78419200
H	-2.78515200	-4.46068200	-0.74428500
H	-4.52514400	-1.05179700	-2.71041500
H	-4.55173400	-3.48304200	-2.19583900

C	-0.77663700	0.11046100	1.72176800
C	0.04959200	0.98896000	2.44600600
C	-1.83894900	-0.54488200	2.36413400
C	-0.19633900	1.19303000	3.80400900
H	0.87662600	1.51241100	1.96221800
C	-2.07209900	-0.32941700	3.72258900
H	-2.48610400	-1.21807400	1.81199200
C	-1.25039900	0.53770800	4.44391300
H	0.44565400	1.86957600	4.36110100
H	-2.89701500	-0.83869600	4.21328800
H	-1.43273500	0.70344000	5.50249300
C	-0.44090400	1.43129700	-0.87878100
C	-1.34554200	2.42385700	-0.47015300
C	0.41195800	1.66968400	-1.96764500
C	-1.40207000	3.63995700	-1.15078500
H	-1.99266900	2.25482100	0.38545400
C	0.35162000	2.89100000	-2.64013500
H	1.13658500	0.91749700	-2.26094700
C	-0.55380500	3.87396800	-2.23519600
H	-2.09994900	4.40682600	-0.82678500
H	1.01953600	3.07446800	-3.47686300
H	-0.59391900	4.82481000	-2.75966000
O	2.53394700	2.23053300	0.94921000
H	2.33795700	2.78273200	0.17718500

TS1

C	1.47502200	0.10427400	-0.63545500
H	1.48125300	-0.04725300	-1.71541400
C	2.53401600	0.35002100	0.14618400
H	1.98685000	0.43343800	1.40583400
C	3.89240100	0.51675000	-0.36766000
O	4.37175300	1.57290500	-0.74227100
O	4.60978400	-0.63863500	-0.28803500
C	5.98875900	-0.51919300	-0.66222400
H	6.50495200	0.20276800	-0.02274400
H	6.41475000	-1.51541300	-0.53222300
H	6.08608500	-0.19644000	-1.70301500
P	-0.21036300	0.02801600	0.05620000
C	-1.16446000	-0.23220800	-1.52624400
C	-0.87434800	-1.37355200	-2.29528700
C	-2.13987900	0.65853800	-1.99320700
C	-1.53524000	-1.61115900	-3.49852900
H	-0.13057800	-2.08701700	-1.94911900
C	-2.80661600	0.41749200	-3.19828200
H	-2.38464200	1.54696600	-1.42111900
C	-2.50515800	-0.71408700	-3.95373100
H	-1.29554300	-2.49765500	-4.07950500
H	-3.56048700	1.11993000	-3.54370100
H	-3.02202000	-0.89902500	-4.89157100
C	-0.71690200	-1.47622200	0.97571500
C	0.22732400	-2.27281800	1.63817300
C	-2.06177800	-1.87570700	0.94817400
C	-0.17559700	-3.45067900	2.26497400
H	1.26298300	-1.96133900	1.67601000
C	-2.46255900	-3.04190700	1.60222300
H	-2.79864000	-1.28789800	0.40893900
C	-1.51897500	-3.83329200	2.25706400
H	0.56343400	-4.06583100	2.77065700
H	-3.50867200	-3.33516900	1.58592700
H	-1.82793800	-4.74790500	2.75616700
C	-0.91770500	1.59303900	0.68256400
C	-1.91744500	1.60690000	1.66453000
C	-0.45320600	2.80326700	0.14701600
C	-2.45093200	2.82088400	2.09841800
H	-2.26578200	0.67688200	2.10241500
C	-0.98946900	4.01360200	0.58925800
H	0.33734100	2.80180500	-0.59777400
C	-1.99052900	4.02520100	1.56207200
H	-3.22235600	2.82377200	2.86365500
H	-0.61855400	4.94677500	0.17456000
H	-2.40549200	4.96865000	1.90585200
O	1.02602000	0.36216400	2.13687200
H	0.87773400	1.27337700	2.43616300

intC

C	0.74297800	0.31158000	0.69003800
H	0.56093300	1.10034700	1.42278500
C	2.02480200	-0.07264600	0.59572600
H	2.37219800	-0.82060000	-0.10971900
C	3.05789000	0.52304000	1.47795100
O	2.87250900	1.34510600	2.35557400
O	4.28440100	0.01665500	1.18730700
C	5.35857600	0.52392100	1.98905200
H	5.19211500	0.29827000	3.04635900
H	6.25789000	0.02300700	1.62811800
H	5.45011200	1.60758600	1.87238600
P	-0.74643200	-0.07440300	-0.48049300
C	-1.95872200	-0.43395900	0.88190200
C	-1.55939100	-0.56376100	2.22398100
C	-3.31681300	-0.62650900	0.57542200
C	-2.48779100	-0.85657600	3.22421700
H	-0.51837900	-0.44648300	2.50195100
C	-4.24501500	-0.91097400	1.57659200
H	-3.63173400	-0.57716800	-0.45884200
C	-3.83519800	-1.02397500	2.90535400
H	-2.15238100	-0.95343400	4.25327500
H	-5.28980500	-1.05335200	1.31328600
H	-4.55828000	-1.24831600	3.68518600
C	-0.63011600	1.74573600	-0.94165300
C	-1.05158700	2.73677800	-0.04289200
C	-0.12748100	2.13621500	-2.19268200
C	-0.97700200	4.08713000	-0.39022500
H	-1.44882500	2.45773300	0.92929400
C	-0.03146500	3.48709300	-2.52727300
H	0.19386500	1.38597100	-2.90942700
C	-0.46005300	4.46665500	-1.62915200
H	-1.31884500	4.84150800	0.31353300
H	0.37202000	3.77349400	-3.49508600
H	-0.39300500	5.51819400	-1.89454400
C	0.04619700	-1.62441300	-1.15021100
C	0.39404300	-2.65150900	-0.26141700
C	0.29699800	-1.80099200	-2.51742700
C	0.97313300	-3.83126800	-0.72985800
H	0.20753100	-2.53707300	0.80205000
C	0.90812600	-2.96711700	-2.98118500
H	-0.01214800	-1.03851600	-3.22258800
C	1.24289400	-3.98747100	-2.09039500
H	1.21821700	-4.62488700	-0.02893800

H	1.10687900	-3.08293500	-4.04349000
H	1.70540600	-4.90125000	-2.45412500
O	-1.90023400	-0.25998000	-1.80399500
H	-2.36070200	0.57782700	-1.97035400

TS2

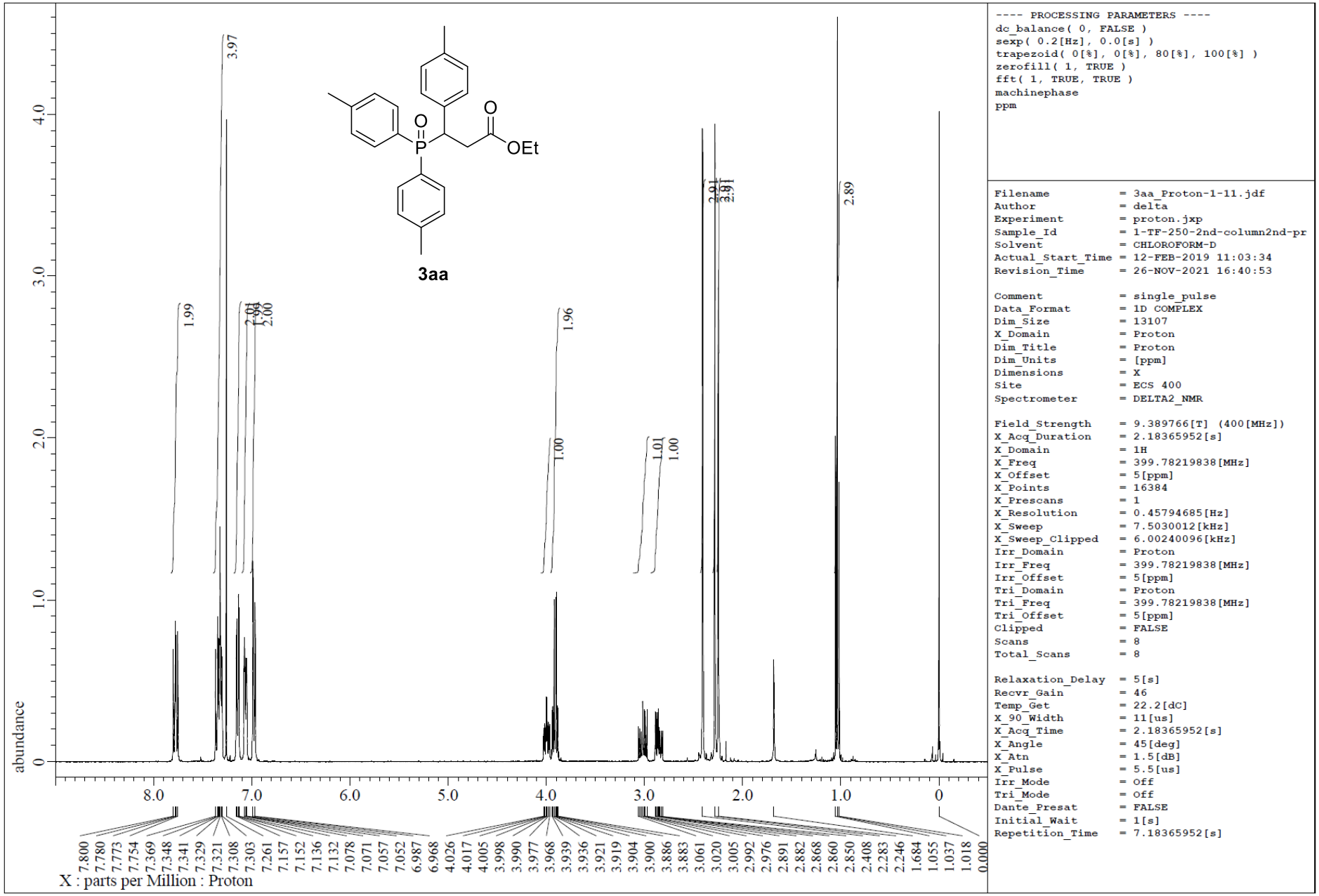
C	0.88214100	0.49800900	0.32881800
H	0.96809100	0.13393900	1.35078100
C	1.73016100	1.53317600	-0.06269100
H	1.61113600	2.06316600	-1.00084600
C	2.90072400	1.78548200	0.73685400
O	3.19768000	1.23764200	1.79445800
O	3.67986600	2.78171300	0.19367000
C	4.84074700	3.11138900	0.95407300
H	5.50198700	2.24568100	1.06244400
H	5.34565700	3.90395400	0.39704700
H	4.57277700	3.46542600	1.95508600
P	-0.62452700	0.09779100	-0.45245000
O	-0.53691600	-0.15047700	-2.06891700
H	-1.04732000	0.54139600	-2.52847300
C	-1.80340700	1.52999300	-0.44724000
C	-3.11204200	1.37044900	-0.94188700
C	-1.41802700	2.77829700	0.06782900
C	-4.00755500	2.43819100	-0.93531300
H	-3.44016400	0.40318000	-1.31674600
C	-2.32135800	3.84375600	0.07784400
H	-0.40948400	2.91117000	0.44713000
C	-3.61170900	3.67777500	-0.42537400
H	-5.01488100	2.30213400	-1.31946500
H	-2.01129500	4.80552200	0.47700200
H	-4.31070500	4.50976900	-0.41787200
C	-1.58356600	-1.21402100	0.34367500
C	-1.92070000	-2.37326700	-0.36727900
C	-2.02737400	-1.04596000	1.66337500
C	-2.69727400	-3.35793200	0.24181600
H	-1.55862700	-2.50630200	-1.38146800
C	-2.78558000	-2.04565800	2.27342800
H	-1.78845800	-0.14021500	2.21425700
C	-3.12421100	-3.19846600	1.56224300
H	-2.95748400	-4.25605800	-0.31102600
H	-3.11690200	-1.91904600	3.30012000
H	-3.72080400	-3.97250300	2.03706700
C	1.28923100	-1.38887300	-0.42951900
C	1.36812600	-2.45765100	0.46777600
C	2.11680500	-1.39036500	-1.55449700
C	2.23098300	-3.53178500	0.22429500
H	0.75547200	-2.47134200	1.36804100
C	2.96245500	-2.46867200	-1.81674700
H	2.11681600	-0.53358500	-2.22521900
C	3.02175100	-3.54471500	-0.92523500
H	2.28704100	-4.35405400	0.93471500
H	3.58583700	-2.46662400	-2.70858000
H	3.69228400	-4.37841300	-1.11841100

3

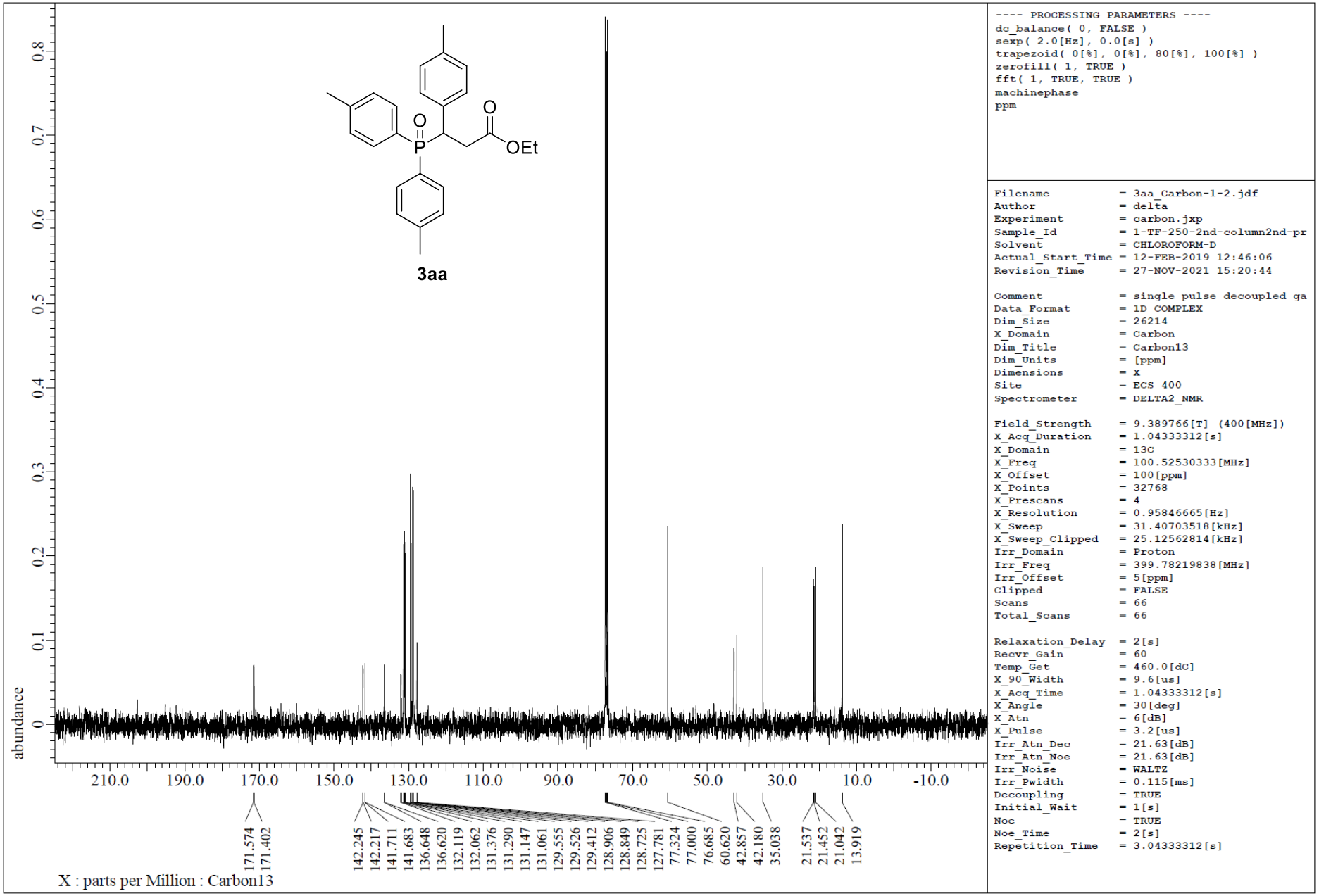
C	0.67732900	-0.75022100	0.80661300
H	1.27364900	-0.11128000	1.46539500
C	1.59764100	-1.91722100	0.39841800
H	1.62586000	-2.64807900	1.21825500
C	3.02290100	-1.43910800	0.17454000
O	3.53559800	-0.49766400	0.74689100
O	3.67853900	-2.23880400	-0.68272900
C	5.03195600	-1.85067700	-0.97084000
H	5.63444500	-1.84069600	-0.05851100
H	5.40675700	-2.59790200	-1.67099700
H	5.04697900	-0.85635100	-1.42383500
P	0.40352600	0.32693900	-0.72624500
O	1.50871200	0.09075100	-1.72455000
H	1.25664800	-2.44555200	-0.49482400
C	0.34479900	2.03884400	-0.07611900
C	-0.70889800	2.92666200	-0.33205900
C	1.46882900	2.49661800	0.63557300
C	-0.65334900	4.24142600	0.13549600
H	-1.57284100	2.59794200	-0.90014700
C	1.52012700	3.80987100	1.09938100
H	2.30995000	1.83006500	0.81073200
C	0.45708300	4.68309200	0.85468400
H	-1.47788200	4.91985500	-0.06696900
H	2.39290200	4.15313000	1.64827000
H	0.49864400	5.70659300	1.21804900
C	-1.22954600	-0.04947400	-1.46575600
C	-1.20214200	-0.50094600	-2.79403100
C	-2.46531800	0.08787600	-0.81200500
C	-2.38971400	-0.81207100	-3.45783400
H	-0.24178700	-0.59694700	-3.29144500
C	-3.64989300	-0.22093700	-1.48065500
H	-2.50830000	0.43042400	0.21685600
C	-3.61367900	-0.67195400	-2.80242200
H	-2.35814200	-1.16031400	-4.48679800
H	-4.60135600	-0.11257400	-0.96699800
H	-4.53916800	-0.91247300	-3.31931400
C	-0.57044800	-1.15716000	1.55939700
C	-1.03746600	-0.35507900	2.61249900
C	-1.28849300	-2.31997100	1.24262200
C	-2.18974600	-0.69749700	3.32101500
H	-0.48797500	0.54435200	2.88041600
C	-2.43602600	-2.66916200	1.95521200
H	-0.95306900	-2.95787100	0.42969700
C	-2.89403500	-1.85804700	2.99473400
H	-2.53027200	-0.06235800	4.13467700
H	-2.97434100	-3.57656400	1.69422400
H	-3.78784500	-2.13093800	3.54925500

5. References

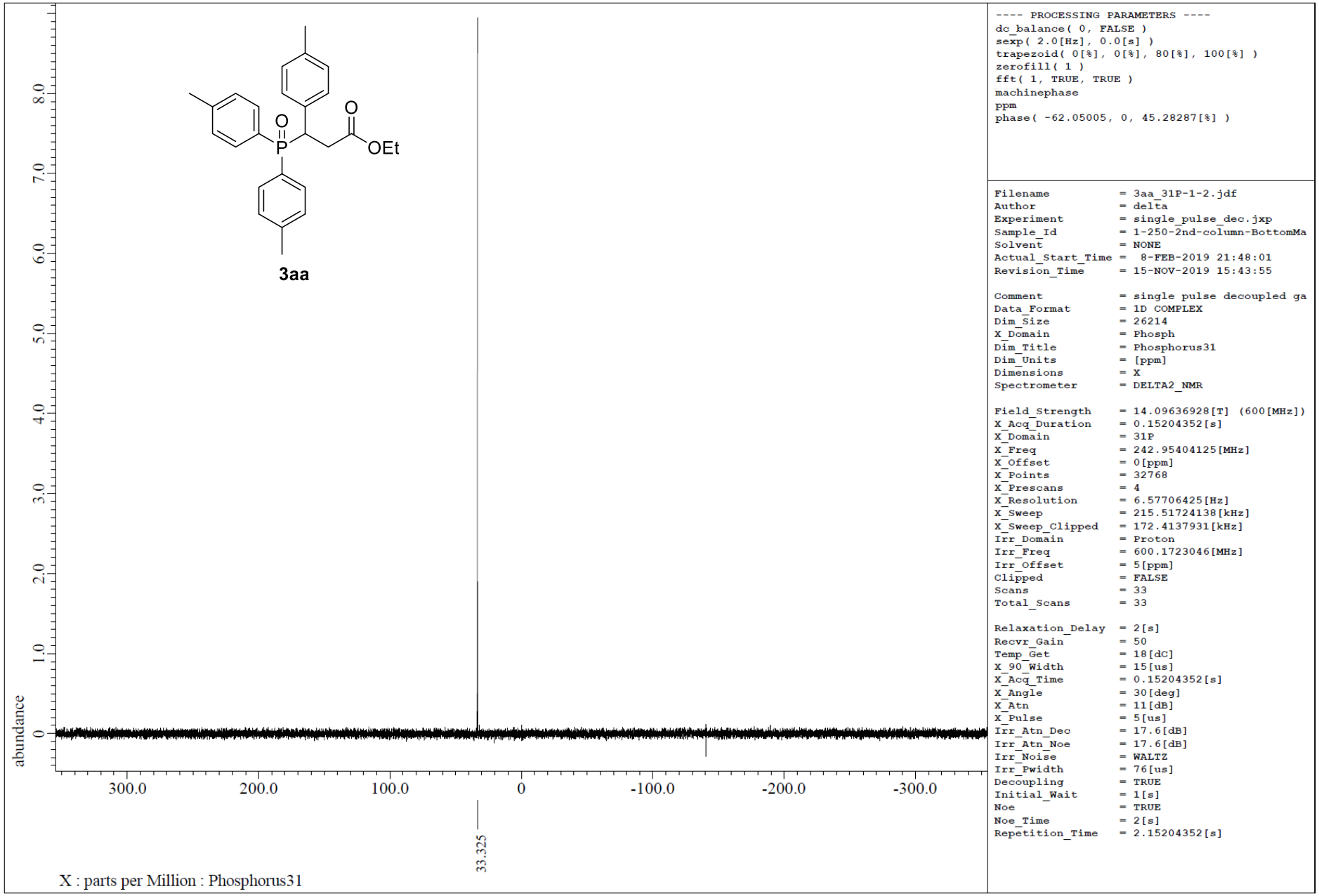
1. **1d**: Liu, Z.; Wu, J.; yang, S. *Org. Lett.* **2017**, *19*, 5434-5437.
2. **1e**: Jeschke, J.; Korb, M.; Rueffer, T.; Gaebler, C.; Lang, H. *Adv. Synth. Catal.* **2015**, *357*, 4069-4081.
3. **1h**: Le Gall, E.; Ben Aissi, K.; Lachaise, I.; Troupel, M. *Synlett*, **2006**, *6*, 954-956.
4. **1i**: Goto, A.; Otake, K.; Kubo, O.; Sawama, Y.; Maegawa, T.; Fujioka, H. *Chem.: Eur. J.* **2012**, *18*, 11423-11432.
5. **1j**: Jeschke, J.; Korb, M.; Rueffer, T.; Gaebler, C.; Lang, H. *Adv. Synth. Catal.* **2015**, *357*, 4069-4081.
6. **1l**: Goto, A.; Otake, K.; Kubo, O.; Sawama, Y.; Maegawa, T.; Fujioka, H. *Chem.: Eur. J.* **2012**, *18*, 11423-11432.
7. **1m**: Elard, M.; Denis, J.; Ferrieira, M.; Bricout, H.; Landy, D.; Tilloy, S.; Monflier, E. *Catal. Today,* **2015**, *247*, 47-54.
8. **2c**: Aioub, A. G.; Higginson, C. J.; Finn, M. G. *Org. Lett.* **2019**, *30*, 406-408.
9. **2d**: Liu, L.; Sun, K.; Su, L.; Dong, J.; Cheng, L.; Zhu, X.; Au, C.; Zhou, Y.; Yin, S. *Org. Lett.* **2018**, *20*, 4023-4027.
10. **2e**: Feray, L.; Bertrand, M. P. *Eur. J. Org. Chem.* **2008**, *18*, 3164-3170.
11. **2f**: Ramachandran, P. V.; Rudd, M. T.; Reddy, M. V. R. *Tetrahedron Lett*. **2005**, *46*, 2547-2549.
12. **2g**: Coles, N. T.; Mahon, M. F.; Webster, R. L. *Chem. Commun*. **2018**, *54*, 10443-10446.
13. **2h**: Andra, L.; Miesch, L. *Org. Biomol. Chem.* **2019**, *17*, 5688-5692.
14. **2i**: Ramachandran, P. V.; Rudd, M. T.; Reddy, M. V. R. *Tetrahedron Lett*. **2005**, *46*, 2547-2549.
15. Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
16. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789
17. Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
18. CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org).



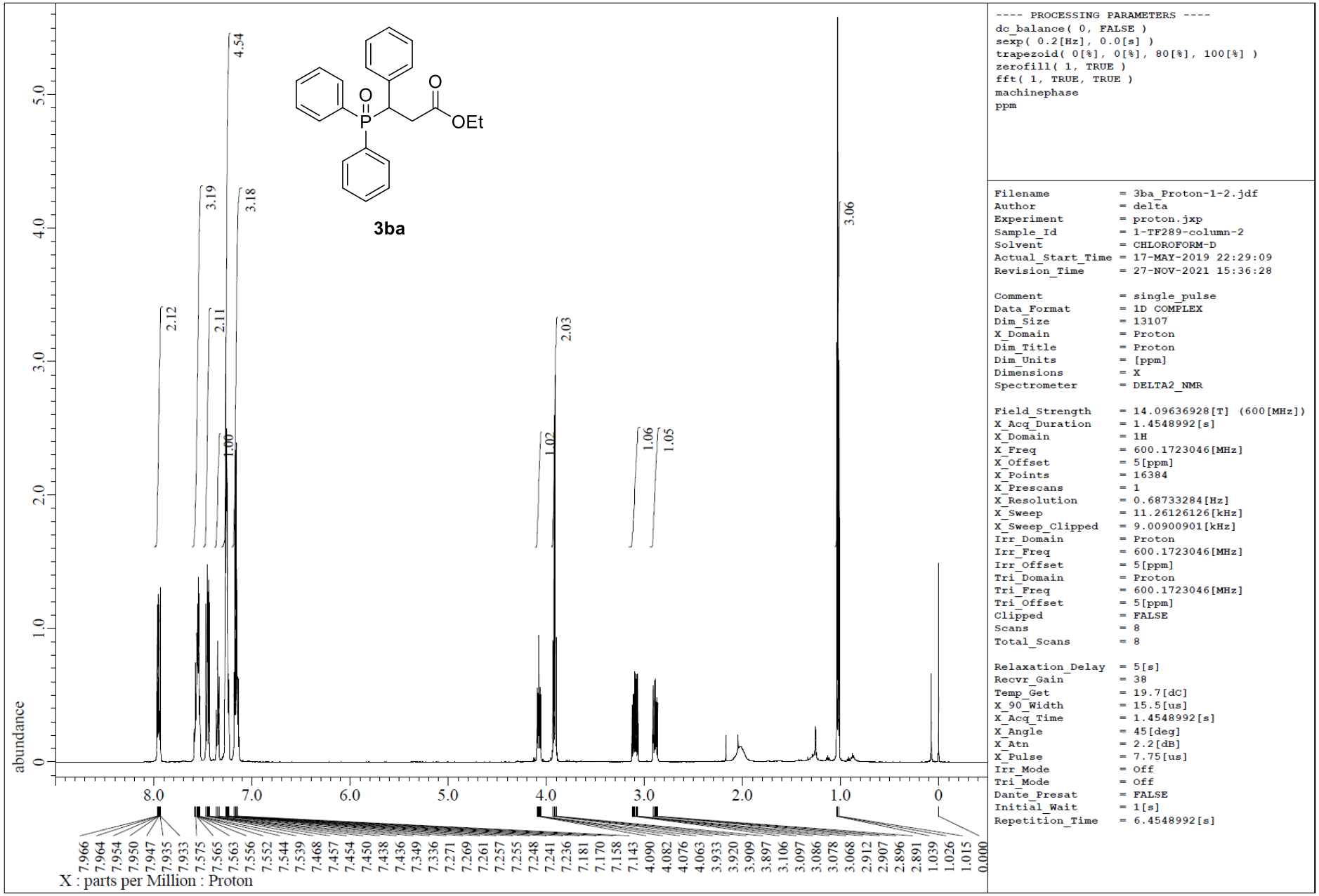
[1] H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



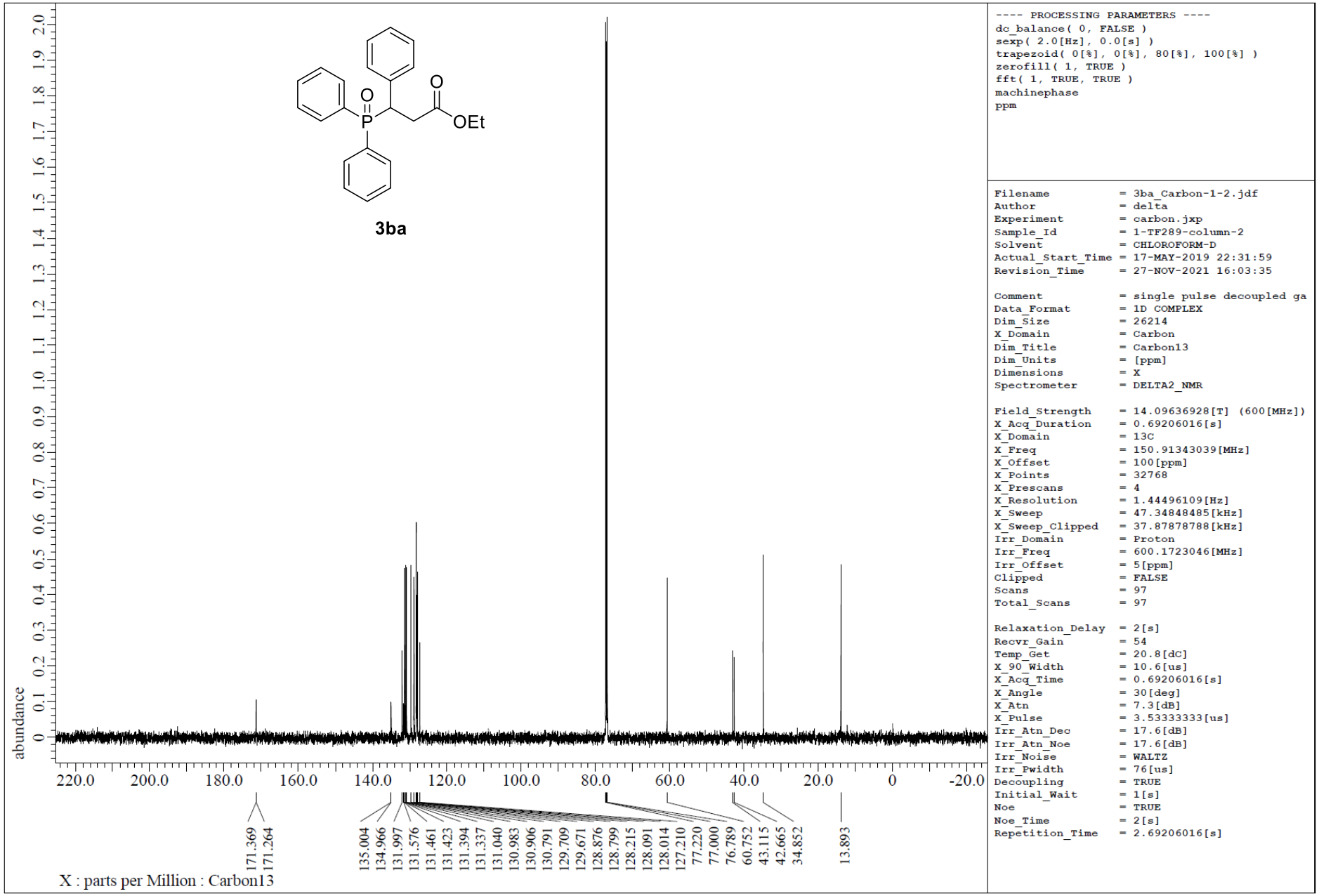
^{13}C NMR spectrum of **3aa** (101 MHz, $CDCl_3$)



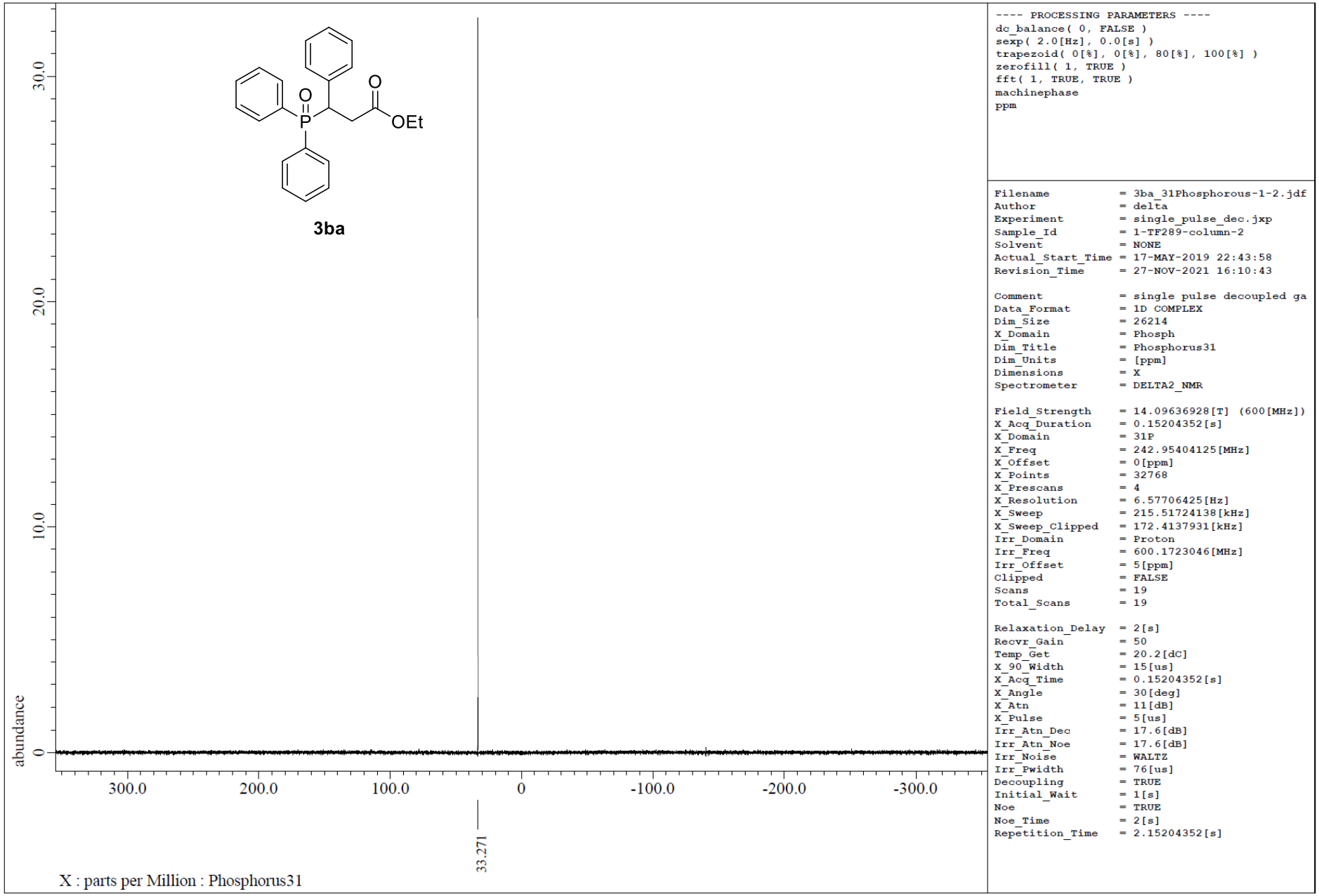
^{31}P NMR spectrum of **3aa** (243 MHz, $CDCl_3$)



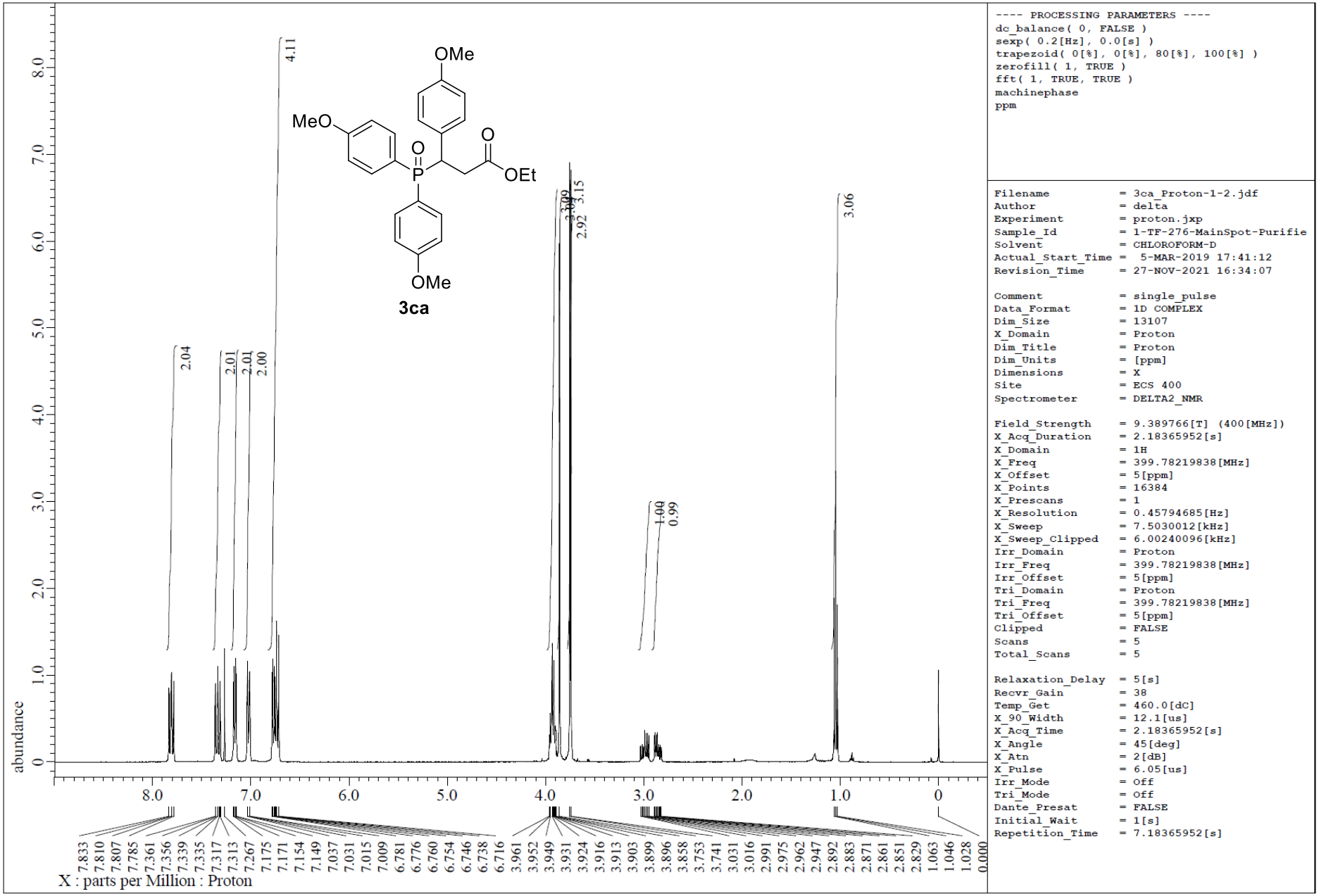
[1] H NMR spectrum of **3ba** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3ba** (151 MHz, $CDCl_3$)



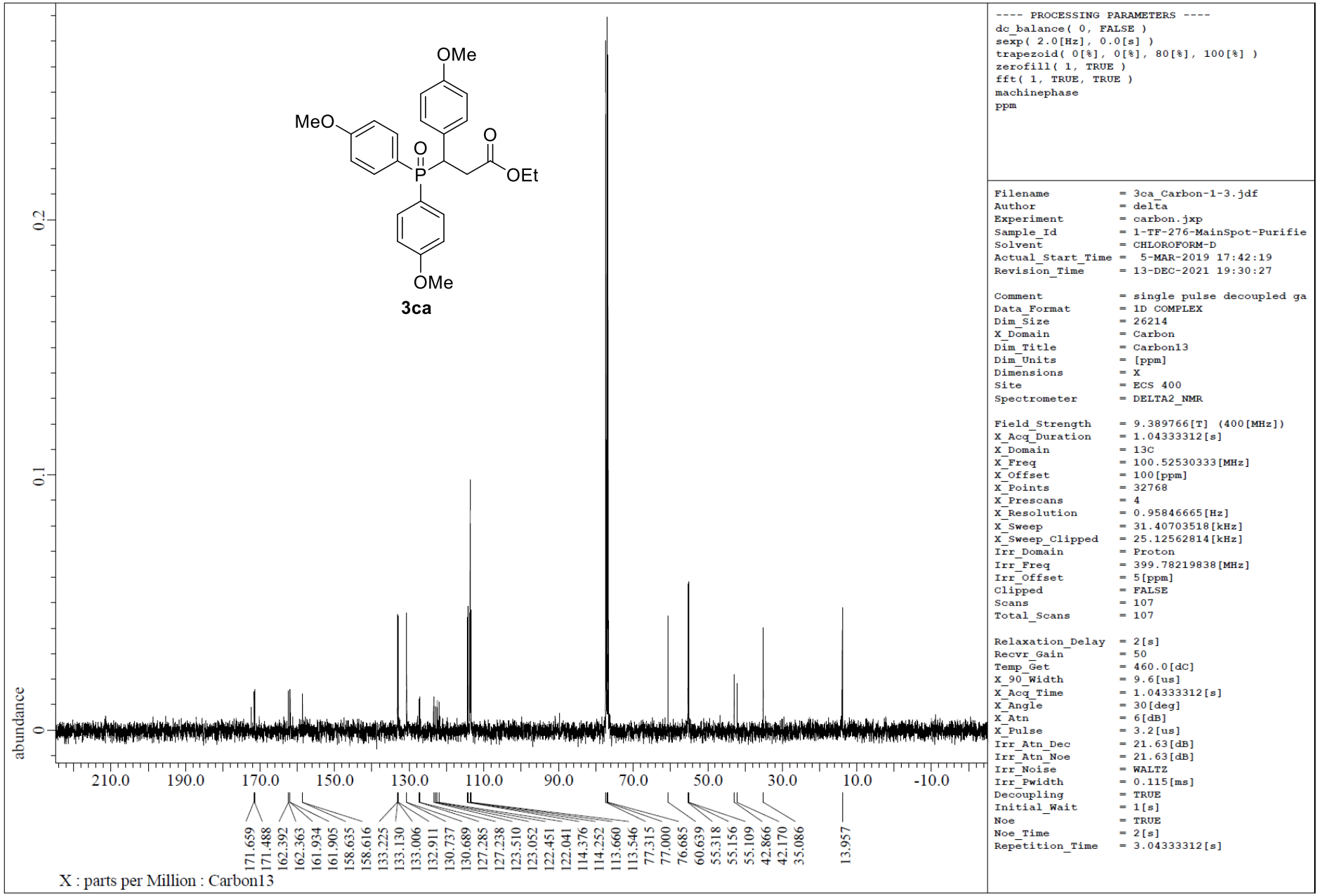
^{31}P NMR spectrum of **3ba** (243 MHz, $CDCl_3$)




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3ca_Proton-1-2.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 1-TF-276-MainSpot-Purifie
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  5-MAR-2019 17:41:12
Revision_Time       = 27-NOV-2021 16:34:07

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 2.18365952[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.45794685[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 5
Total_Scans         = 5

Relaxation_Delay    = 5[s]
Recvr_Gain          = 38
Temp_Get            = 460.0[dC]
X_90_Width          = 12.1[us]
X_Acq_Time          = 2.18365952[s]
X_Angle             = 45[deg]
X_Atn               = 2[dB]
X_Pulse             = 6.05[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 7.18365952[s]
```

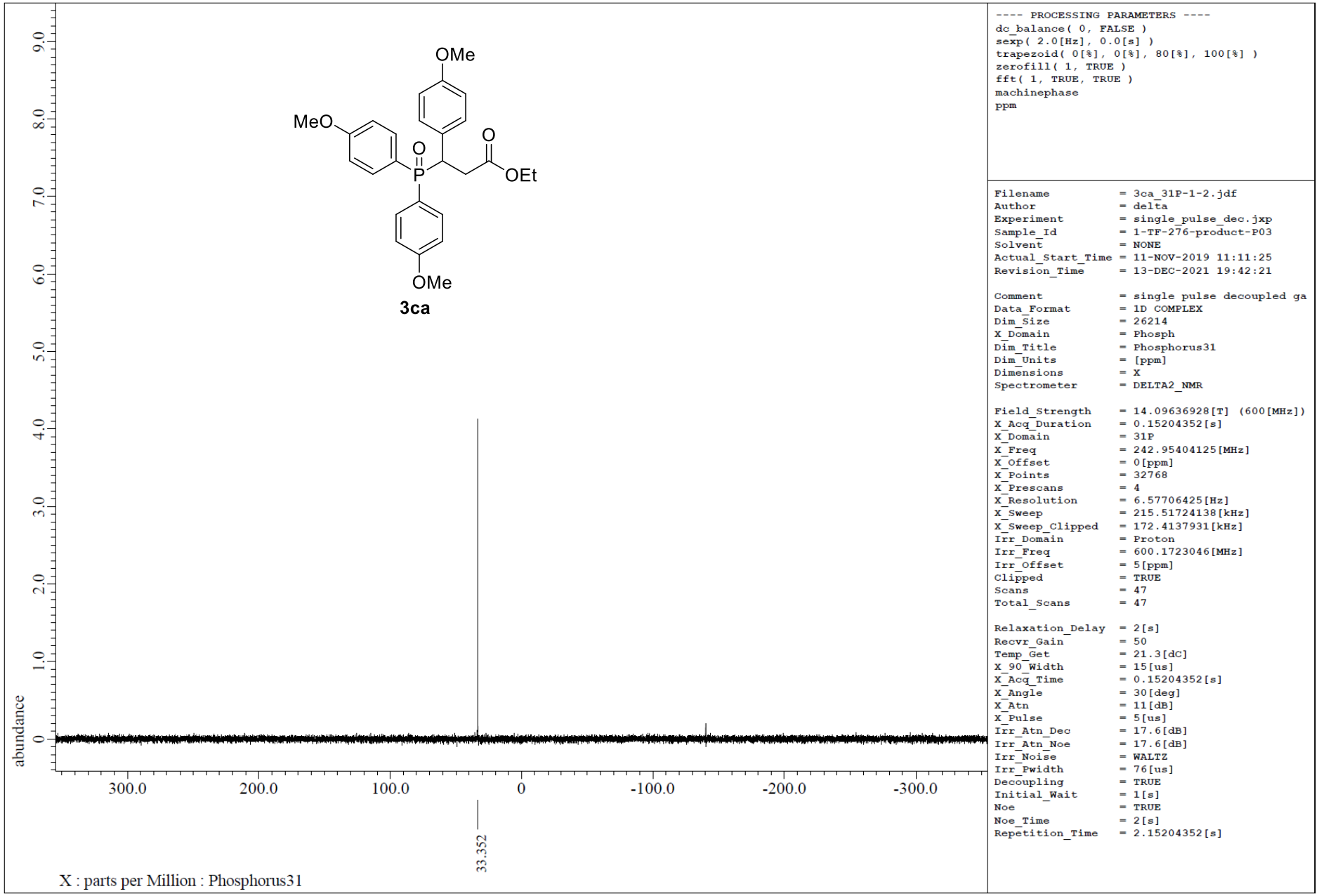
^{1}H NMR spectrum of **3ca** (400 MHz, $CDCl_3$)



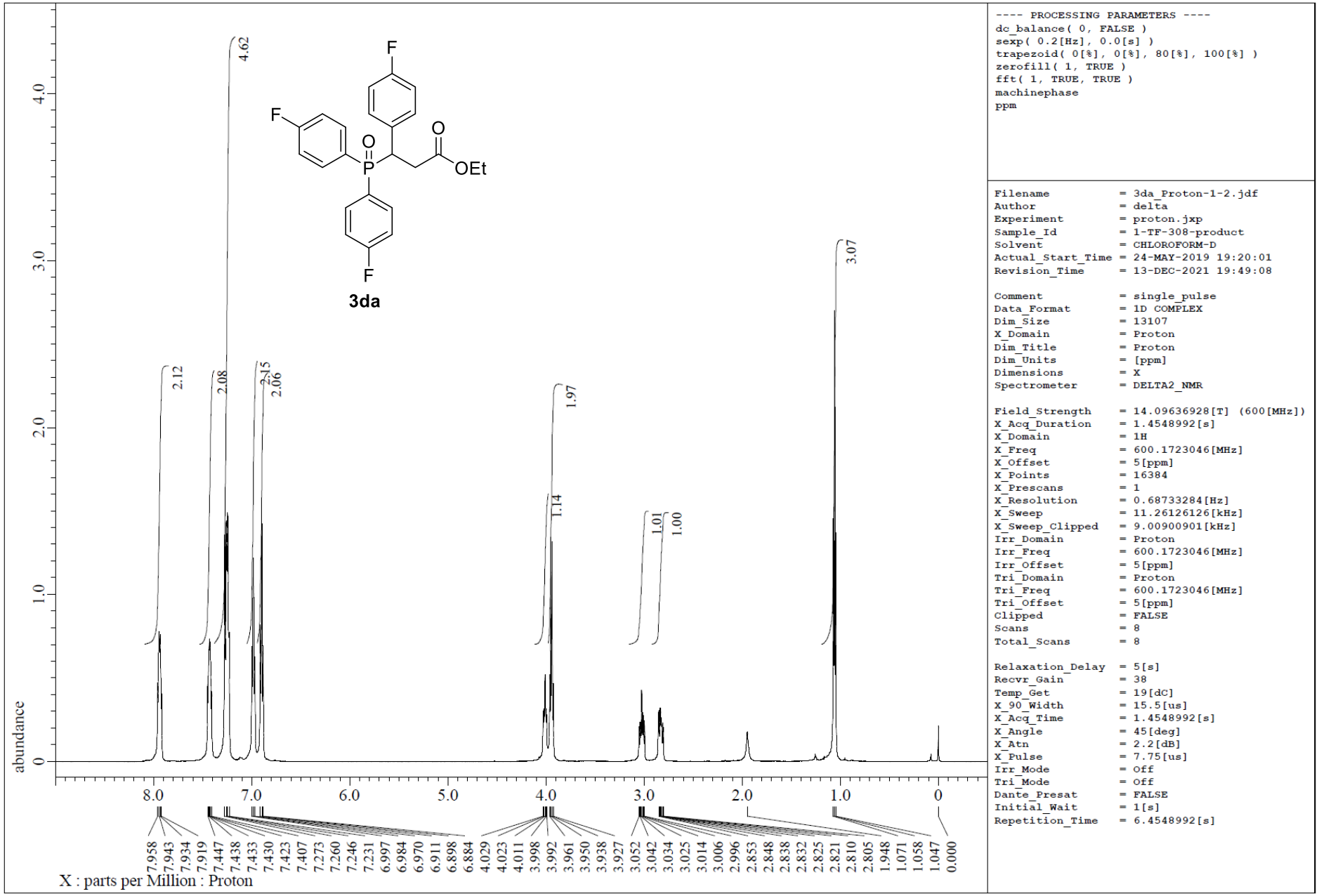

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3ca_Carbon-1-3.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 1-TF-276-MainSpot-Purifie
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  5-MAR-2019 17:42:19
Revision_Time       = 13-DEC-2021 19:30:27

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 107
Total_Scans         = 107

Relaxation_Delay    = 2[s]
Recvr_Gain          = 50
Temp_Get            = 460.0[dC]
X_90_Width          = 9.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
X_Atn               = 6[dB]
X_Pulse             = 3.2[us]
Irr_Atn_Dec         = 21.63[dB]
Irr_Atn_Noe         = 21.63[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 3.04333312[s]
```

^{13}C NMR spectrum of **3ca** (101 MHz, $CDCl_3$)



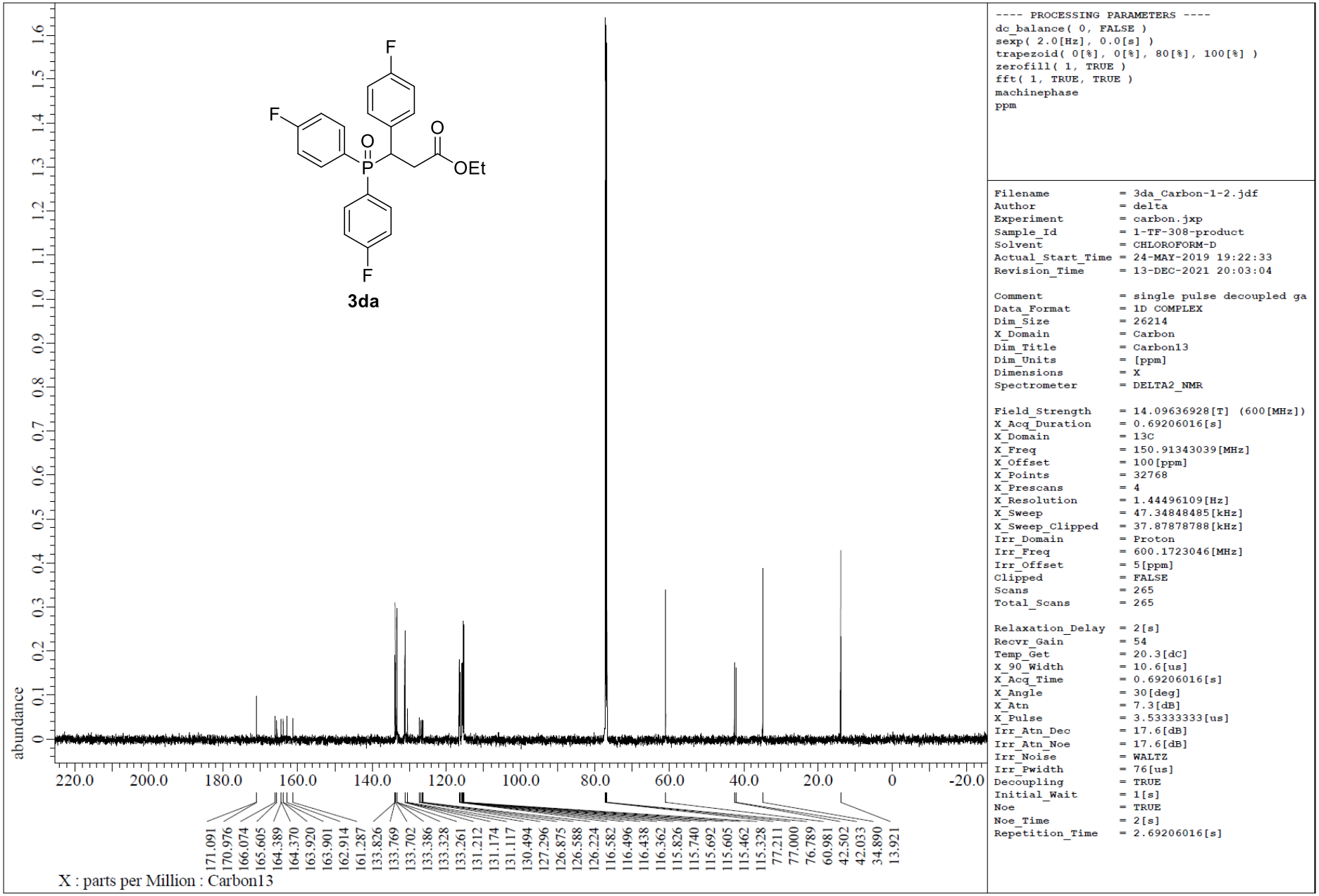
^{31}P NMR spectrum of **3ca** (243 MHz, $CDCl_3$)



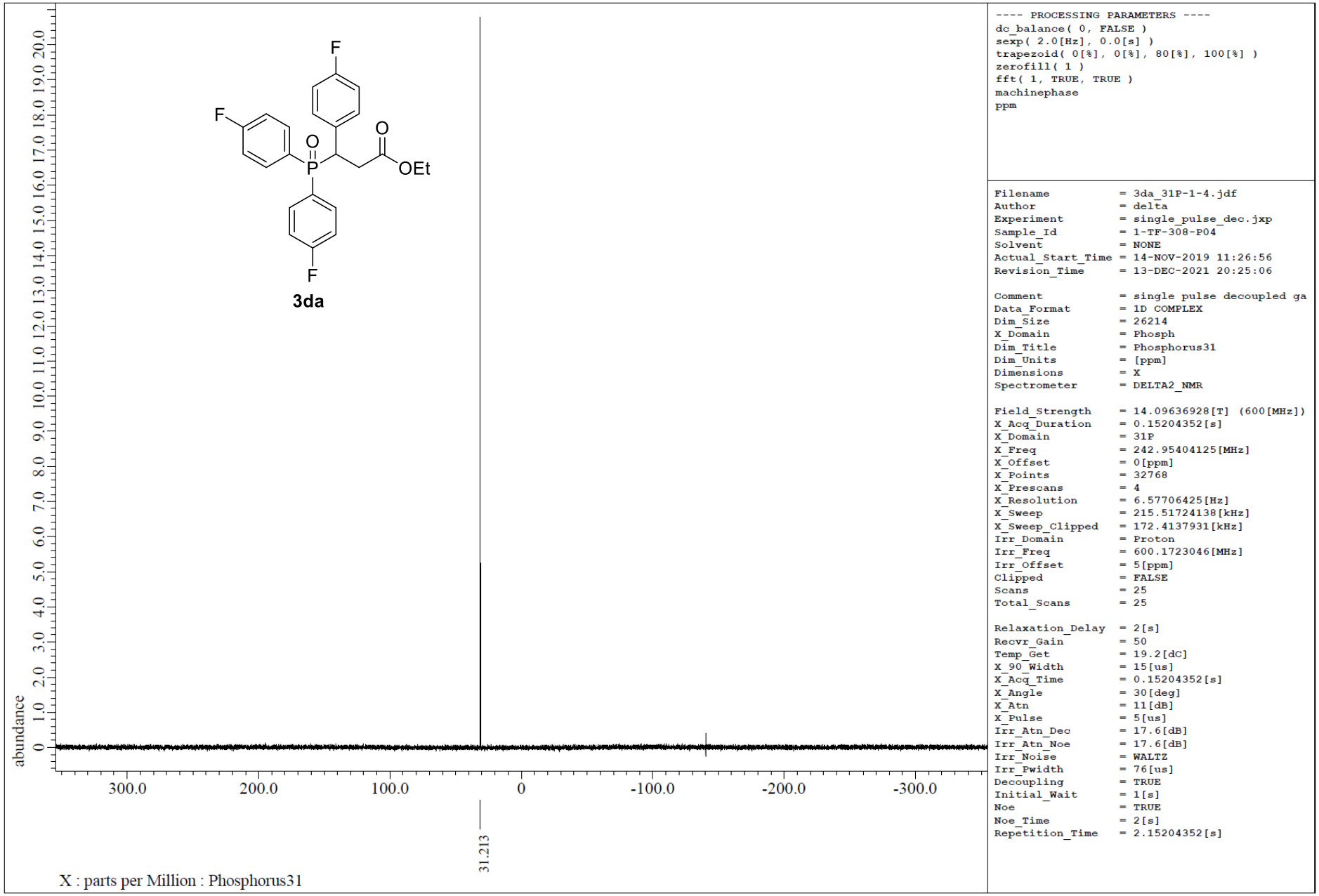

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3da_Proton-1-2.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 1-TF-308-product
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 24-MAY-2019 19:20:01
Revision_Time       = 13-DEC-2021 19:49:08

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 38
Temp_Get            = 19[dC]
X_90_Width          = 15.5[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 2.2[dB]
X_Pulse             = 7.75[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

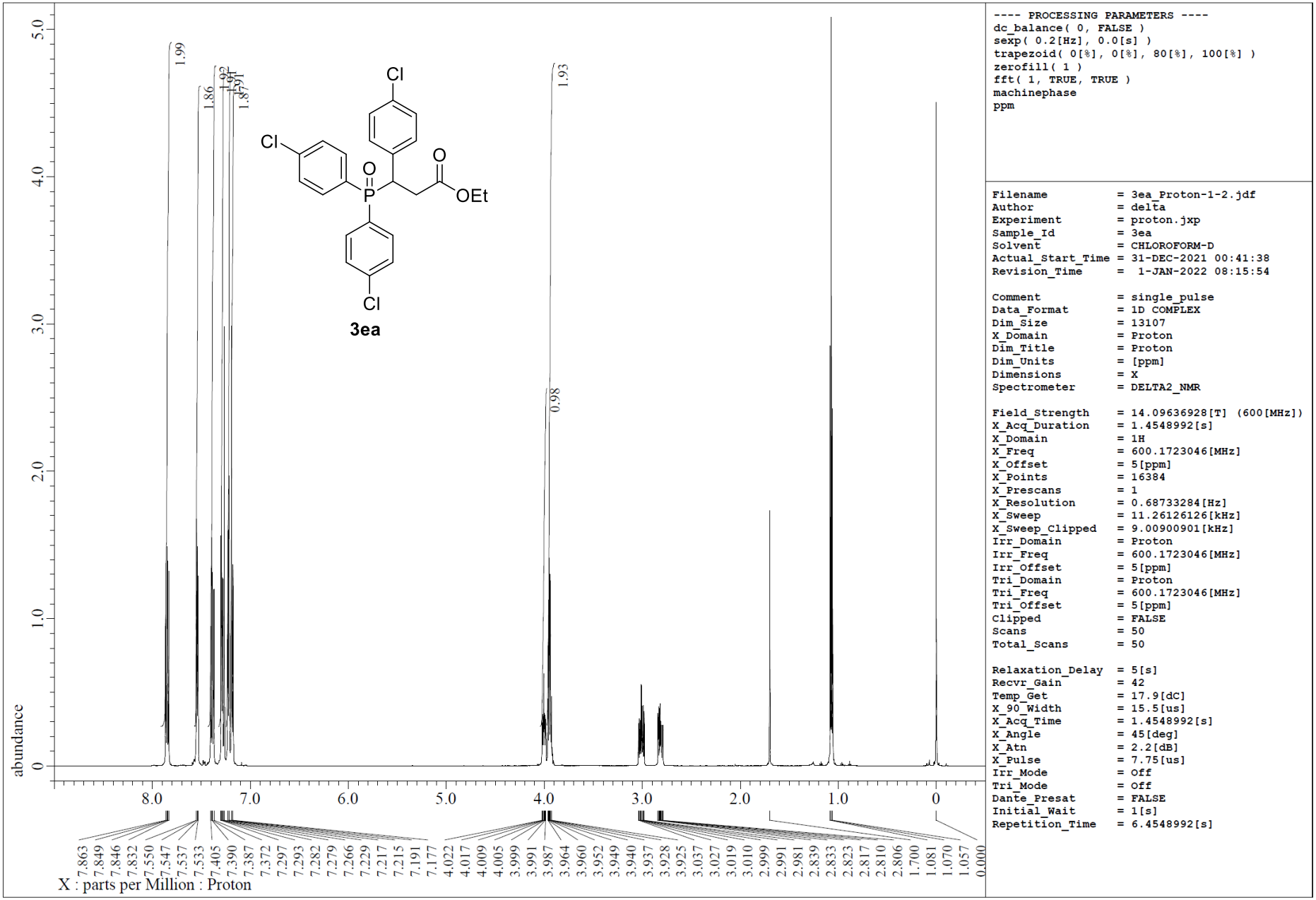
^{1}H NMR spectrum of **3da** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3da** (151 MHz, $CDCl_3$)



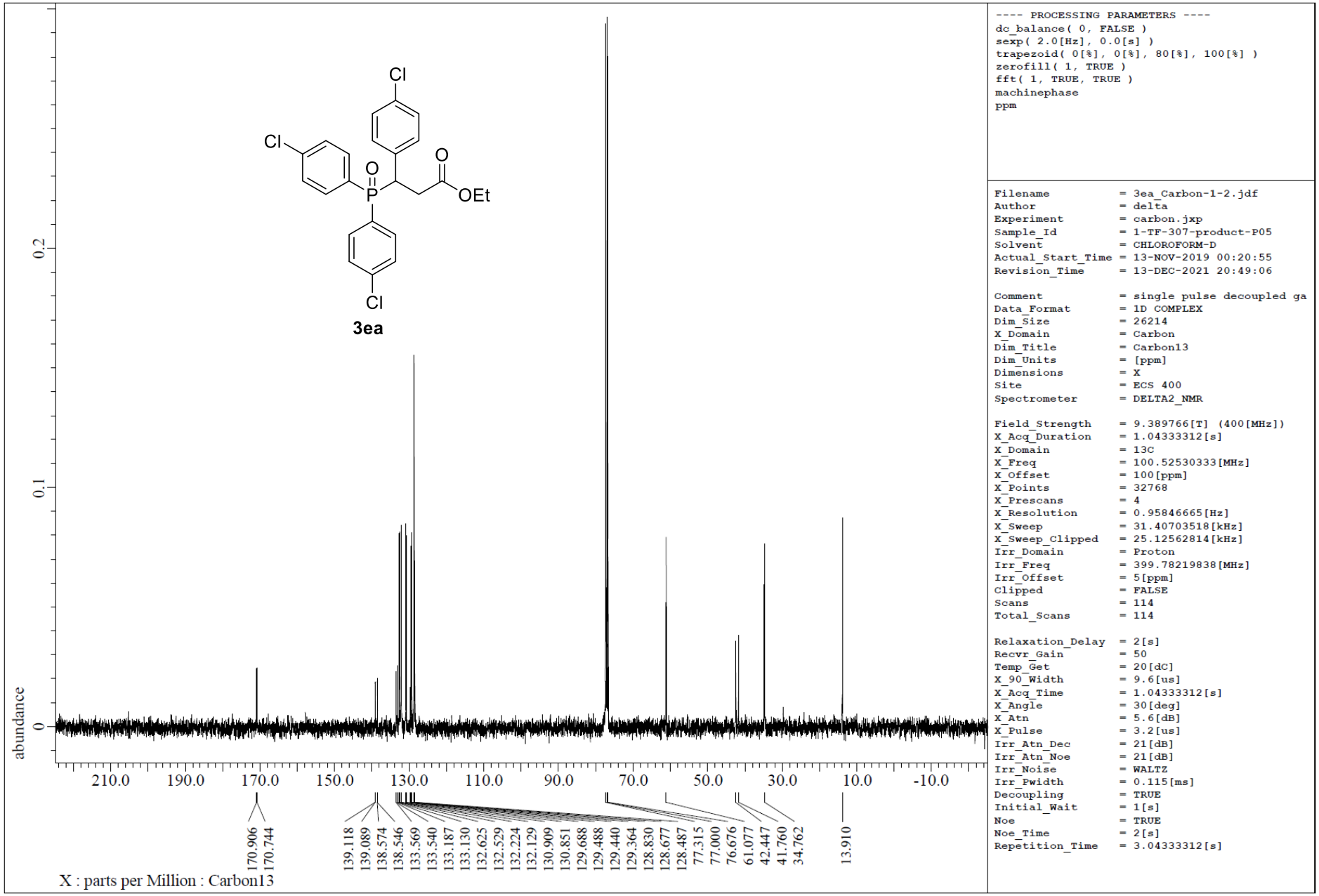
^{31}P NMR spectrum of **3da** (243 MHz, $CDCl_3$)



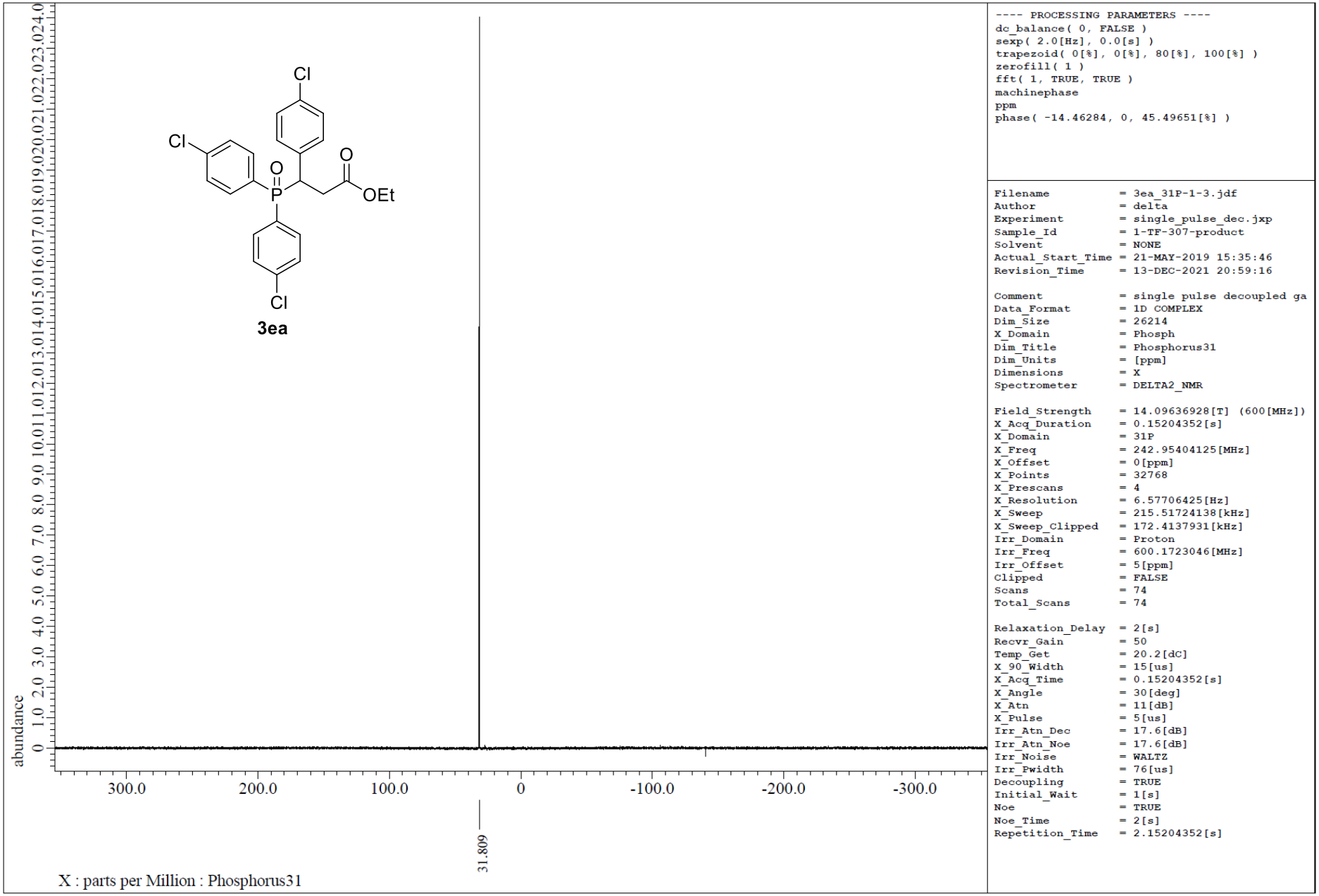

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3ea_Proton-1-2.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 3ea
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 31-DEC-2021 00:41:38
Revision_Time       =  1-JAN-2022 08:15:54

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 1.4548992[s]
X_Domain            = 1H
X_Freq              = 600.1723046[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.68733284[Hz]
X_Sweep             = 11.26126126[kHz]
X_Sweep_Clipped     = 9.00900901[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 600.1723046[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 50
Total_Scans         = 50

Relaxation_Delay    = 5[s]
Recvr_Gain          = 42
Temp_Get            = 17.9[dC]
X_90_Width          = 15.5[us]
X_Acq_Time          = 1.4548992[s]
X_Angle             = 45[deg]
X_Atn               = 2.2[dB]
X_Pulse             = 7.75[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 6.4548992[s]
```

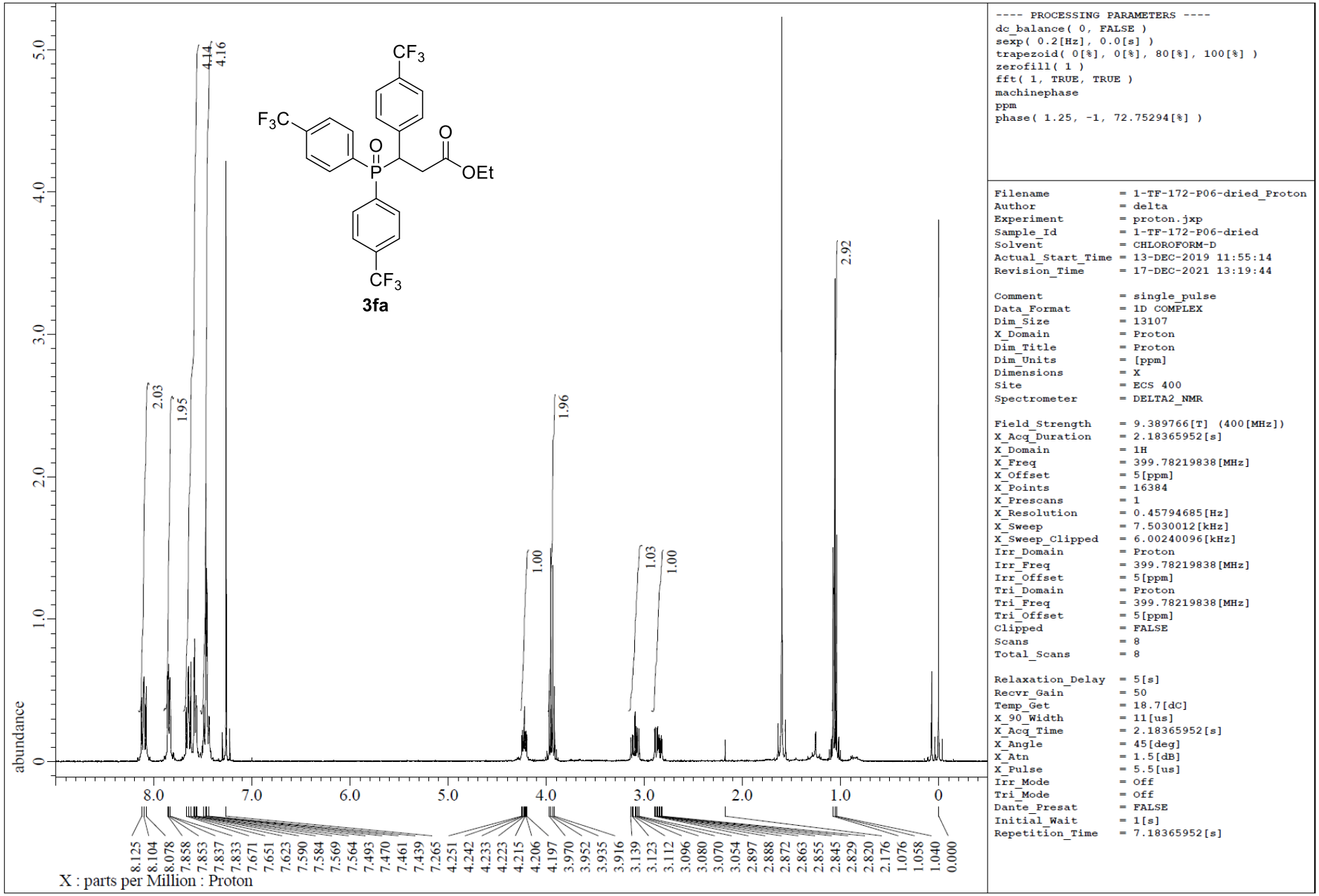
^{1}H NMR spectrum of **3ea** (600 MHz, $CDCl_3$)



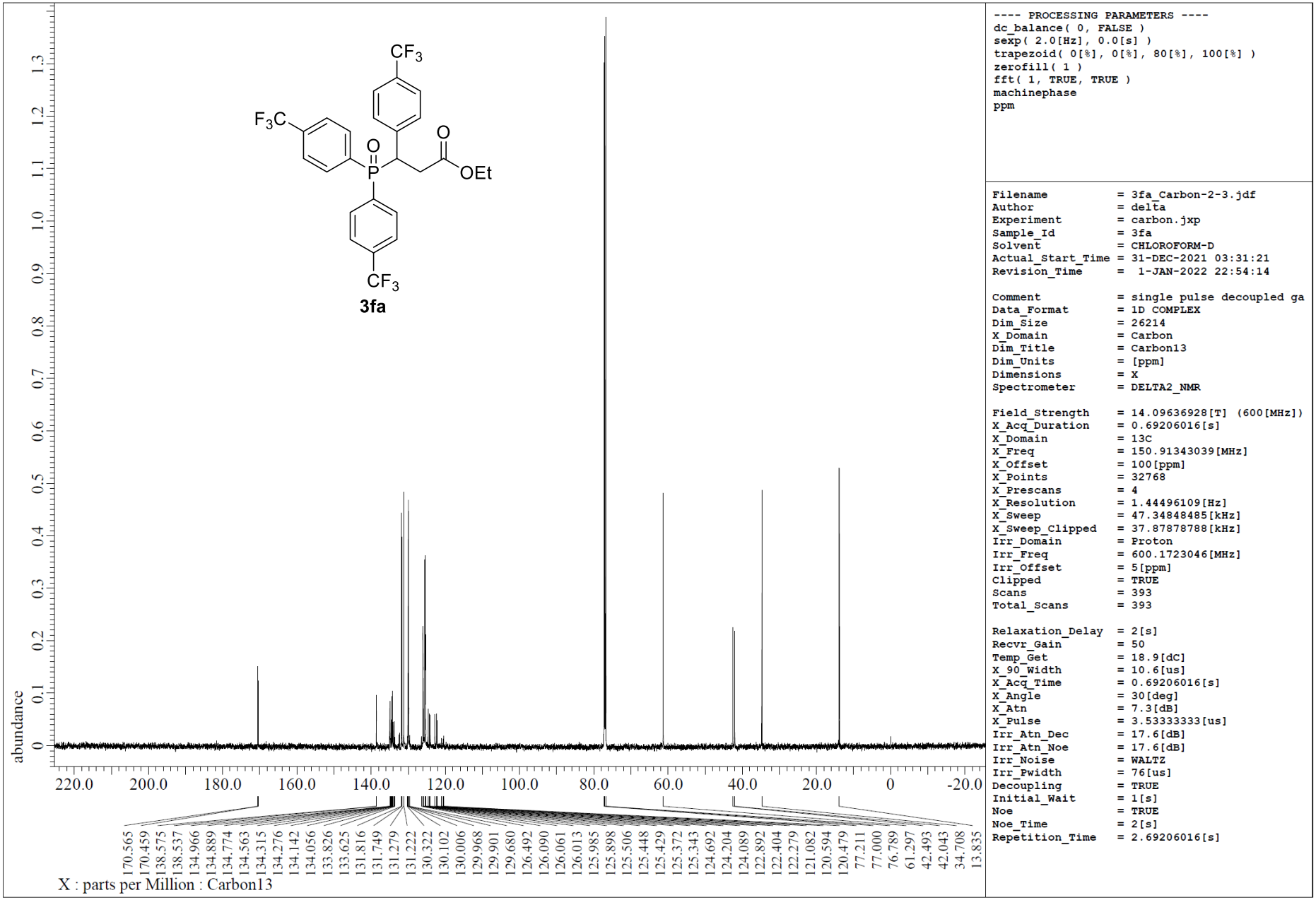
^{13}C NMR spectrum of **3ea** (101 MHz, $CDCl_3$)



^{31}P NMR spectrum of **3ea** (243 MHz, $CDCl_3$)



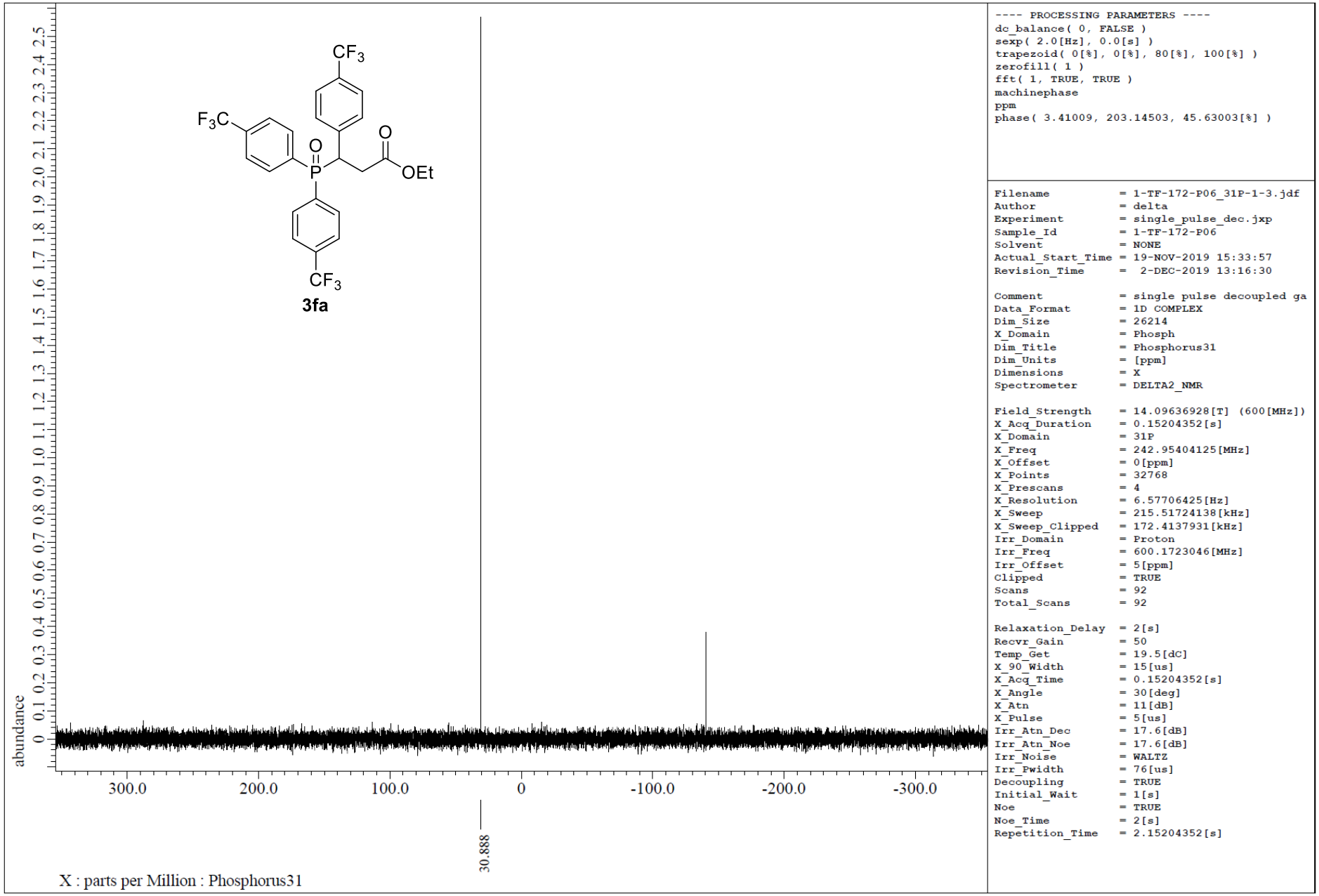
[1] H NMR spectrum of **3fa** (400 MHz, $CDCl_3$)



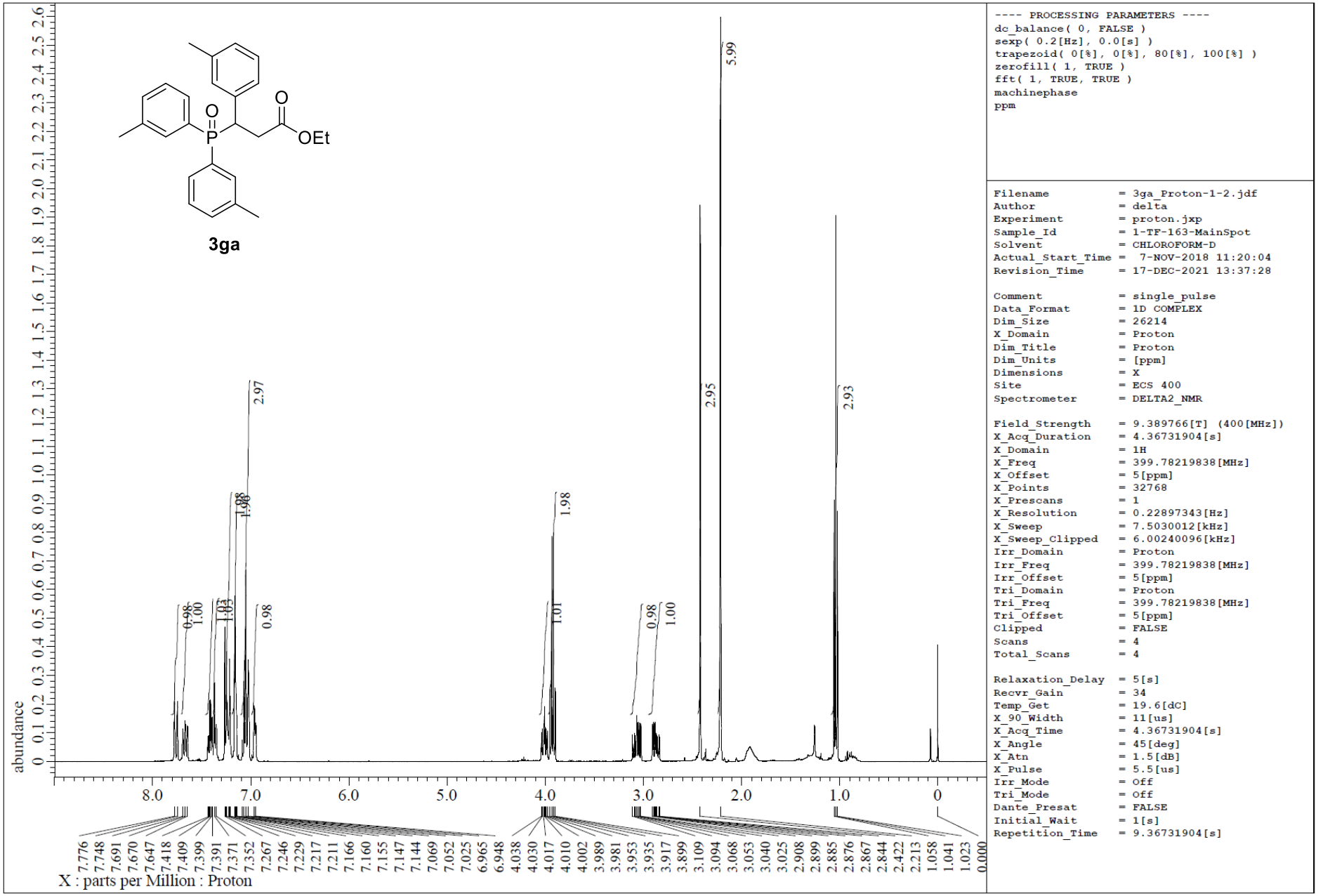

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3fa_Carbon-2-3.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 3fa
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 31-DEC-2021 03:31:21
Revision_Time       =  1-JAN-2022 22:54:14

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = TRUE
Scans               = 393
Total_Scans         = 393

Relaxation_Delay    = 2[s]
Recvr_Gain          = 50
Temp_Get            = 18.9[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 7.3[dB]
X_Pulse             = 3.53333333[us]
Irr_Atn_Dec         = 17.6[dB]
Irr_Atn_Noe         = 17.6[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 76[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

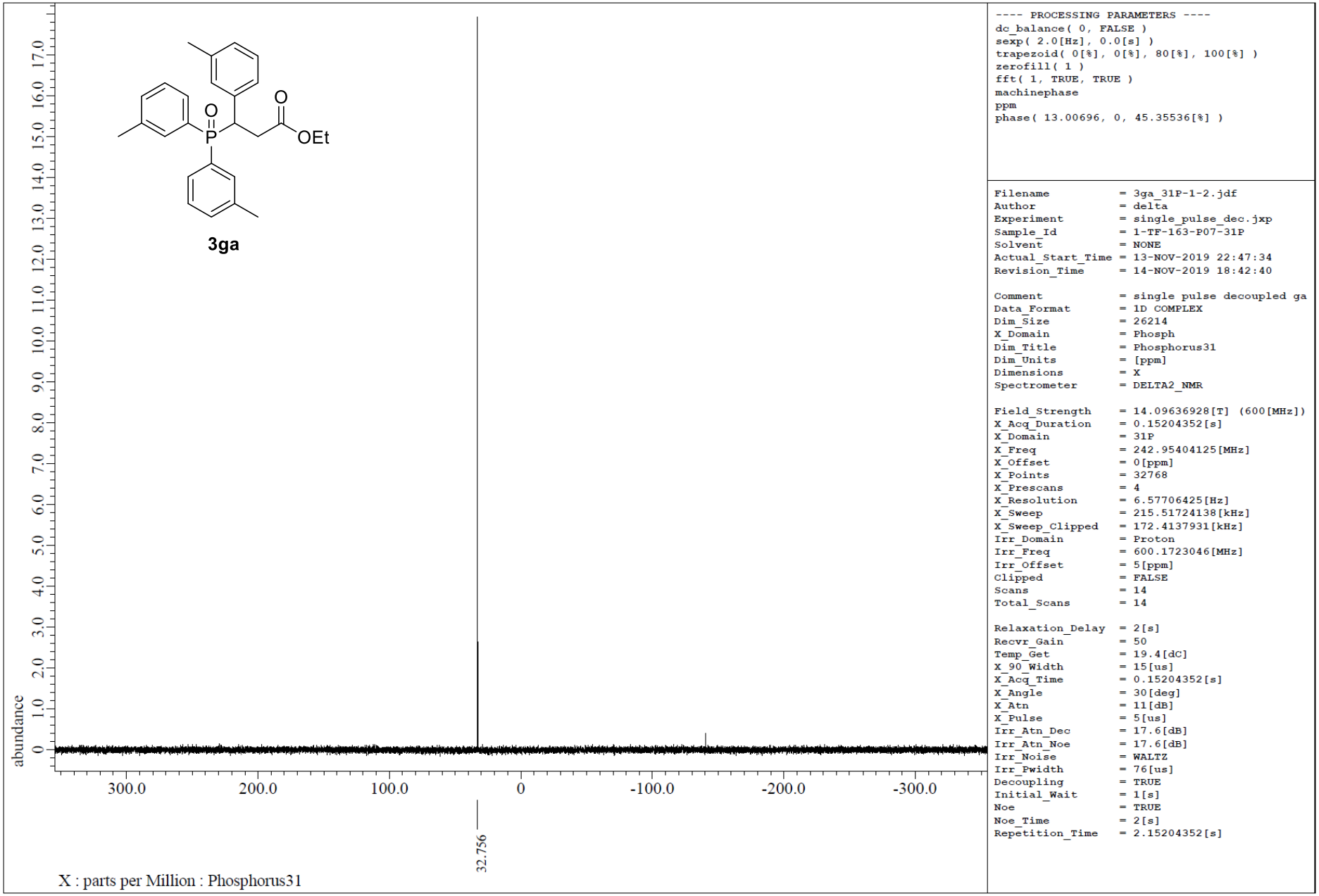
^{13}C NMR spectrum of **3fa** (151 MHz, $CDCl_3$)



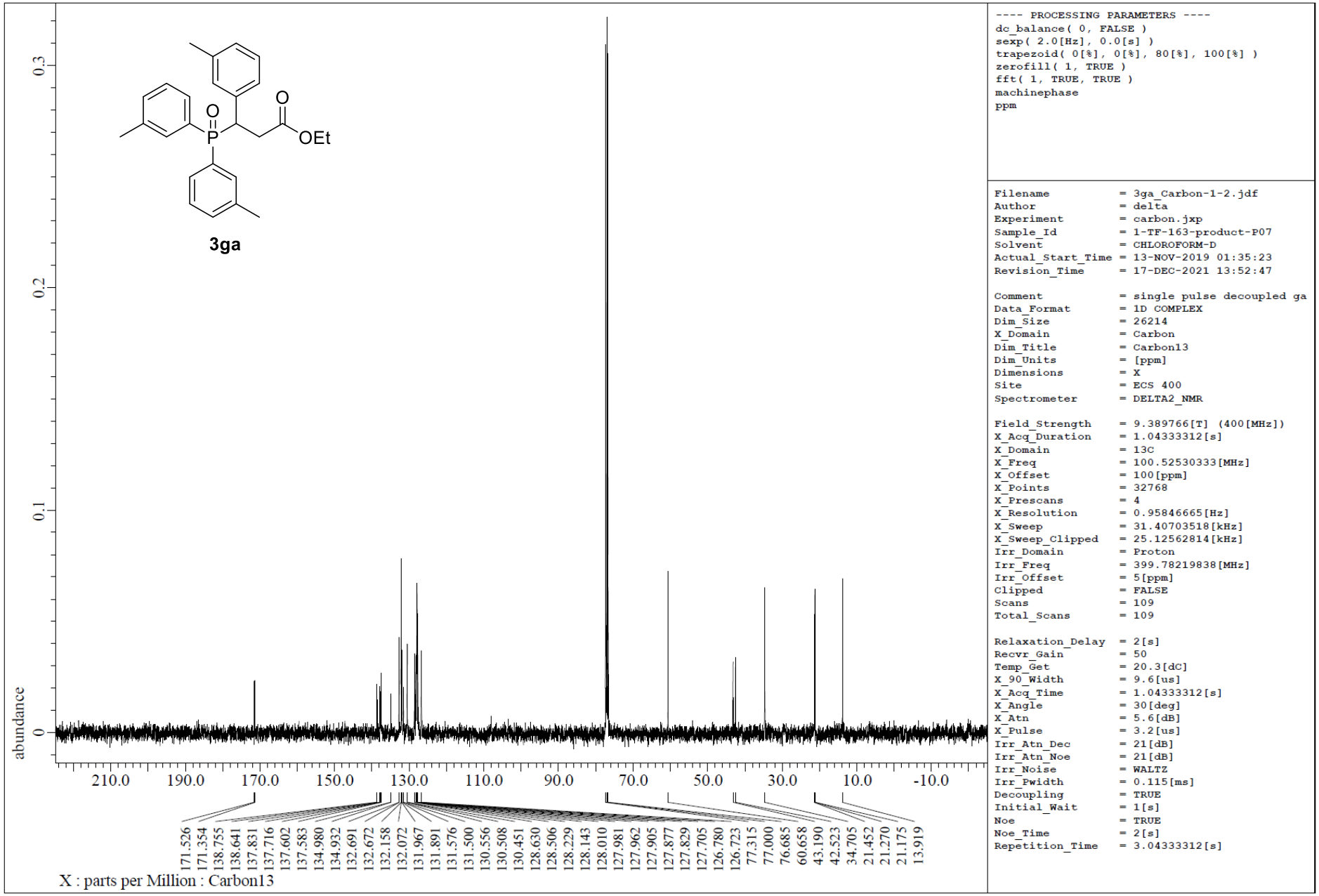
^{31}P NMR spectrum of **3fa** (243 MHz, $CDCl_3$)



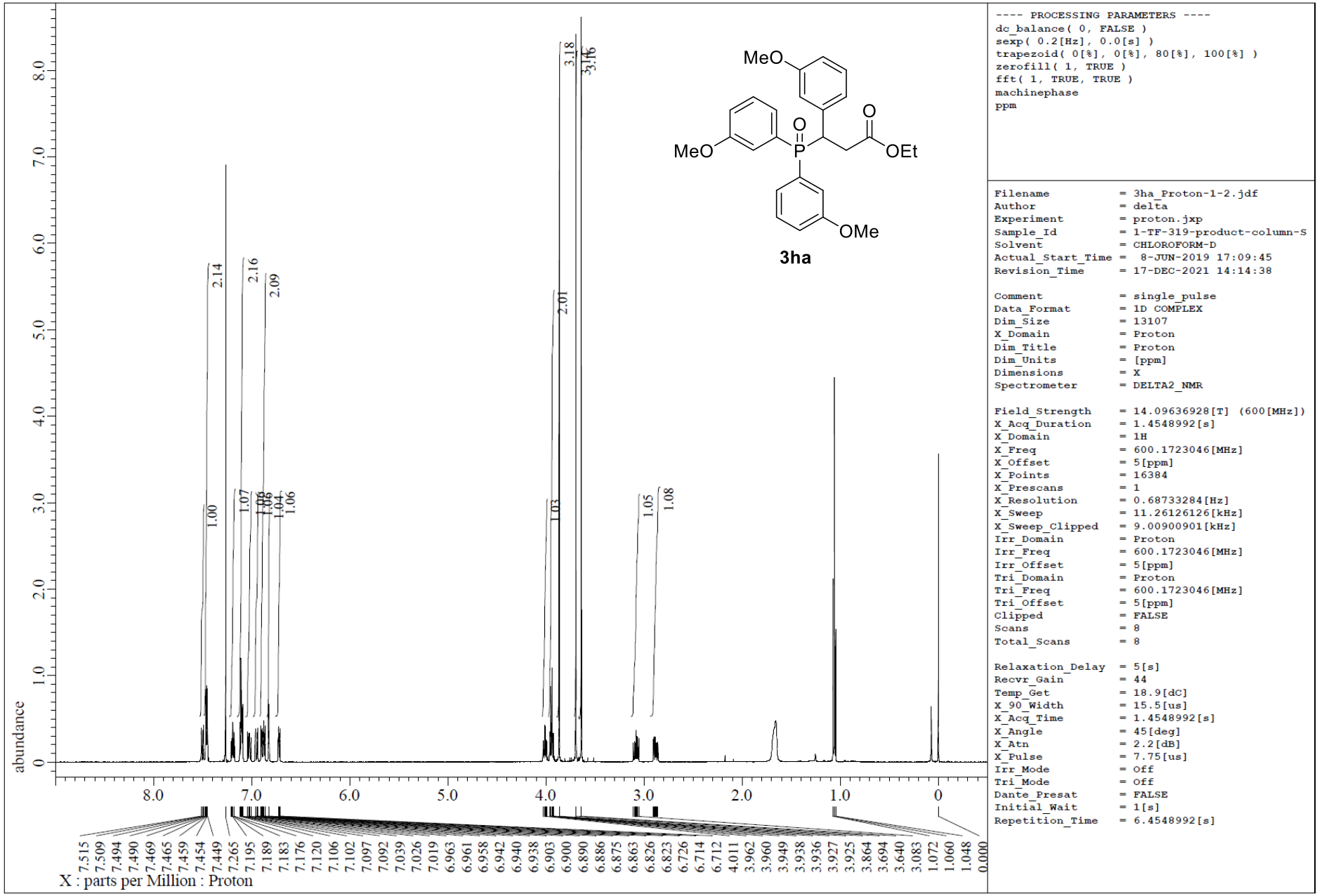
[1] H NMR spectrum of **3ga** (400 MHz, $CDCl_3$)



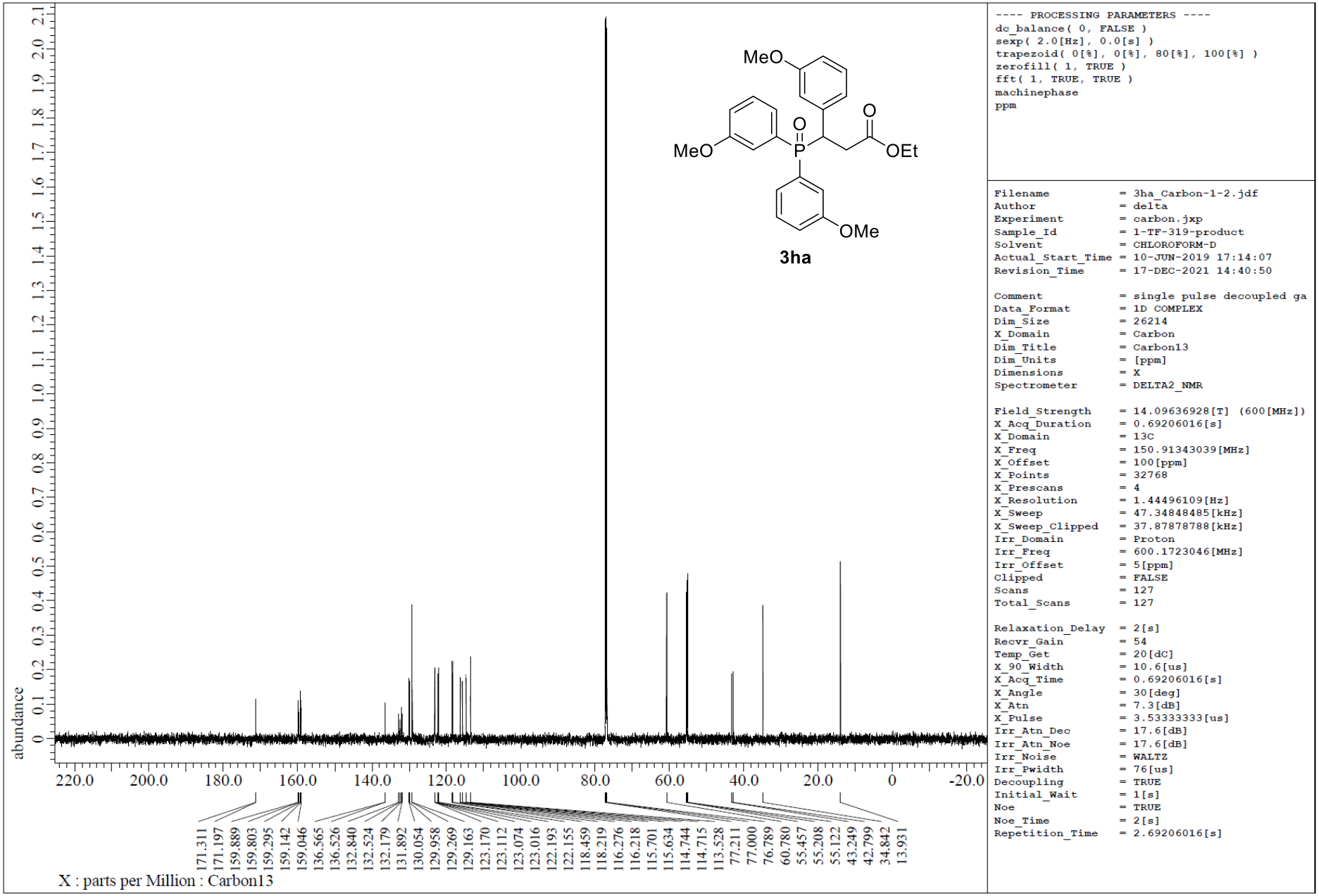
^{13}C NMR spectrum of **3ga** (101 MHz, $CDCl_3$)



^{31}P NMR spectrum of **3ga** (243 MHz, $CDCl_3$)



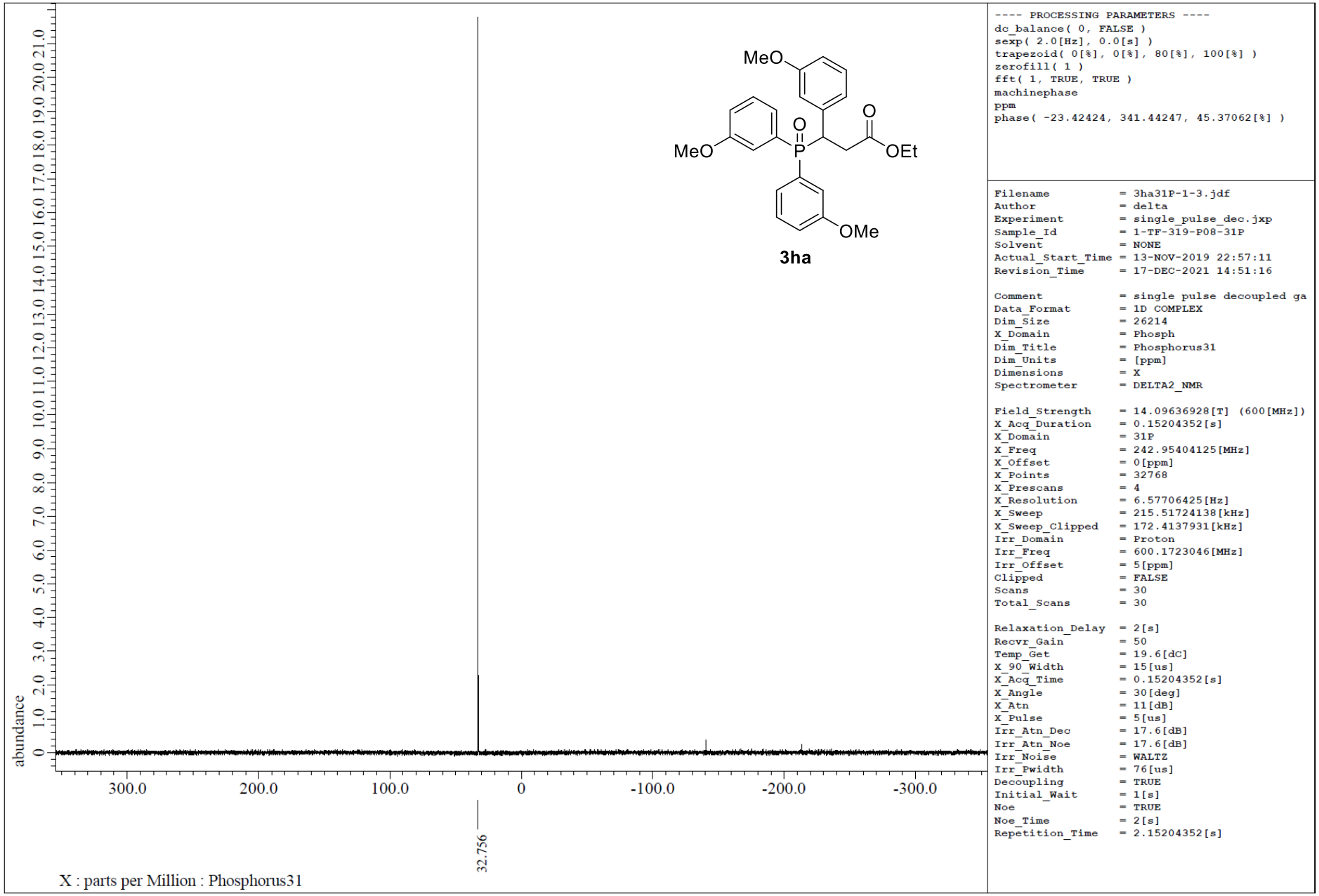
[1] H NMR spectrum of **3ha** (600 MHz, $CDCl_3$)



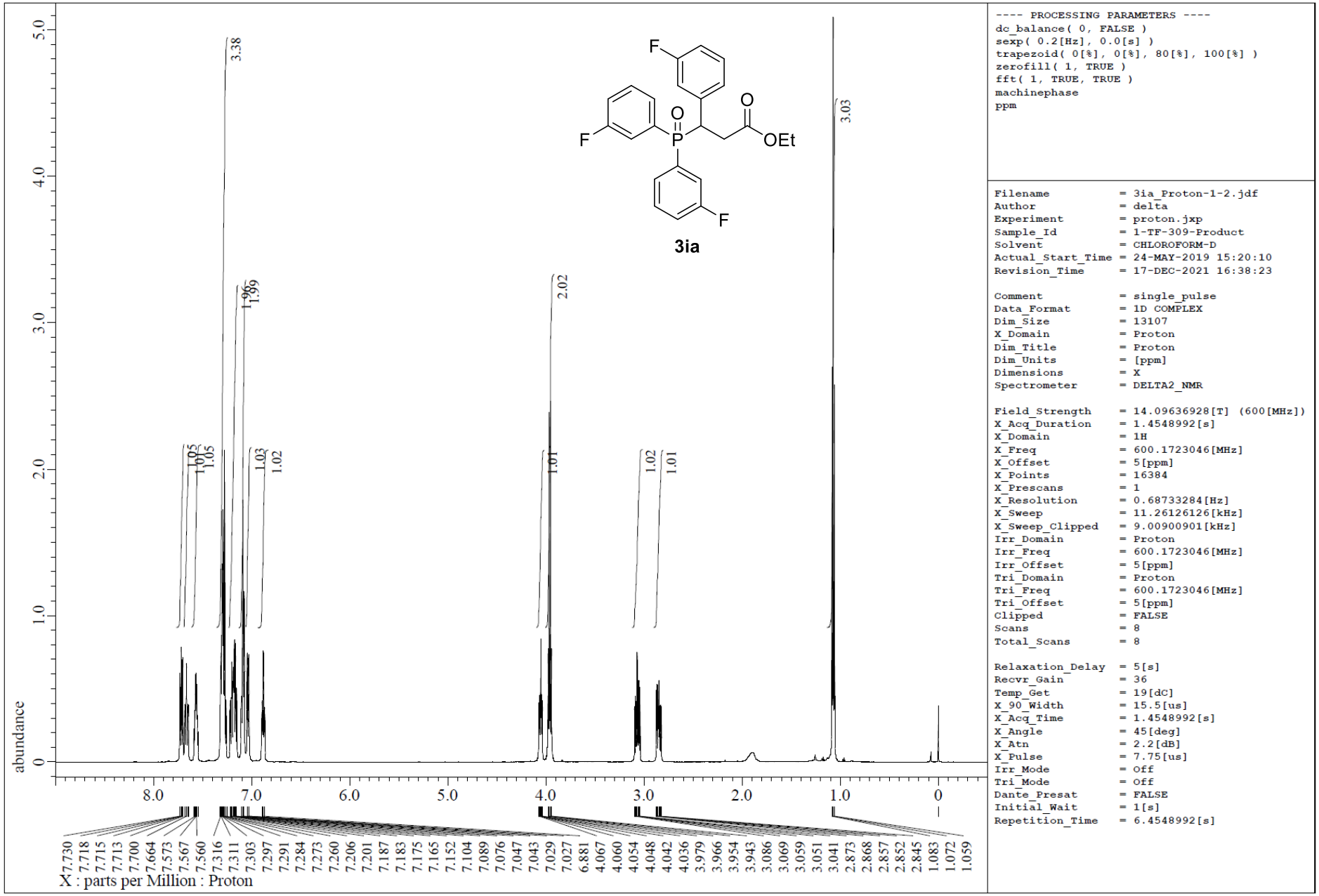

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3ha_Carbon-1-2.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 1-TF-319-product
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 10-JUN-2019 17:14:07
Revision_Time       = 17-DEC-2021 14:40:50

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 127
Total_Scans         = 127

Relaxation_Delay    = 2[s]
Recvr_Gain          = 54
Temp_Get            = 20[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 7.3[dB]
X_Pulse             = 3.53333333[us]
Irr_Atn_Dec         = 17.6[dB]
Irr_Atn_Noe         = 17.6[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 76[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

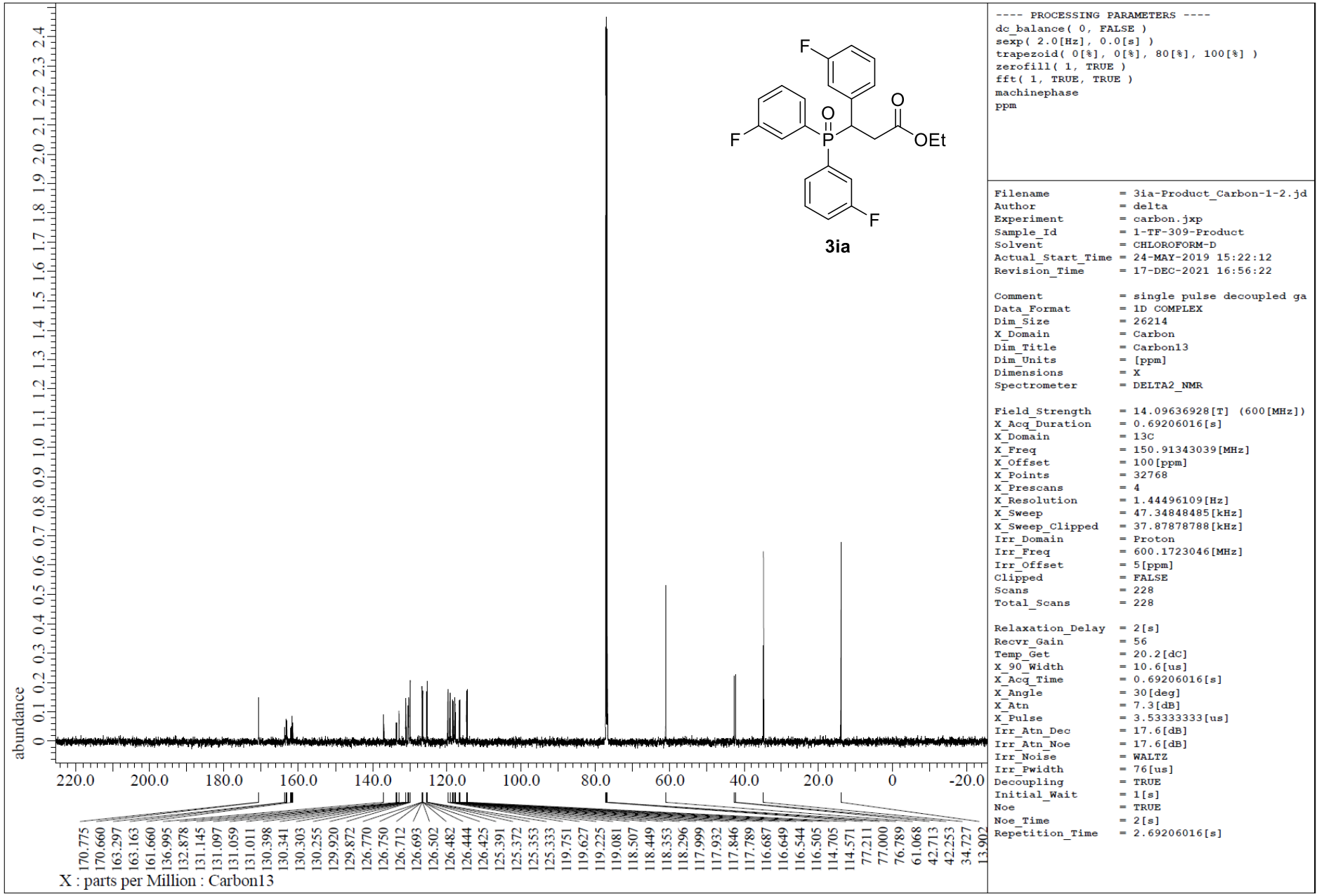
^{13}C NMR spectrum of **3ha** (151 MHz, $CDCl_3$)



^{31}P NMR spectrum of **3ha** (243 MHz, $CDCl_3$)



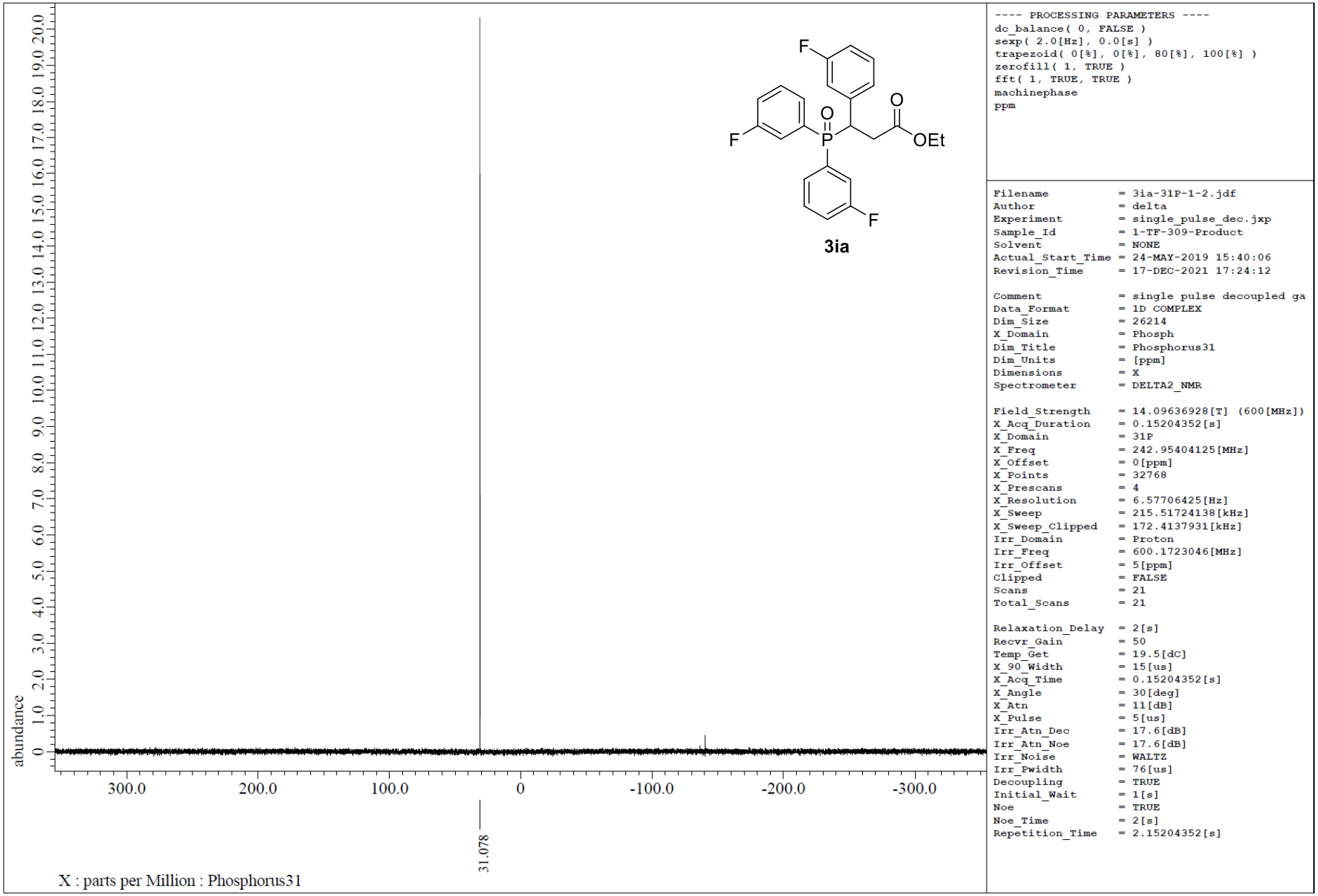
[1] H NMR spectrum of **3ia** (600 MHz, $CDCl_3$)



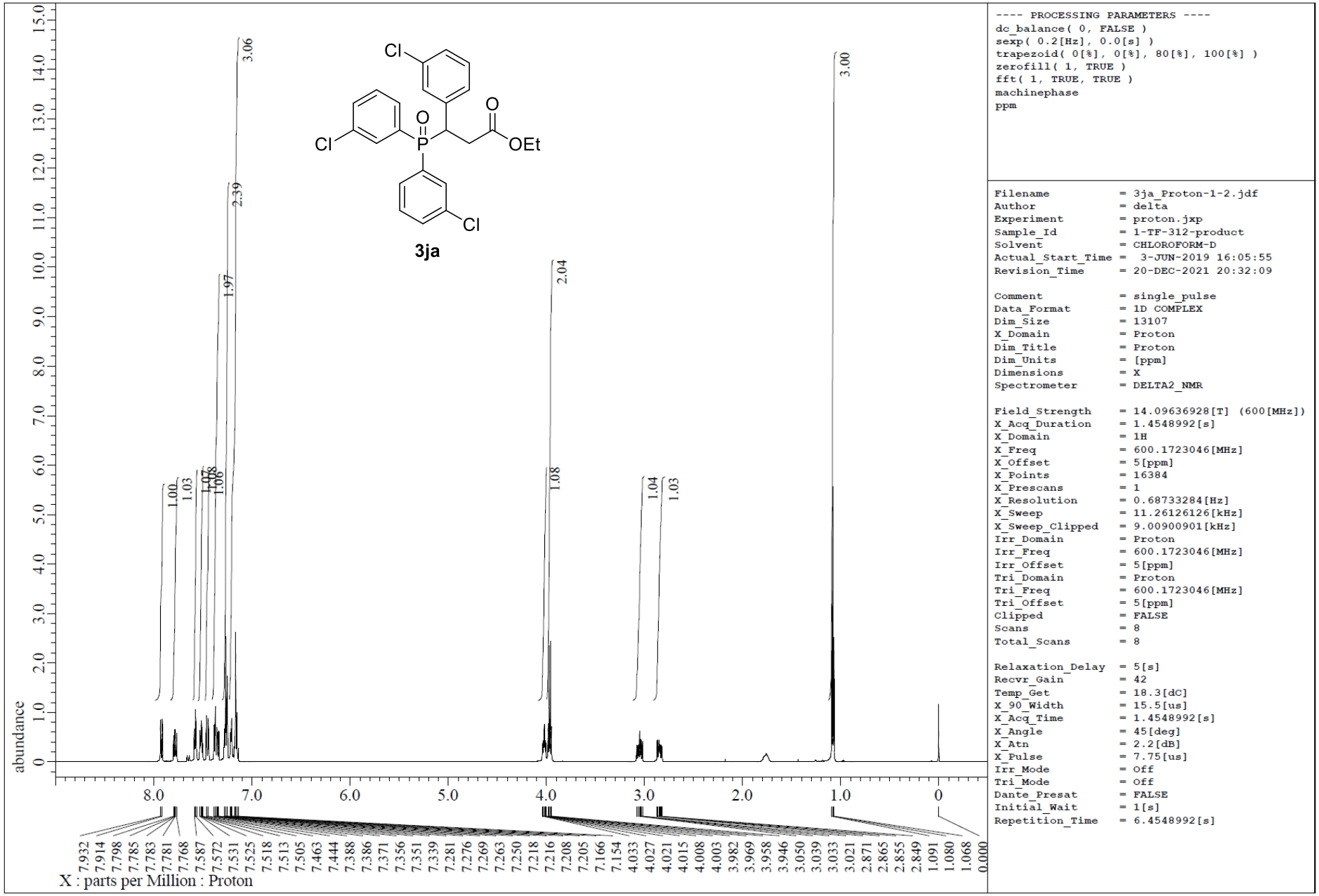

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

Filename	= 3ia-Product_Carbon-1-2.jd
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= 1-TF-309-Product
Solvent	= CHLOROFORM-D
Actual_Start_Time	= 24-MAY-2019 15:22:12
Revision_Time	= 17-DEC-2021 16:56:22
Comment	= single pulse decoupled ga
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
X_Domain	= Carbon
Dim_Title	= Carbon13
Dim_Units	= [ppm]
Dimensions	= X
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09636928[T] (600[MHz])
X_Acq_Duration	= 0.69206016[s]
X_Domain	= 13C
X_Freq	= 150.91343039[MHz]
X_Offset	= 100[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.44496109[Hz]
X_Sweep	= 47.34848485[kHz]
X_Sweep_Clipped	= 37.87878788[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723046[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 228
Total_Scans	= 228
Relaxation_Delay	= 2[s]
Recvr_Gain	= 56
Temp_Get	= 20.2[dC]
X_90_Width	= 10.6[us]
X_Acq_Time	= 0.69206016[s]
X_Angle	= 30[deg]
X_Atn	= 7.3[dB]
X_Pulse	= 3.53333333[us]
Irr_Atn_Dec	= 17.6[dB]
Irr_Atn_Noe	= 17.6[dB]
Irr_Noise	= WALTZ
Irr_Pwidth	= 76[us]
Decoupling	= TRUE
Initial_Wait	= 1[s]
Noe	= TRUE
Noe_Time	= 2[s]
Repetition_Time	= 2.69206016[s]

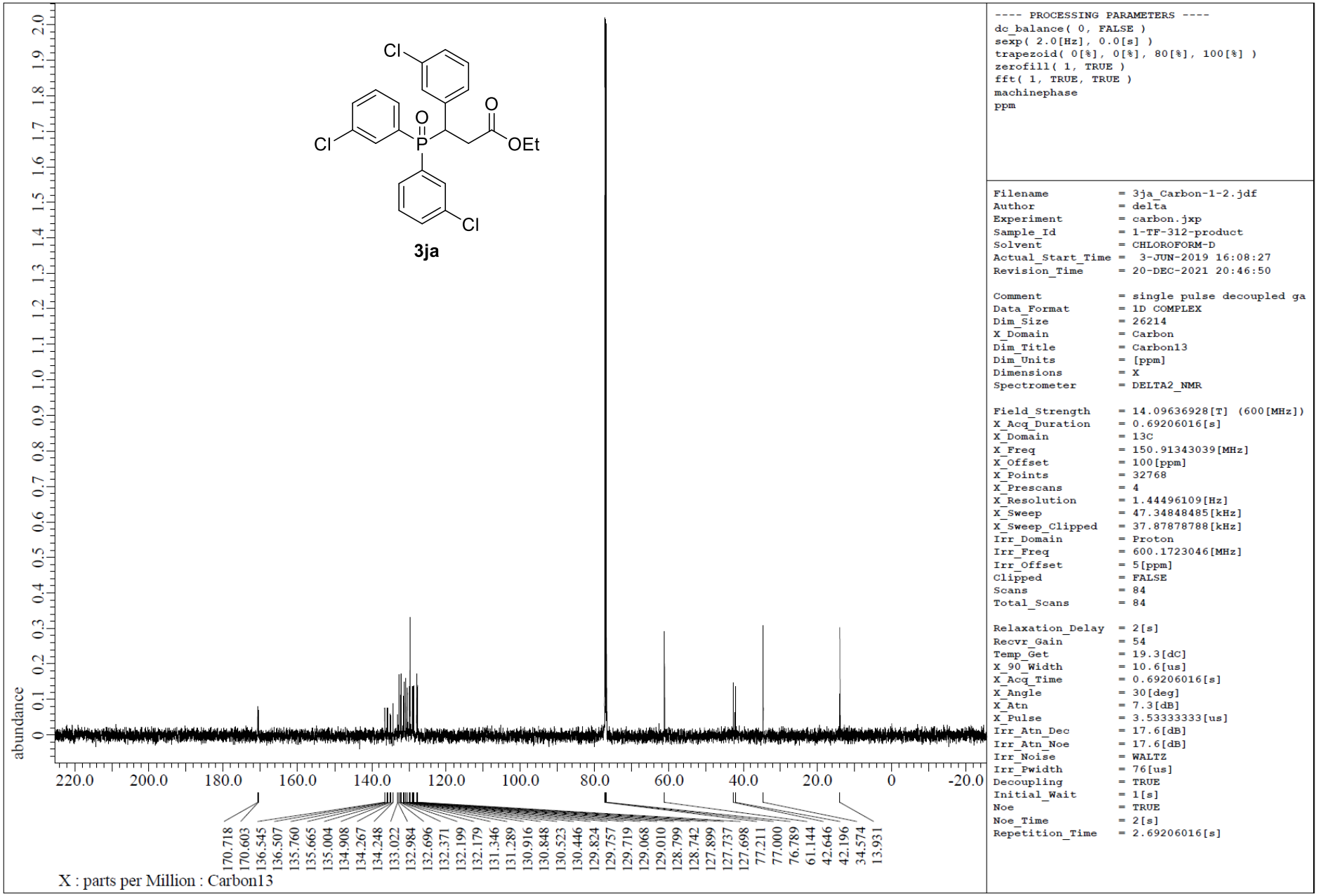
^{13}C NMR spectrum of **3ia** (151 MHz, $CDCl_3$)



^{31}P NMR spectrum of **3ia** (243 MHz, $CDCl_3$)



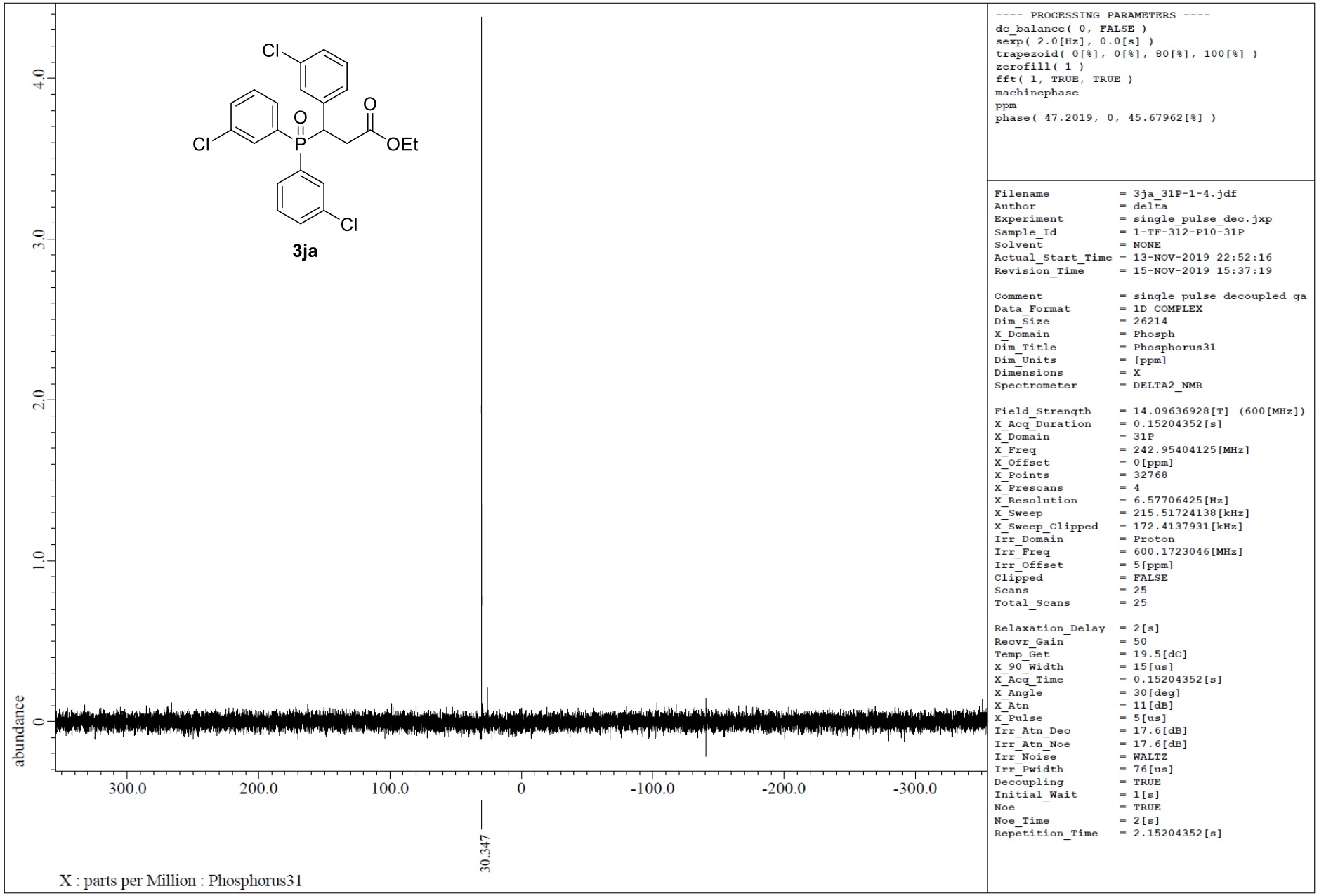
[1] H NMR spectrum of **3ja** (600 MHz, $CDCl_3$)



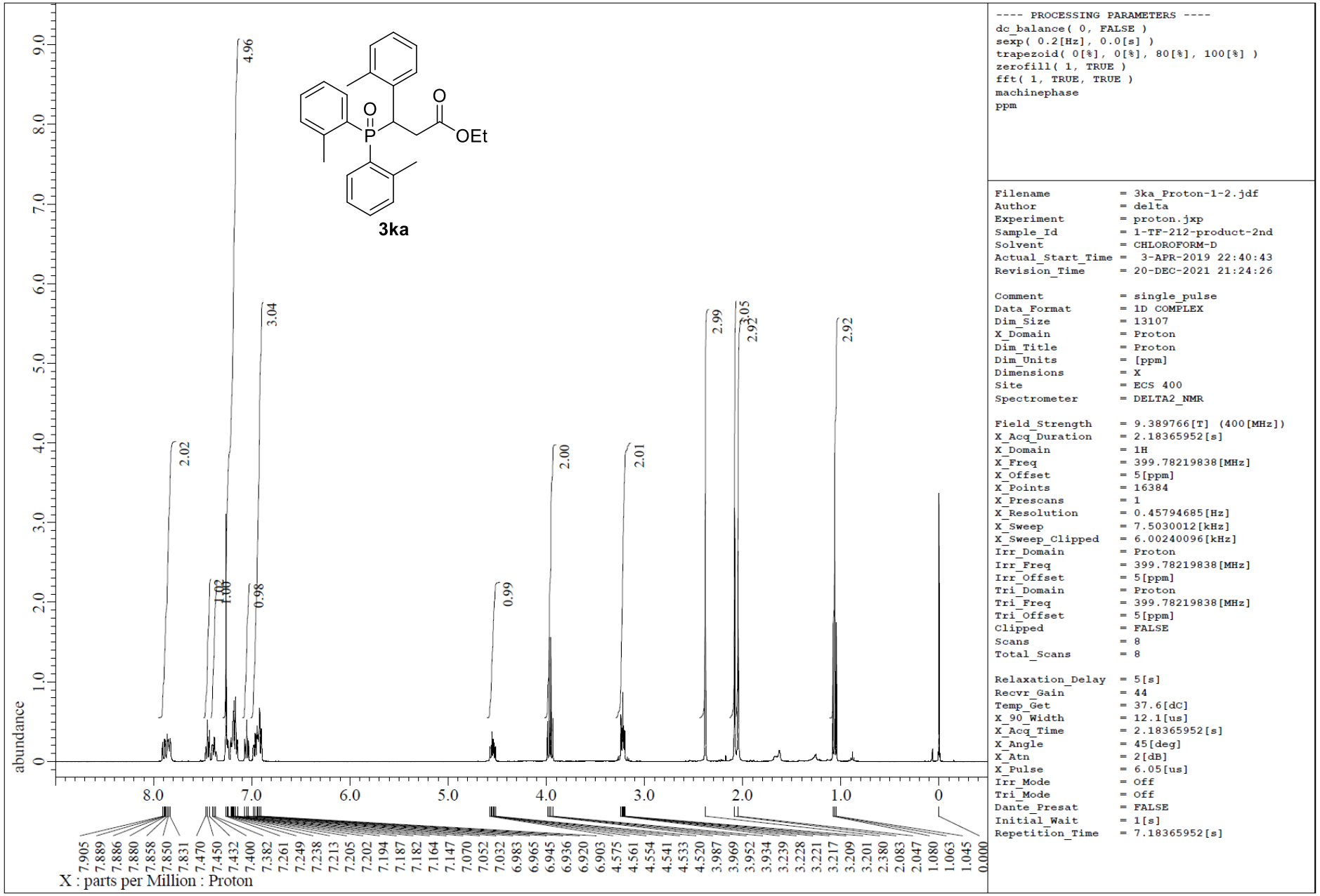

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3ja_Carbon-1-2.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 1-TF-312-product
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  3-JUN-2019 16:08:27
Revision_Time       = 20-DEC-2021 20:46:50

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 84
Total_Scans         = 84

Relaxation_Delay    = 2[s]
Recvr_Gain          = 54
Temp_Get            = 19.3[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 7.3[dB]
X_Pulse             = 3.53333333[us]
Irr_Atn_Dec         = 17.6[dB]
Irr_Atn_Noe         = 17.6[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 76[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

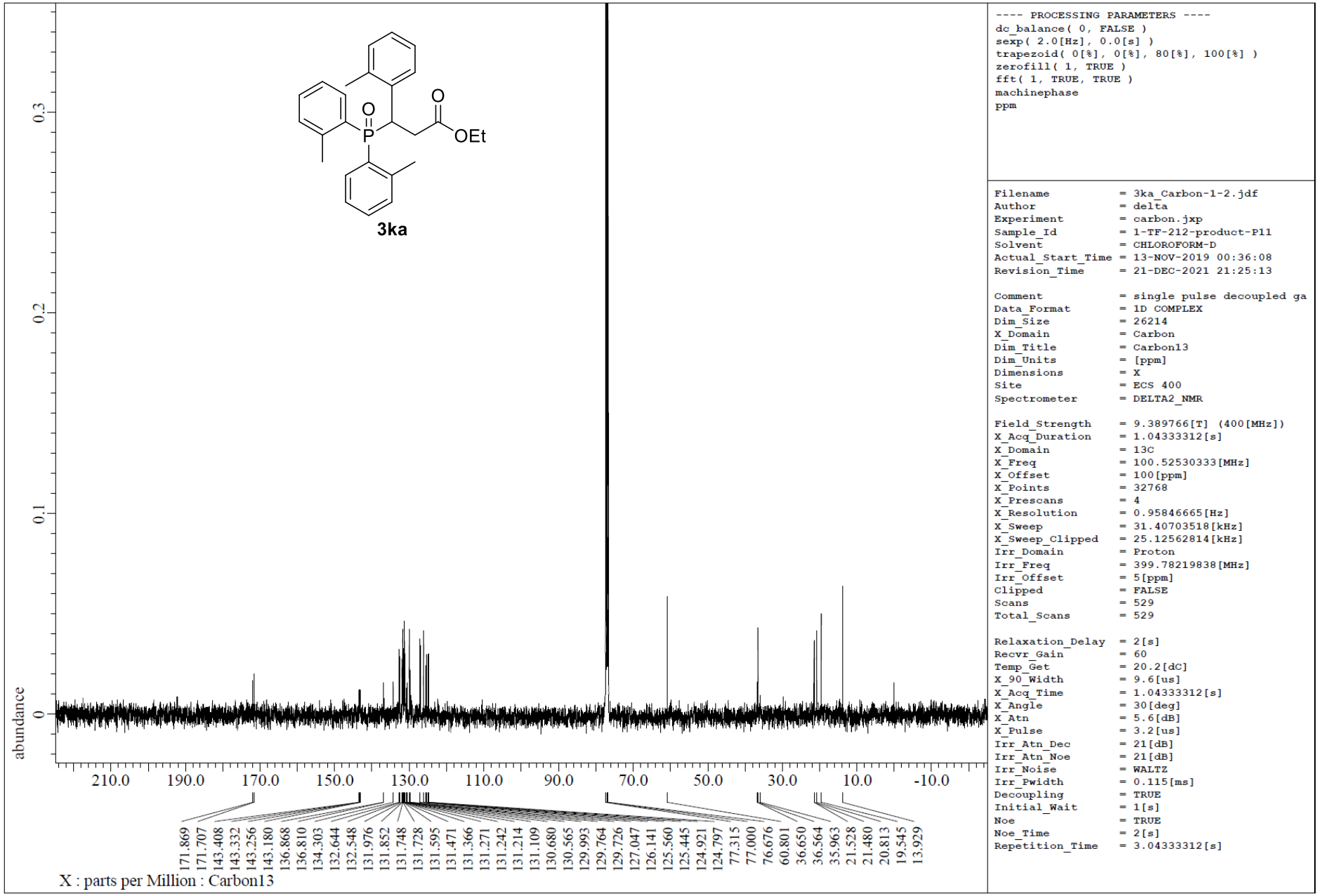
^{13}C NMR spectrum of **3ja** (151 MHz, $CDCl_3$)



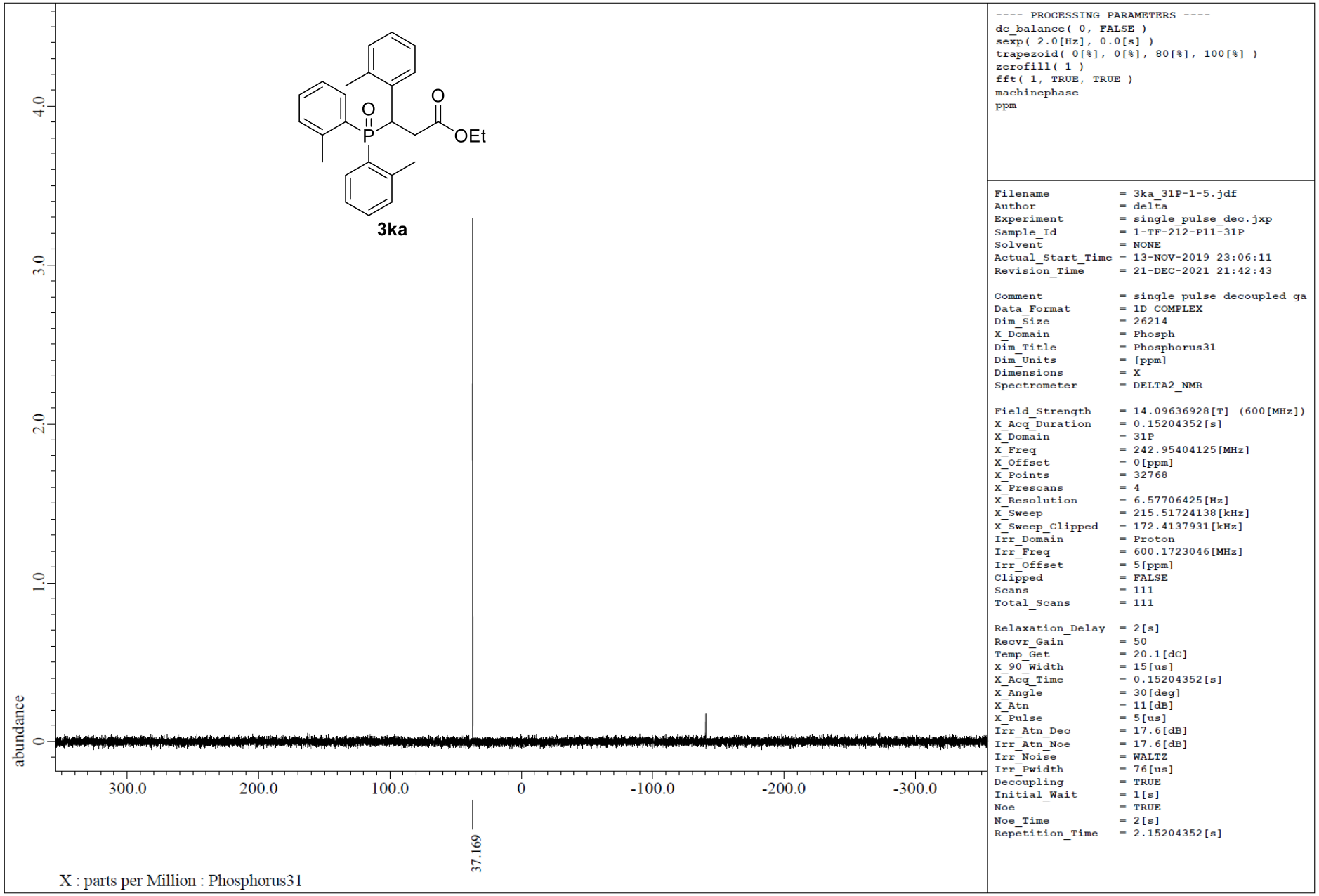
^{31}P NMR spectrum of **3ja** (243 MHz, $CDCl_3$)



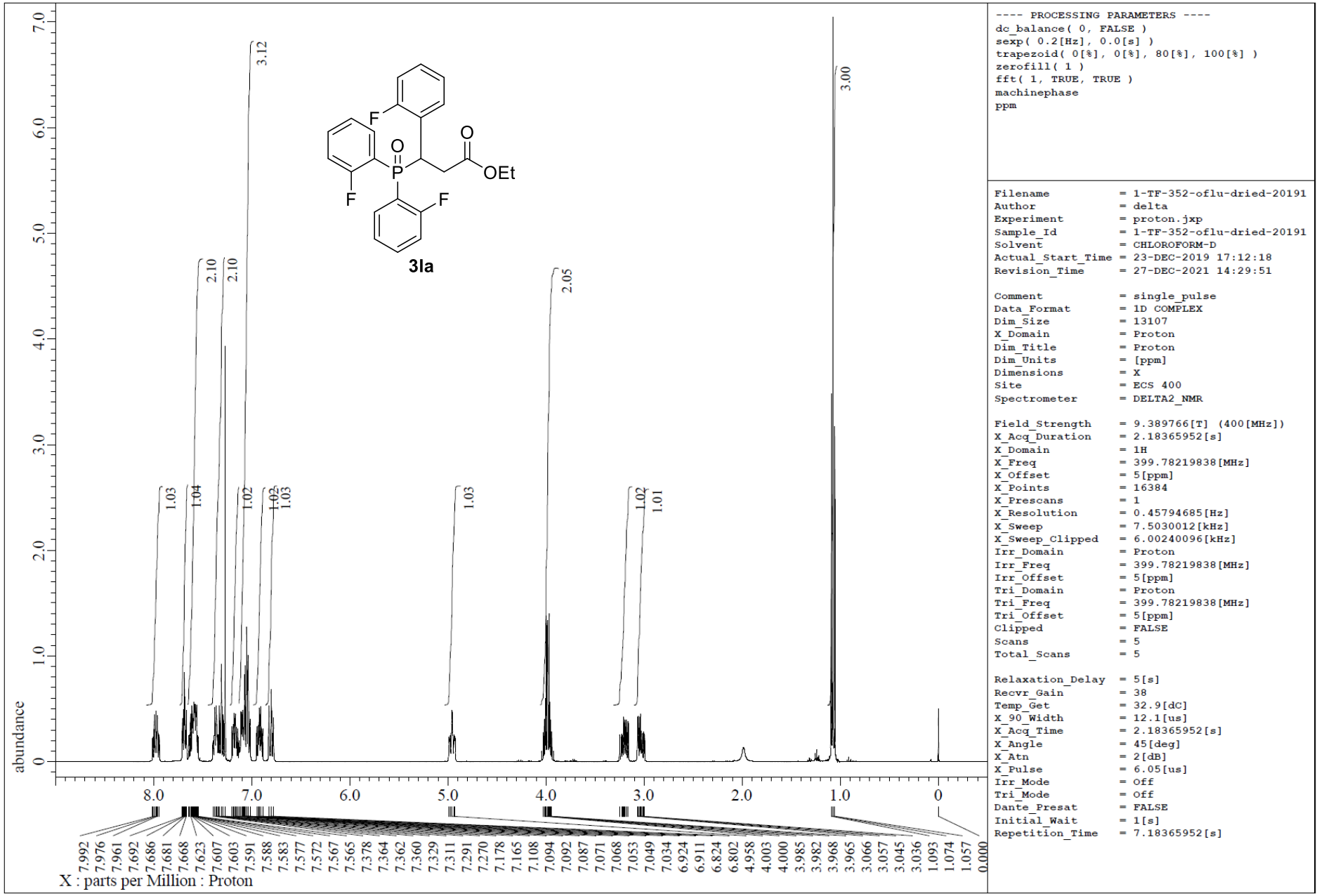
^{1}H NMR spectrum of **3ka** (400 MHz, $CDCl_3$)



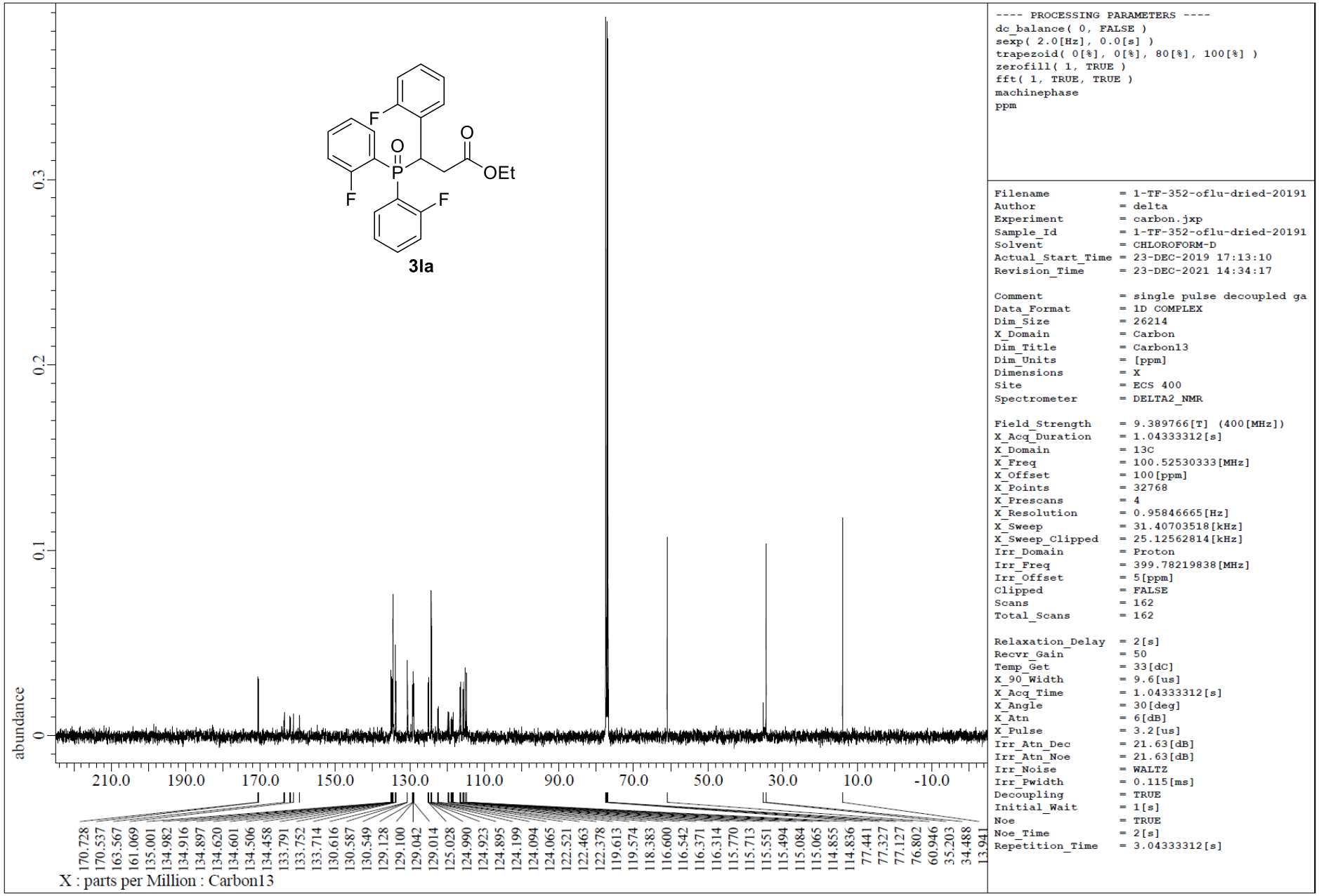
^{13}C NMR spectrum of **3ka** (101 MHz, $CDCl_3$)



^{31}P NMR spectrum of **3ka** (243 MHz, $CDCl_3$)



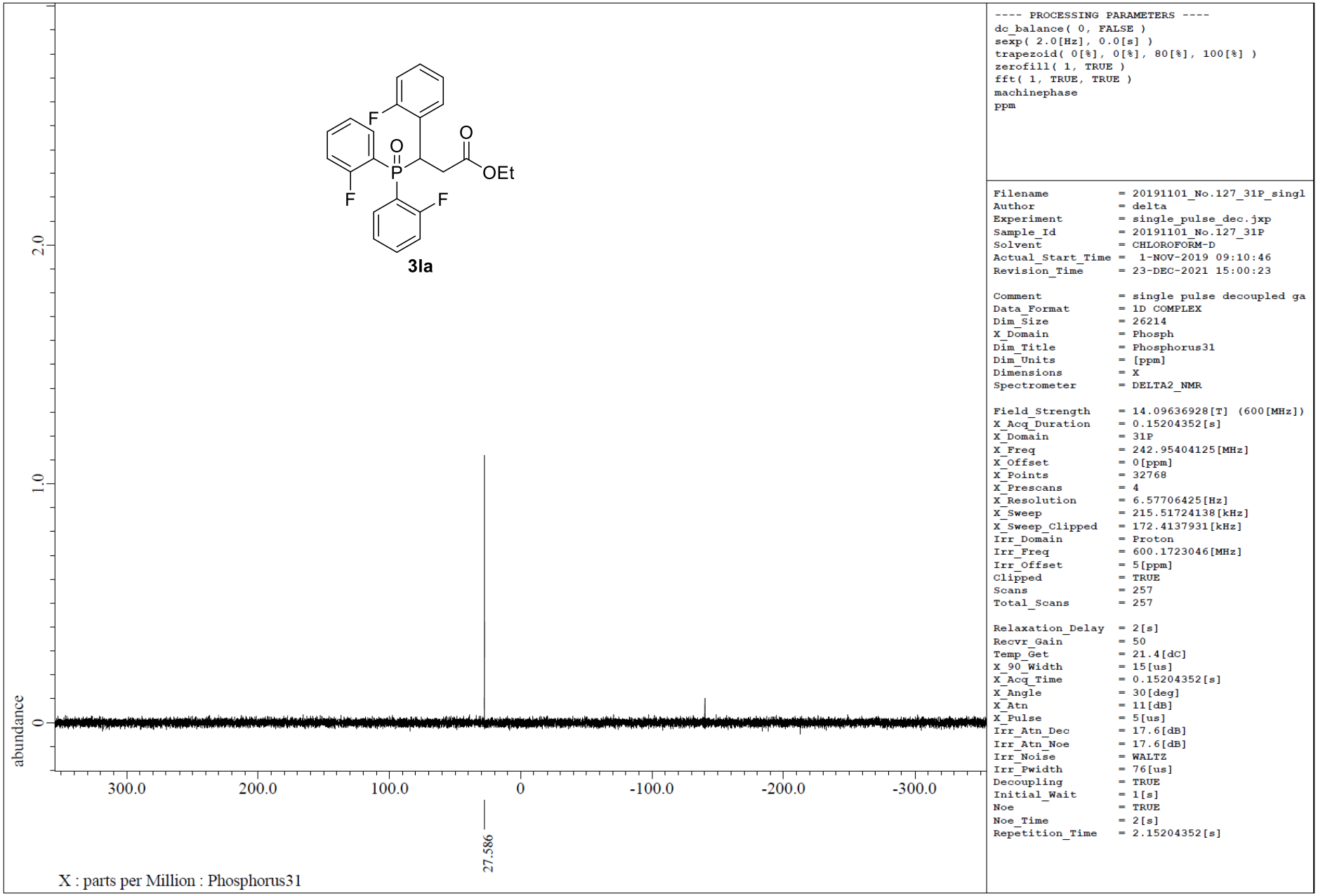
[1] H NMR spectrum of **3la** (400 MHz, $CDCl_3$)



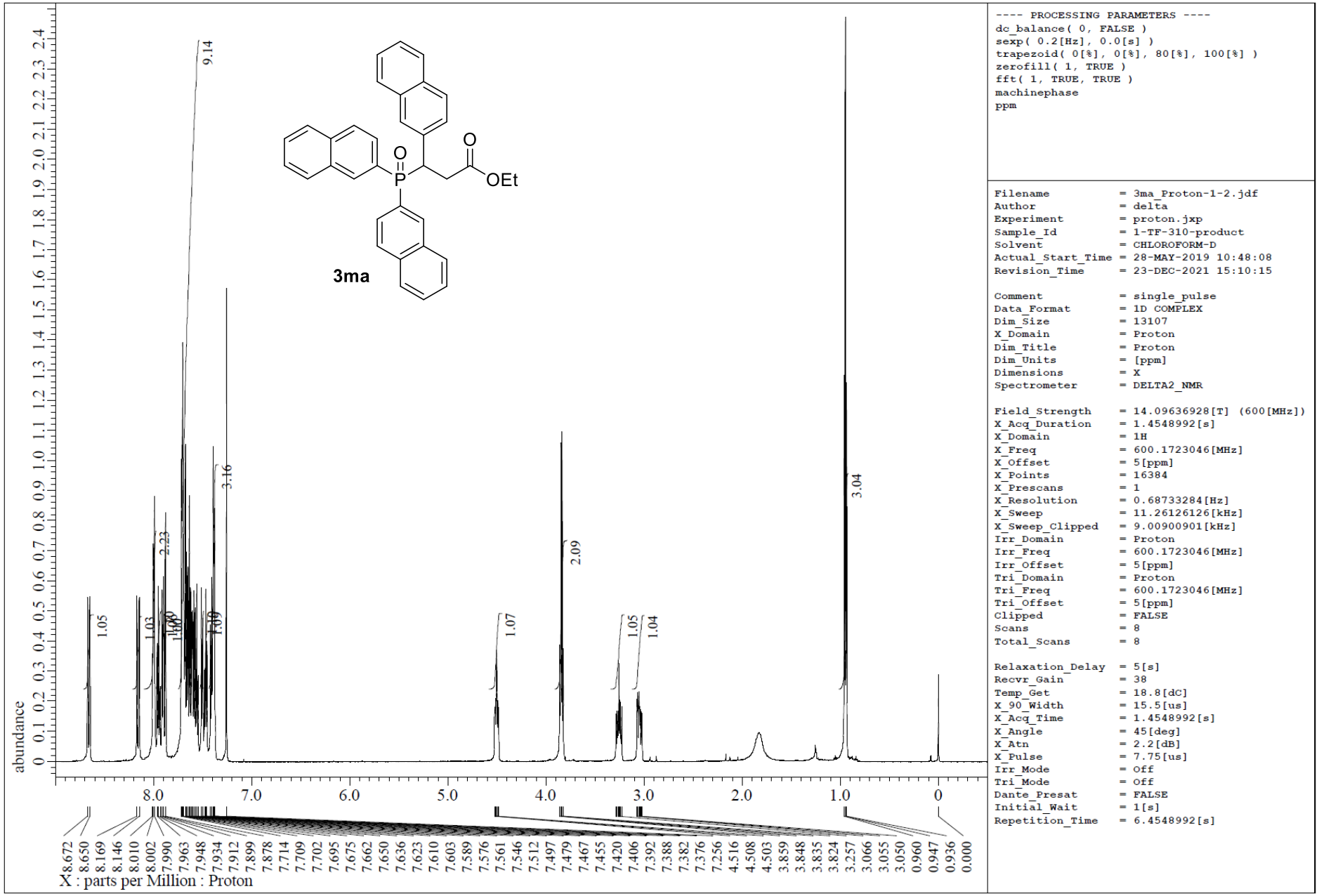

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 1-TF-352-oflu-dried-20191
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 1-TF-352-oflu-dried-20191
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 23-DEC-2019 17:13:10
Revision_Time       = 23-DEC-2021 14:34:17

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 1.04333312[s]
X_Domain            = 13C
X_Freq              = 100.52530333[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 0.95846665[Hz]
X_Sweep             = 31.40703518[kHz]
X_Sweep_Clipped     = 25.12562814[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 162
Total_Scans         = 162

Relaxation_Delay    = 2[s]
Recvr_Gain          = 50
Temp_Get            = 33[dC]
X_90_Width          = 9.6[us]
X_Acq_Time          = 1.04333312[s]
X_Angle             = 30[deg]
X_Atn               = 6[dB]
X_Pulse             = 3.2[us]
Irr_Atn_Dec         = 21.63[dB]
Irr_Atn_Noe         = 21.63[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 0.115[ms]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 3.04333312[s]
```

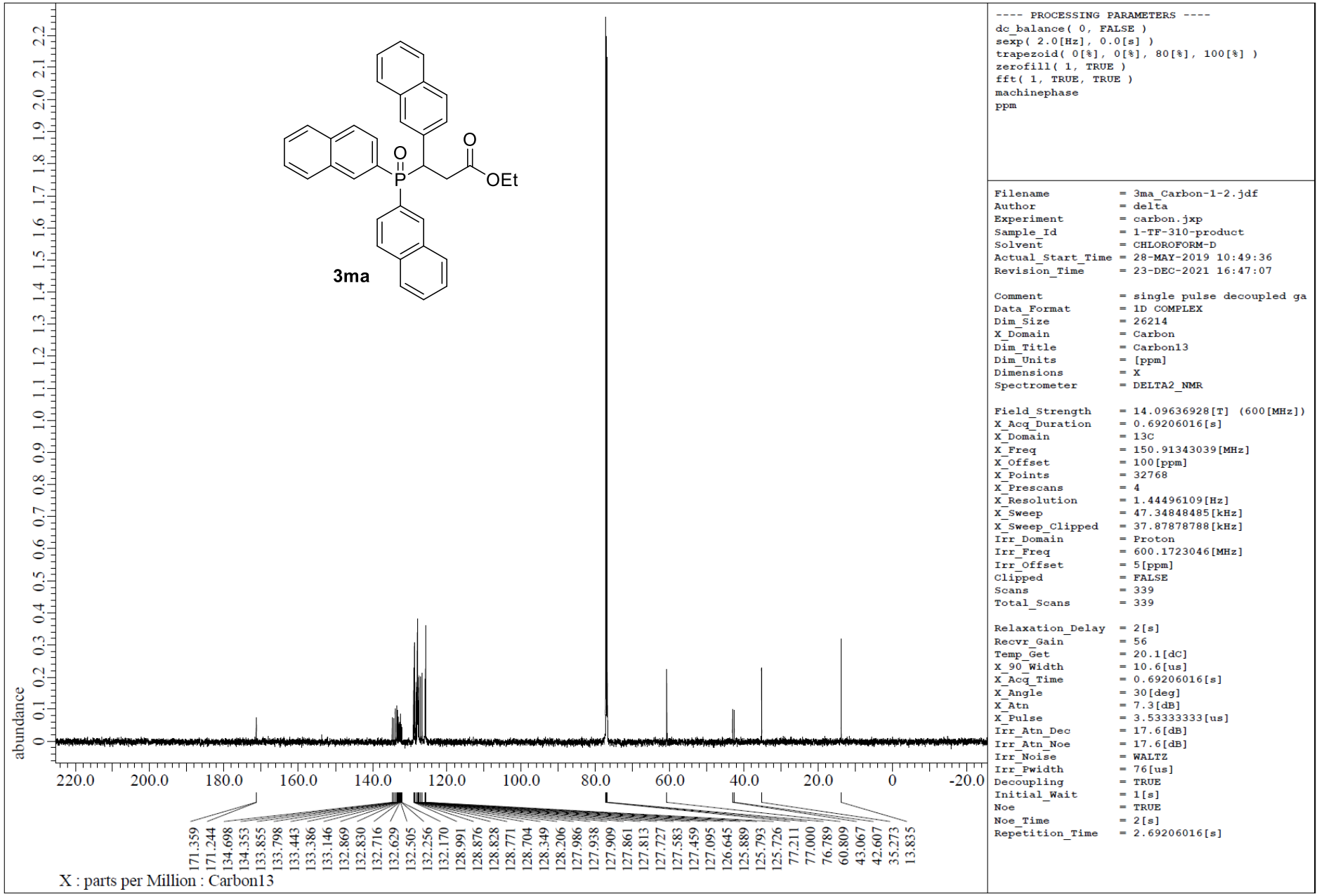
^{13}C NMR spectrum of **3la** (101 MHz, $CDCl_3$)



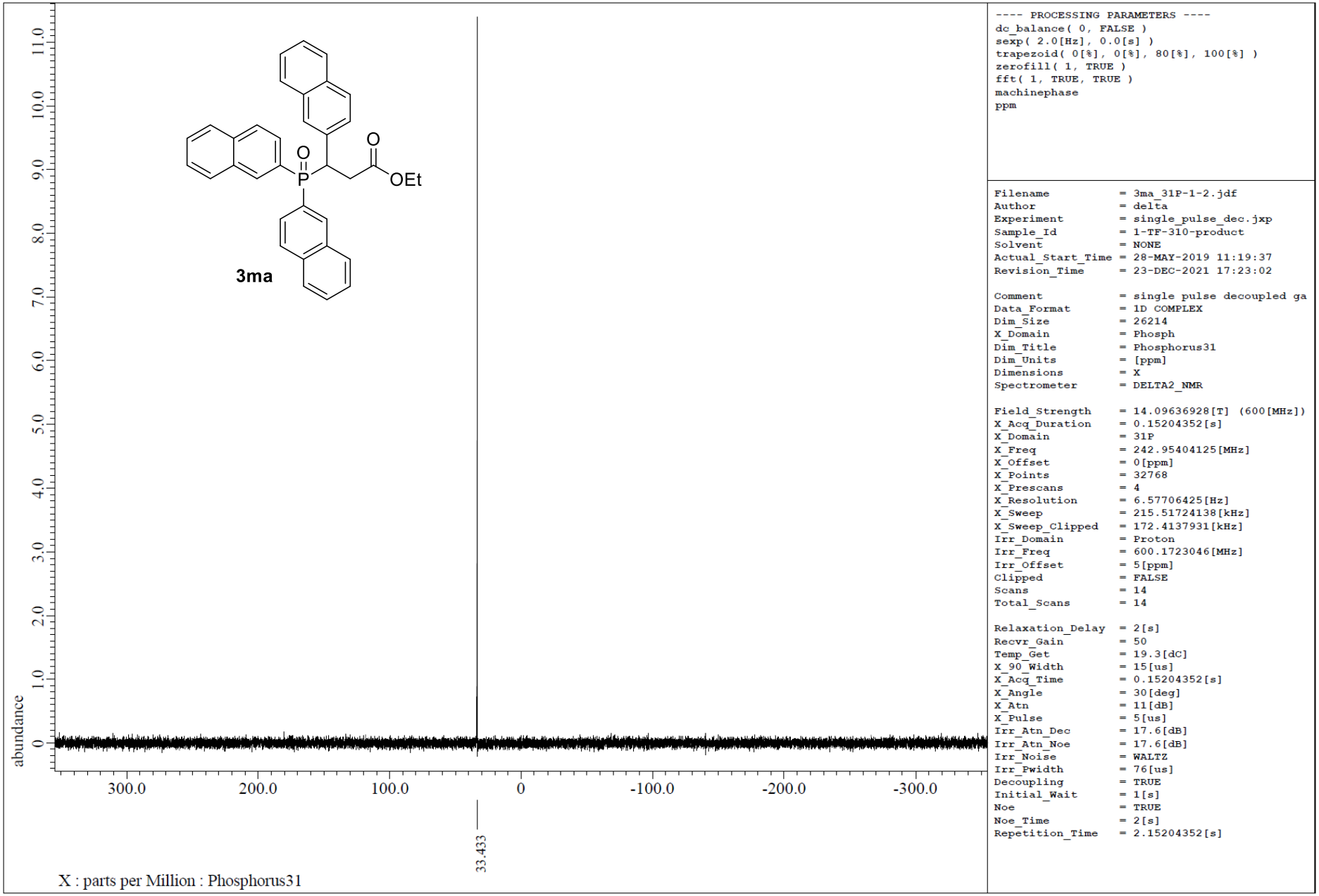
^{31}P NMR spectrum of **3la** (243 MHz, $CDCl_3$)



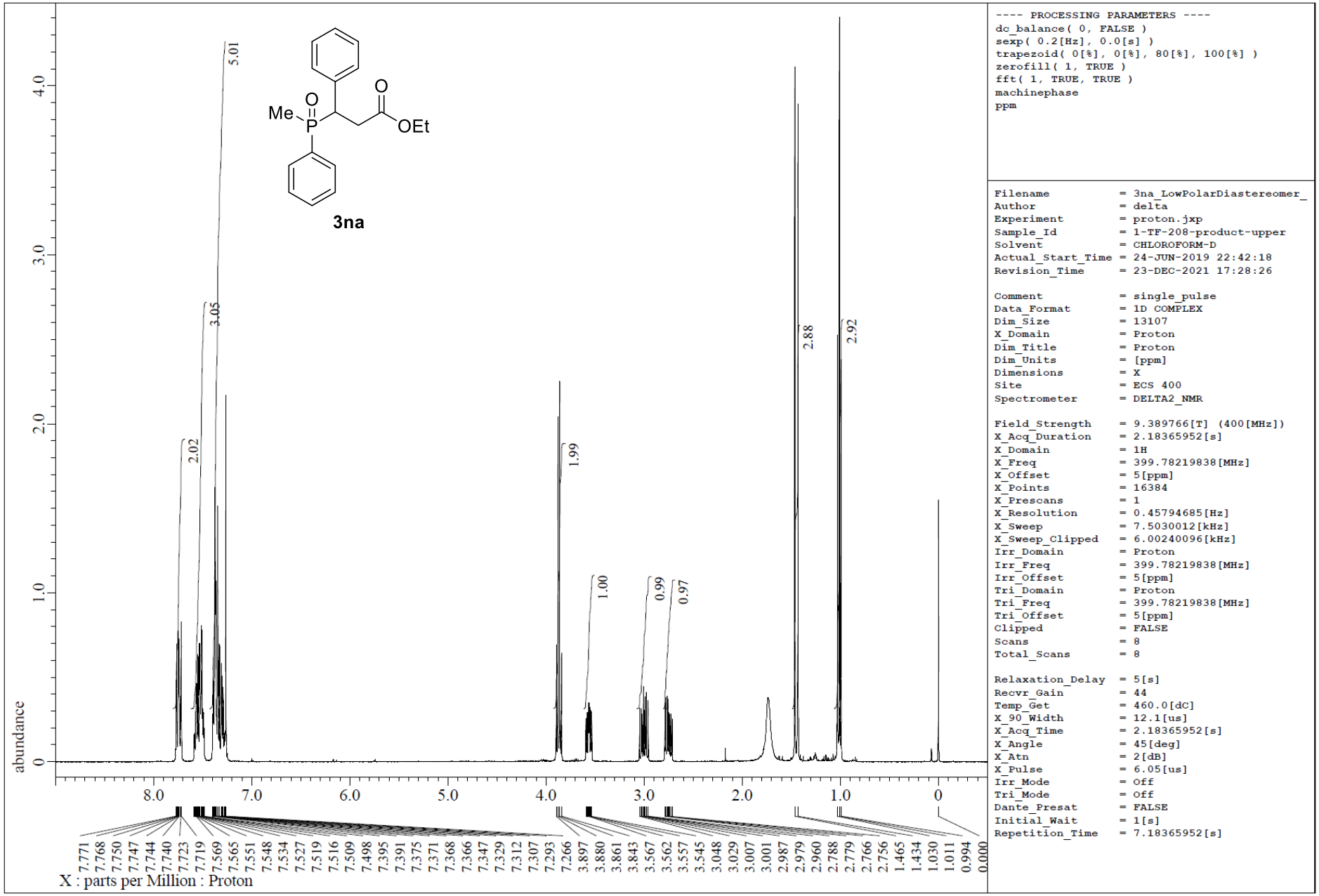
[1] H NMR spectrum of **3ma** (600 MHz, $CDCl_3$)



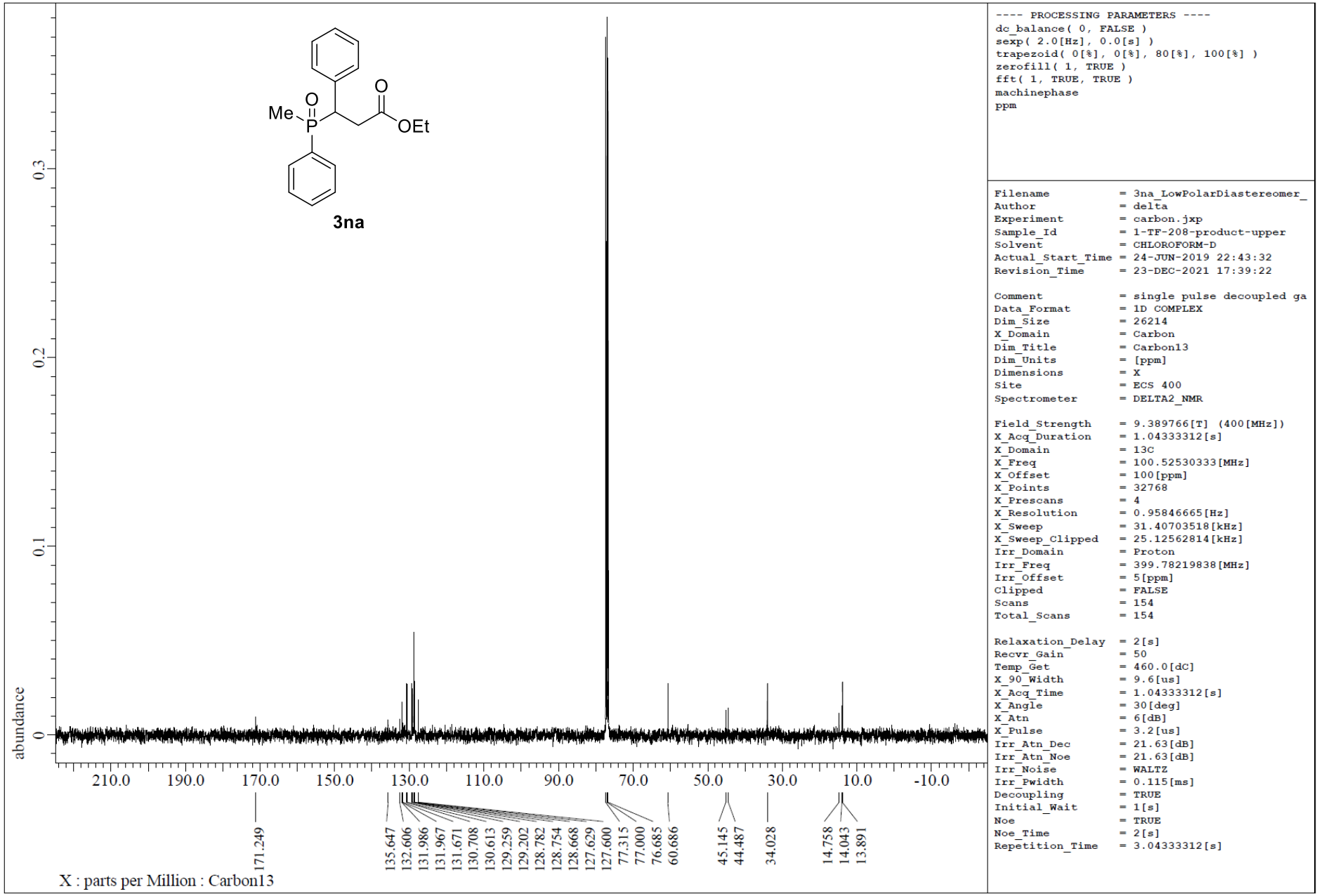
^{13}C NMR spectrum of **3ma** (151 MHz, $CDCl_3$)



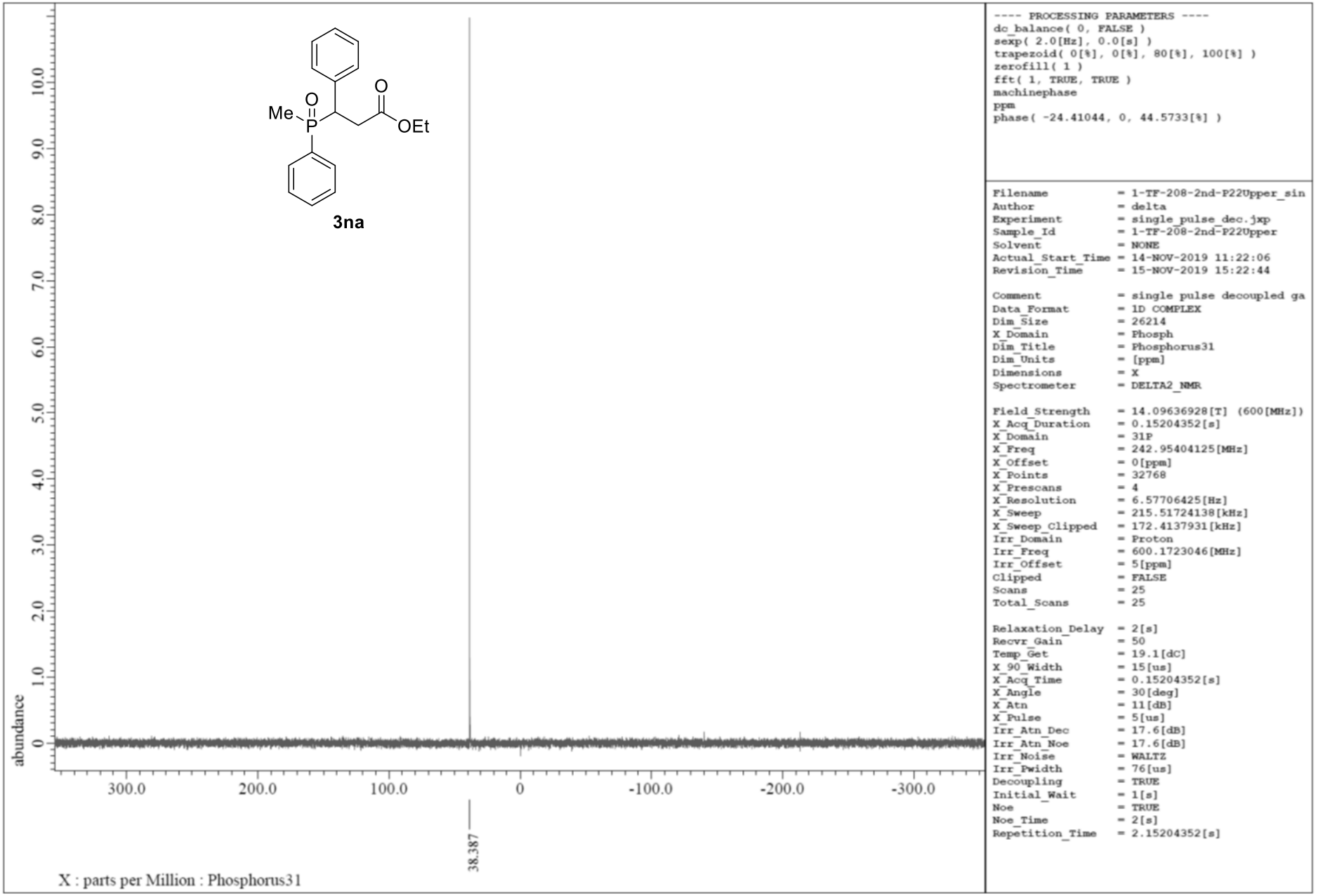
^{31}P NMR spectrum of **3ma** (243 MHz, $CDCl_3$)



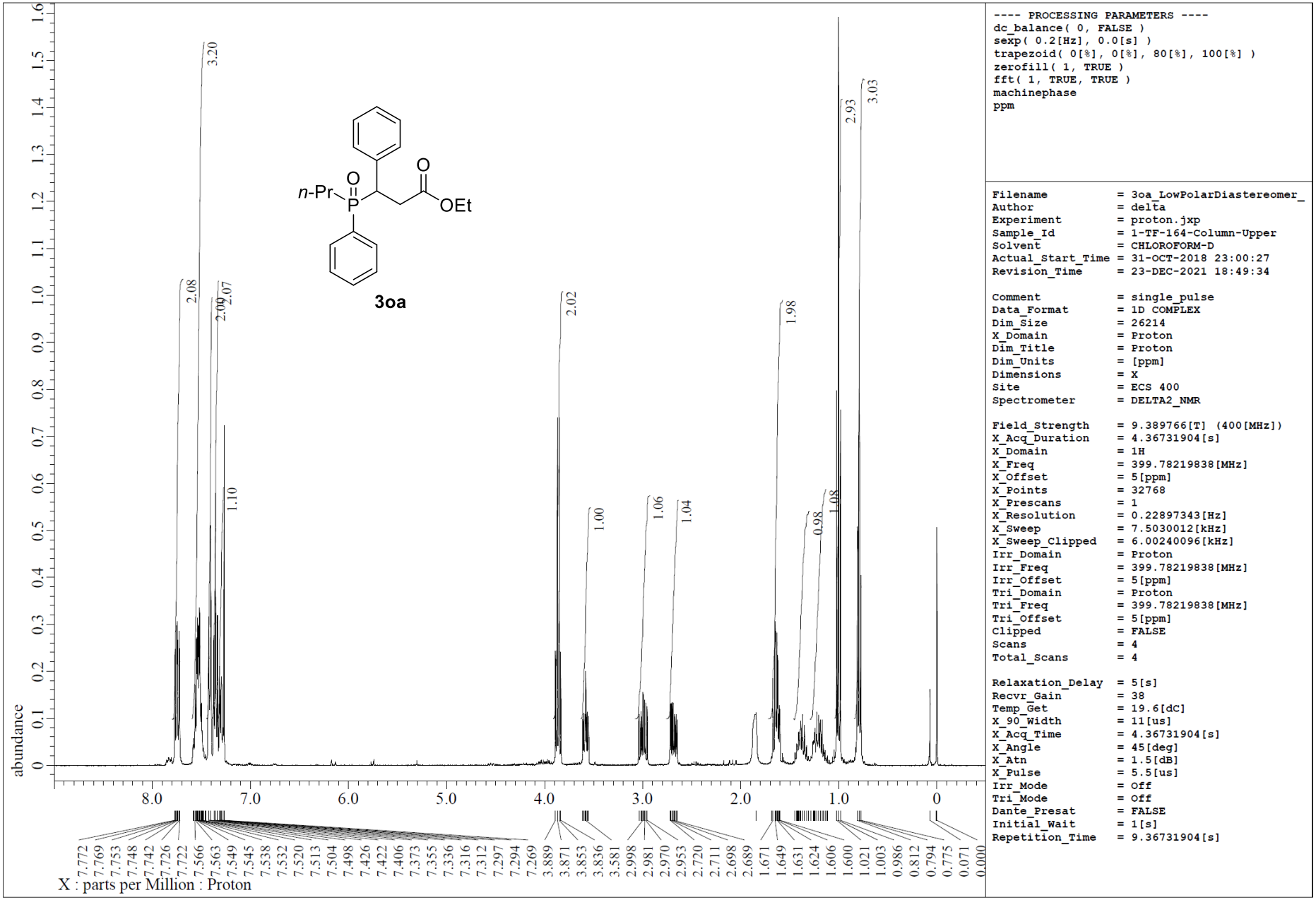
^{1}H NMR spectrum of **3na** (400 MHz, $CDCl_3$)



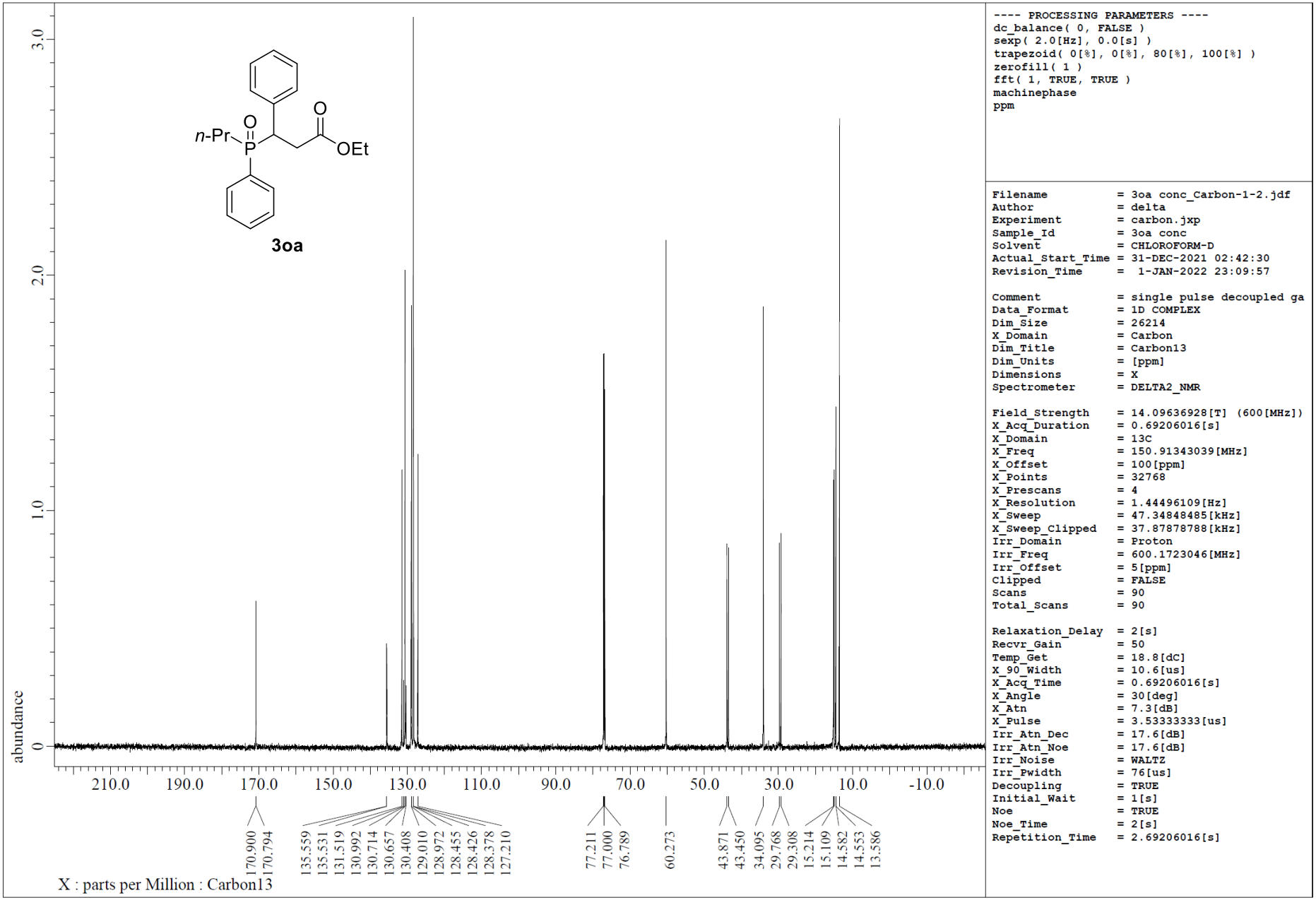
^{13}C NMR spectrum of **3na** (101 MHz, $CDCl_3$)



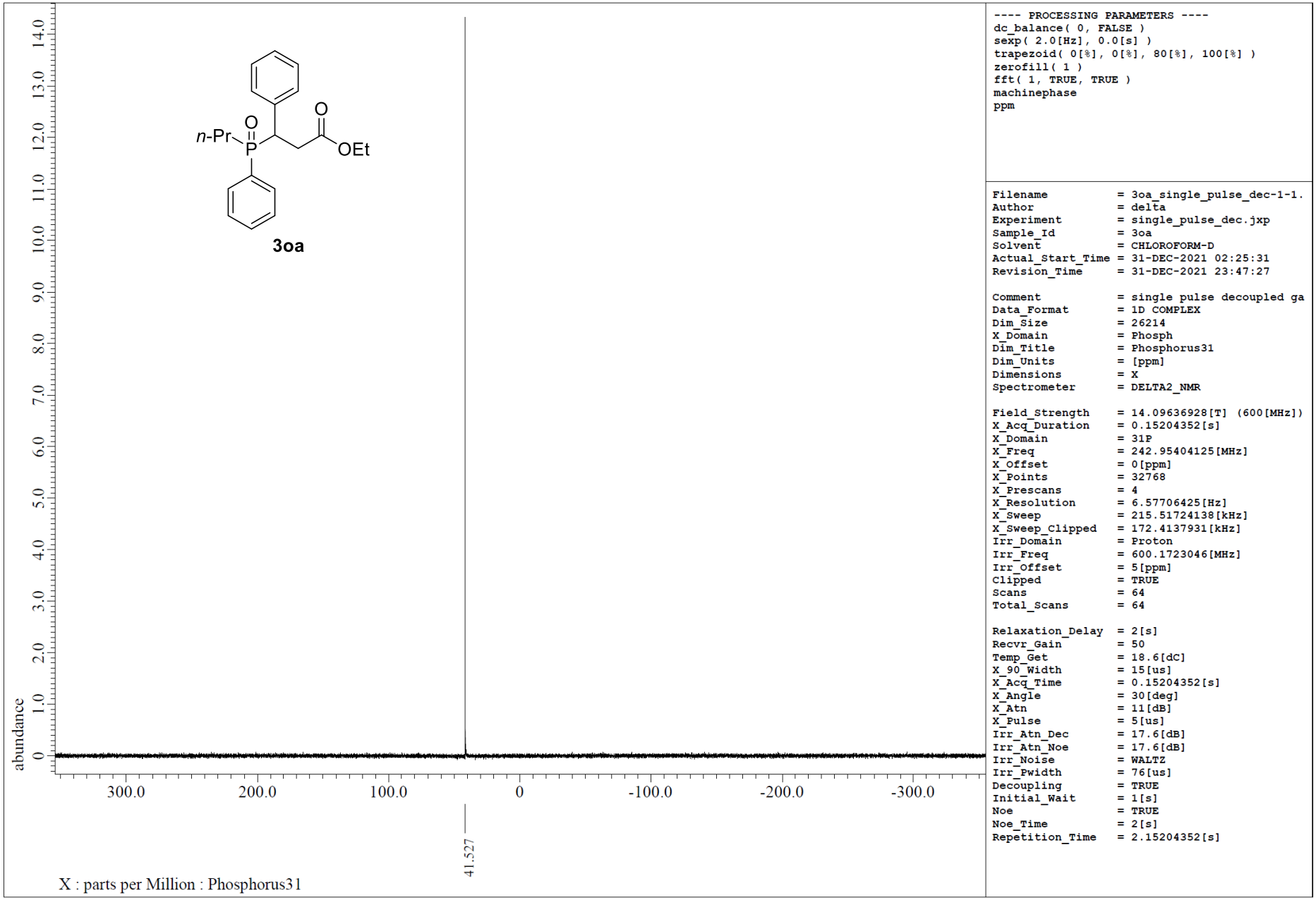
^{31}P NMR spectrum of **3na** (243 MHz, $CDCl_3$)



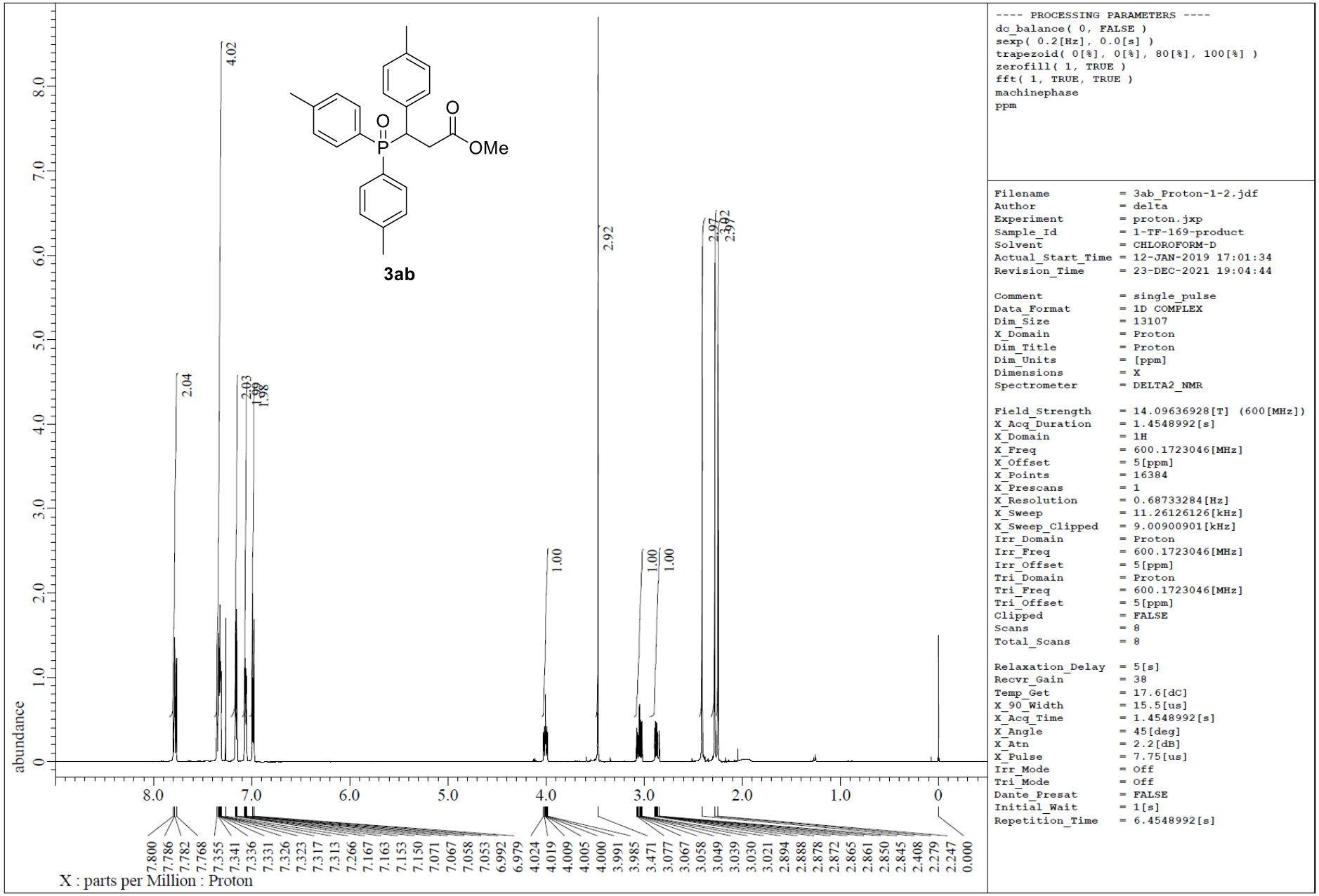
^{1}H NMR spectrum of **3oa** (400 MHz, $CDCl_3$)



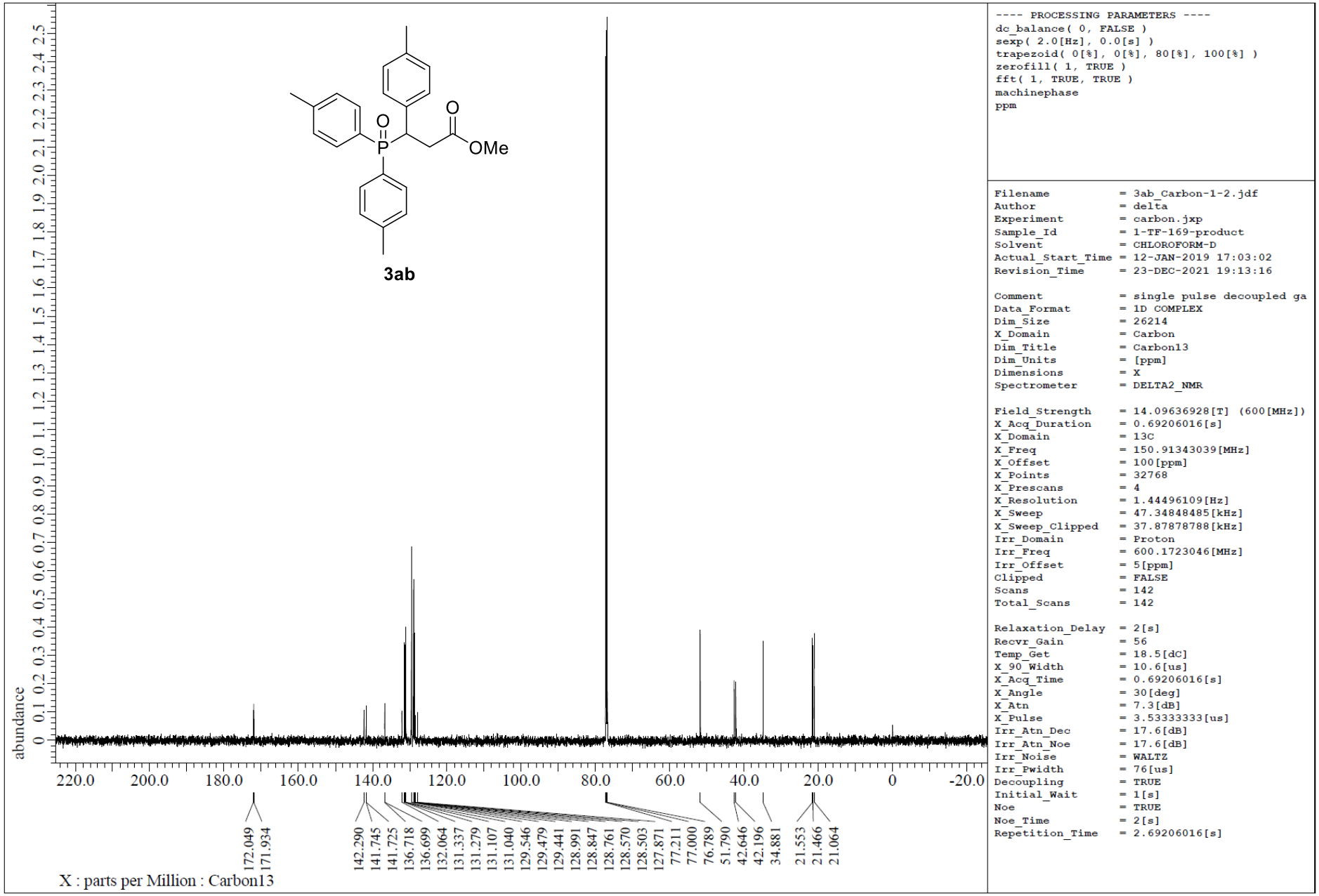
^{13}C NMR spectrum of **3oa** (101 MHz, $CDCl_3$)



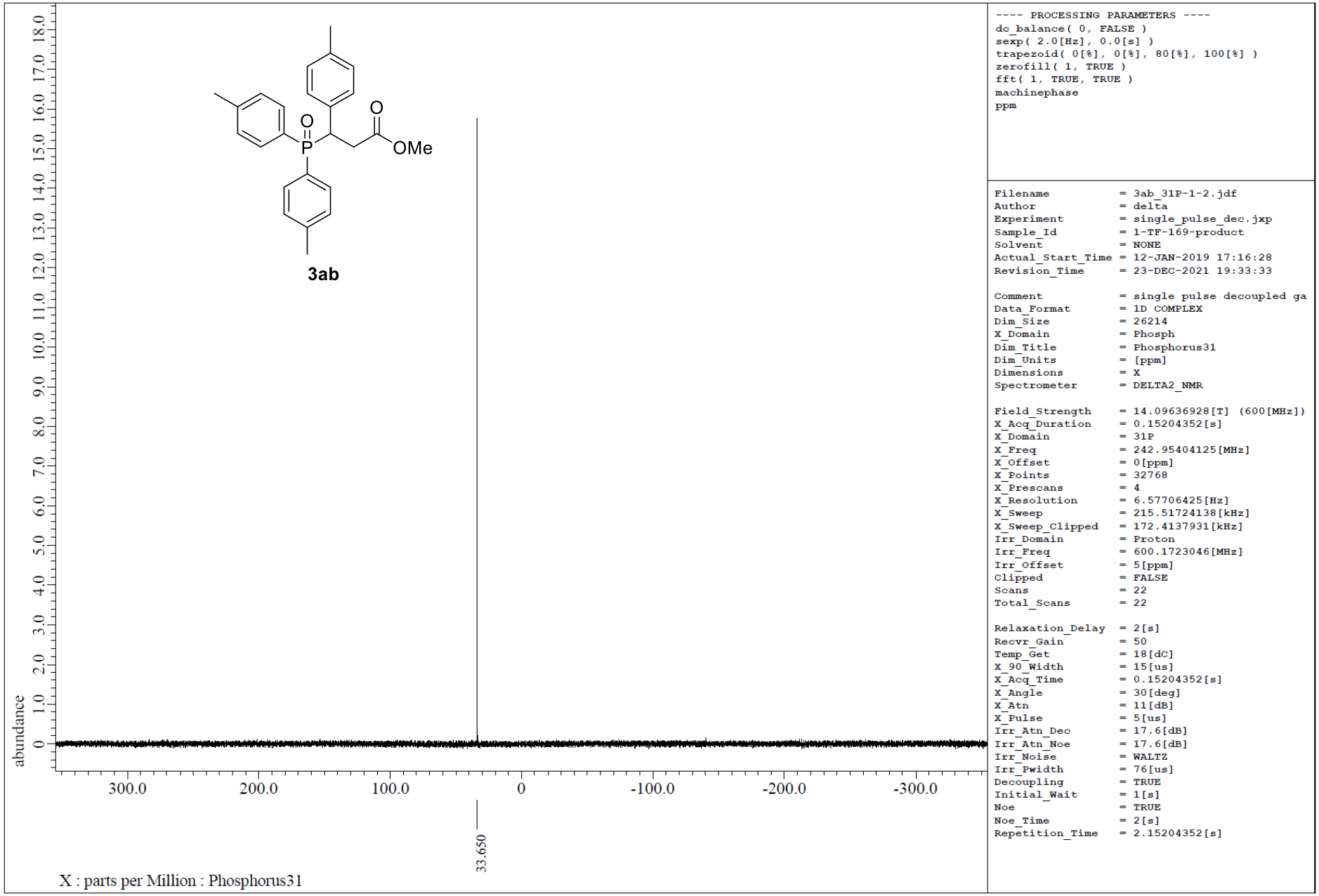
^{31}P NMR spectrum of **3oa** (243 MHz, $CDCl_3$)



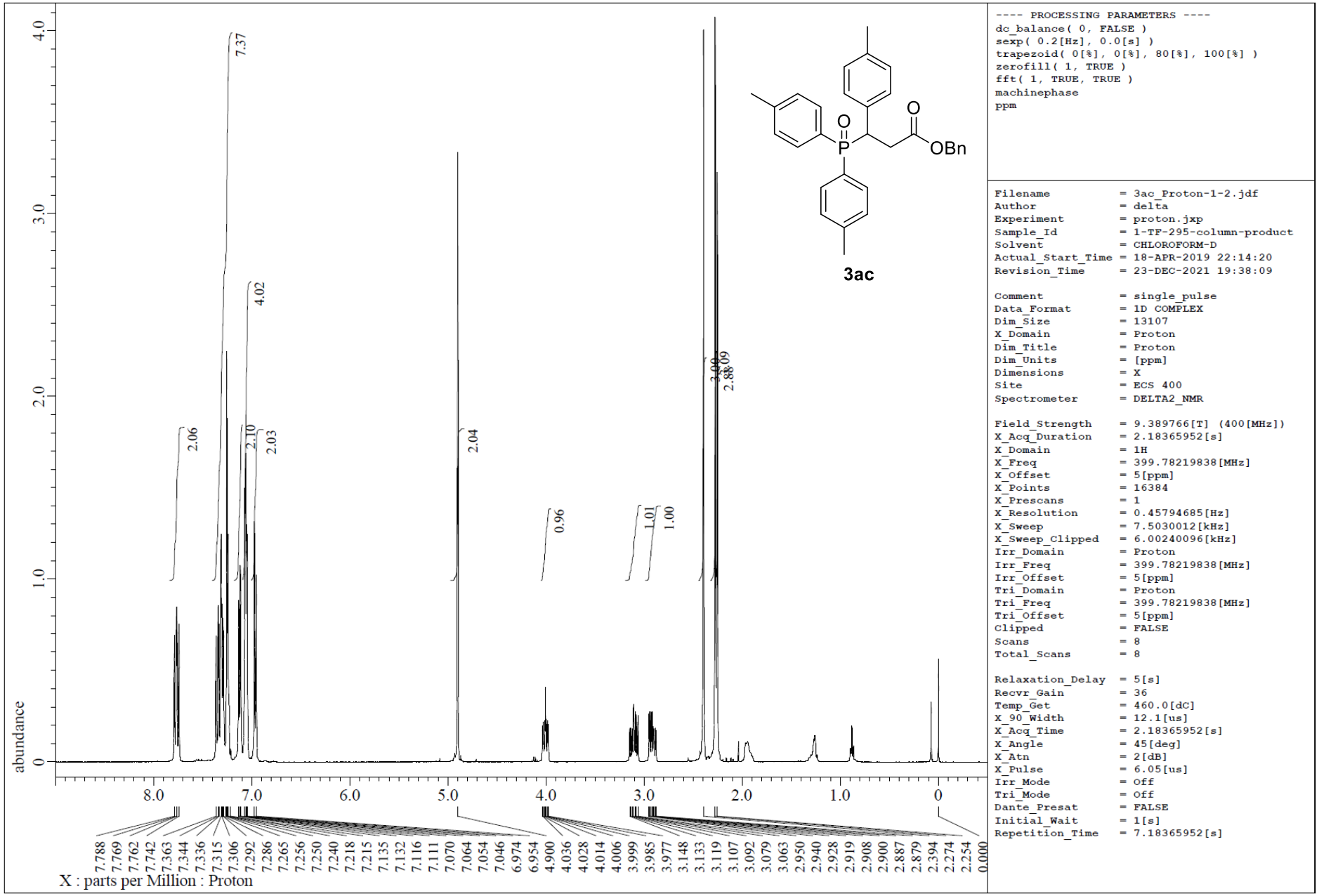
[1] H NMR spectrum of **3ab** (600 MHz, $CDCl_3$)



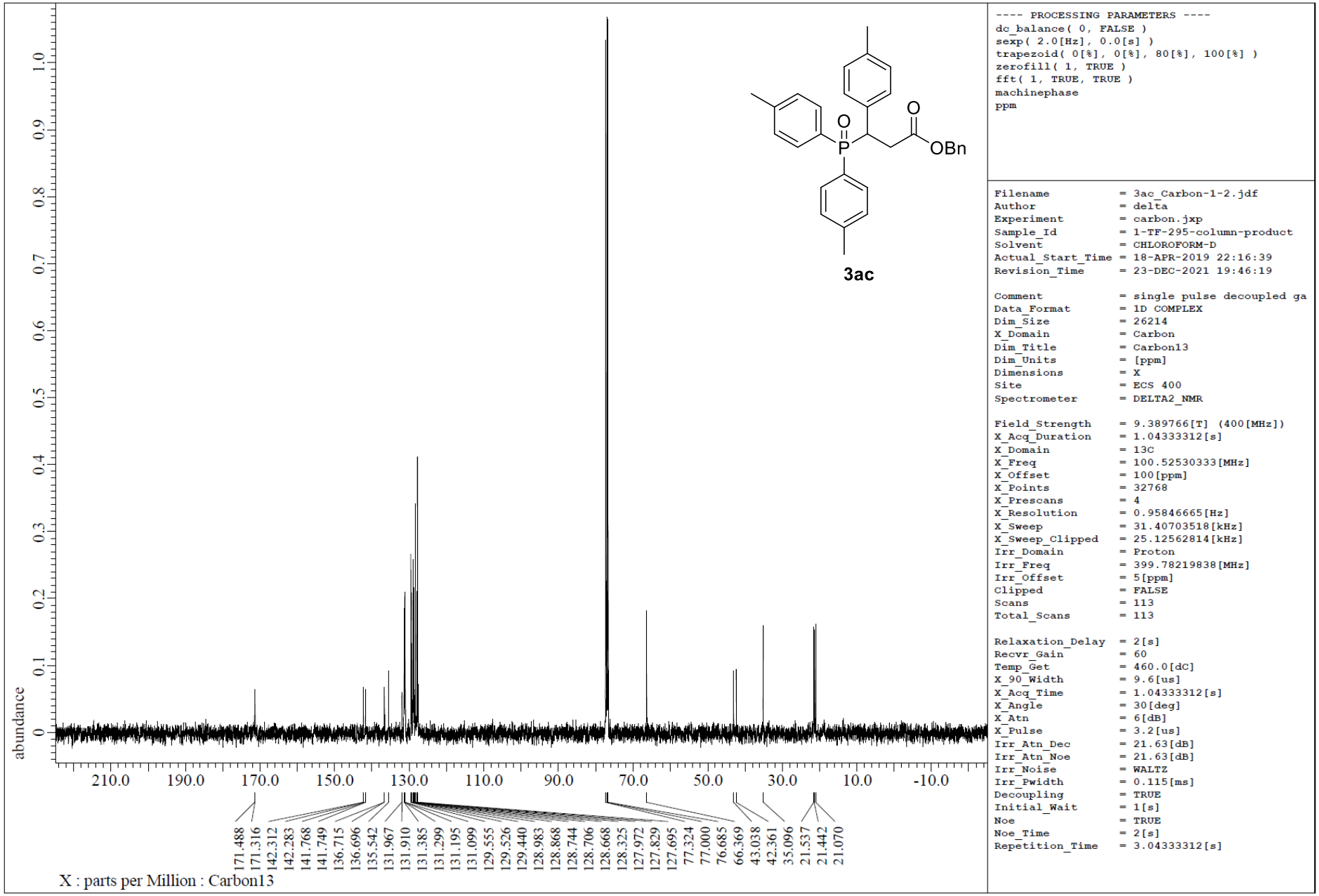
^{13}C NMR spectrum of **3ab** (151 MHz, $CDCl_3$)



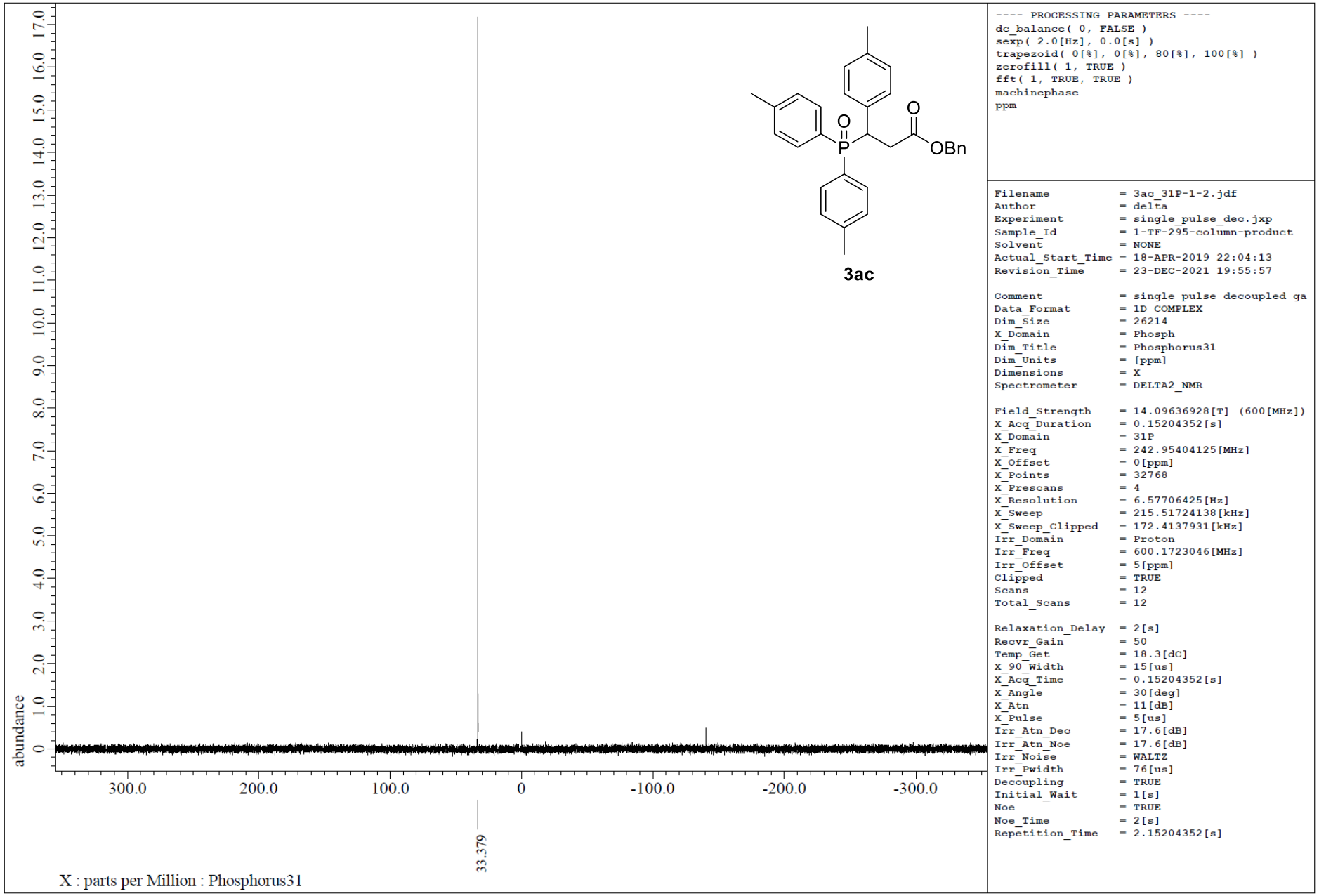
^{31}P NMR spectrum of **3ab** (243 MHz, $CDCl_3$)



[1] H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)



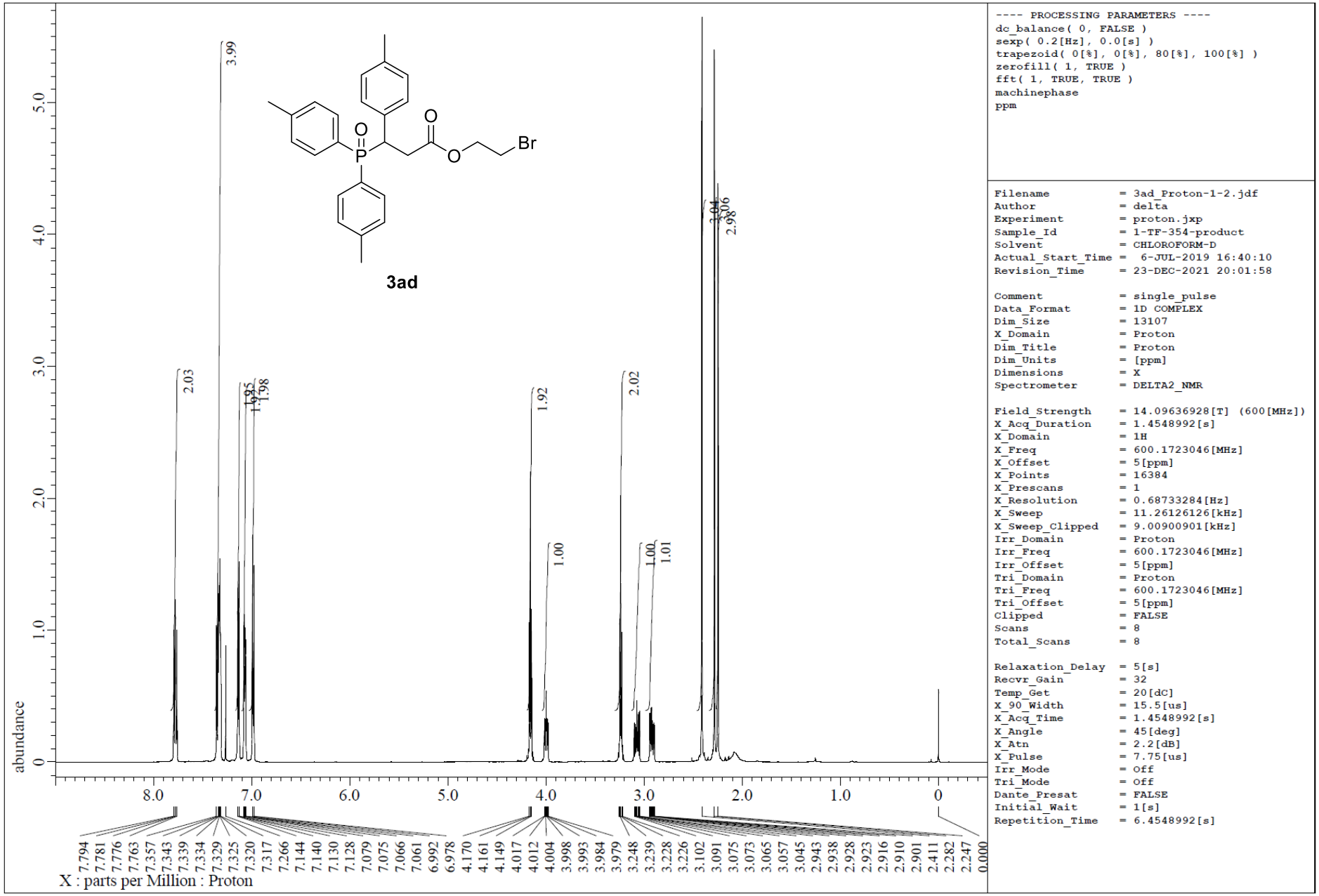
^{13}C NMR spectrum of **3ac** (101 MHz, $CDCl_3$)



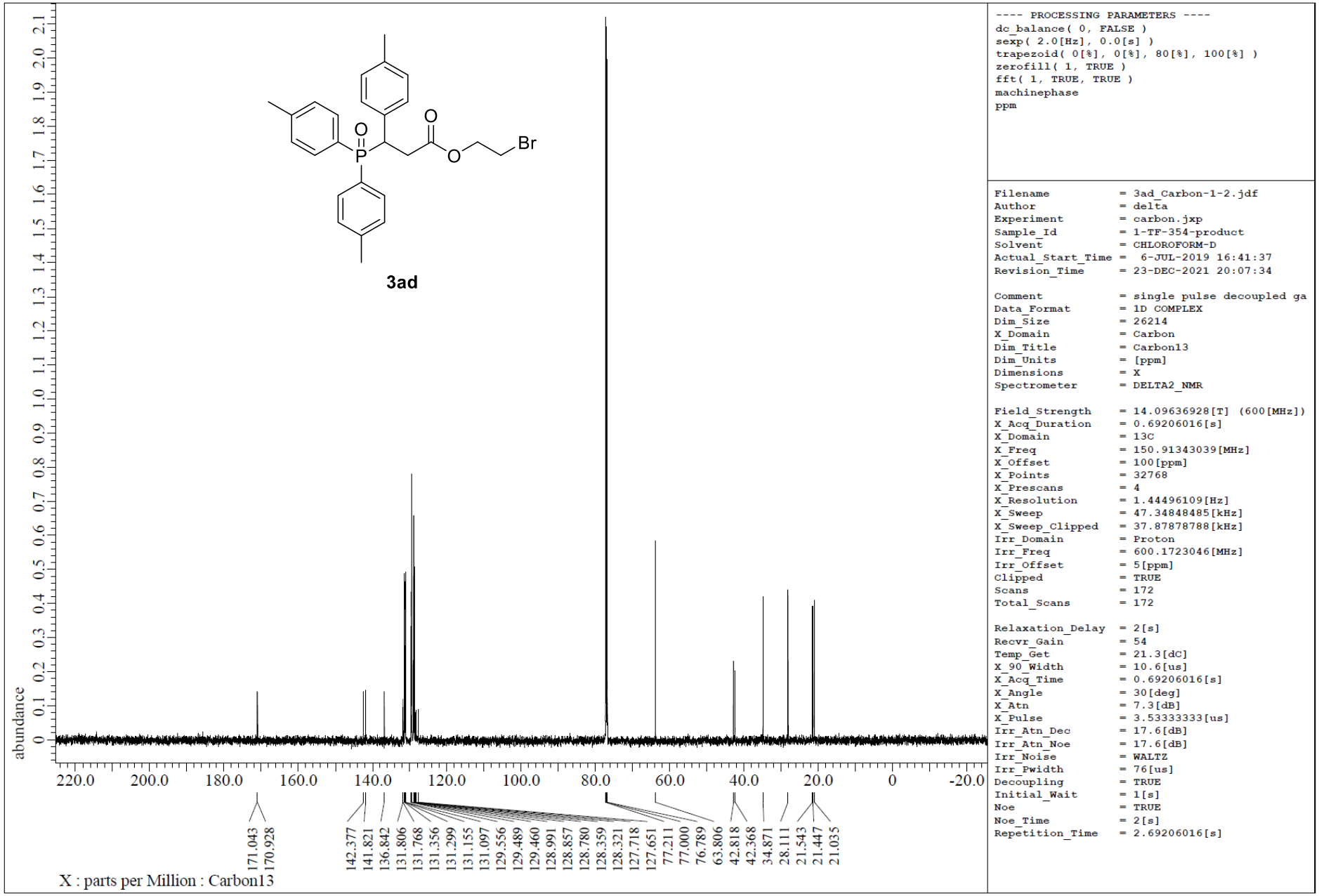

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename           = 3ac_31P-1-2.jdf
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = 1-TF-295-column-product
Solvent            = NONE
Actual_Start_Time  = 18-APR-2019 22:04:13
Revision_Time      = 23-DEC-2021 19:55:57

Comment            = single pulse decoupled ga
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
X_Domain           = Phosph
Dim_Title          = Phosphorus31
Dim_Units          = [ppm]
Dimensions         = X
Spectrometer       = DELTA2_NMR

Field_Strength     = 14.09636928[T] (600[MHz])
X_Acq_Duration     = 0.15204352[s]
X_Domain           = 31P
X_Freq             = 242.95404125[MHz]
X_Offset           = 0[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 6.57706425[Hz]
X_Sweep            = 215.51724138[kHz]
X_Sweep_Clipped    = 172.4137931[kHz]
Irr_Domain         = Proton
Irr_Freq           = 600.1723046[MHz]
Irr_Offset         = 5[ppm]
Clipped            = TRUE
Scans              = 12
Total_Scans        = 12

Relaxation_Delay   = 2[s]
Recvr_Gain         = 50
Temp_Get           = 18.3[dC]
X_90_Width         = 15[us]
X_Acq_Time         = 0.15204352[s]
X_Angle            = 30[deg]
X_Atn              = 11[dB]
X_Pulse            = 5[us]
Irr_Atn_Dec        = 17.6[dB]
Irr_Atn_Noe        = 17.6[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 76[us]
Decoupling         = TRUE
Initial_Wait       = 1[s]
Noe                = TRUE
Noe_Time           = 2[s]
Repetition_Time    = 2.15204352[s]
```

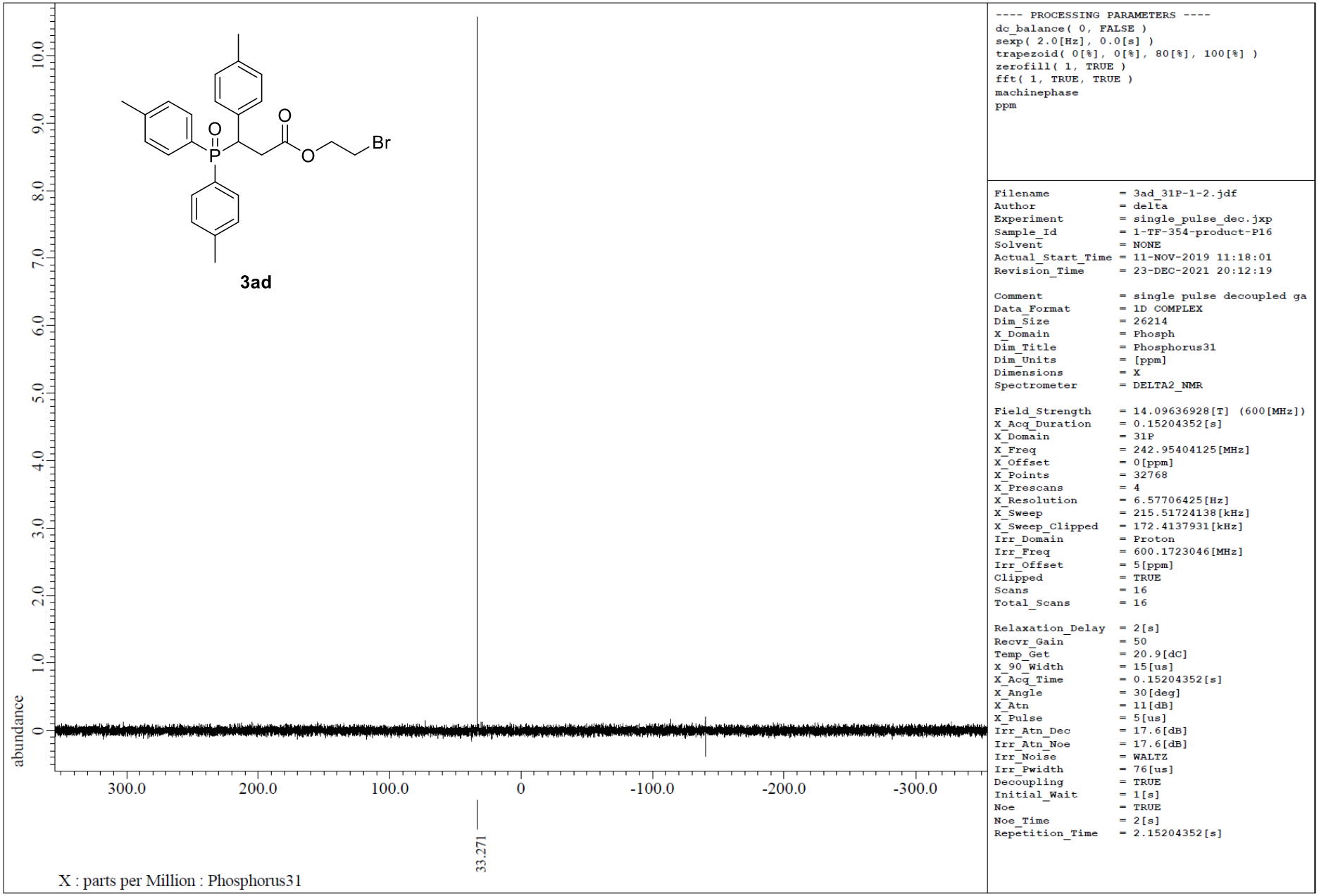
^{31}P NMR spectrum of **3ac** (243 MHz, $CDCl_3$)



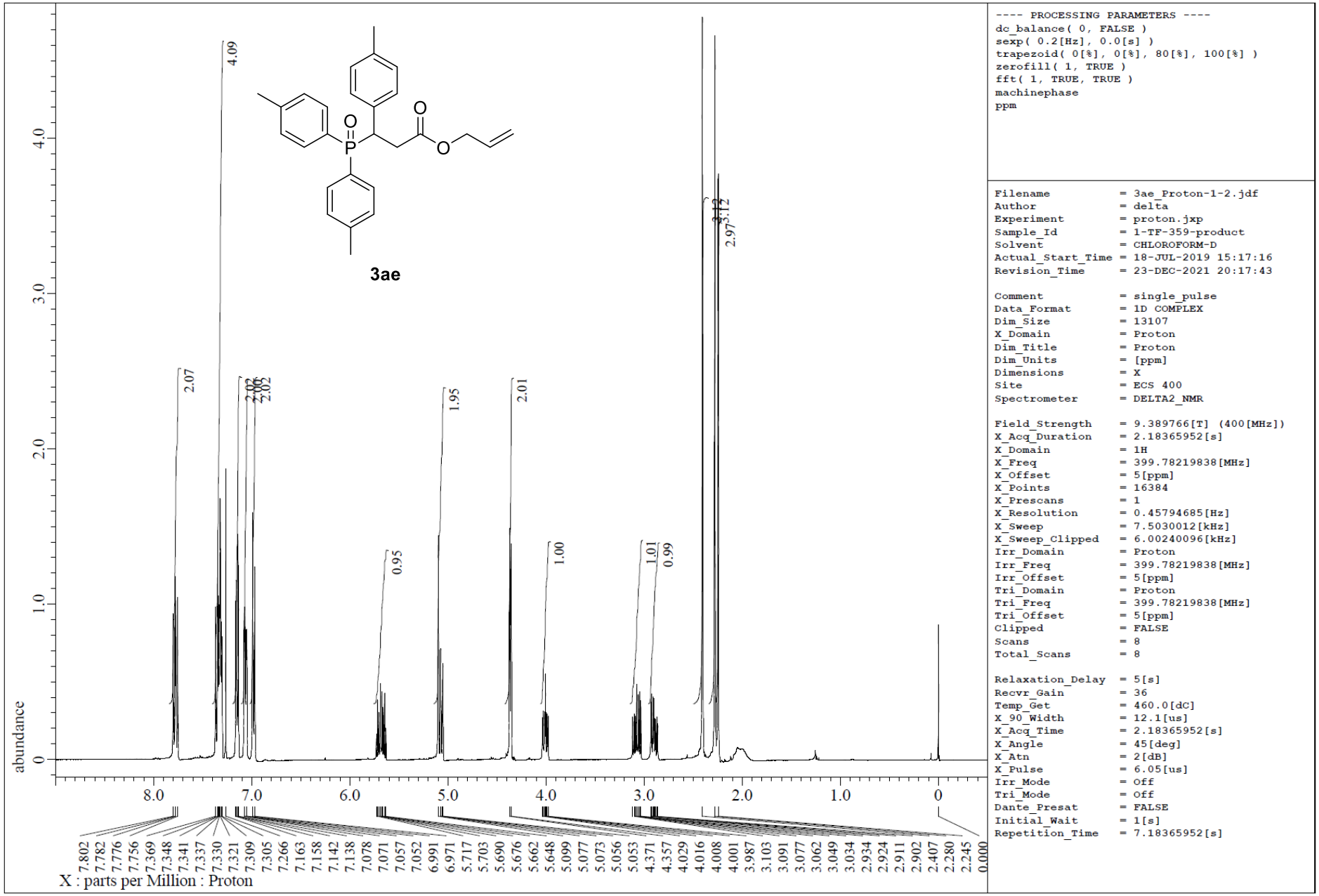
[1] H NMR spectrum of **3ad** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3ad** (151 MHz, $CDCl_3$)



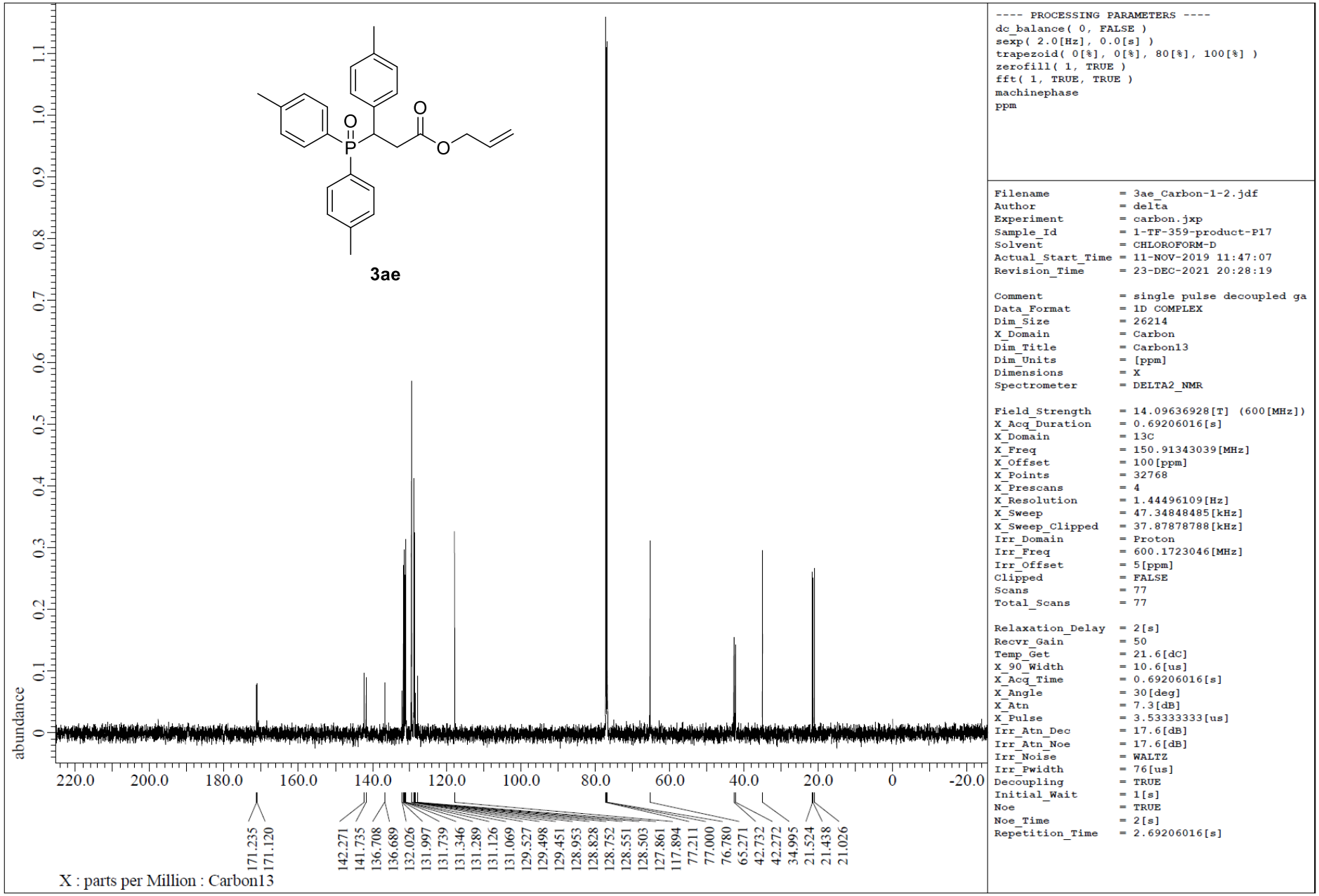
^{31}P NMR spectrum of **3ad** (243 MHz, $CDCl_3$)



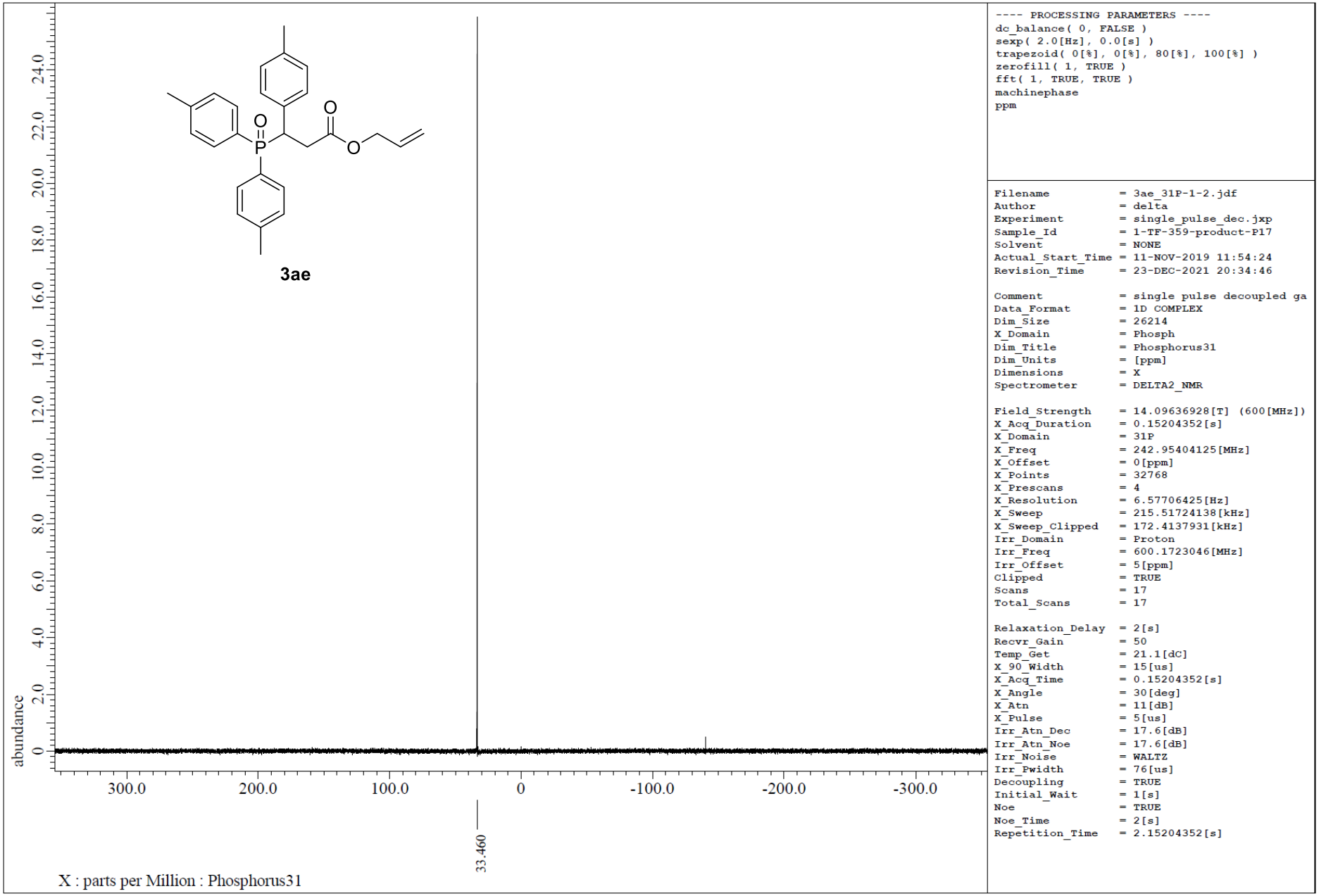

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3ae_Proton-1-2.jdf
Author              = delta
Experiment          = proton.jxp
Sample_Id           = 1-TF-359-product
Solvent             = CHLOROFORM-D
Actual_Start_Time   = 18-JUL-2019 15:17:16
Revision_Time       = 23-DEC-2021 20:17:43

Comment             = single_pulse
Data_Format         = 1D COMPLEX
Dim_Size            = 13107
X_Domain            = Proton
Dim_Title           = Proton
Dim_Units           = [ppm]
Dimensions          = X
Site                = ECS 400
Spectrometer        = DELTA2_NMR

Field_Strength      = 9.389766[T] (400[MHz])
X_Acq_Duration      = 2.18365952[s]
X_Domain            = 1H
X_Freq              = 399.78219838[MHz]
X_Offset            = 5[ppm]
X_Points            = 16384
X_Prescans          = 1
X_Resolution        = 0.45794685[Hz]
X_Sweep             = 7.5030012[kHz]
X_Sweep_Clipped     = 6.00240096[kHz]
Irr_Domain          = Proton
Irr_Freq            = 399.78219838[MHz]
Irr_Offset          = 5[ppm]
Tri_Domain          = Proton
Tri_Freq            = 399.78219838[MHz]
Tri_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 8
Total_Scans         = 8

Relaxation_Delay    = 5[s]
Recvr_Gain          = 36
Temp_Get            = 460.0[dC]
X_90_Width          = 12.1[us]
X_Acq_Time          = 2.18365952[s]
X_Angle             = 45[deg]
X_Atn               = 2[dB]
X_Pulse             = 6.05[us]
Irr_Mode            = Off
Tri_Mode            = Off
Dante_Presat        = FALSE
Initial_Wait        = 1[s]
Repetition_Time     = 7.18365952[s]
```

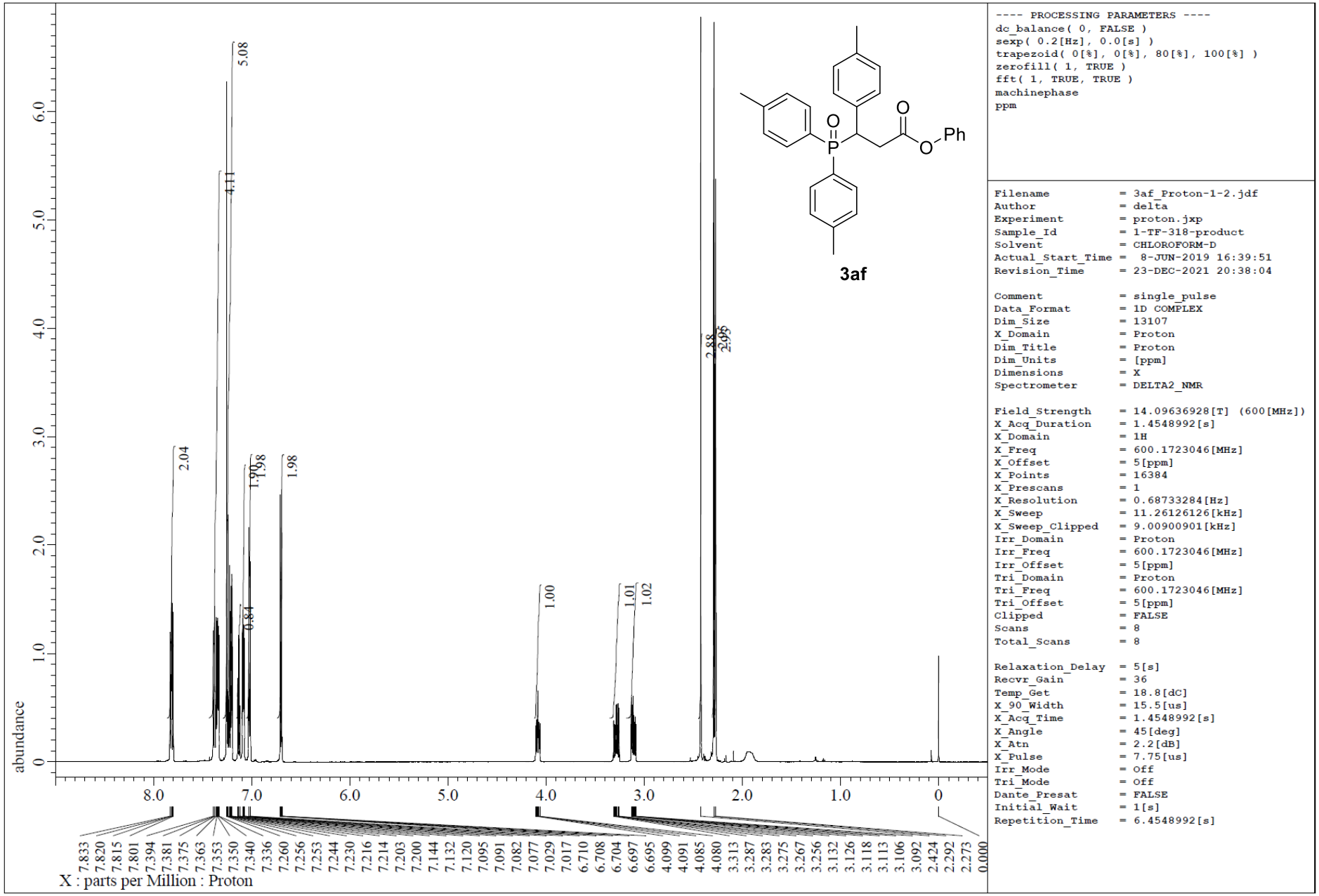
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)



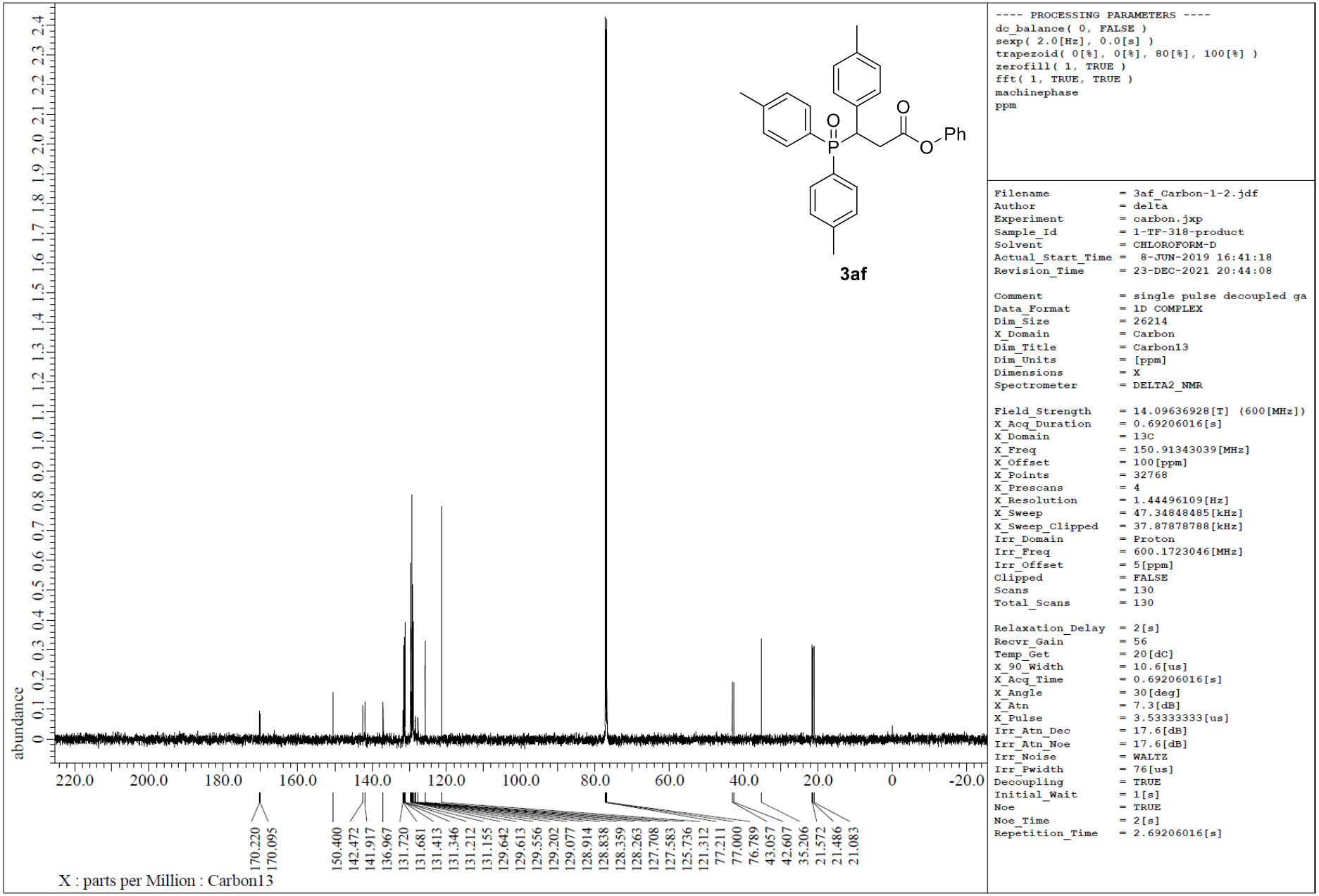
^{13}C NMR spectrum of **3ae** (151 MHz, $CDCl_3$)



^{31}P NMR spectrum of **3ae** (243 MHz, $CDCl_3$)



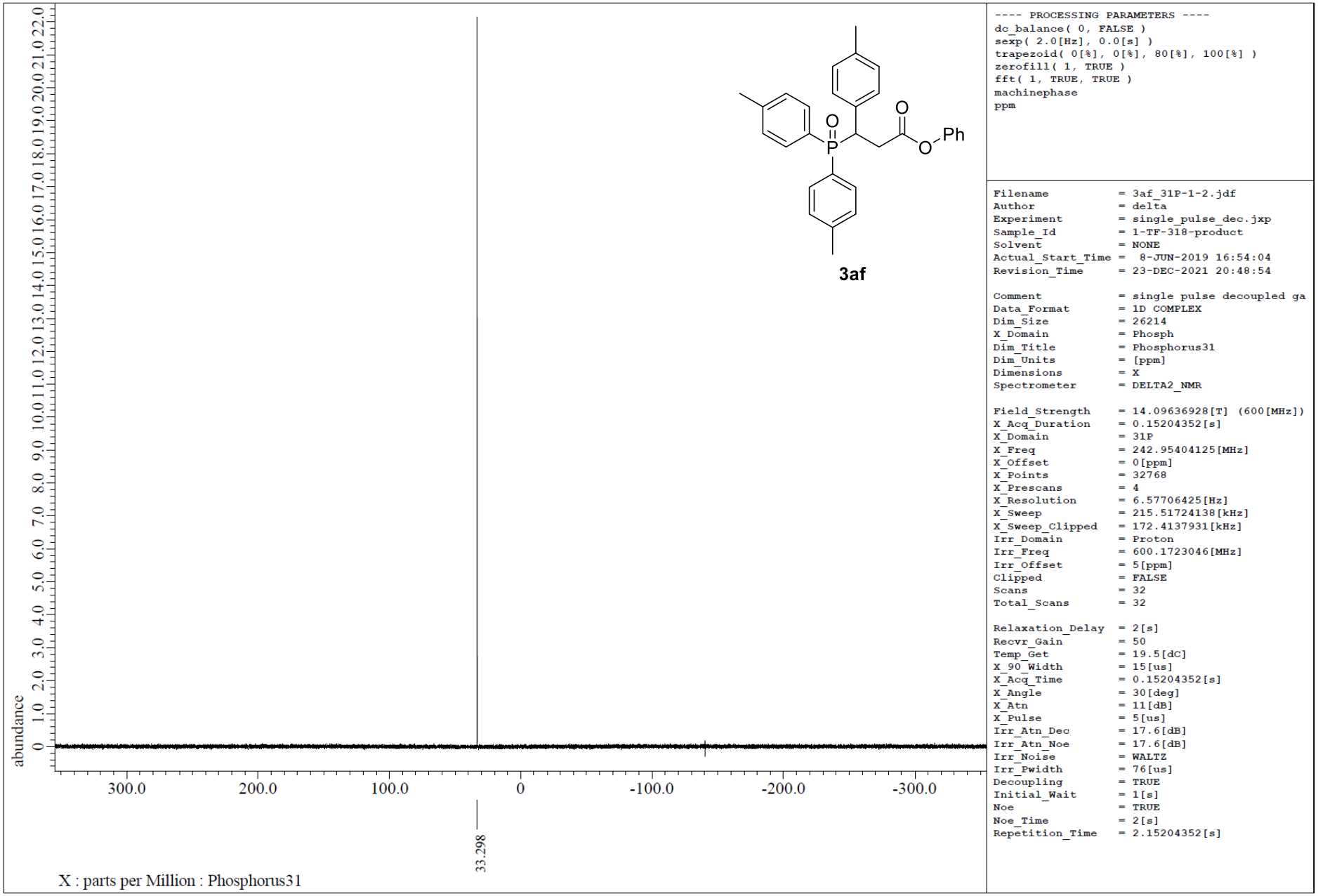
[1] H NMR spectrum of **3af** (600 MHz, $CDCl_3$)



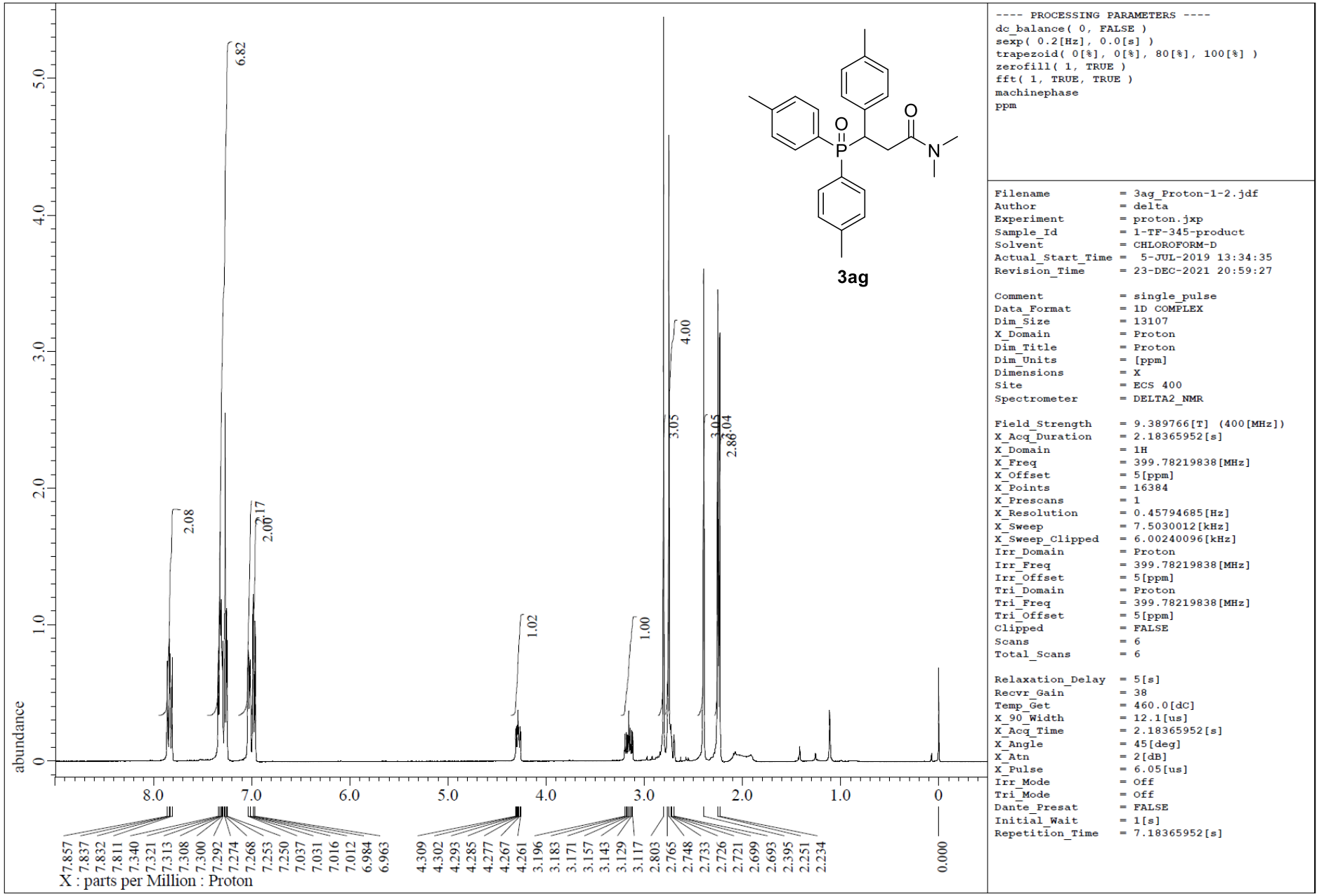

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1, TRUE )
fft( 1, TRUE, TRUE )
machinephase
ppm
```

```
Filename            = 3af_Carbon-1-2.jdf
Author              = delta
Experiment          = carbon.jxp
Sample_Id           = 1-TF-318-product
Solvent             = CHLOROFORM-D
Actual_Start_Time   =  8-JUN-2019 16:41:18
Revision_Time       = 23-DEC-2021 20:44:08

Comment             = single pulse decoupled ga
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
X_Domain            = Carbon
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Spectrometer        = DELTA2_NMR

Field_Strength      = 14.09636928[T] (600[MHz])
X_Acq_Duration      = 0.69206016[s]
X_Domain            = 13C
X_Freq              = 150.91343039[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.44496109[Hz]
X_Sweep             = 47.34848485[kHz]
X_Sweep_Clipped     = 37.87878788[kHz]
Irr_Domain          = Proton
Irr_Freq            = 600.1723046[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 130
Total_Scans         = 130

Relaxation_Delay    = 2[s]
Recvr_Gain          = 56
Temp_Get            = 20[dC]
X_90_Width          = 10.6[us]
X_Acq_Time          = 0.69206016[s]
X_Angle             = 30[deg]
X_Atn               = 7.3[dB]
X_Pulse             = 3.53333333[us]
Irr_Atn_Dec         = 17.6[dB]
Irr_Atn_Noe         = 17.6[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 76[us]
Decoupling          = TRUE
Initial_Wait        = 1[s]
Noe                 = TRUE
Noe_Time            = 2[s]
Repetition_Time     = 2.69206016[s]
```

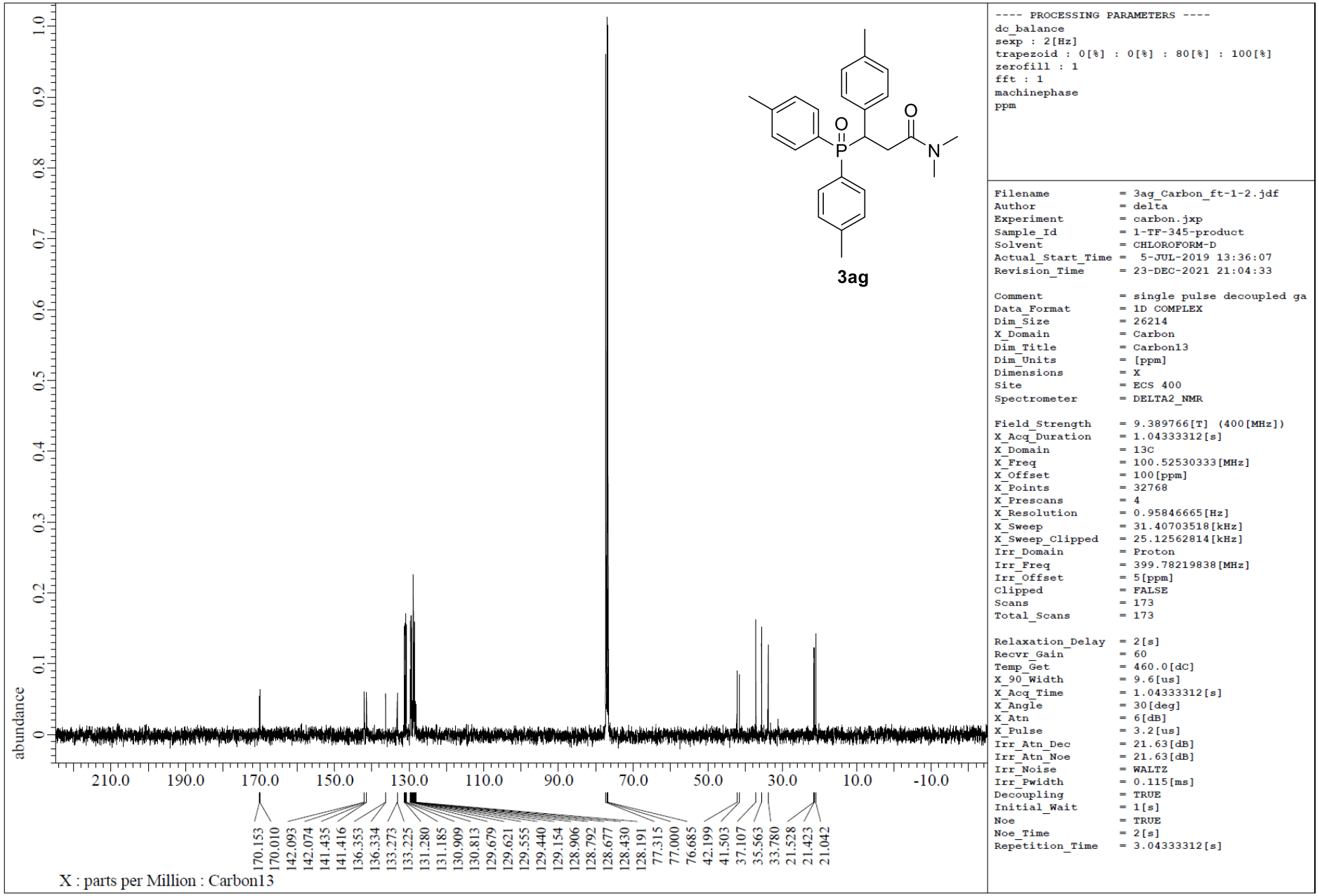
^{13}C NMR spectrum of **3af** (151 MHz, $CDCl_3$)



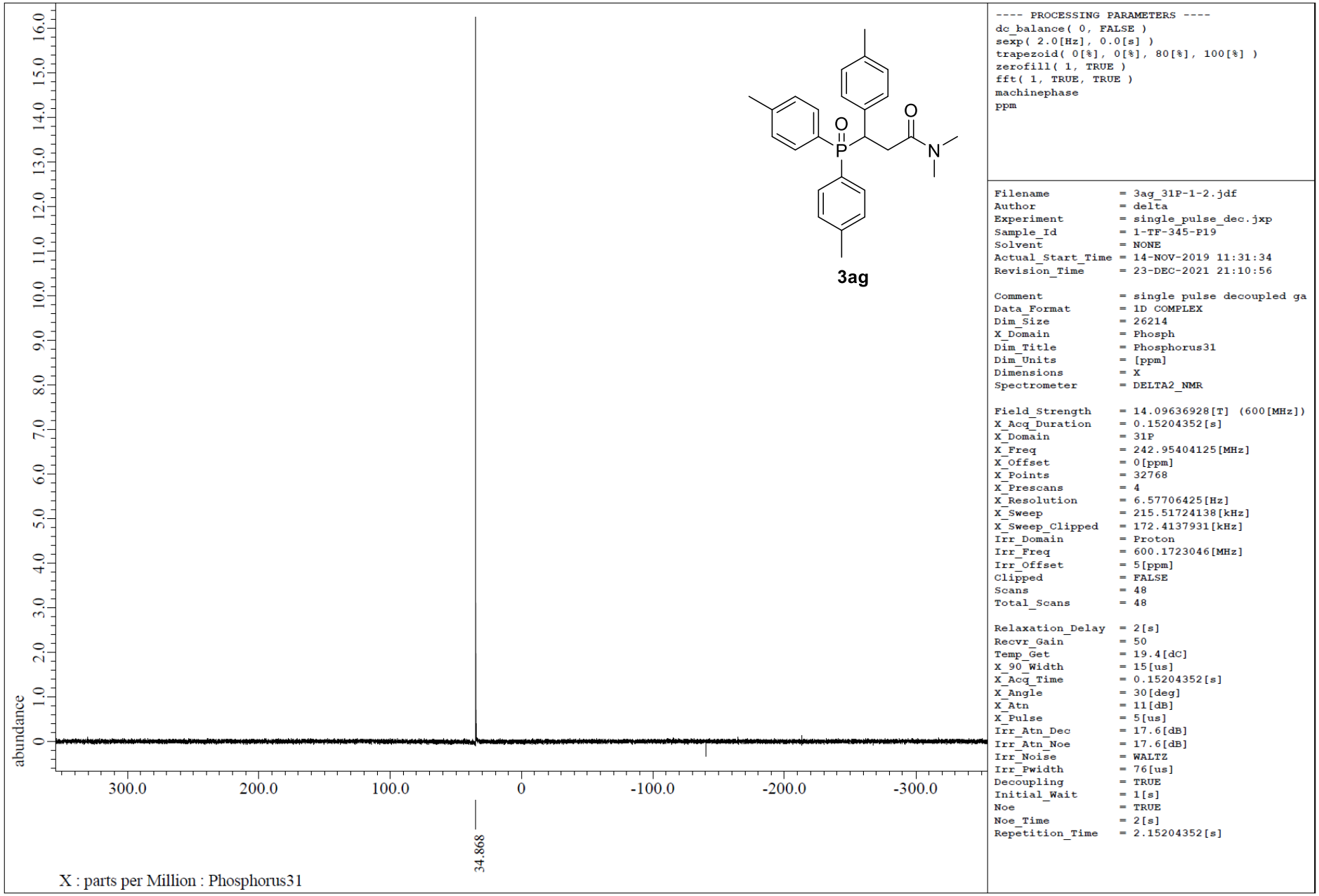
^{31}P NMR spectrum of **3af** (243 MHz, $CDCl_3$)



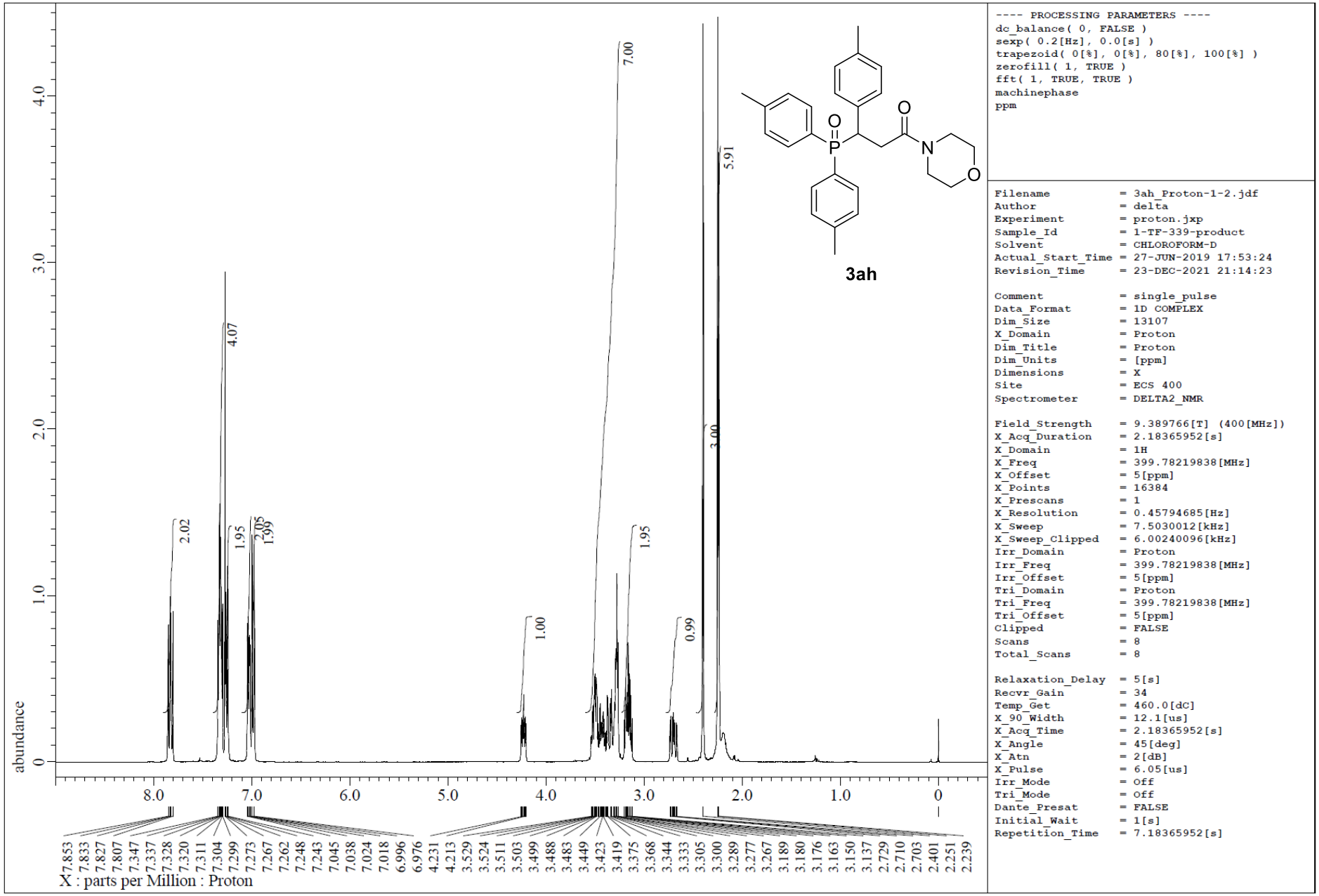
[1] H NMR spectrum of **3ag** (400 MHz, $CDCl_3$)



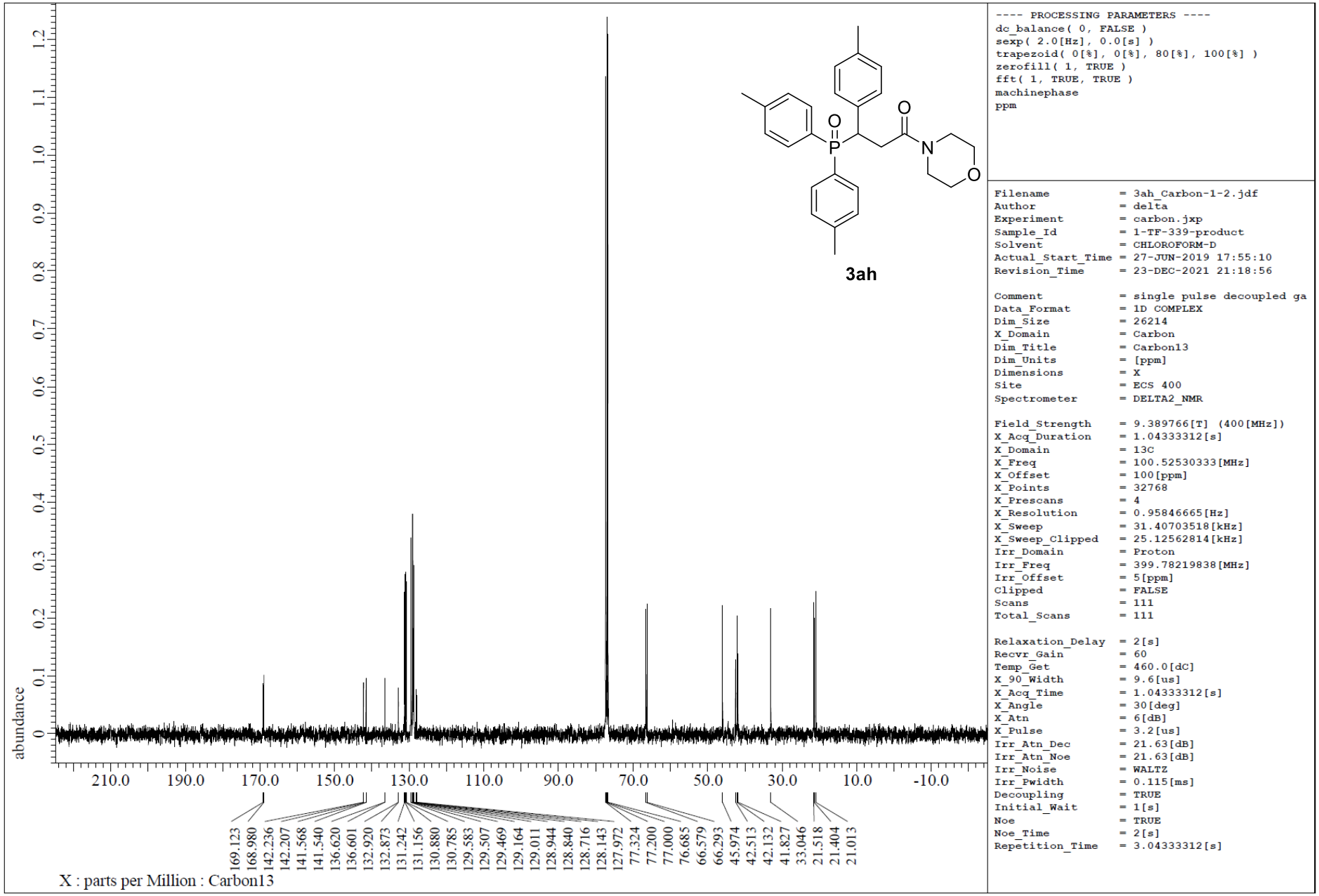
^{13}C NMR spectrum of **3ag** (101 MHz, $CDCl_3$)



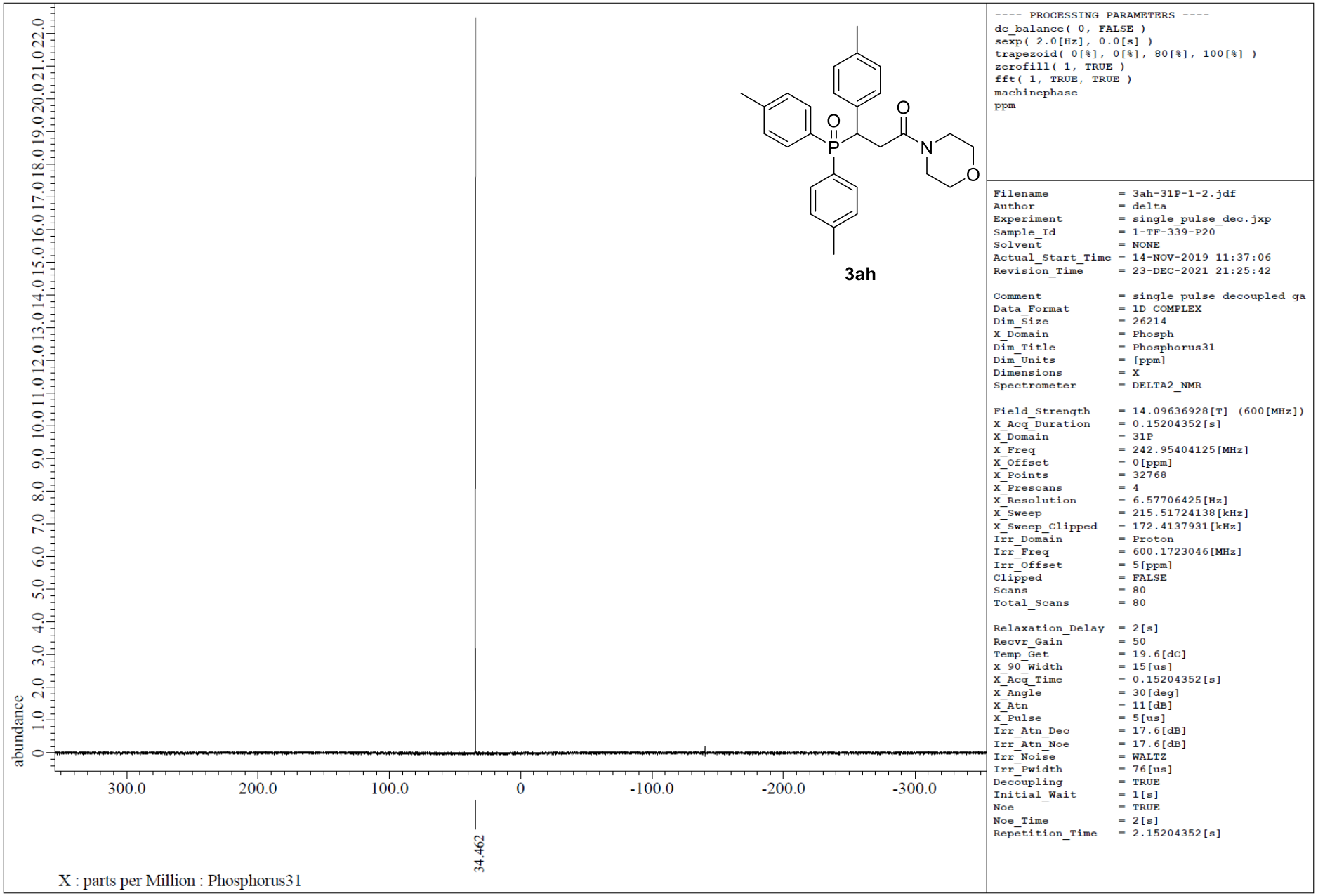
^{31}P NMR spectrum of **3ag** (243 MHz, $CDCl_3$)



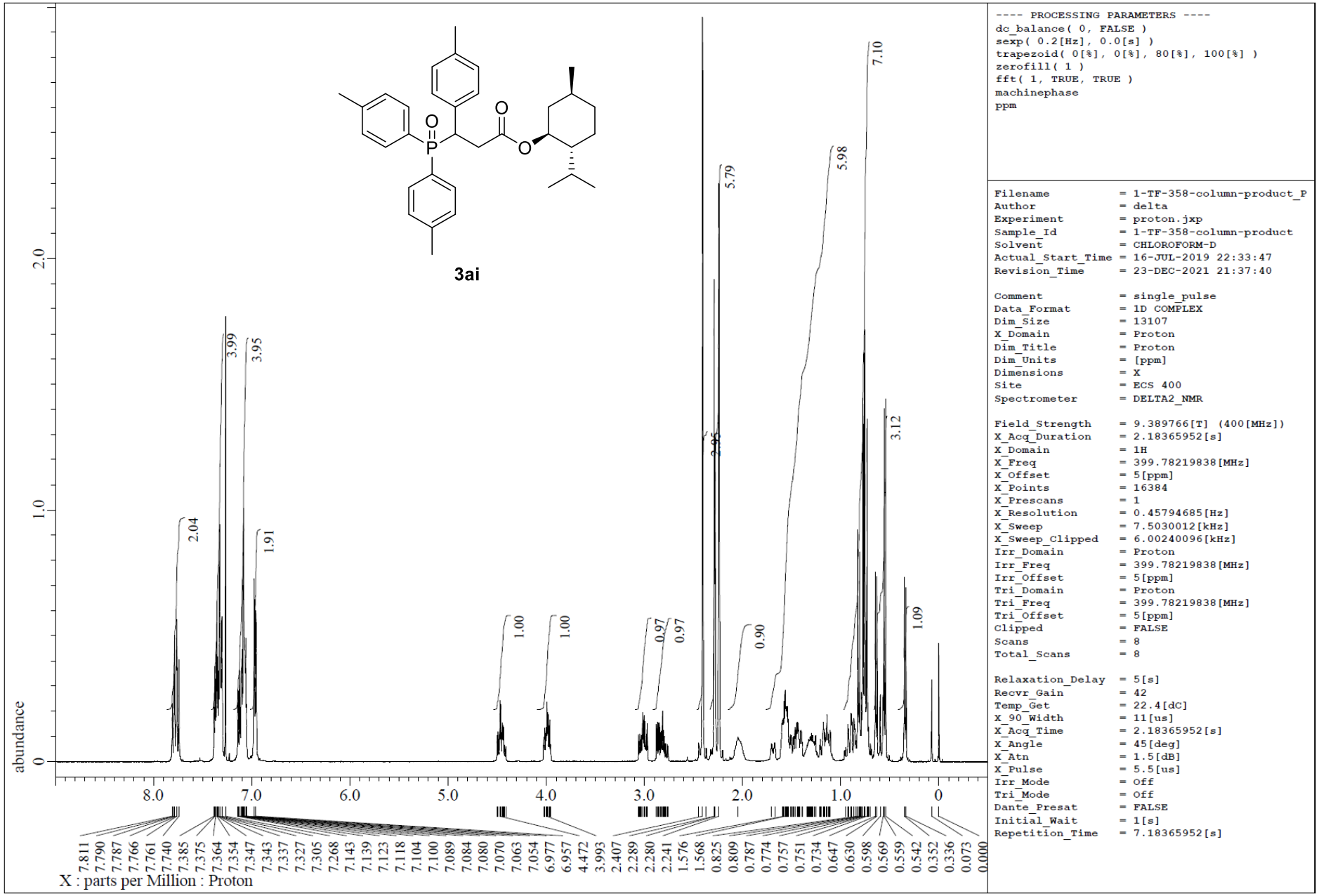
[1] H NMR spectrum of **3ah** (400 MHz, $CDCl_3$)



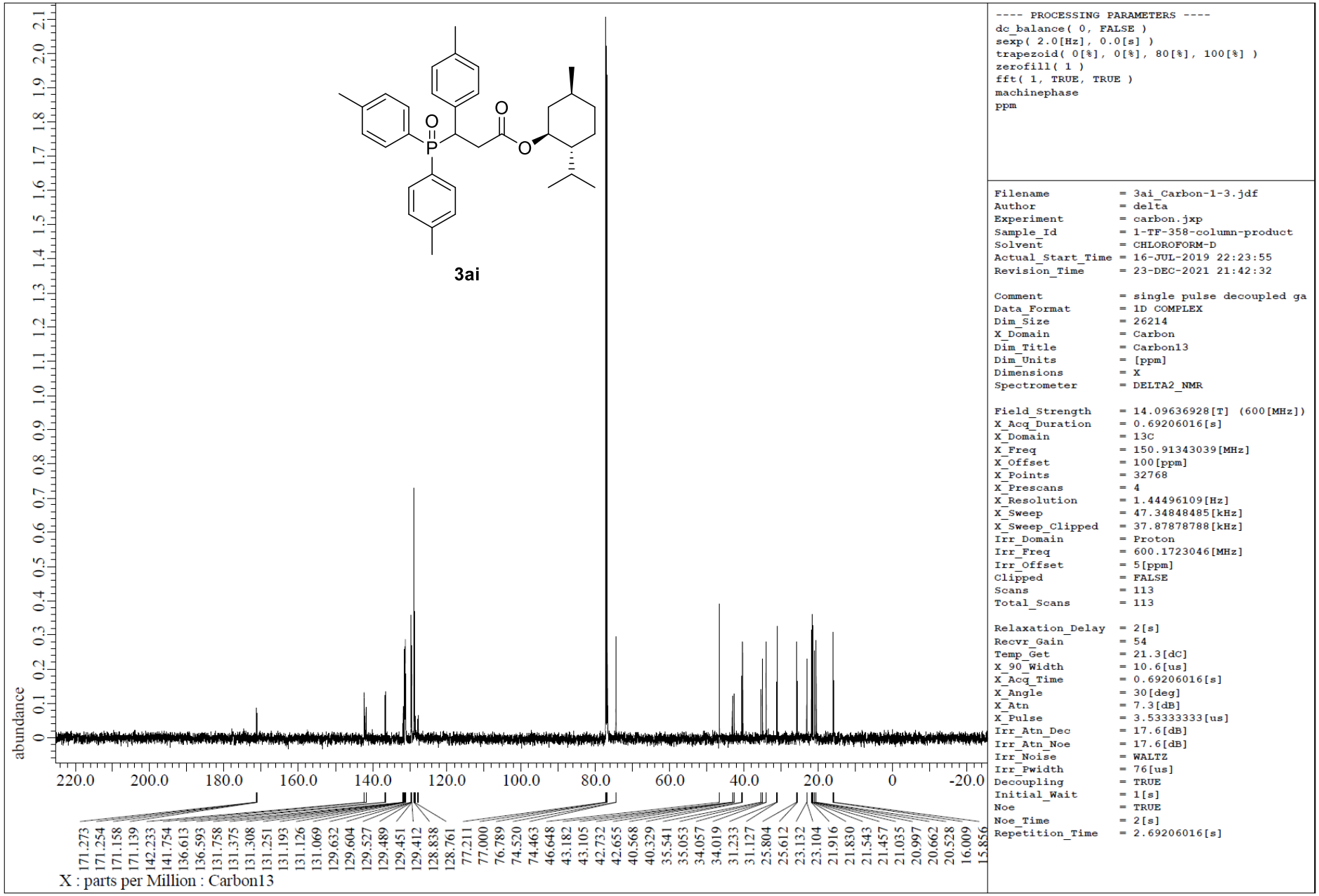
^{13}C NMR spectrum of **3ah** (101 MHz, $CDCl_3$)



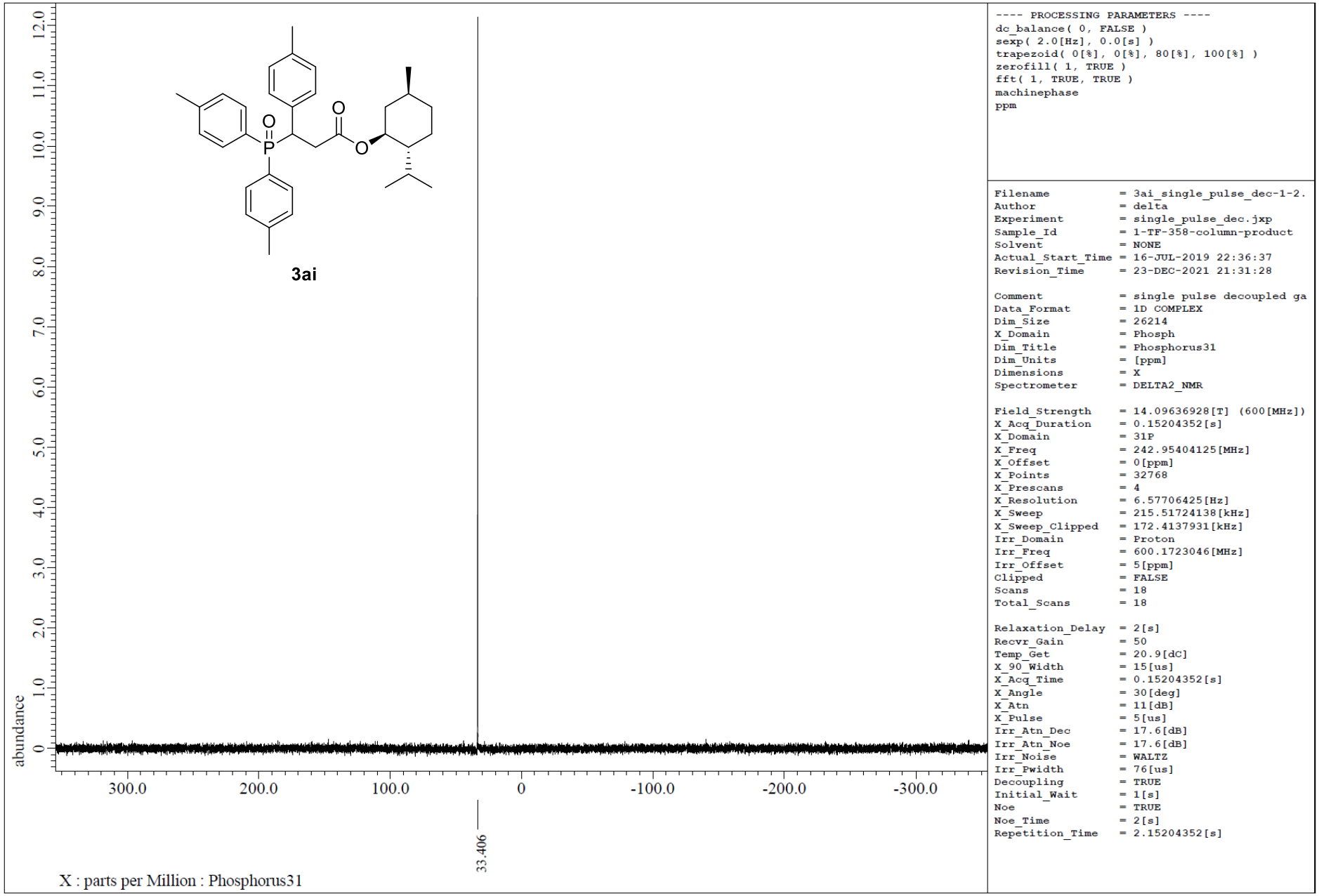
^{31}P NMR spectrum of **3ah** (243 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3ai** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3ai** (151 MHz, $CDCl_3$)



^{31}P NMR spectrum of **3ai** (243 MHz, $CDCl_3$)