Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Highly Efficient Nucleophilic Substitution Reaction Between $R_2P(O)H$ and Triarylmethanols to Phosphorus-Substituted Triarylmethanes

Long Chen,[a*] Xin-Yue Fang,[a] and Yun-Xiang Zou[a]

[a] *Antibiotics Research and Re-evaluation Key Laboratory of Sichuan Province, Sichuan Industrial Institute of Antibiotics, Chengdu University, 168 Hua Guan Road, Chengdu 610052, P. R. China*

E-mail: chenlong@cdu.edu.cn

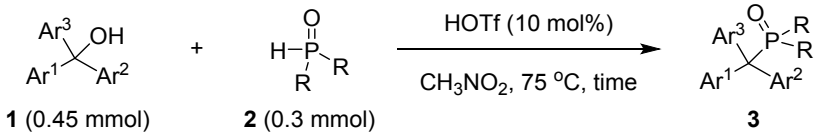
Contents **page**

General: Reactions were monitored by thin layer chromatography using UV light to visualize the reaction course. Purification of reaction products were carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 spectrometer. The ^{31}P NMR spectra were recorded at 162 MHz with 85% H_3PO_4 as external standard. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

All reactions were run under an atmosphere of air. Anhydrous THF and toluene were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous acetone was distilled over anhydrous $CaSO_4$ and stored over MS 4Å. Anhydrous halogenated solvents and CH_3CN were prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous ethyl acetate was prepared by first dried in anhydrous Na_2SO_4 and then distilled over P_2O_5 and stored over MS 4Å. Anhydrous CH_3NO_2 was prepared by first dried in anhydrous Na_2SO_4 and then distilled under reduced pressure. Triarylmethanols **1** were prepared according to the literature report.[1] Commercially available HOTf (trifluoromethanesulfonic acid) was used as received.

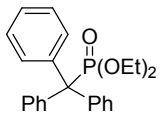
[1]. M. Horn and H. Mayr, *Chem. Eur. J.*, 2010, **16**, 7469.

General procedure for the nucleophilic substitution reaction between $R_2P(O)H$ and triarylmethanols



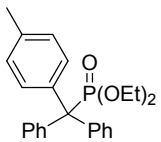
1 (0.45 mmol) **2** (0.3 mmol) **3**

The reaction was carried out under an air atmosphere. To a 5-mL vial were added triarylmethanols **1** (0.45 mmol, 1.5 equivs), $R_2P(O)H$ **2** (0.3 mmol, 1.0 equiv) and 1.0 mL of anhydrous CH_3NO_2. After adding HOTf (4.5 mg, 10 mol%) which was prepared as a solution in CH_3NO_2, the reaction mixture was stirred at 75 °C till almost full conversion of **2** by TLC analysis. The reaction mixture was directly subjected to column chromatography using petrol ether/ethyl acetate (generally 6:1 to 3:1, v:v) as the eluent to afford the desired products **3** or **4**.



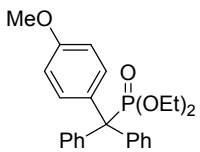
3a

Column chromatography afforded the desired product **3a**[2] in 90% yield (102.6 mg) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.25 (m, 15H), 4.06-3.96 (m, 2H), 3.87-3.77 (m, 2H), 1.09 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 130.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.8, 126.8 (d, $J_{C\text{-}P}$ = 1.0 Hz), 63.3 (d, $J_{C\text{-}P}$ = 8.0 Hz), 63.0 (d, $J_{C\text{-}P}$ = 135.0 Hz), 16.2, 16.1; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 25.9.



3b

Column chromatography afforded **3b** in 92% yield (108.7 mg) as white solid; Mp: 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.35 (m, 4H), 7.32-7.27 (m, 6H), 7.24-7.22 (m, 2H), 7.12-7.10 (m, 2H), 4.08-3.98 (m, 2H), 3.89-3.79 (m, 2H), 2.36 (s, 3H), 1.11 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.6, 138.4, 136.4, 130.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 130.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 128.5, 127.7, 126.8, 63.3 (d, $J_{C\text{-}P}$ = 5.0 Hz), 62.5 (d, $J_{C\text{-}P}$ = 90.0 Hz), 20.9, 16.2, 16.1; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 26.2; IR (neat): 3756, 2920, 1493, 1241, 1046, 954, 700, 624 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{27}O_3P$ $[M+H]^+$: 395.1771, Found: 395.1769.

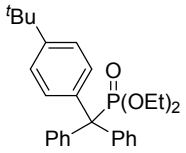


3c

Column chromatography afforded the desired product **3c** in 95% yield (116.8 mg) as white solid; Mp: 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.25 (m, 4H),

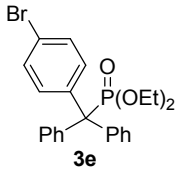
[2] R. Palchaudhuri, V. Nesterenko and P. J. Hergenrother, *J. Am. Chem. Soc.*, 2008, **130**, 10274.

7.21-7.14 (m, 8H), 6.74-6.72 (m, 2H), 3.98-3.88 (m, 2H), 3.79-3.71 (m, 2H), 3.69 (s, 3H), 1.02 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.2 (d, $J_{C\text{-}P}$ = 1.0 Hz), 141.8 (d, $J_{C\text{-}P}$ = 5.0 Hz), 133.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 7.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.7, 126.7, 113.0, 63.2 (d, $J_{C\text{-}P}$ = 8.0), 62.1 (d, $J_{C\text{-}P}$ = 136.0 Hz), 55.1, 16.13, 16.08; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 26.2; IR (neat): 2920, 1602, 1295, 1049, 948, 890, 741, 700 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{27}O_4P$ $[M+H]^+$: 411.1720, Found: 411.1719.



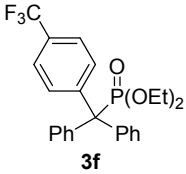
3d

Column chromatography afforded the desired product **3d** in 80% yield (104.6 mg) as white solid; Mp: 128-130 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.25 (m, 4H), 7.21-7.12 (m, 10 H), 3.96-3.87 (m, 2H), 3.78-3.68 (m, 2H), 1.22 (s, 9H), 0.98 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 149.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 141.7 (d, $J_{C\text{-}P}$ = 5.0 Hz), 138.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.6, 126.7 (d, $J_{C\text{-}P}$ = 1.0 Hz), 124.6, 63.1 (d, $J_{C\text{-}P}$ = 8.0 Hz), 61.8, 34.2, 31.2, 16.04, 15.98; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 26.2; IR (neat): 3070, 1600, 1493, 1243, 1015, 952, 754, 699 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{33}O_3P$ $[M+H]^+$: 437.2240, Found: 437.2239.



3e

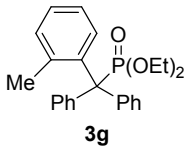
Column chromatography afforded the desired product **3e** in 47% yield (64.6 mg) as white solid; Mp: 118-120 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.39 (m, 2H), 7.34-7.22 (m, 10H), 7.21-7.20 (m, 2H), 4.07-3.97 (m, 2H), 3.88-3.78 (m, 2H), 1.10 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 140.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 132.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.8 (d, $J_{C\text{-}P}$ = 1.0 Hz), 130.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.9, 127.0 (d, $J_{C\text{-}P}$ = 1.0 Hz), 121.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 63.3 (d, $J_{C\text{-}P}$ = 8.0 Hz), 62.4 (d, $J_{C\text{-}P}$ = 135.0 Hz), 16.11, 16.06; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 25.4; IR (neat): 3348, 2918, 2815, 1596, 1240, 1043, 1009, 947, 701 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{24}BrO_3P$ $[M+H]^+$: 459.0719, Found: 459.0719.



3f

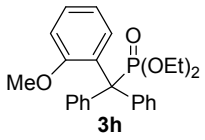
Column chromatography afforded the desired product **3f** in 40% yield (53.8 mg) as white solid; Mp: 123-125 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.24-7.18 (m, 10 H), 4.00-3.91 (m, 2H), 3.82-3.72 (m, 2H), 1.02 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 146.0 (d, $J_{C\text{-}P}$ = 5.0 Hz), 140.8 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 128.9 (q, $J_{C\text{-}F}$ = 85.0 Hz), 128.2, 127.2 (d, $J_{C\text{-}P}$ = 1.0 Hz), 124.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.0 Hz), 63.5 (d, $J_{C\text{-}P}$ = 8.0 Hz), 62.2, 16.1, 16.0; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 25.2; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) : δ = -62.4; IR (neat): 2979, 2930, 2355, 1445, 1241, 1070, 949, 703, 686 cm^{-1}; HRMS (ESI): Exact mass calcd for

$C_{24}H_{24}F_3O_3P$ $[M+H]^+$: 449.1488, Found: 449.1488.



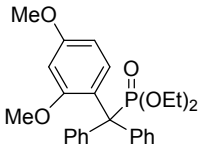
3g

Column chromatography afforded the desired product **3g** in 60% yield (70.9 mg) as white solid; Mp: 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12-8.11 (m, 1H), 7.57-7.56 (m, 4H), 7.29-7.24 (m, 4H), 7.24-7.22 (m, 4H), 7.05-7.03 (m, 1H), 3.88-3.82 (m, 2H), 3.64-3.63 (m, 2H), 1.32 (s, 3H), 1.03 (t, J = 4.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 140.6 (d, J_{C-P} = 2.0 Hz), 139.3 (d, J_{C-P} = 9.0 Hz), 138.6 (d, J_{C-P} = 6.0 Hz), 132.8, 131.5 (d, J_{C-P} = 4.0 Hz), 130.7 (d, J_{C-P} = 4.0 Hz), 127.6, 127.1, 126.7, 125.4, 63.3 (d, J_{C-P} = 6.0 Hz), 63.2 (d, J_{C-P} = 87.0 Hz), 23.0, 16.10, 16.06; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 26.3; IR (neat): 2920, 1645, 1597, 1490, 1239, 1015, 958, 736, 698 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{27}O_3P$ $[M+H]^+$: 395.1771, Found: 395.1772.



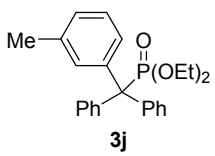
3h

Column chromatography afforded product **3h** in 80% yield (98.4 mg) as white solid; Mp: 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82-7.80 (m, 1H), 7.43-7.41 (m, 4H), 7.24-7.10 (m, 7H), 6.95-6.91 (m, 1H), 6.74-6.72 (m, 1H), 3.84-3.75 (m, 2H), 3.67-3.57 (m, 2H), 3.05 (s, 3H), 0.95 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.0 (d, J_{C-P} = 12.0 Hz), 139.6 (d, J_{C-P} = 7.0 Hz), 131.6 (d, J_{C-P} = 6.0 Hz), 130.2 (d, J_{C-P} = 5.0 Hz), 128.6, 127.0 (d, J_{C-P} = 1.0 Hz), 126.3 (d, J_{C-P} = 3.0 Hz), 120.3, 113.2, 63.1 (d, J_{C-P} = 8.0 Hz), 61.4 (d, J_{C-P} = 133.0 Hz), 54.9, 16.1, 16.0; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 25.4; IR (neat): 2927, 1596, 1491, 1242, 1024, 986, 697 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{27}O_4P$ $[M+H]^+$: 411.1720, Found: 411.1720.



3i

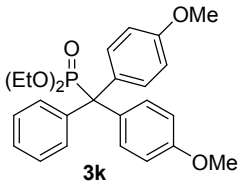
Column chromatography afforded product **3i** in 88% yield (116.2 mg) as red oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77-7.74 (m, 1H), 7.50-7.48 (m, 4H), 7.26-7.16 (m, 6H), 6.54-6.52 (m, 1H), 6.39-6.38 (m, 1H), 3.90-3.82 (m, 2H), 3.80 (s, 3H), 3.73-3.66 (m, 2H), 3.12 (s, 3H), 1.02 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.0, 159.0 (d, J_{C-P} = 12.0 Hz), 139.8 (d, J_{C-P} = 7.0 Hz), 131.9 (d, J_{C-P} = 6.0 Hz), 130.1 (d, J_{C-P} = 6.0 Hz), 126.9 (d, J_{C-P} = 2.0 Hz), 126.1 (d, J_{C-P} = 1.0 Hz), 123.8 (d, J_{C-P} = 3.0 Hz), 103.7, 100.5, 63.0 (d, J_{C-P} = 8.0 Hz), 60.8 (d, J_{C-P} = 134.0 Hz), 55.1, 54.8, 16.00, 15.95; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 25.7; IR (neat): 2922, 1493, 1286, 1047, 959, 696 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{29}O_5P$ $[M+H]^+$: 441.1825, Found: 441.1826.



3j

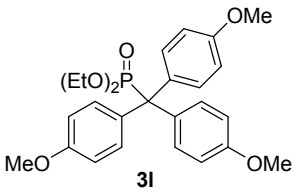
Column chromatography afforded **3j** in 76% yield (89.8 mg) as white solid; Mp: 90-

92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.31 (m, 4H), 7.29-7.23 (m, 6H), 7.23-7.15 (m, 2H), 7.12-7.11 (m, 1H), 7.07-7.06 (m, 1H), 4.04-3.98 (m, 2H), 3.85-3.78 (m, 2H), 2.27 (s, 3H), 1.09 (t, J = 8.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 141.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 137.2, 131.3 (d, $J_{C\text{-}P}$ = 4.0 Hz), 130.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.7, 127.6, 126.8, 63.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 62.8 (d, $J_{C\text{-}P}$ = 90.0 Hz), 21.7, 16.14, 16.10; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 26.8; IR (neat): 2983, 1598, 1490, 1235, 1050, 959, 701 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{27}O_3P$ $[M+H]^+$: 395.1771, Found: 395.1770.



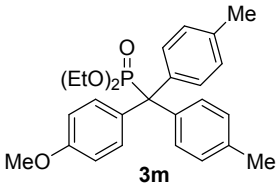
3k

Column chromatography afforded **3k** in 80% yield (105.6 mg) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.31 (m, 2H), 7.26-7.21 (m, 7H), 6.81-6.79 (m, 4H), 4.03-3.96 (m, 2H), 3.84-3.77 (m, 2H), 3.76 (s, 6H), 1.09 (t, J = 8.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.2 (d, $J_{C\text{-}P}$ = 2.0 Hz), 142.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 133.8 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 7.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 1.0 Hz), 126.8, 113.1 (d, $J_{C\text{-}P}$ = 1.0 Hz), 63.2 (d, $J_{C\text{-}P}$ = 8.0 Hz), 61.4 (d, $J_{C\text{-}P}$ = 136.0 Hz), 55.2, 16.22, 16.17; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 27.1; IR (neat): 3359, 2918, 2849, 1508, 1291, 1185, 1021, 958, 797, 741 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{29}O_5P$ $[M+H]^+$: 441.1825, Found: 441.1826.



3l

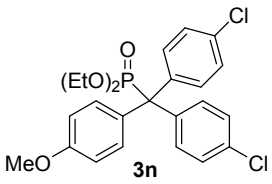
Column chromatography afforded the desired product **3l**[2] in 94% yield (132.5 mg) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.21 (m, 6H), 6.81-6.78 (m, 6H), 4.02-3.96 (m, 2H), 3.83-3.78 (m, 2H), 3.76 (s, 9H), 1.10 (t, J = 4.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.2, 134.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 113.0, 63.1 (d, $J_{C\text{-}P}$ = 7.0 Hz), 60.7 (d, $J_{C\text{-}P}$ = 136.0 Hz), 55.1, 16.3, 16.2; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 27.3.



3m

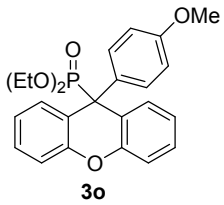
Column chromatography afforded the desired product **3m** in 92% yield (120.8 mg) as white solid; Mp: 89-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.22 (m, 6H), 7.10-7.07 (m, 4H), 6.81-6.80 (m, 2H), 4.05-3.99 (m, 2H), 3.86-3.80 (m, 2H), 3.76 (s, 3H), 2.31 (s, 6H), 1.11 (t, J = 4.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.1 (d, $J_{C\text{-}P}$ = 1.0 Hz), 138.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 136.2 (d, $J_{C\text{-}P}$ = 1.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 128.3, 112.9, 63.0 (d, $J_{C\text{-}P}$ = 8.0 Hz), 61.3 (d, $J_{C\text{-}P}$ = 136.0 Hz), 55.0, 20.8, 16.1, 16.0; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 27.3; IR (neat): 2982, 1509, 1441, 1291, 1186, 1020, 953, 809, 741 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{26}H_{31}O_4P$

$[M+H]^+$: 439.2033, Found: 439.2033.



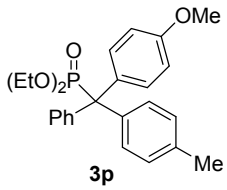
3n

Column chromatography afforded the desired product **3n** in 81% yield (116.2 mg) as white solid; Mp: 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.22 (m, 8H), 7.28-7.16 (m, 2H), 6.81-6.80 (m, 2H), 4.05-3.98 (m, 2H), 3.86-3.79 (m, 2H), 3.77 (s, 3H), 1.11 (t, J = 4.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.5, 140.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 128.0, 113.3, 63.4 (d, $J_{C\text{-}P}$ = 8.0 Hz), 61.1 (d, $J_{C\text{-}P}$ = 137.0 Hz), 55.1, 16.2, 16.1; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 26.0; IR (neat): 2940, 1604, 1509, 1286, 1096, 960, 793, 668 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{25}Cl_2O_4P$ $[M+H]^+$: 479.0940, Found: 479.0941.



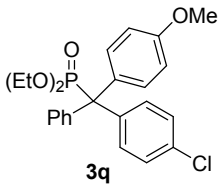
3o

Column chromatography afforded **3o** in 85% yield (108.1 mg) as white solid; Mp: 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (m, 2H), 7.21-7.18 (m, 2H), 7.07-7.05 (d, J = 8.0 Hz, 2H), 6.98-6.96 (m, 2H), 6.96-6.90 (m, 2H), 6.84 (d, J = 8.0 Hz, 2H), 3.82-3.79 (m, 3H), 3.79 (s, 3H), 3.78-3.76 (m, 1H), 1.11 (t, J = 4.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.1, 151.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 136.3, 132.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 122.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 122.3 (d, $J_{C\text{-}P}$ = 8.0 Hz), 115.8 (d, $J_{C\text{-}P}$ = 2.0 Hz), 113.3, 63.4 (d, $J_{C\text{-}P}$ = 8.0 Hz), 55.1, 50.9 (d, $J_{C\text{-}P}$ = 143.0 Hz), 16.2, 16.1; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 27.2; IR (neat): 3649, 2927, 1601, 1477, 1282, 1125, 1022, 948, 872, 764 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{25}O_5P$ $[M+H]^+$: 425.1512, Found: 425.1512.



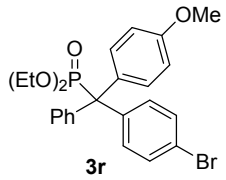
3p

Column chromatography afforded the desired product **3p** in 88% yield (111.9 mg) as white solid; Mp: 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.32 (m, 2H), 7.27-7.19 (m, 7H), 7.08-7.06 (m, 2H), 6.81-6.79 (m, 2H), 4.03-3.97 (m, 2H), 3.84-3.78 (m, 2H), 3.77 (s, 3H), 2.32 (s, 3H), 1.09 (t, J = 4.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.2 (d, $J_{C\text{-}P}$ = 1.0 Hz), 142.0 (d, $J_{C\text{-}P}$ = 5.0 Hz), 138.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 136.4 (d, $J_{C\text{-}P}$ = 1.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 7.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 1.0 Hz), 127.7, 126.7 (d, $J_{C\text{-}P}$ = 2.0 Hz), 113.0, 63.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 61.8 (d, $J_{C\text{-}P}$ = 136.0 Hz), 55.1, 20.9, 16.2, 16.1; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 27.0; IR (neat): 2918, 1509, 1443, 1294, 1186, 1020, 955, 810, 739, 707 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{29}O_4P$ $[M+H]^+$: 425.1876, Found: 425.1876.



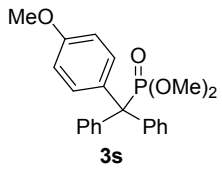
3q

Column chromatography afforded the desired product **3q** in 83% yield (110.6 mg) as white solid; Mp: 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.23 (m, 9H), 7.22-7.19 (m, 2H), 6.82-6.80 (m, 2H), 4.03-3.99 (m, 2H), 3.84-3.80 (m, 2H), 3.78 (s, 3H), 1.10 (t, J = 4.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.3, 141.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 140.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 132.7, 132.0 (d, $J_{C\text{-}P}$ = 4.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.9, 127.0, 113.2, 63.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 63.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 61.6 (d, $J_{C\text{-}P}$ = 90.0 Hz), 55.1, 16.2, 16.1; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 26.4; IR (neat): 2927, 1608, 1490, 1232, 1095, 948, 794, 709 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{26}ClO_4P$ [M+H]$^+$: 445.1330, Found: 445.1331.



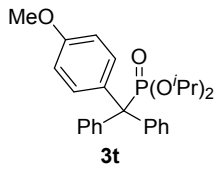
3r

Column chromatography afforded the desired product **3r** in 85% yield (124.4 mg) as white solid; Mp: 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.39 (m, 2H), 7.32-7.25 (m, 5H), 7.23-7.20 (m, 4H), 6.83-6.81 (m, 2H), 4.04-4.00 (m, 2H), 3.86-3.79 (m, 2H), 3.77 (s, 3H), 1.11 (t, J = 4.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.3, 141.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 141.1 (d, $J_{C\text{-}P}$ = 4.0 Hz), 132.3, 131.6, 130.8, 130.4 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.9, 121.0, 113.2, 63.34 (d, $J_{C\text{-}P}$ = 3.0 Hz), 63.29 (d, $J_{C\text{-}P}$ = 3.0 Hz), 61.7 (d, $J_{C\text{-}P}$ = 91.0 Hz), 55.1, 16.2, 16.1; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 26.3; IR (neat): 2922, 1608, 1443, 1233, 1050, 956, 740 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{26}BrO_4P$ [M+H]$^+$: 489.0825, Found: 489.0829.



3s

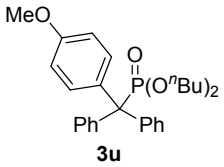
Column chromatography afforded the desired product **3s**[2] in 90% yield (103.1 mg) as white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.18 (m, 10 H), 7.14-7.13 (m, 2H), 6.76-6.74 (m, 2H), 3.72 (s, 3H), 3.51 (s, 3H), 3.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.4, 141.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 133.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.5 (d, $J_{C\text{-}P}$ = 7.0 Hz), 127.9, 127.0, 113.2, 62.2 (d, $J_{C\text{-}P}$ = 135.0 Hz), 55.1, 53.8 (d, $J_{C\text{-}P}$ = 8.0 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 28.8.



3t

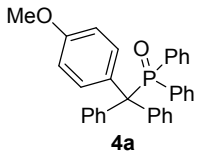
Column chromatography afforded the desired product **3t** in 78% yield (102.5 mg) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.21 (m, 4H), 7.20-7.15 (m, 8H), 6.74-6.72 (m, 2H), 4.51-4.43 (m, 2H), 3.73 (s, 3H), 1.09 (d, J = 6.0 Hz, 6H), 0.86 (d, J = 6.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.2, 142.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 134.0 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.7, 126.7, 113.0, 72.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 62.3 (d, $J_{C\text{-}P}$ = 136.0 Hz), 55.2, 24.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 23.1 (d, $J_{C\text{-}P}$ = 6.0 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 24.3; IR (neat): 2978, 1607, 1240, 1103, 972, 793, 700 cm^{-1}; HRMS (ESI):

Exact mass calcd for $C_{26}H_{31}O_4P$ $[M+H]^+$: 439.2033, Found: 439.2032.



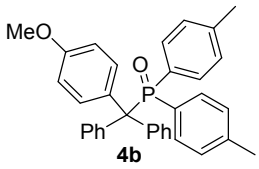
3u

Column chromatography afforded the desired product **3u** in 90% yield (125.8 mg) as yellow solid; Mp: 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.24 (m, 4H), 7.23-7.14 (m, 8H), 6.76-6.73 (m, 2H), 3.90-3.83 (m, 2H), 3.72 (s, 3H), 3.70-3.62 (m, 2H), 1.39-1.27 (m, 4H), 1.15-1.06 (m, 4H), 0.73 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.2 (d, $J_{C\text{-}P}$ = 2.0 Hz), 141.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 133.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.7 (d, $J_{C\text{-}P}$ = 1.0 Hz), 113.1, 66.8 (d, $J_{C\text{-}P}$ = 8.0 Hz), 62.3 (d, $J_{C\text{-}P}$ = 136.0 Hz), 55.1, 32.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 18.6, 13.5; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 26.0; IR (neat): 2958, 1604, 1508, 1464, 1293, 1191, 1030, 977, 701 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{28}H_{35}O_4P$ $[M+H]^+$: 467.2346, Found: 467.2345.



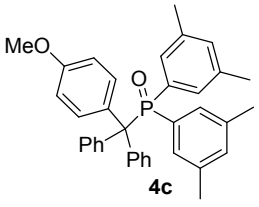
4a

Column chromatography afforded the desired product **4a** in 91% yield (129.4 mg) as white powder; Mp: 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.39 (m, 2H), 7.28-7.21 (m, 16 H), 7.14-7.11 (m, 4H), 6.77-6.76 (m, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.5, 133.5 (d, $J_{C\text{-}P}$ = 5.0 Hz), 132.9, 132.7, 132.1, 131.7, 131.4, 127.9, 127.8, 127.7, 127.1, 113.0, 64.0 (d, $J_{C\text{-}P}$ = 42.0 Hz), 55.2; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.0; IR (neat): 3068, 2838, 1607, 1508, 1436, 1251, 1104, 1031, 932, 712 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{32}H_{27}O_2P$ $[M+H]^+$: 475.1821, Found: 475.1820.



4b

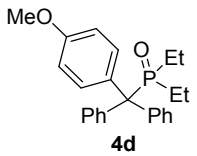
Column chromatography afforded the desired product **4b** in 83% yield (125.0 mg) as white powder; Mp: 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.20 (m, 11 H), 7.03-6.97 (m, 9 H), 6.77-6.75 (m, 2H), 3.81 (s, 3H), 2.31 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.4, 141.6, 133.5, 133.4, 132.9, 131.7, 129.6, 128.9, 128.6 (d, $J_{C\text{-}P}$ = 8.0 Hz), 127.7, 127.0, 112.9, 63.9 (d, $J_{C\text{-}P}$ = 43.0 Hz), 55.2, 21.4; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.3; IR (neat): 2960, 1601, 1462, 1255, 1027, 936, 715, 696 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{34}H_{31}O_2P$ $[M+H]^+$: 503.2134, Found: 503.2130.



4c

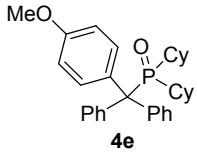
Column chromatography afforded the desired product **4c** in 84% yield (133.6 mg) as white powder; Mp: 171-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.17 (m, 12 H), 7.02 (s, 2H), 6.77-6.76 (m, 2H), 6.66-6.64 (m, 4H), 3.81 (s, 3H), 2.14 (s, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.4, 137.1 (d, $J_{C\text{-}P}$ = 8.0 Hz), 133.1, 132.8, 132.2, 131.9, 131.6, 131.23, 131.18, 127.6, 126.9, 112.9, 64.1 (d, $J_{C\text{-}}$

$_P$ = 41.0 Hz), 55.3, 21.2; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.4; IR (neat): 2948, 1597, 1508, 1255, 1029, 889, 697 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{36}H_{35}O_2P$ $[M+H]^+$: 531.2447, Found: 531.2446.



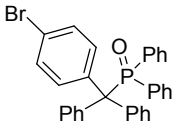
4d

Column chromatography afforded the desired product **4d** in 90% yield (102.1 mg) as colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (brs, 5H), 7.29-7.27 (m, 5H), 7.23-7.21 (m, 2H), 6.83-6.81 (m, 2H), 3.78 (s, 3H), 1.90-1.81 (m, 2H), 1.51-1.44 (m, 2H), 1.07 (t, J = 4.0 Hz, 3H), 1.04 (t, J = 4.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.1, 131.8, 130.5, 128.0, 126.7, 113.3, 61.9 (d, $J_{C\text{-}P}$ = 39.0 Hz), 55.1, 21.1 (d, $J_{C\text{-}P}$ = 44.0 Hz), 6.8, 6.7; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 58.5; IR (neat): 3100, 2938, 1610, 1500, 1430, 1251, 1104, 1036, 950, 712 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{27}O_2P$ $[M+H]^+$: 379.1821, Found: 379.1815.



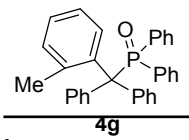
4e

Column chromatography afforded the desired product **4e**[3] in 60% yield (87.5 mg) as white powder; Mp: 145-147 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.69 (m, 4H), 7.26-7.23 (m, 4H), 7.19-7.13 (m, 3H), 7.06-7.04 (m, 2H), 6.81-6.68 (m, 2H), 3.76 and 3.68 (s × 2, in total 3H), 1.93-1.91 (m, 2H), 1.82-1.76 (m, 2H), 1.64-1.60 (m, 2H), 1.49-1.44 (m, 4H), 1.25-1.1.17 (m, 4H), 1.07-0.99 (m, 4H), 0.87-0.81 (m, 2H), 0.64-0.52 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.7, 157.5, 145.5, 138.7, 137.3, 133.5, 132.4, 130.8, 128.0, 127.9, 127.7, 127.3, 126.0, 113.3, 113.1, 62.1 (d, $J_{C\text{-}P}$ = 35.0 Hz), 55.4, 55.0, 37.3 (d, $J_{C\text{-}P}$ = 39.0 Hz), 27.7, 27.5, 27.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 26.7 (d, $J_{C\text{-}P}$ = 8.0 Hz), 25.8 ; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 56.1; IR (neat): 3100, 1601, 1490, 1170, 1080, 1008, 809, 701 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{32}H_{39}O_2P$ $[M+H]^+$: 487.2760, Found: 487.2762.



4f

Column chromatography afforded the desired product **4f** in 79% yield (124.0 mg) as white powder; Mp: 145-147 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 2H), 7.29-7.27 (m, 2H), 7.23-7.13 (m, 16H), 7.07-7.03 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 133.5, 133.4, 133.3, 132.4, 131.8, 131.7, 131.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 131.5, 130.9, 128.0, 127.4, 121.4, 64.2 (d, $J_{C\text{-}P}$ = 63.0 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 34.7; IR (neat): 3070, 1594, 1486, 1178, 1091, 1008, 809, 697 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{31}H_{24}BrOP$ $[M+H]^+$: 523.0821, Found: 523.0824.

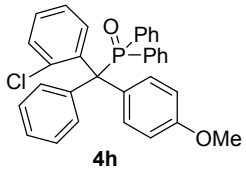


4g

Column chromatography afforded the desired product **4g** in 83% yield (114.0 mg) as white powder; Mp: 208-210 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.30-8.29 (m, 1H),

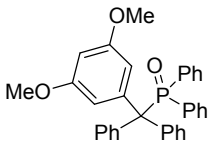
[3] T. Shibata, K. Iino, Y. Sugimura, *Heterocycles*, 1986, **24**, 1331.

7.39-7.34 (m, 6H), 7.27-7.24 (m, 5H), 7.18-7.11 (m, 7H), 7.00-6.99 (m, 1H), 6.88-6.85 (m, 4H), 1.31 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.7, 139.3, 139.2, 133.6, 133.5, 133.0, 132.1, 131.3, 130.9 (d, J_{C-P} = 6.0 Hz), 127.64, 127.57, 127.4, 127.0, 125.4, 64.6 (d, J_{C-P} = 40.0 Hz), 23.0; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 36.1; IR (neat): 3059, 2346, 1492, 1433, 1172, 1087, 748, 696 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{32}H_{27}OP$ $[M+H]^+$: 459.1872, Found: 459.1870.



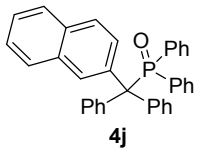
4h

Column chromatography afforded the desired product **4h** in 51% yield (77.7 mg) as colorless oil; Mp: 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56-8.55 (m, 1H), 7.41-7.32 (m, 4H), 7.25-7.14 (m, 12 H), 6.95-6.94 (m, 2H), 6.92-6.85 (m, 2H), 6.80-6.78 (m, 2H), 3.83 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.7, 141.0, 136.1 (d, J_{C-P} = 7.0 Hz), 134.0, 133.62 (d, J_{C-P} = 2.0 Hz), 133.56, 133.4 (d, J_{C-P} = 2.0 Hz), 132.4, 132.23 (d, J_{C-P} = 6.0 Hz), 132.16 (d, J_{C-P} = 3.0 Hz), 131.5, 128.2, 127.63, 127.62 (d, J_{C-P} = 12.0 Hz), 127.3, 127.2, 126.3, 112.4, 63.3 (d, J_{C-P} = 41.0 Hz), 55.2; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 36.1; IR (neat): 2926, 1604, 1465, 1251, 1031, 850, 792, 693 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{32}H_{26}ClO_2P$ $[M+H]^+$: 509.1432, Found: 509.1430.



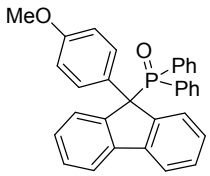
4i

Column chromatography afforded the desired product **4i** in 79% yield (119.4 mg) as white powder; Mp: 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.40 (m, 3H), 7.29-7.21 (m, 14H), 7.18-7.15 (m, 4H), 6.53 (s, 1H), 6.39 (s, 1H), 3.56 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 160.0, 133.4 (d, J_{C-P} = 6.0 Hz), 132.8, 132.2, 131.8, 131.4, 128.0, 127.9, 127.8, 127.3, 110.4, 99.6, 64.9 (d, J_{C-P} = 42.0 Hz), 55.1; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.1; IR (neat): 2927, 2359, 1681, 1475, 1064, 997, 899, 697 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{33}H_{29}O_3P$ $[M+H]^+$: 505.1927, Found: 505.1926.



4j

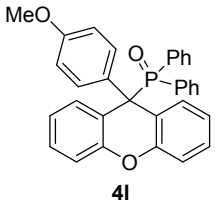
Column chromatography afforded the desired product **4j** in 74% yield (109.7 mg) as white powder; Mp: 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (s, 1H), 7.72-7.70 (m, 1H), 7.62-7.59 (m, 1H), 7.52-7.51 (m, 1H), 7.41-7.20 (m, 11 H), 7.17-7.05 (m, 12 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 133.5 (d, J_{C-P} = 7.0 Hz), 132.62, 132.57, 132.1, 132.0 (d, J = 5.0 Hz), 131.7, 131.4 (d, J_{C-P} = 3.0 Hz), 130.0 (d, J_{C-P} = 4.0 Hz), 128.5, 127.9, 127.80, 127.77, 127.3 (d, J_{C-P} = 6.0 Hz), 127.1, 126.3, 125.9, 64.7 (d, J_{C-P} = 63.0 Hz); $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 34.9; IR (neat): 3061, 2212, 1598, 1495, 1436, 1173, 1037, 932, 727, 692cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{35}H_{27}OP$ $[M+H]^+$: 495.1872, Found: 495.1871.



4k

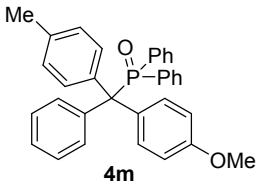
Column chromatography afforded the desired product **4k** in 95% yield (134.5 mg) as

white powder; Mp: 218-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.08 (m, 2H), 7.57-7.56 (m, 2H), 7.44-7.42 (m, 2H), 7.33-7.27 (m, 4H), 7.24-7.22 (m, 2H), 7.12-7.06 (m, 8H), 6.91-6.89 (m, 2H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.0, 143.1, 141.5 (d, J_{C-P} = 3.0 Hz), 132.6 (d, J_{C-P} = 6.0 Hz), 127.9, 127.4 (d, J_{C-P} = 8.0 Hz), 127.0, 119.8, 114.0, 62.5 (d, J_{C-P} = 40.0 Hz), 55.2; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 37.1; IR (neat): 3064, 1604, 1437, 1300, 1251, 1096, 886, 747, 693 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{32}H_{25}O_2P$ $[M+H]^+$: 473.1665, Found: 473.1664.



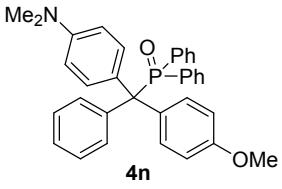
4l

Column chromatography afforded the desired product **4l** in 92% yield (134.7 mg) as white powder; Mp: 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74-7.73 (m, 2H), 7.47-7.40 (m, 6H), 7.26-7.23 (m, 4H), 7.19-7.16 (m, 2H), 7.04-7.02 (m, 2H), 6.94-6.91 (m, 2H), 6.80-6.79 (m, 2H), 6.72-6.71 (m, 2H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.0, 151.5 (d, J = 3.0 Hz), 136.6, 133.3, 133.1 (d, J_{C-P} = 5.0 Hz), 132.4 (d, J_{C-P} = 5.0 Hz), 131.5, 131.1, 130.5, 129.0, 127.5 (d, J_{C-P} = 7.0 Hz), 122.3, 121.6 (d, J_{C-P} = 2.0 Hz), 115.6, 113.3, 55.1, 54.5 (d, J_{C-P} = 44.0 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 29.2; IR (neat): 2956, 2359, 1598, 1475, 1254, 1072, 944, 870, 780, 693 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{32}H_{25}O_3P$ $[M+H]^+$: 489.1614, Found: 489.1612.



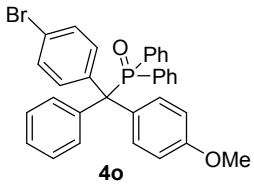
4m

Column chromatography afforded the desired product **4m** in 96% yield (140.5 mg) as white powder; Mp: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.38 (m, 2H), 7.27-7.21 (m, 11H), 7.19-7.12 (m, 6H), 7.03-7.01 (m, 2H), 6.76-6.75 (m, 2H), 3.79 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.4, 136.8, 133.4 (d, J_{C-P} = 5.0 Hz), 132.9, 132.8, 132.2, 131.6, 131.5, 131.3, 128.4, 127.9, 127.8, 127.72, 127.67, 127.0, 112.9, 63.6 (d, J_{C-P} = 43.0 Hz), 55.2, 20.9; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.0; IR (neat): 2955, 2329, 1604, 1510, 1436, 1293, 1178, 1035, 750, 693 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{33}H_{29}O_2P$ $[M+H]^+$: 489.1978, Found: 489.1976.



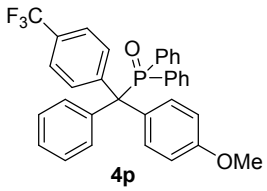
4n

Column chromatography afforded the desired product **4n** in 90% yield (139.6 mg) as white powder; Mp: 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.37 (m, 3H), 7.25-7.14 (m, 15 H), 7.04 (s, 1H), 6.75-6.73 (m, 2H), 6.56 (s, 2H), 3.78 (s, 3H), 2.93 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.3, 133.52, 133.46, 133.1, 132.8, 132.6, 131.6, 131.2, 127.8, 127.7 (d, J_{C-P} = 8.0 Hz), 126.8, 112.9, 111.4, 63.11 (d, J_{C-P} = 43.0 Hz), 55.2, 40.4; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.0; IR (neat): 3301, 2920, 2854, 1610, 1585, 1408 1240, 1045, 965, 750, 690 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{34}H_{32}NO_2P$ $[M+H]^+$: 518.2243, Found: 518.2241.



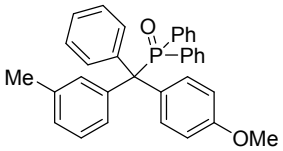
4o

Column chromatography afforded the desired product **4o** in 77% yield (127.5 mg) as white powder; Mp: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.31 (m, 2H), 7.28-7.25 (m, 2H), 7.22-7.11 (m, 11H), 7.09-7.04 (m, 6H), 6.69-6.67 (m, 2H), 3.71 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.6 (d, $J_{C\text{-}P}$ = 1.0 Hz), 133.39 (d, $J_{C\text{-}P}$ = 8.0 Hz), 133.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 132.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 132.5, 131.62 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.55, 131.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.8, 127.9, 127.8, 127.3, 121.2 (d, $J_{C\text{-}P}$ = 1.0 Hz), 113.1, 63.5 (d, $J_{C\text{-}P}$ = 63.0 Hz), 55.2; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 34.7; IR (neat): 3065, 1604, 1508, 1435, 1252, 1177, 1032, 882, 694 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{32}H_{26}BrO_2P$ $[M+H]^+$: 553.0927, Found: 553.0925.



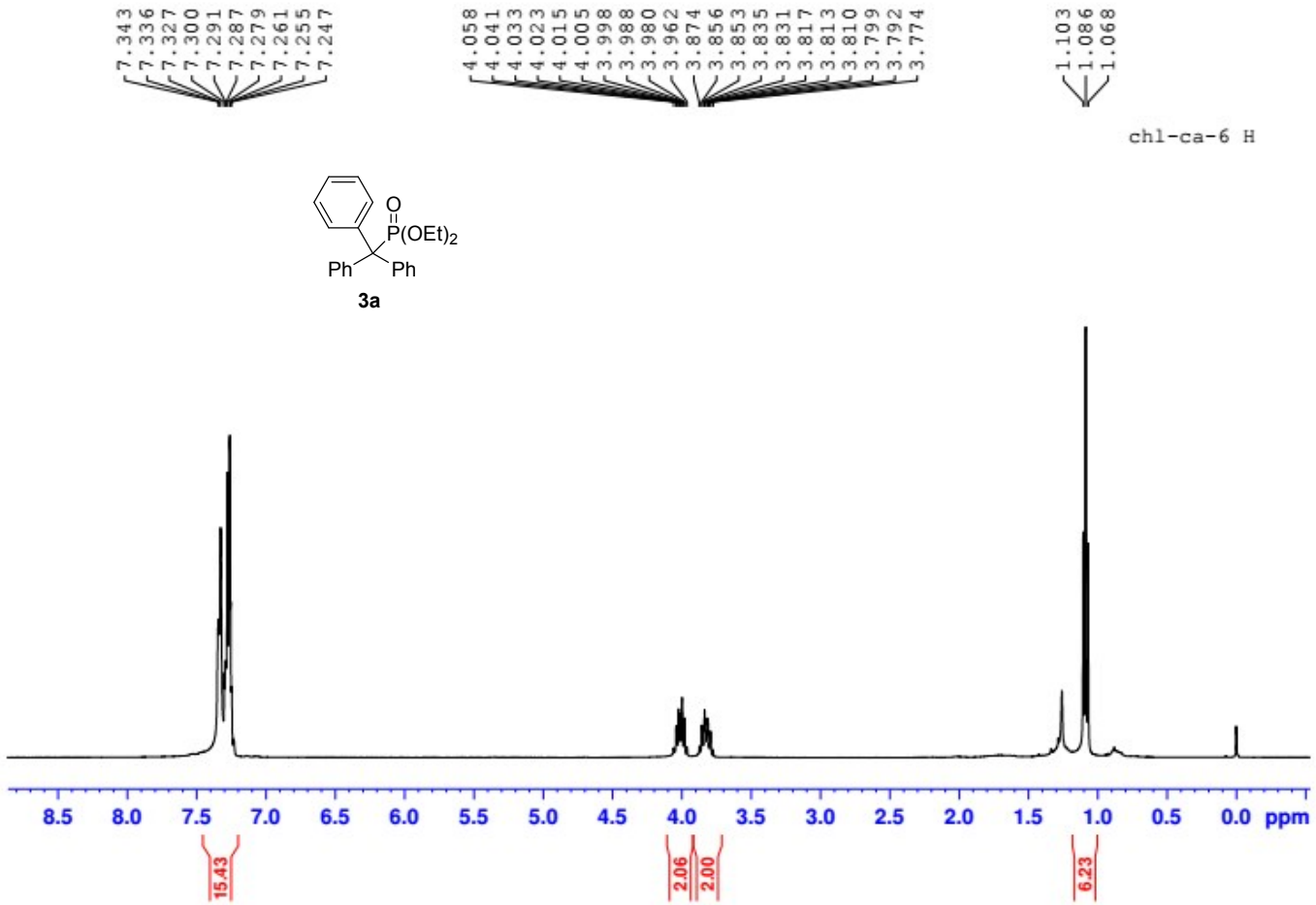
4p

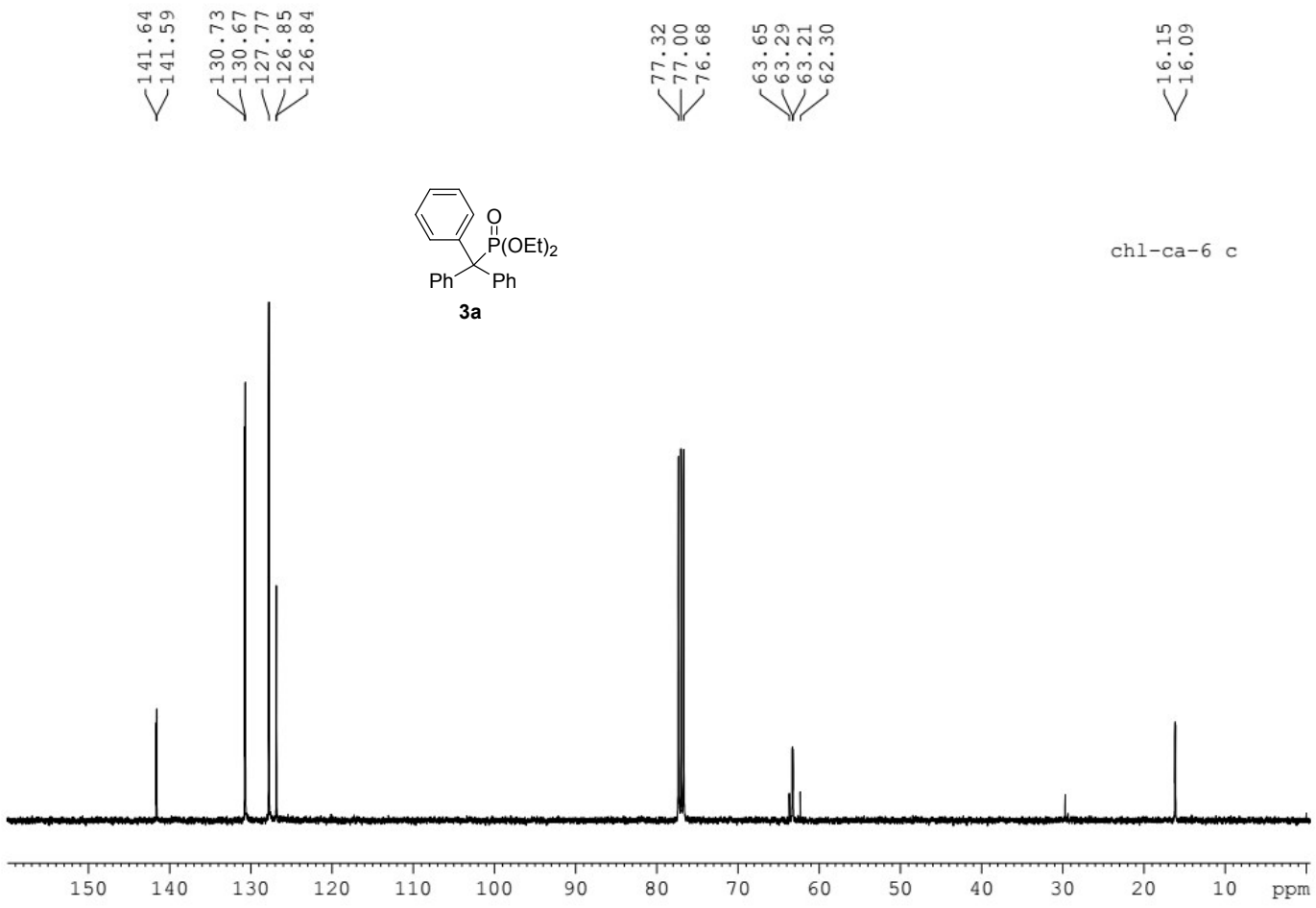
Column chromatography afforded the desired product **4p** in 81% yield (131.7 mg) as white powder; Mp: 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.48 (m, 2H), 7.40-7.38 (m, 2H), 7.34-7.31 (m, 2H), 7.21-7.13 (m, 9H), 7.08-7.03 (m, 6H), 6.71-6.68 (m, 2H), 3.72 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.8 (d, $J_{C\text{-}P}$ = 2.0 Hz), 146.6, 133.44 (d, $J_{C\text{-}P}$ = 3.0 Hz), 133.36 (d, $J_{C\text{-}P}$ = 3.0 Hz), 133.0 (d, $J_{C\text{-}P}$ =5.0 Hz), 132.3, 131.74 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.65 (d, $J_{C\text{-}P}$ = 5.0 Hz), 131.6, 131.4, 128.9 (q, $J_{C\text{-}F}$ = 32.0 Hz), 128.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 127.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.5, 124.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 124.0 (q, $J_{C\text{-}F}$ = 270.0 Hz), 113.2, 63.8 (d, $J_{C\text{-}P}$ = 63.0 Hz), 55.2; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 34.8; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ = -62.4; IR (neat): 3053, 1607, 1509, 1325, 1254, 1117, 1018, 878, 691 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{33}H_{26}F_3O_2P$ $[M+H]^+$: 543.1696, Found: 543.1695.

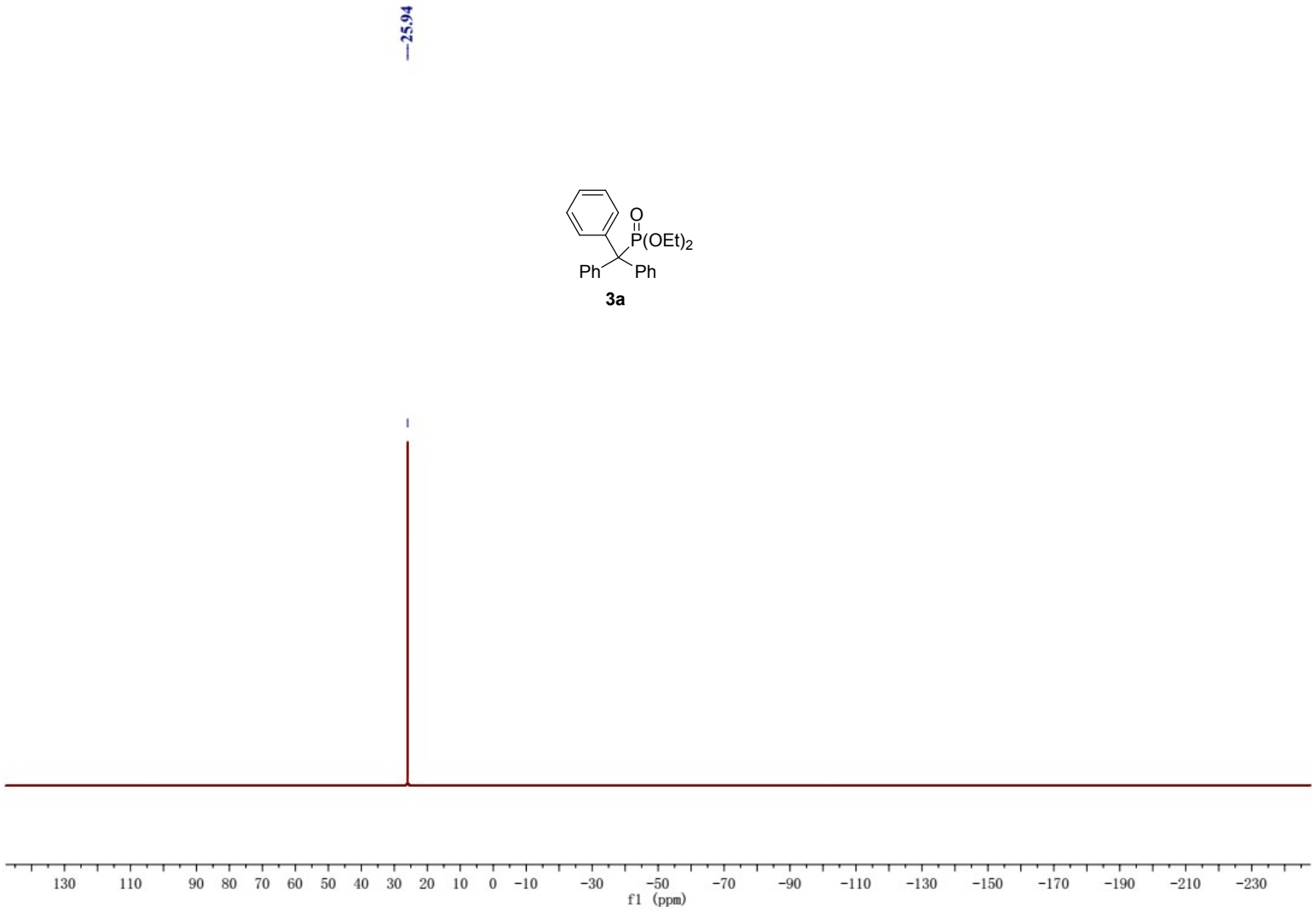


4q

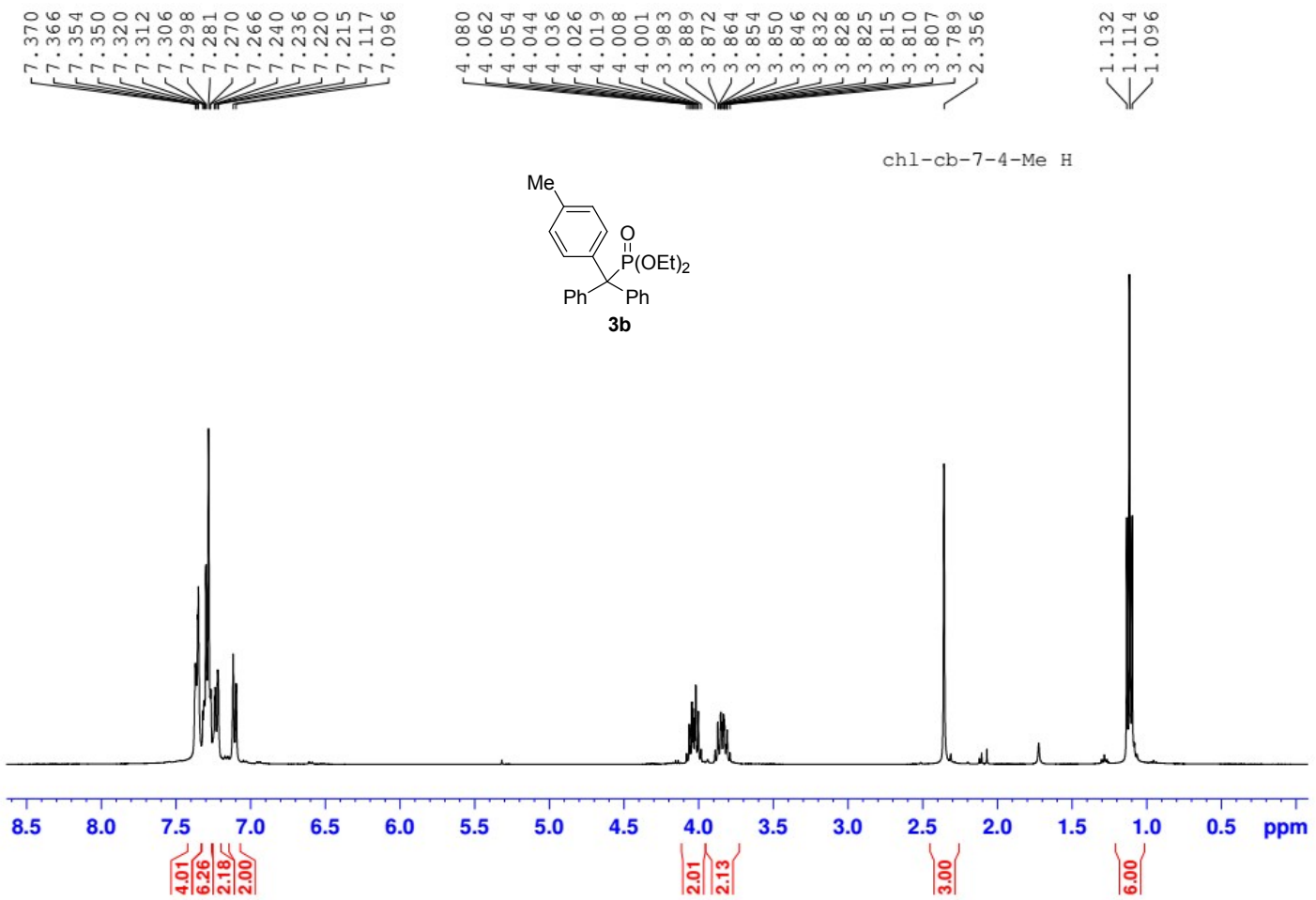
Column chromatography afforded the desired product **4q** in 96% yield (140.5 mg) as white powder; Mp: 161-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.26 (m, 4H), 7.16-7.10 (m, 9H), 7.08-7.03 (m, 4H), 7.01-6.92 (m, 4H), 6.68-6.66 (m, 2H), 3.70 (s, 3H), 2.09 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.4, 136.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 133.5, 133.4, 132.9, 132.8, 132.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 132.0, 131.63, 131.58, 131.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 5.0 Hz), 127.8 (d, $J_{C\text{-}P}$ = 4.0 Hz), 127.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 127.0, 112.9, 63.9 (d, $J_{C\text{-}P}$ = 64.0 Hz), 55.1, 21.5; $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.0; IR (neat): 3059, 1603, 1508, 1436, 1253, 1178, 1033, 927, 791, 701 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{33}H_{29}O_2P$ $[M+H]^+$: 489.1978, Found: 489.1973.

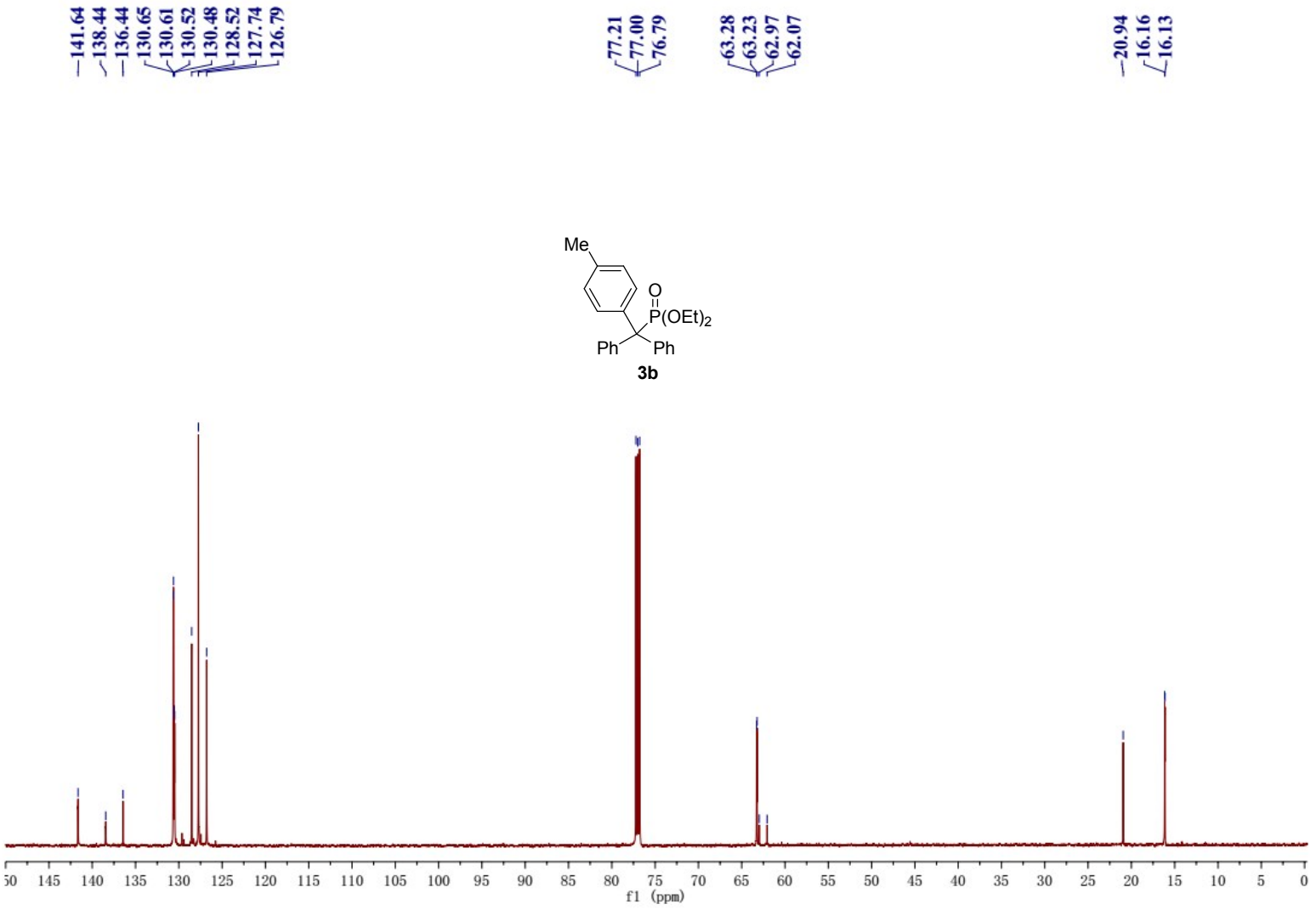

7.343
7.336
7.327
7.300
7.291
7.287
7.279
7.261
7.255
7.247
4.058
4.041
4.033
4.023
4.015
4.005
3.998
3.988
3.980
3.962
3.874
3.856
3.853
3.835
3.831
3.817
3.813
3.810
3.799
3.792
3.774
1.103
1.086
1.068
chl-ca-6 H
O
P(OEt)2
Ph
Ph
3a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
15.43
2.06
2.00
6.23

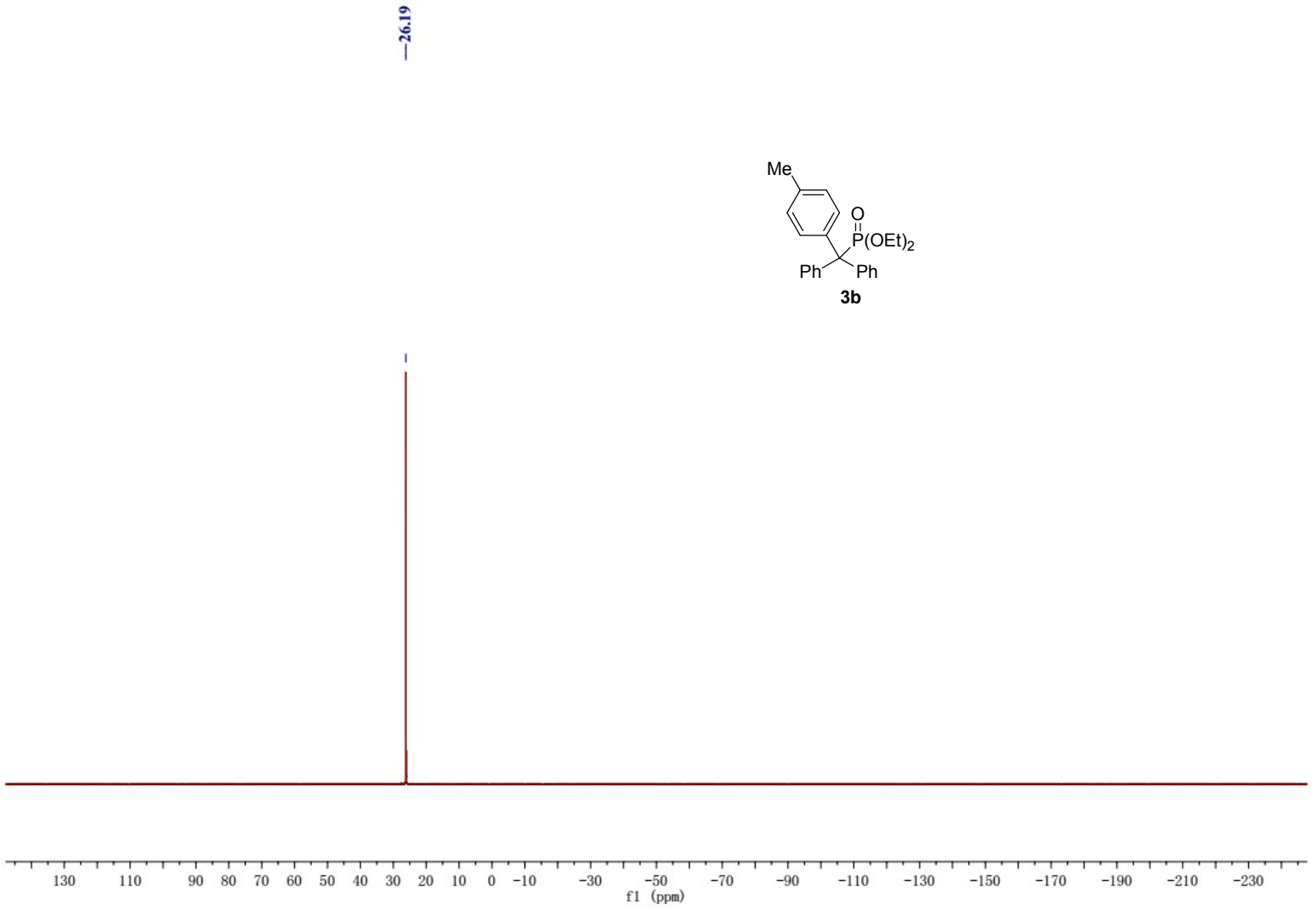

141.64
141.59
130.73
130.67
127.77
126.85
126.84
77.32
77.00
76.68
63.65
63.29
63.21
62.30
16.15
16.09
O
P(OEt)2
Ph
Ph
3a
chl-ca-6 c
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

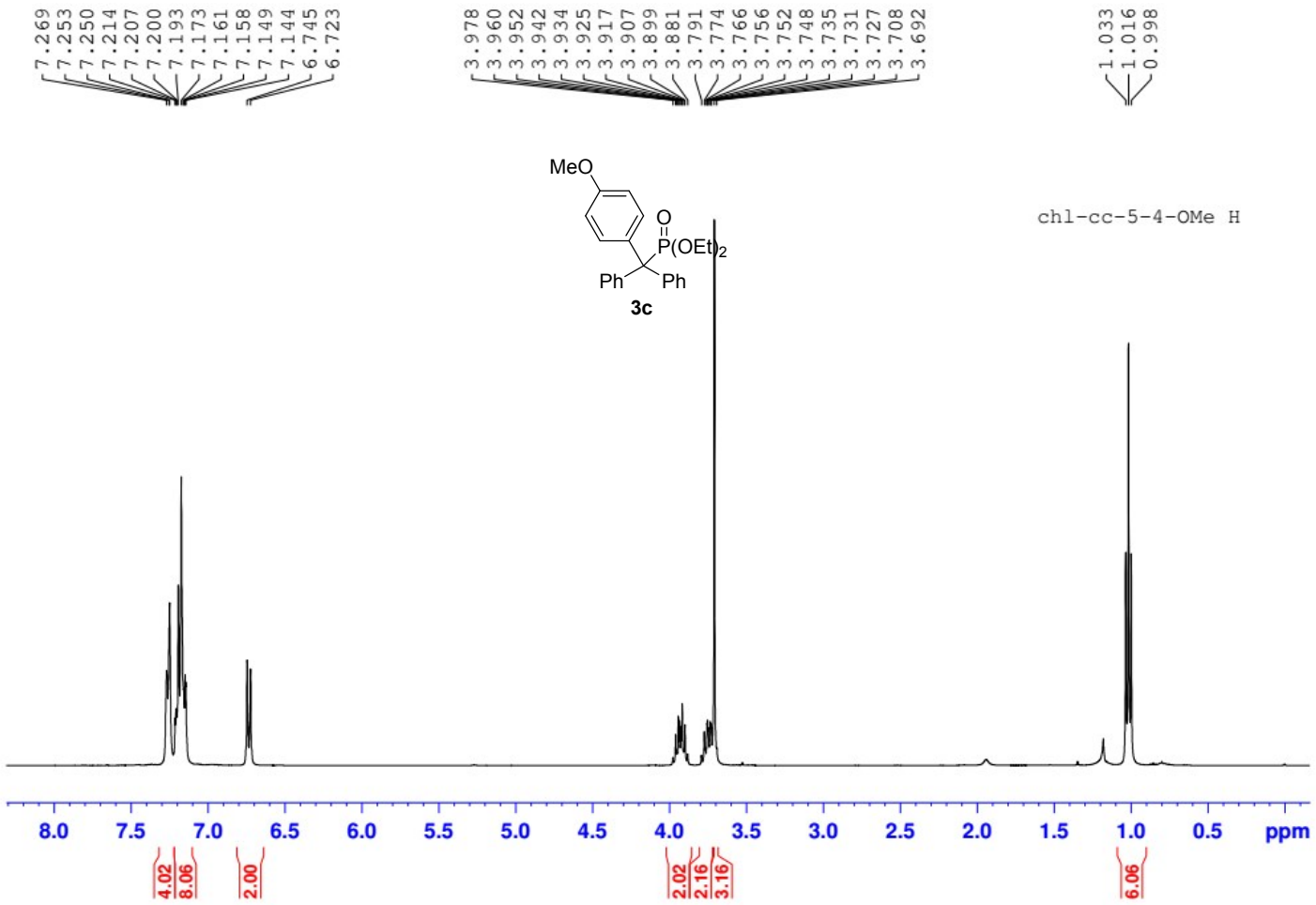

25.94
O
P(OEt)2
Ph
Ph
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

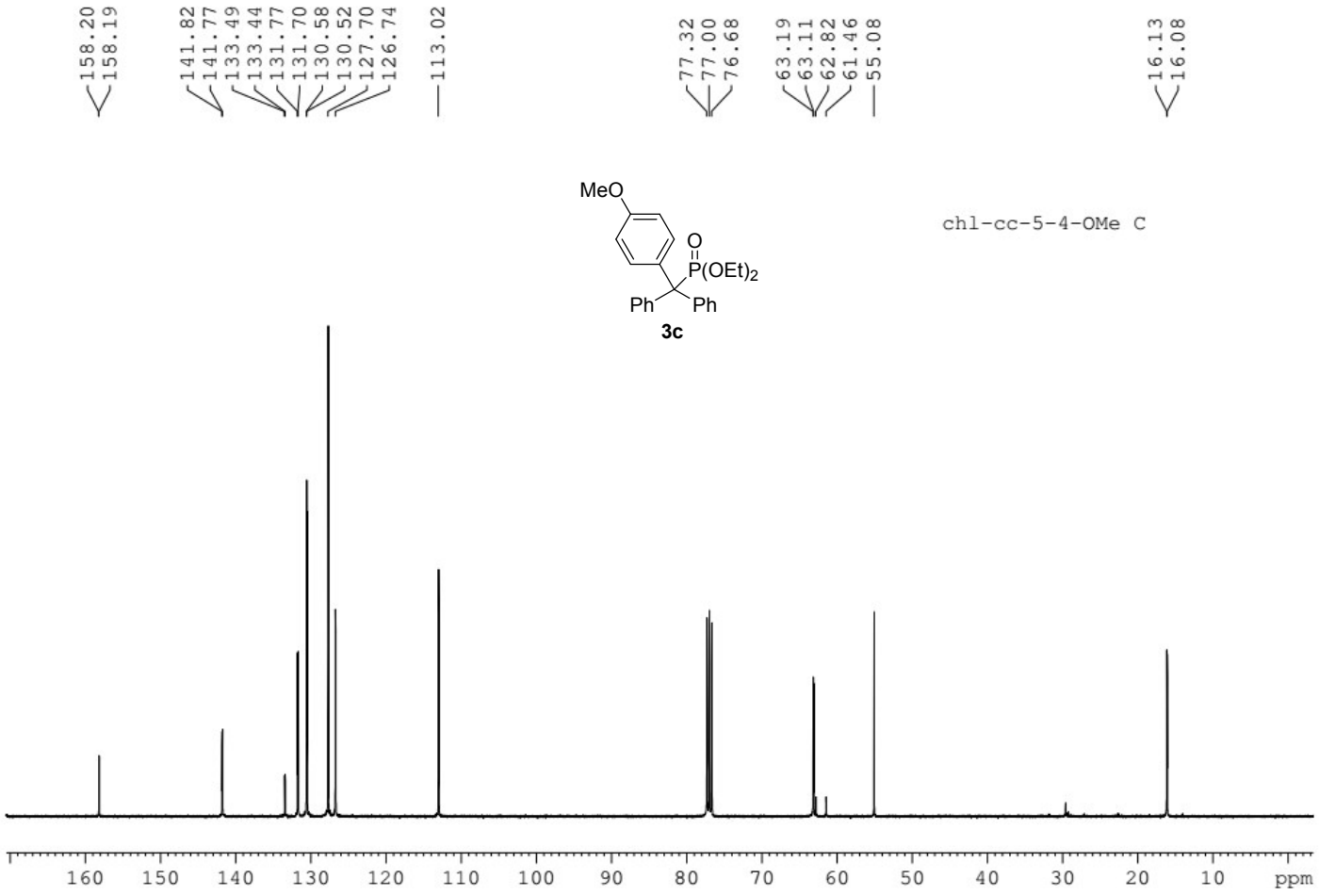
3a

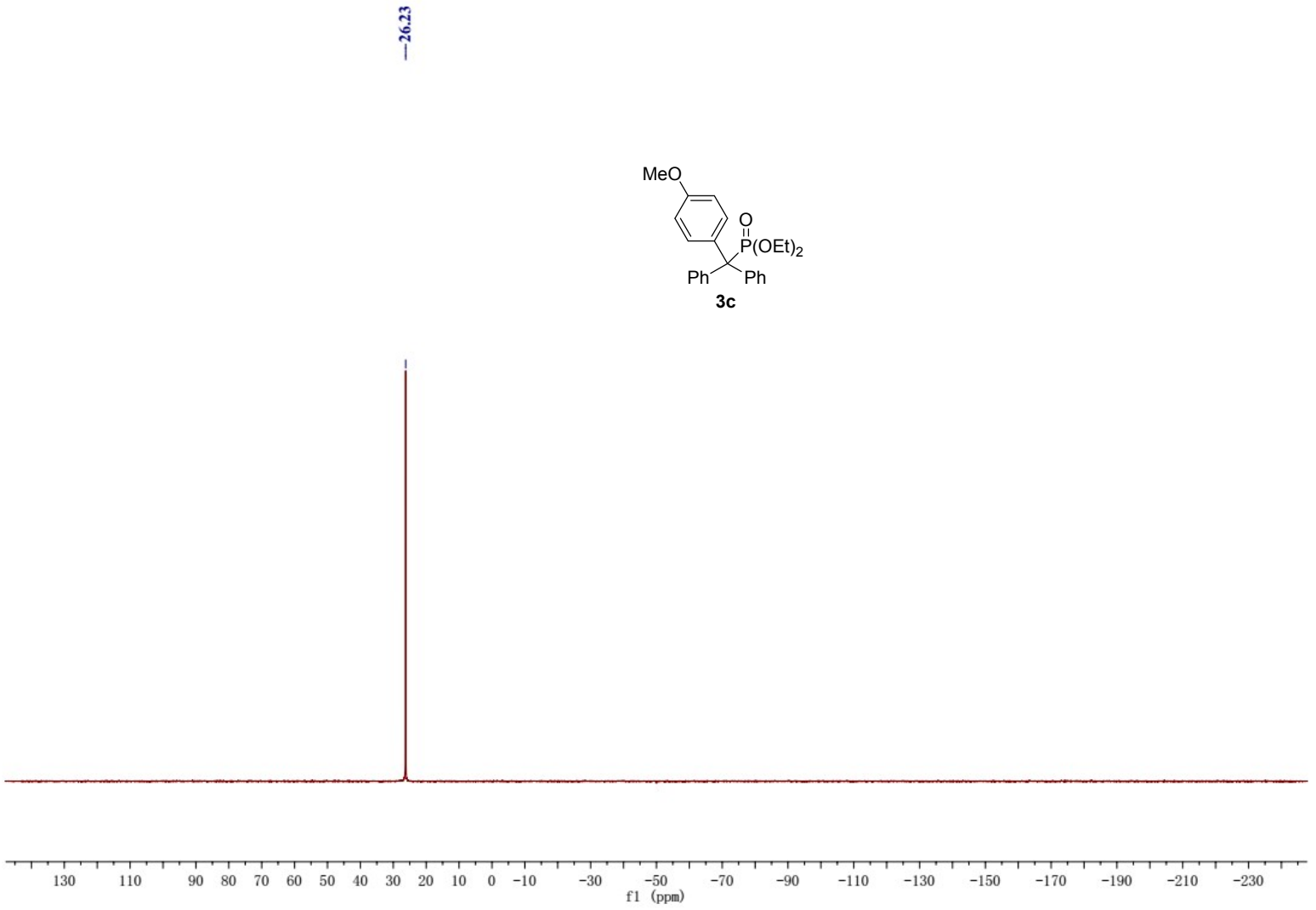

7.370
7.366
7.354
7.350
7.320
7.312
7.306
7.298
7.281
7.270
7.266
7.240
7.236
7.220
7.215
7.117
7.096
4.080
4.062
4.054
4.044
4.036
4.026
4.019
4.008
4.001
3.983
3.889
3.872
3.864
3.854
3.850
3.846
3.832
3.828
3.825
3.815
3.810
3.807
3.789
2.356
1.132
1.114
1.096
chl-cb-7-4-Me H
Me
O
P(OEt)2
Ph
Ph
3b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.01
6.26
2.18
2.00
2.01
2.13
3.00
6.00

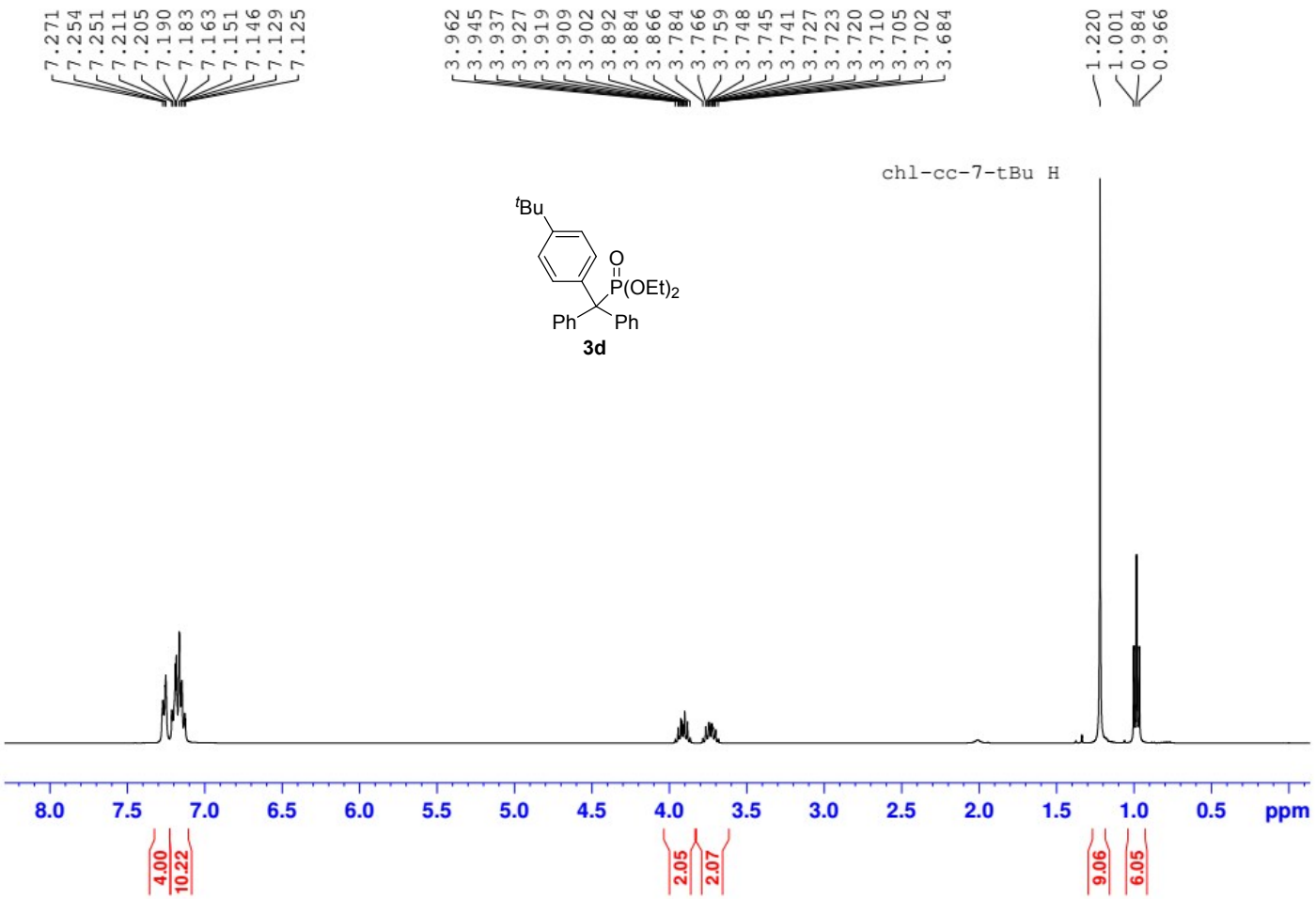

141.64
138.44
136.44
130.65
130.61
130.52
130.48
128.52
127.74
126.79
77.21
77.00
76.79
63.28
63.23
62.97
62.07
20.94
16.16
16.13
Me
O
P(OEt)2
Ph
Ph
3b
f1 (ppm)

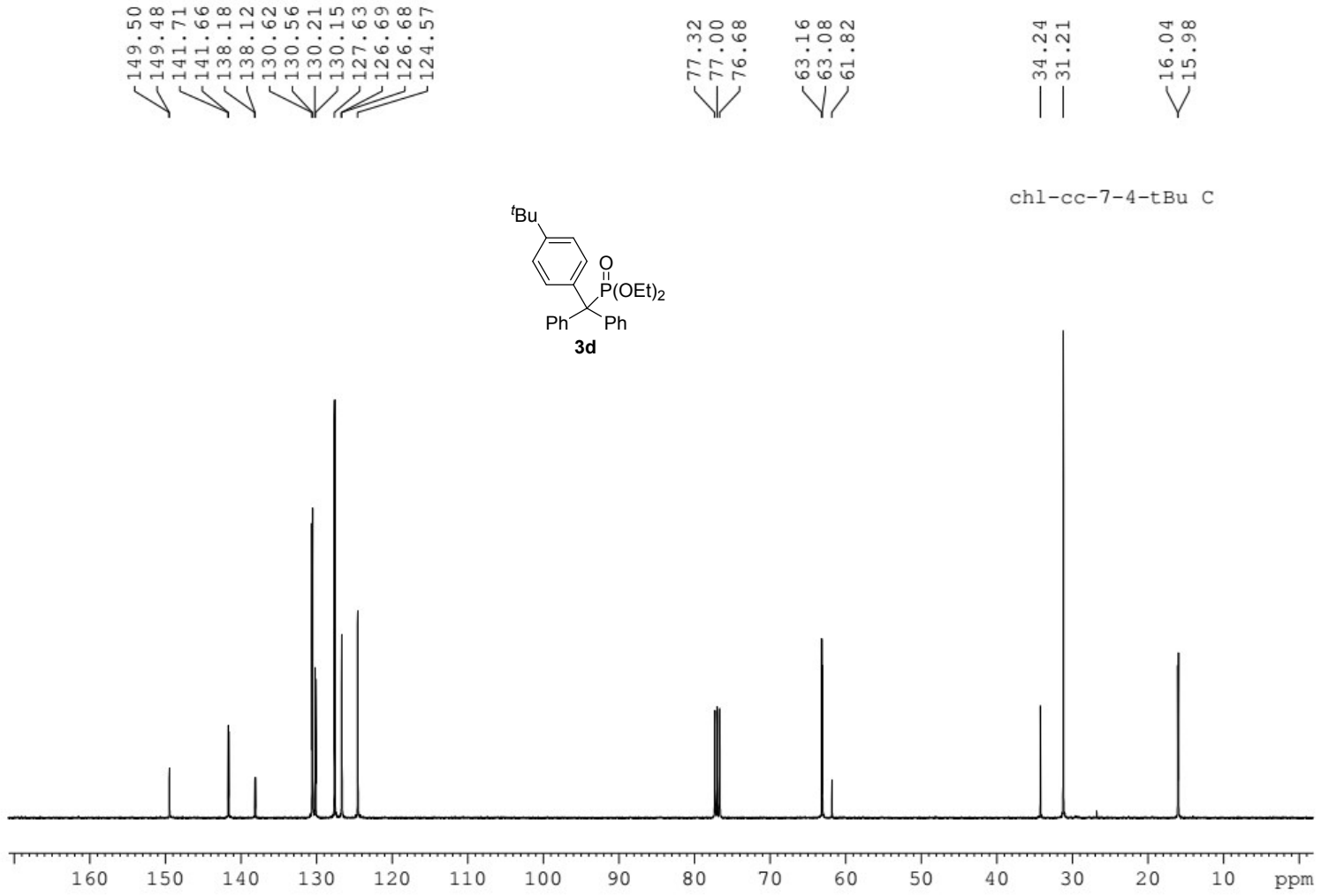

26.19
Me
O
P(OEt)2
Ph
Ph
3b
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

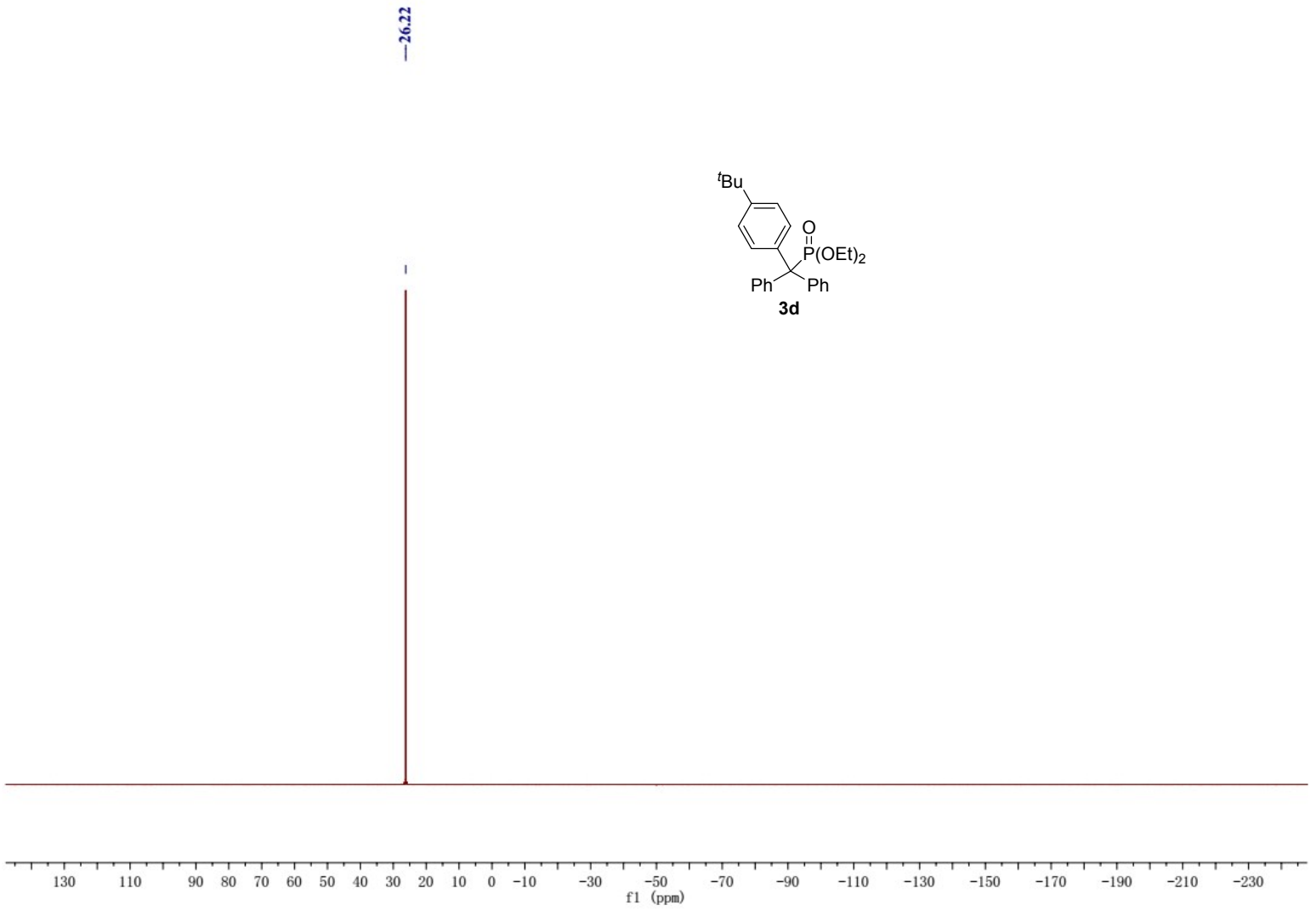

7.269
7.253
7.250
7.214
7.207
7.200
7.193
7.173
7.161
7.158
7.149
7.144
6.745
6.723
3.978
3.960
3.952
3.942
3.934
3.925
3.917
3.907
3.899
3.881
3.791
3.774
3.766
3.756
3.752
3.748
3.735
3.731
3.727
3.708
3.692
1.033
1.016
0.998
MeO
O
P(OEt)2
Ph
Ph
3c
chl-cc-5-4-OMe H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.02
8.06
2.00
2.02
2.16
3.16
6.06

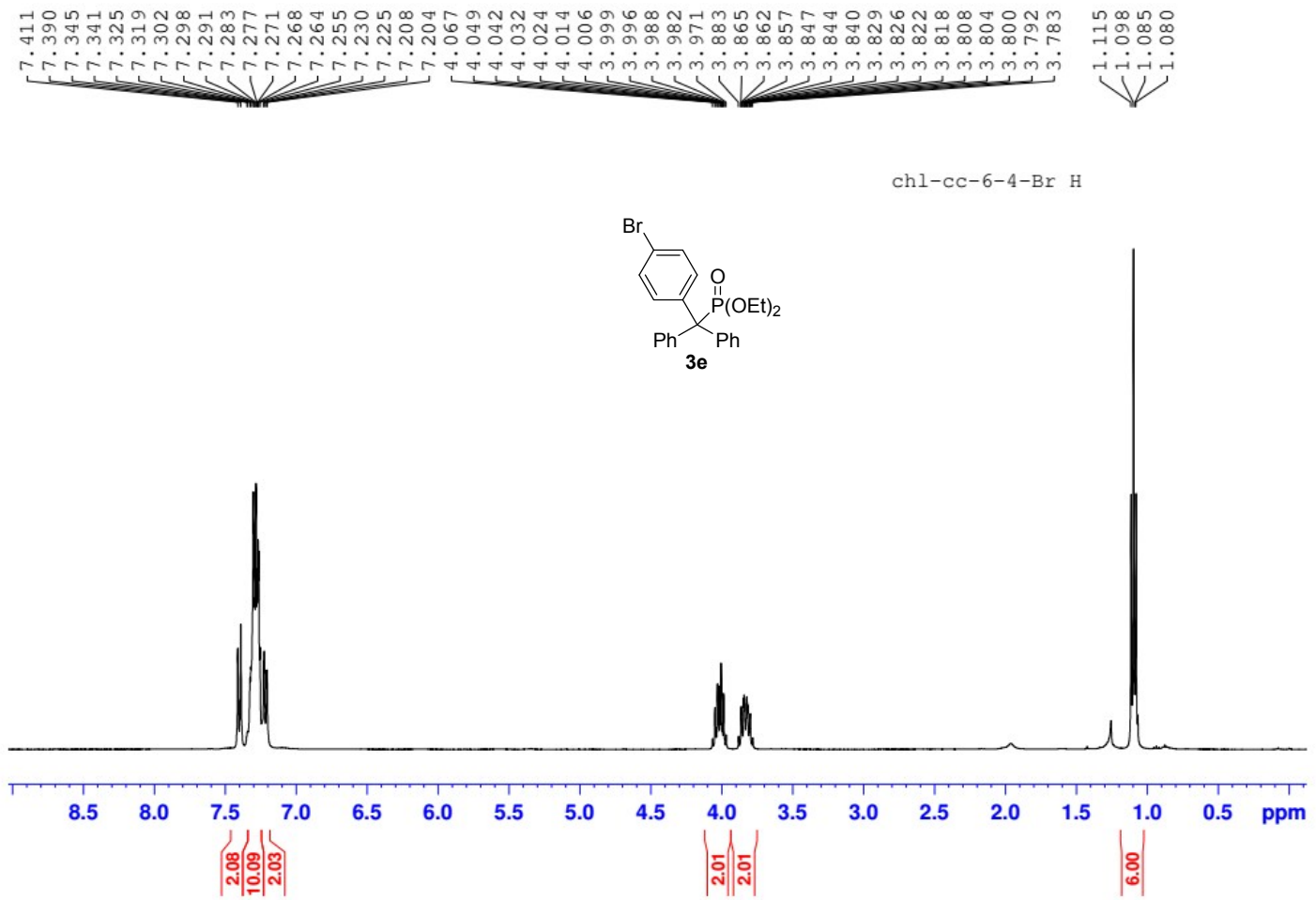

158.20
158.19
141.82
141.77
133.49
133.44
131.77
131.70
130.58
130.52
127.70
126.74
113.02
77.32
77.00
76.68
63.19
63.11
62.82
61.46
55.08
16.13
16.08
MeO
O
P(OEt)2
Ph
Ph
3c
chl-cc-5-4-OMe C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

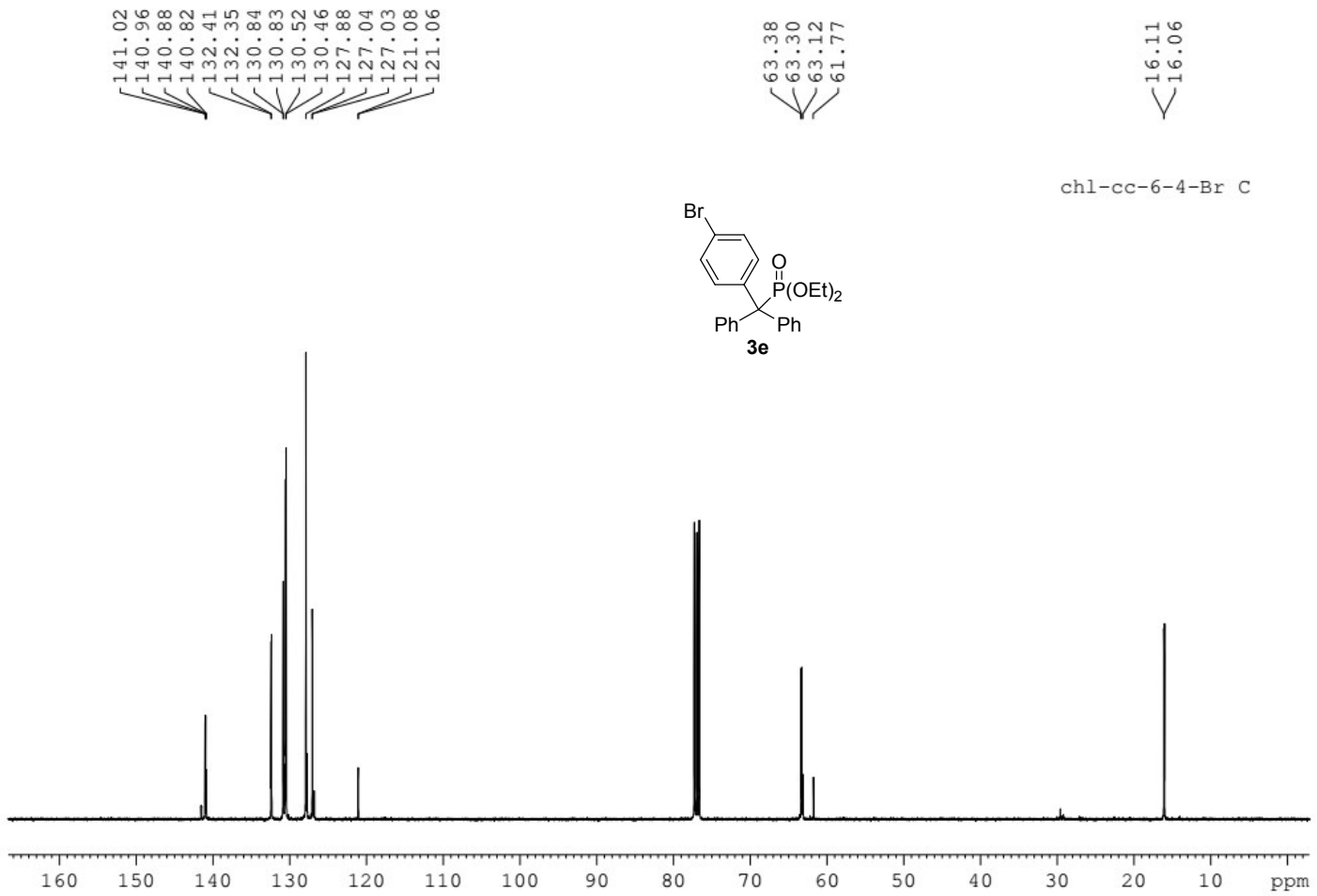

26.23
MeO
O
P(OEt)2
Ph
Ph
3c
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

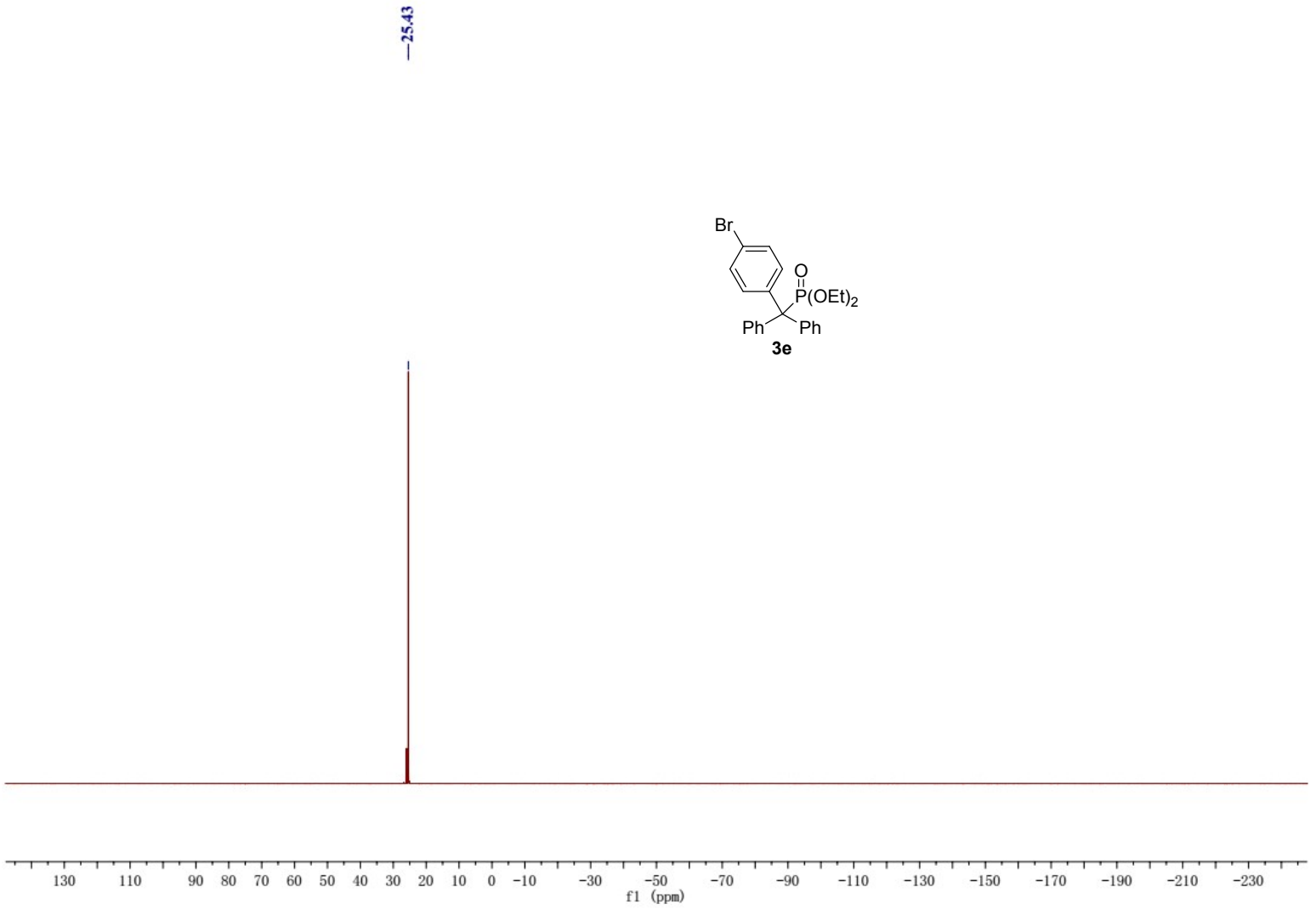

7.271
7.254
7.251
7.211
7.205
7.190
7.183
7.163
7.151
7.146
7.129
7.125
3.962
3.945
3.937
3.927
3.919
3.909
3.902
3.892
3.884
3.866
3.784
3.766
3.759
3.748
3.745
3.741
3.727
3.723
3.720
3.710
3.705
3.702
3.684
1.220
1.001
0.984
0.966
chl-cc-7-tBu H
tBu
O
P(OEt)2
Ph
Ph
3d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.00
10.22
2.05
2.07
9.06
6.05

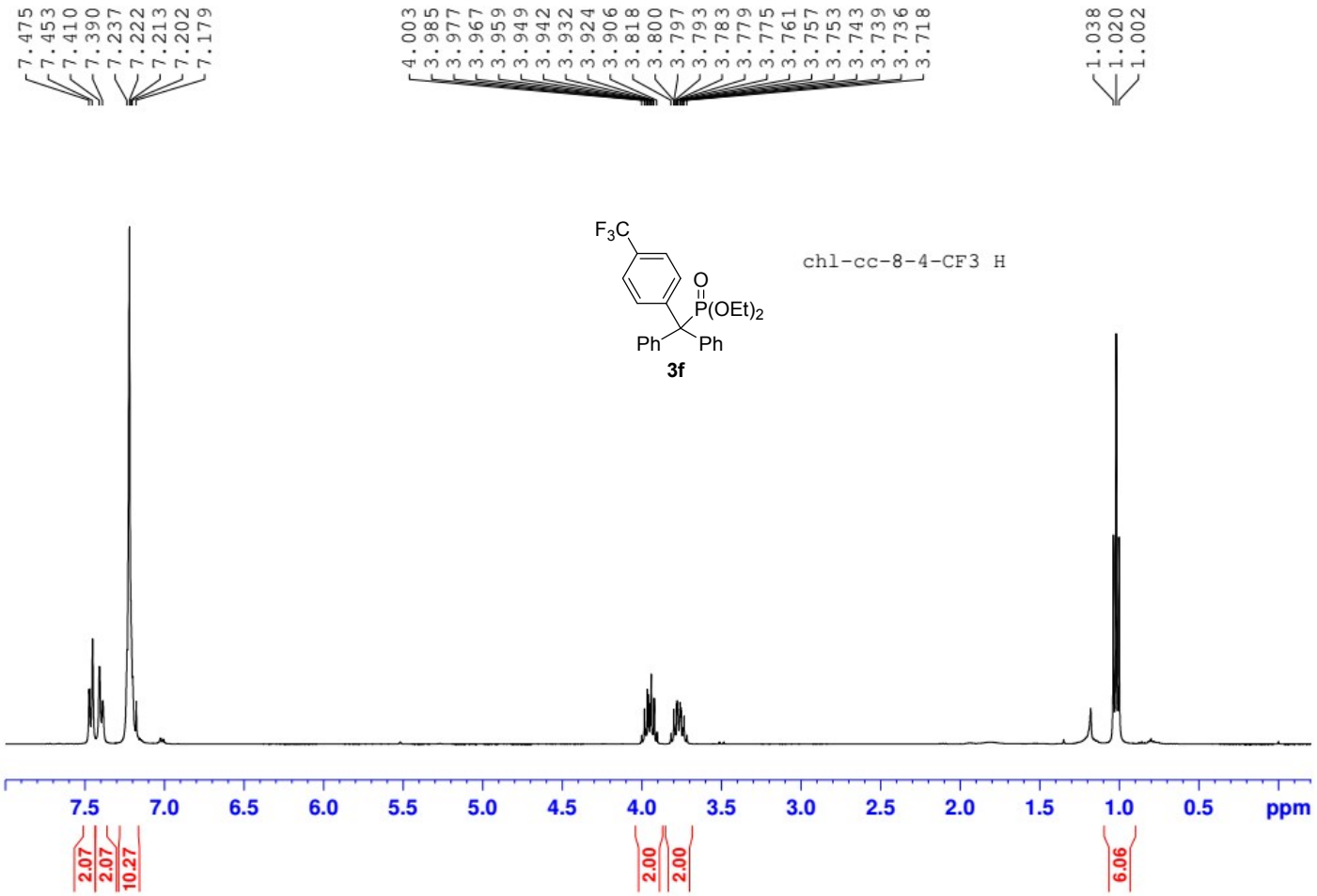

149.50
149.48
141.71
141.66
138.18
138.12
130.62
130.56
130.21
130.15
127.63
126.69
126.68
124.57
77.32
77.00
76.68
63.16
63.08
61.82
34.24
31.21
16.04
15.98
chl-cc-7-4-tBu C
tBu
O
P(OEt)2
Ph
Ph
3d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

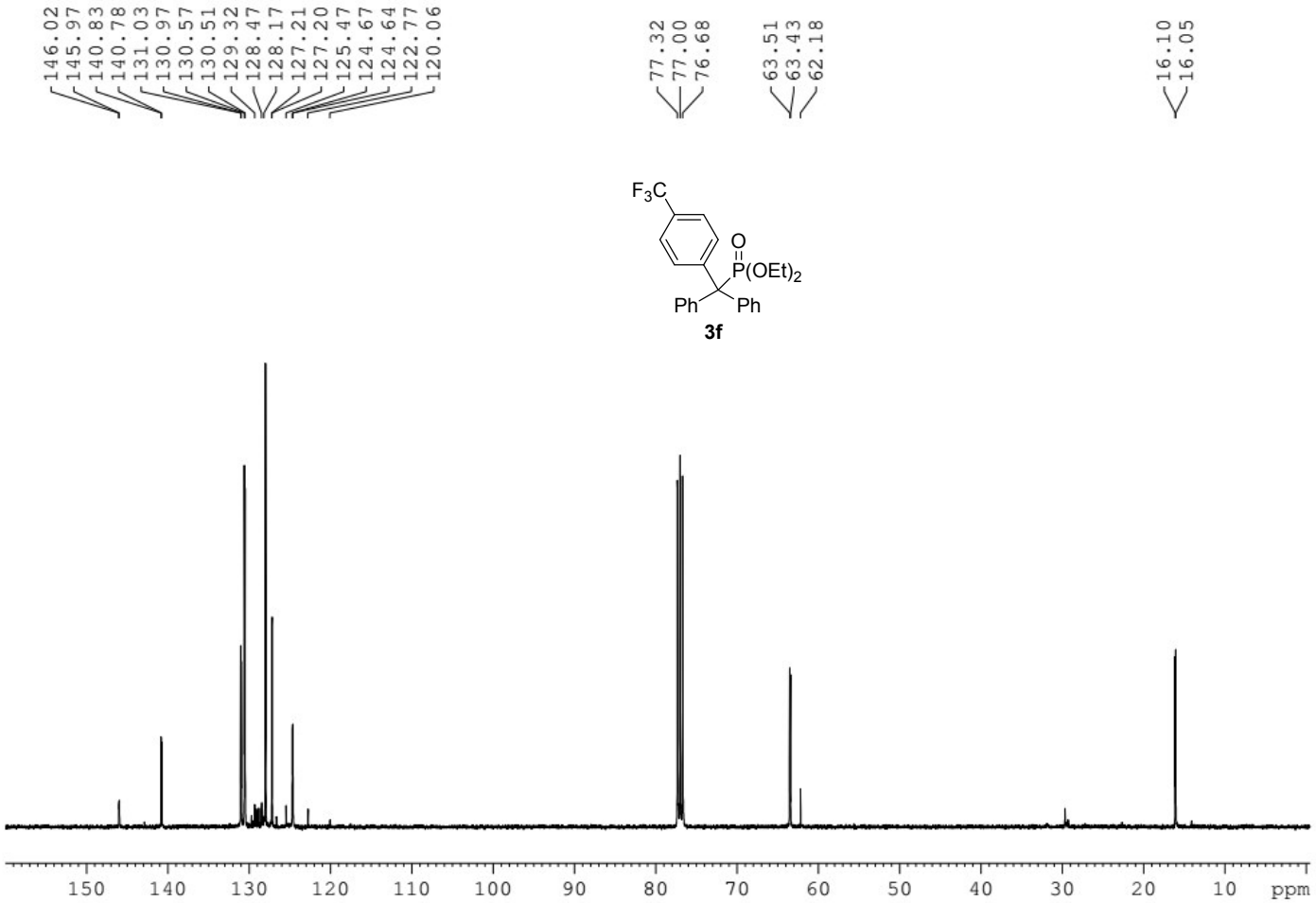

26.22
tBu
O
P(OEt)2
Ph
Ph
3d
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

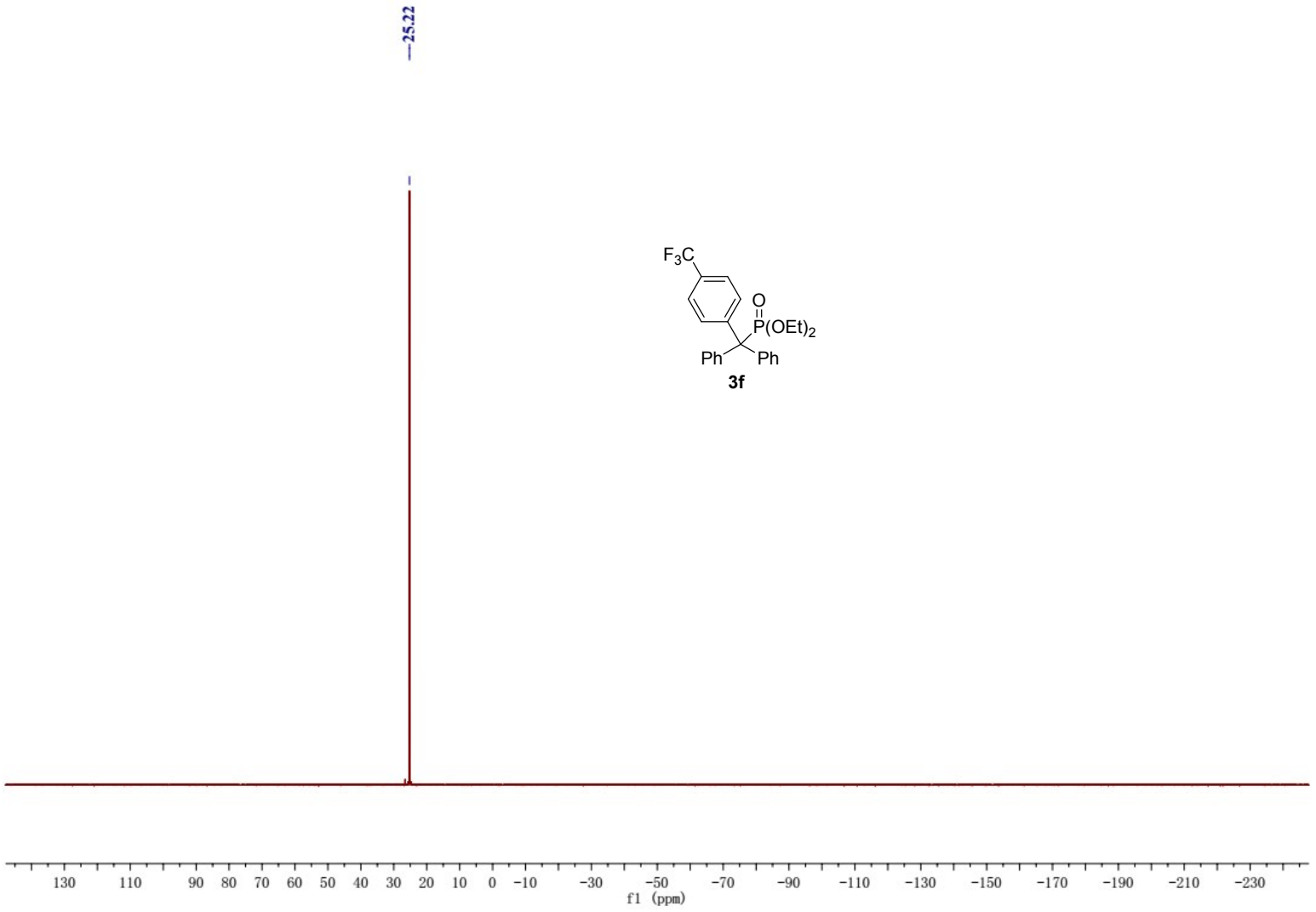

7.411
7.390
7.345
7.341
7.325
7.319
7.302
7.298
7.291
7.283
7.277
7.271
7.268
7.264
7.255
7.230
7.225
7.208
7.204
4.067
4.049
4.042
4.032
4.024
4.014
4.006
3.999
3.996
3.988
3.982
3.971
3.883
3.865
3.862
3.857
3.847
3.844
3.840
3.829
3.826
3.822
3.818
3.808
3.804
3.800
3.792
3.783
1.115
1.098
1.085
1.080
chl-cc-6-4-Br H
Br
O
P(OEt)2
Ph
Ph
3e
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.08
10.09
2.03
2.01
2.01
6.00

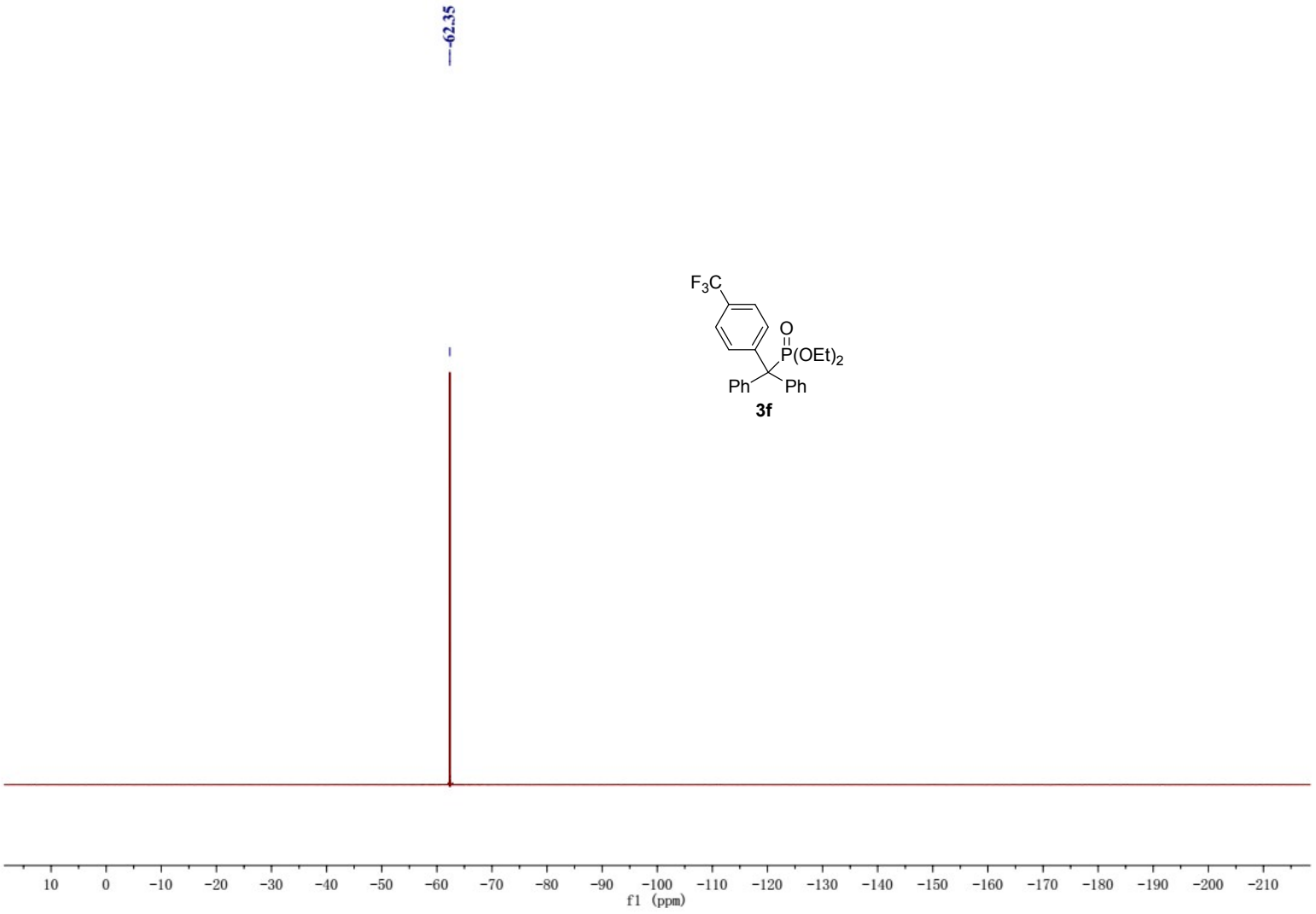

141.02
140.96
140.88
140.82
132.41
132.35
130.84
130.83
130.52
130.46
127.88
127.04
127.03
121.08
121.06
63.38
63.30
63.12
61.77
16.11
16.06
chl-cc-6-4-Br C
Br
O
P(OEt)2
Ph
Ph
3e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


25.43
Br
O
P(OEt)2
Ph
Ph
3e
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

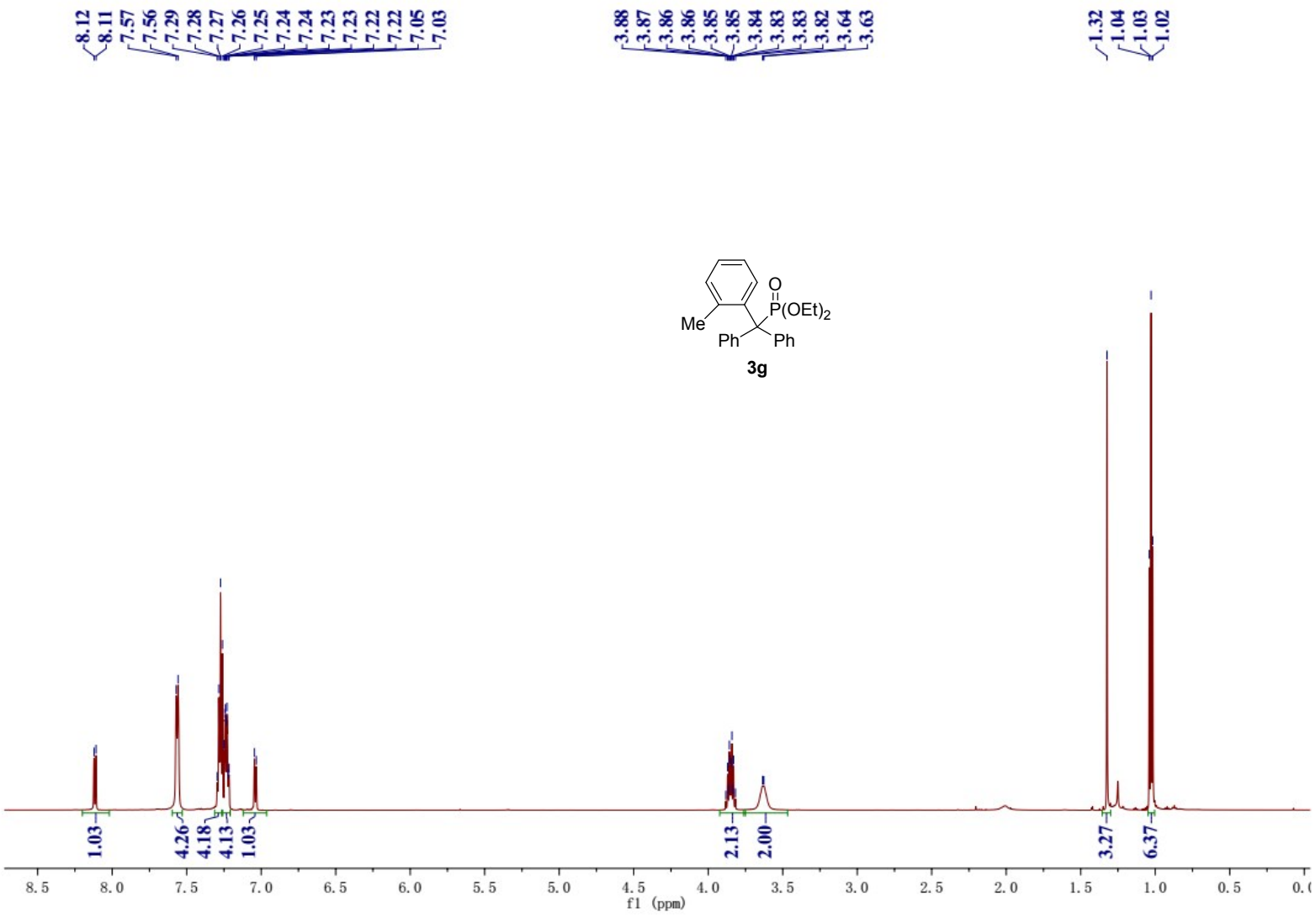

7.475
7.453
7.410
7.390
7.237
7.222
7.213
7.202
7.179
4.003
3.985
3.977
3.967
3.959
3.949
3.942
3.932
3.924
3.906
3.818
3.800
3.797
3.793
3.783
3.779
3.775
3.761
3.757
3.753
3.743
3.739
3.736
3.718
1.038
1.020
1.002
F3C
O
P(OEt)2
Ph
Ph
3f
chl-cc-8-4-CF3 H
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.07
2.07
10.27
2.00
2.00
6.06

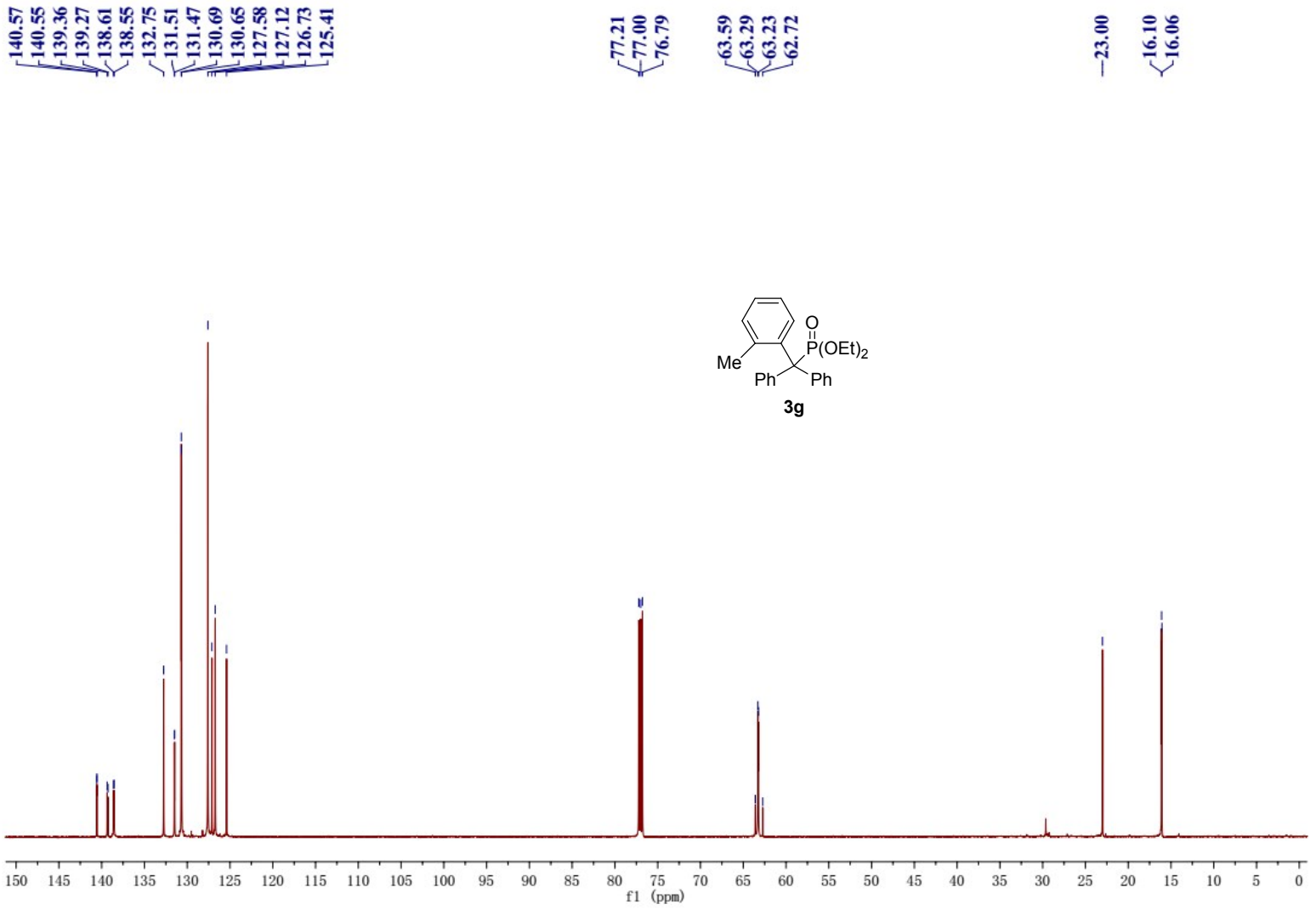

146.02
145.97
140.83
140.78
131.03
130.97
130.57
130.51
129.32
128.47
128.17
127.21
127.20
125.47
124.67
124.64
122.77
120.06
77.32
77.00
76.68
63.51
63.43
62.18
16.10
16.05
F3C
O
P(OEt)2
Ph
Ph
3f
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

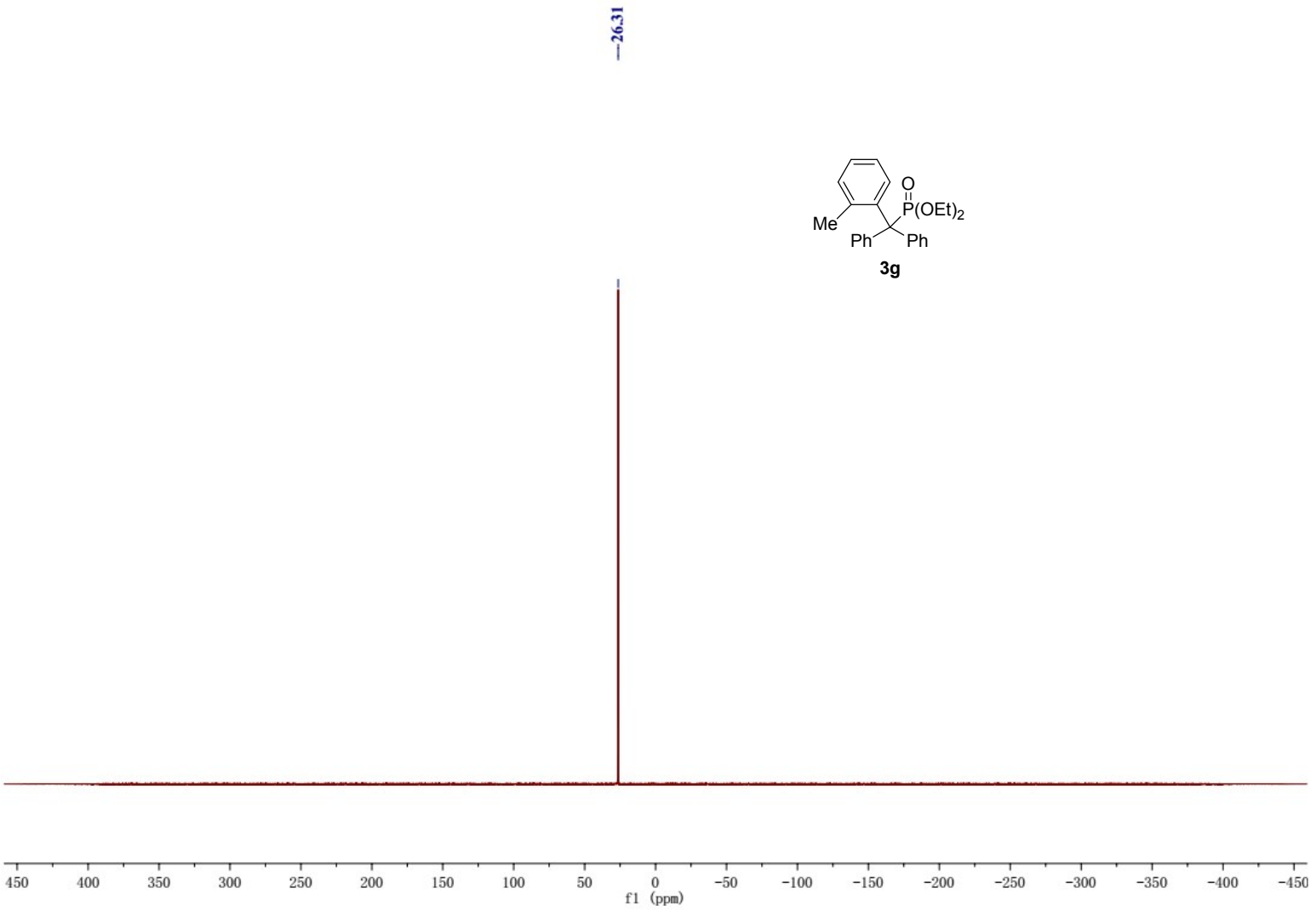

25.22
F3C
O
P(OEt)2
Ph
Ph
3f
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

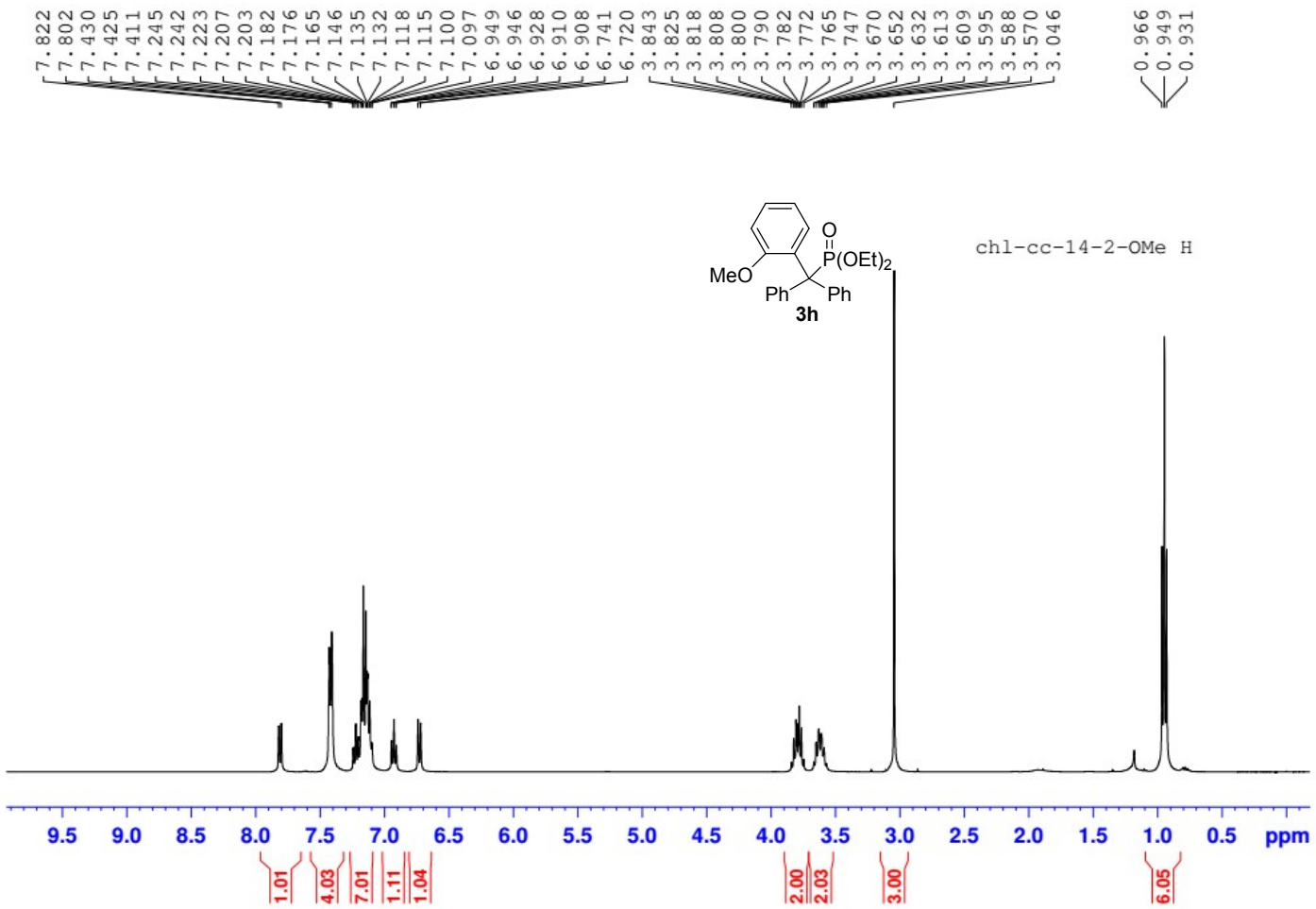

-62.35
F3C
O
P(OEt)2
Ph
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

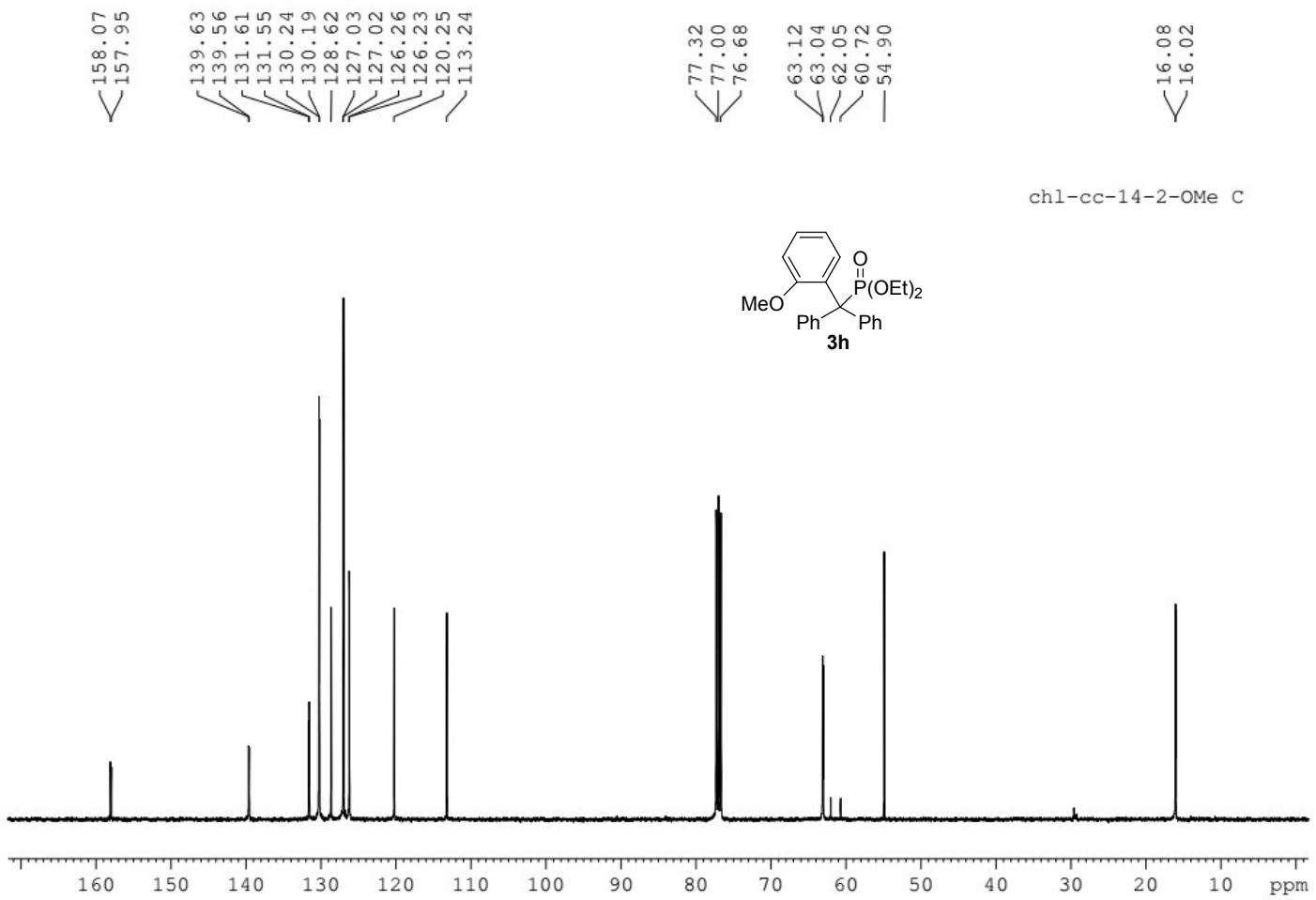
3f

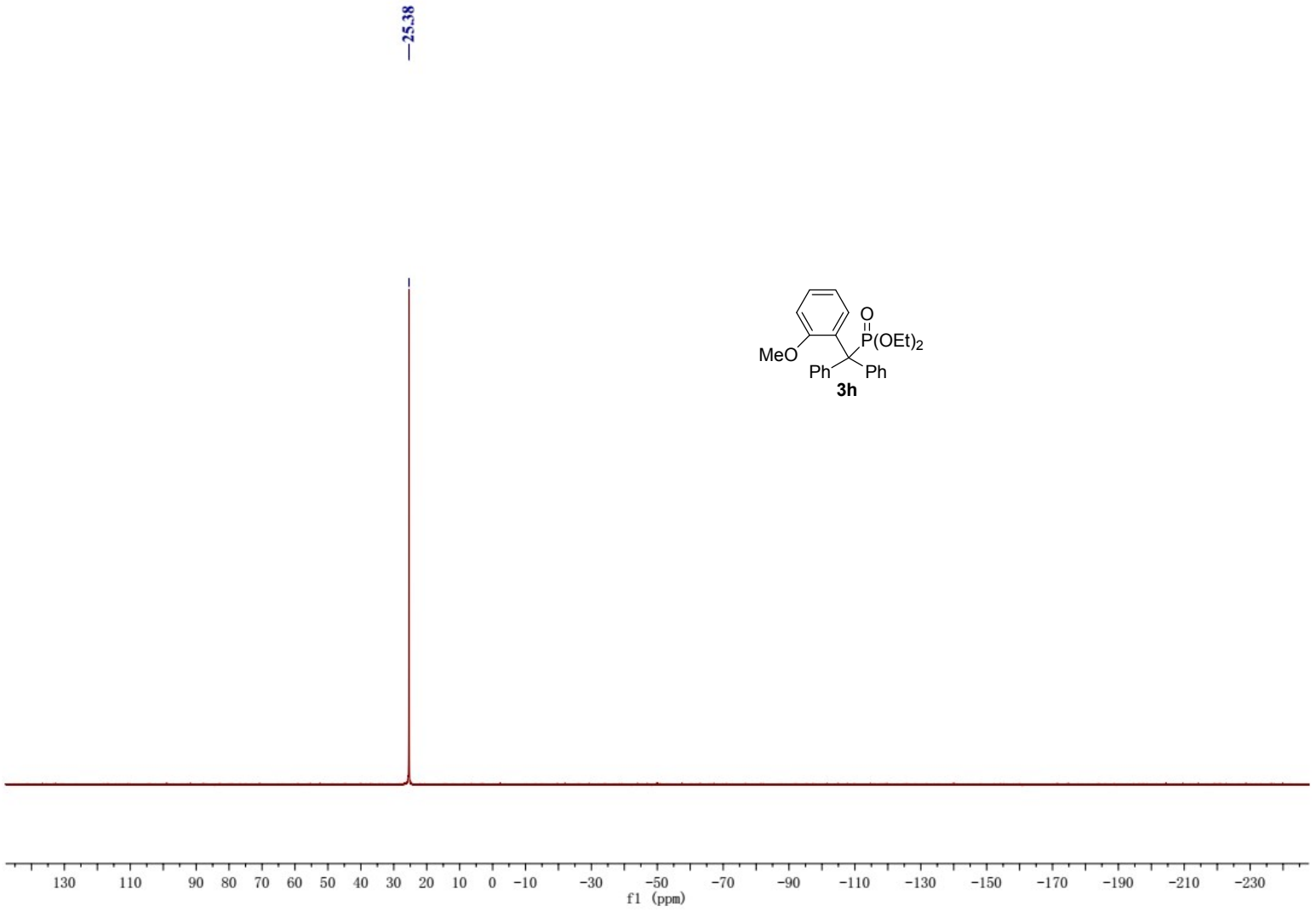

8.12
8.11
7.57
7.56
7.29
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.05
7.03
3.88
3.87
3.86
3.86
3.85
3.85
3.84
3.83
3.83
3.82
3.64
3.63
1.32
1.04
1.03
1.02
O
P(OEt)2
Me
Ph
Ph
3g
1.03
4.26
4.18
4.13
1.03
2.13
2.00
3.27
6.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

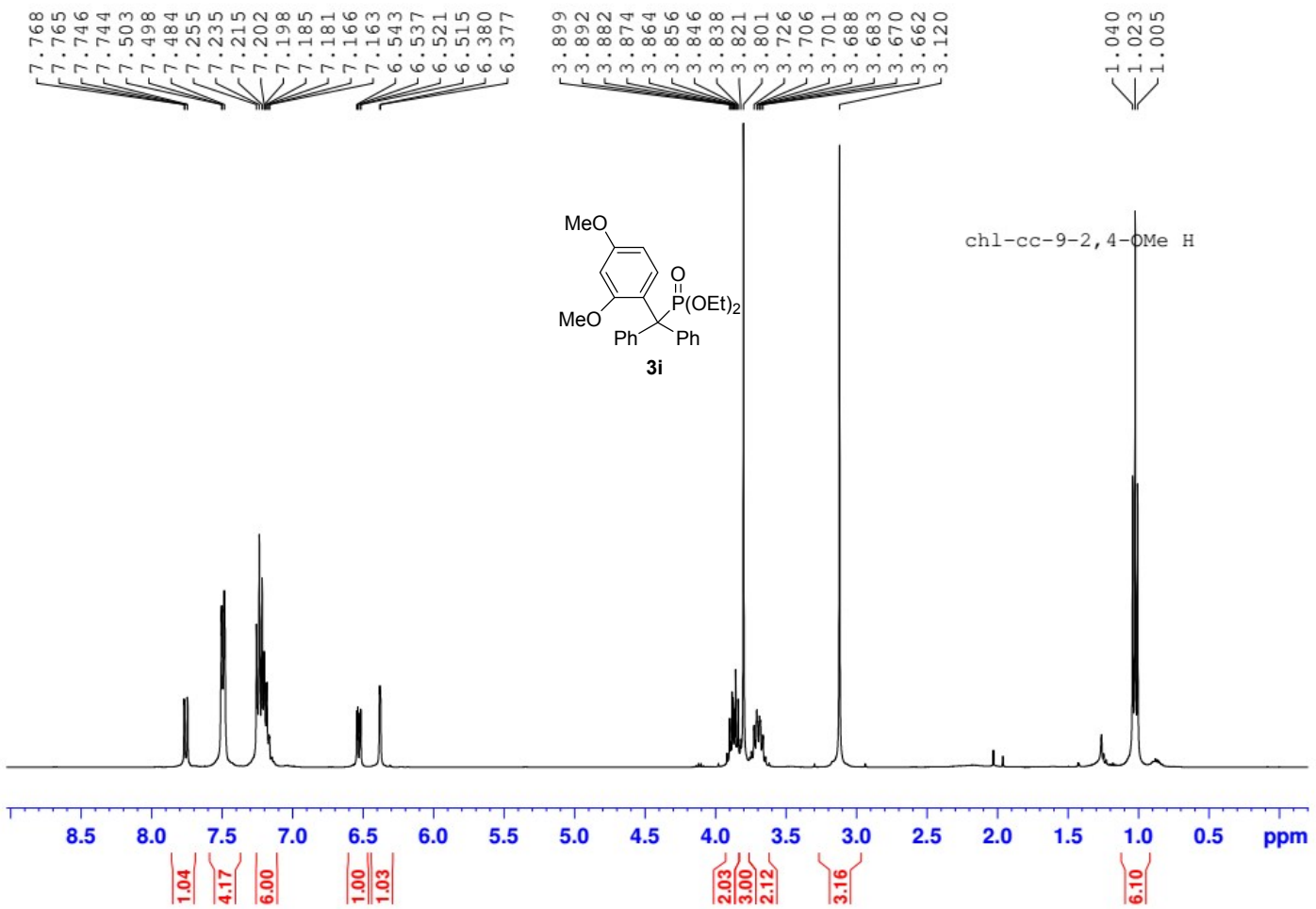

140.57
140.55
139.36
139.27
138.61
138.55
132.75
131.51
131.47
130.69
130.65
127.58
127.12
126.73
125.41
77.21
77.00
76.79
63.59
63.29
63.23
62.72
23.00
16.10
16.06
O
P(OEt)2
Me
Ph
Ph
3g
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

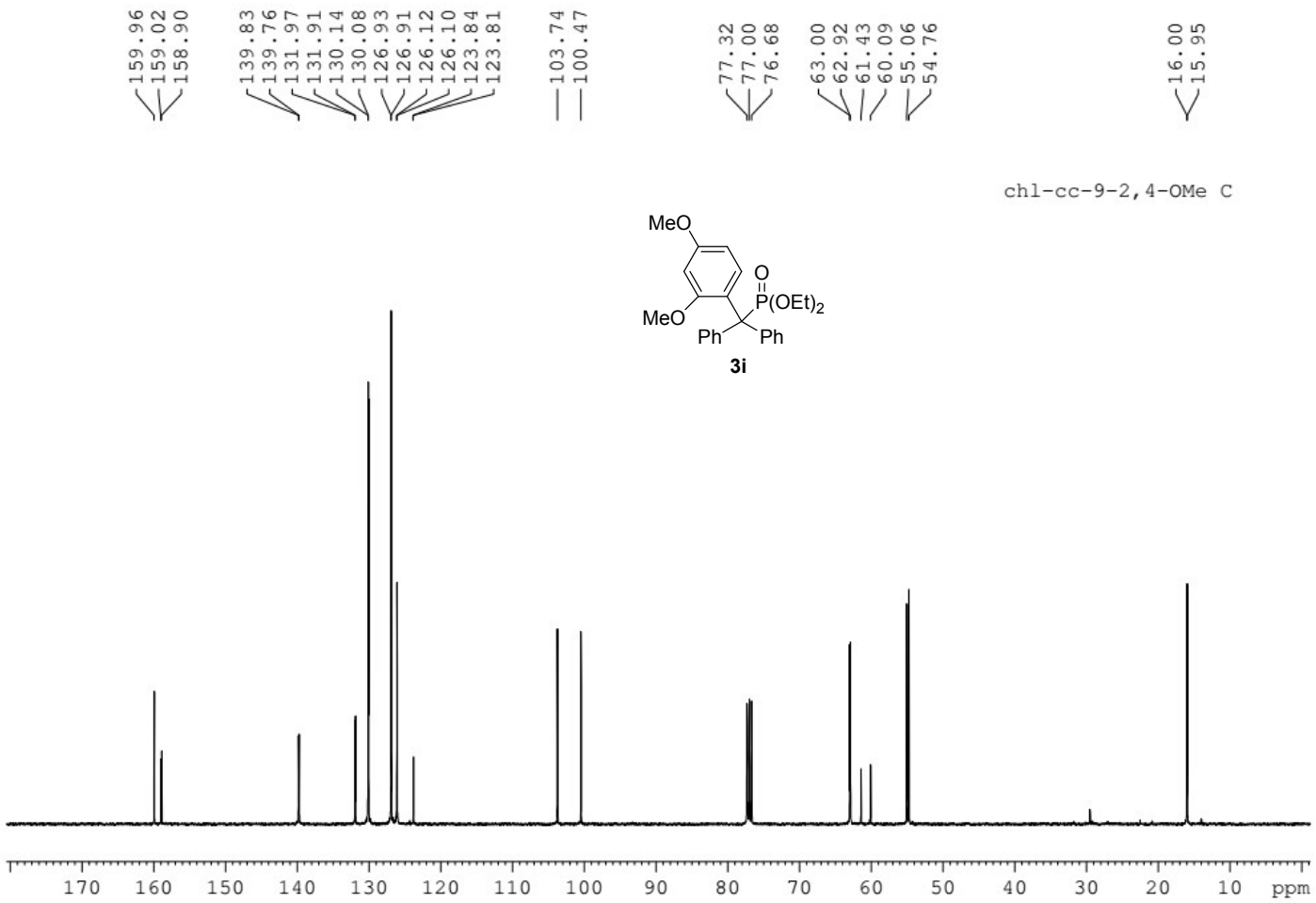

26.31
O
P(OEt)2
Me
Ph
Ph
3g
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

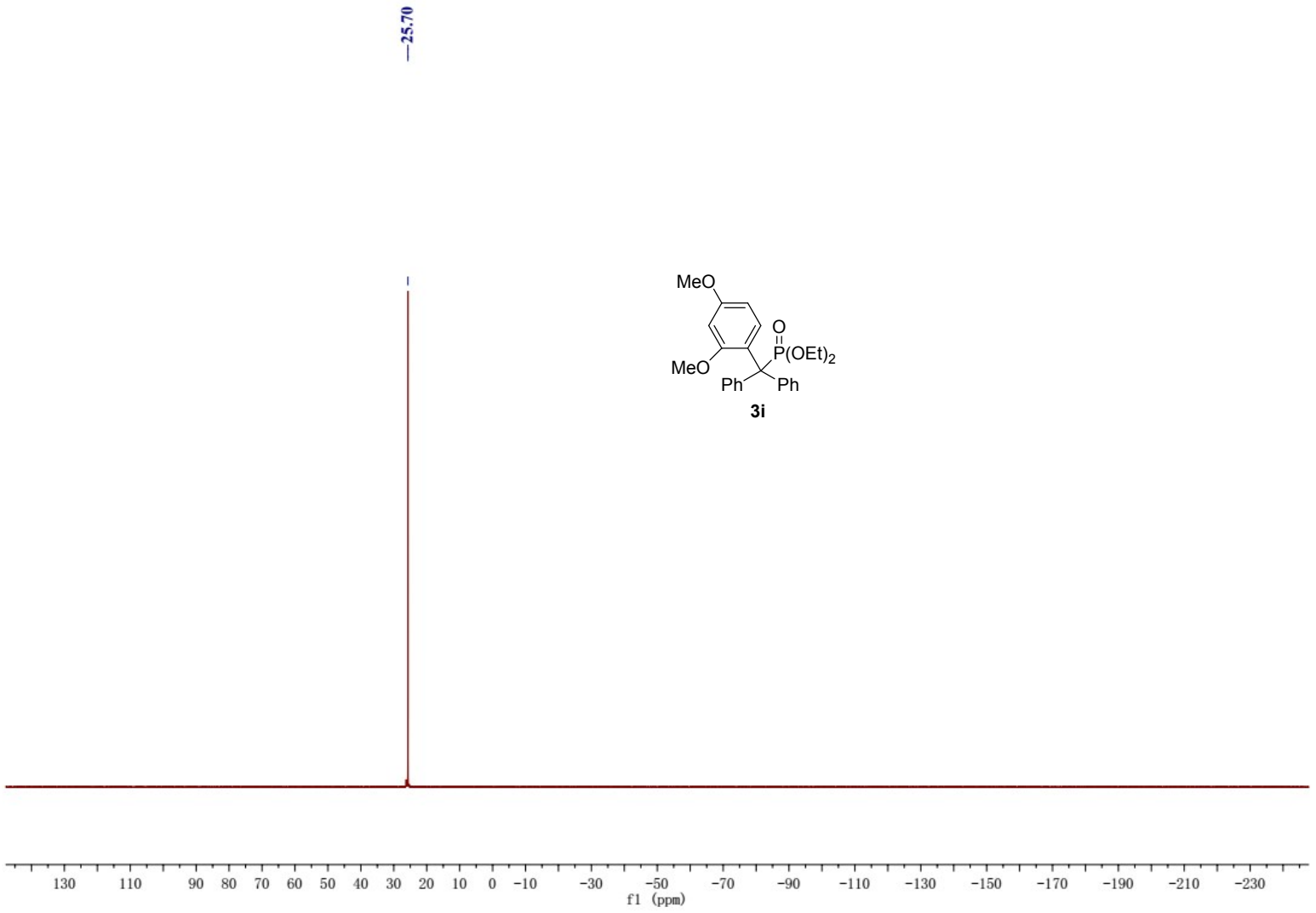

7.822
7.802
7.430
7.425
7.411
7.245
7.242
7.223
7.207
7.203
7.182
7.176
7.165
7.146
7.135
7.132
7.118
7.115
7.100
7.097
6.949
6.946
6.928
6.910
6.908
6.741
6.720
3.843
3.825
3.818
3.808
3.800
3.790
3.782
3.772
3.765
3.747
3.670
3.652
3.632
3.613
3.609
3.595
3.588
3.570
3.046
0.966
0.949
0.931
MeO
O
P(OEt)2
Ph
Ph
3h
ch1-cc-14-2-OMe H
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.01
4.03
7.01
1.11
1.04
2.00
2.03
3.00
6.05


158.07
157.95
139.63
139.56
131.61
131.55
130.24
130.19
128.62
127.03
127.02
126.26
126.23
120.25
113.24
77.32
77.00
76.68
63.12
63.04
62.05
60.72
54.90
16.08
16.02
chl-cc-14-2-OMe C
MeO
O
P(OEt)2
Ph
Ph
3h
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

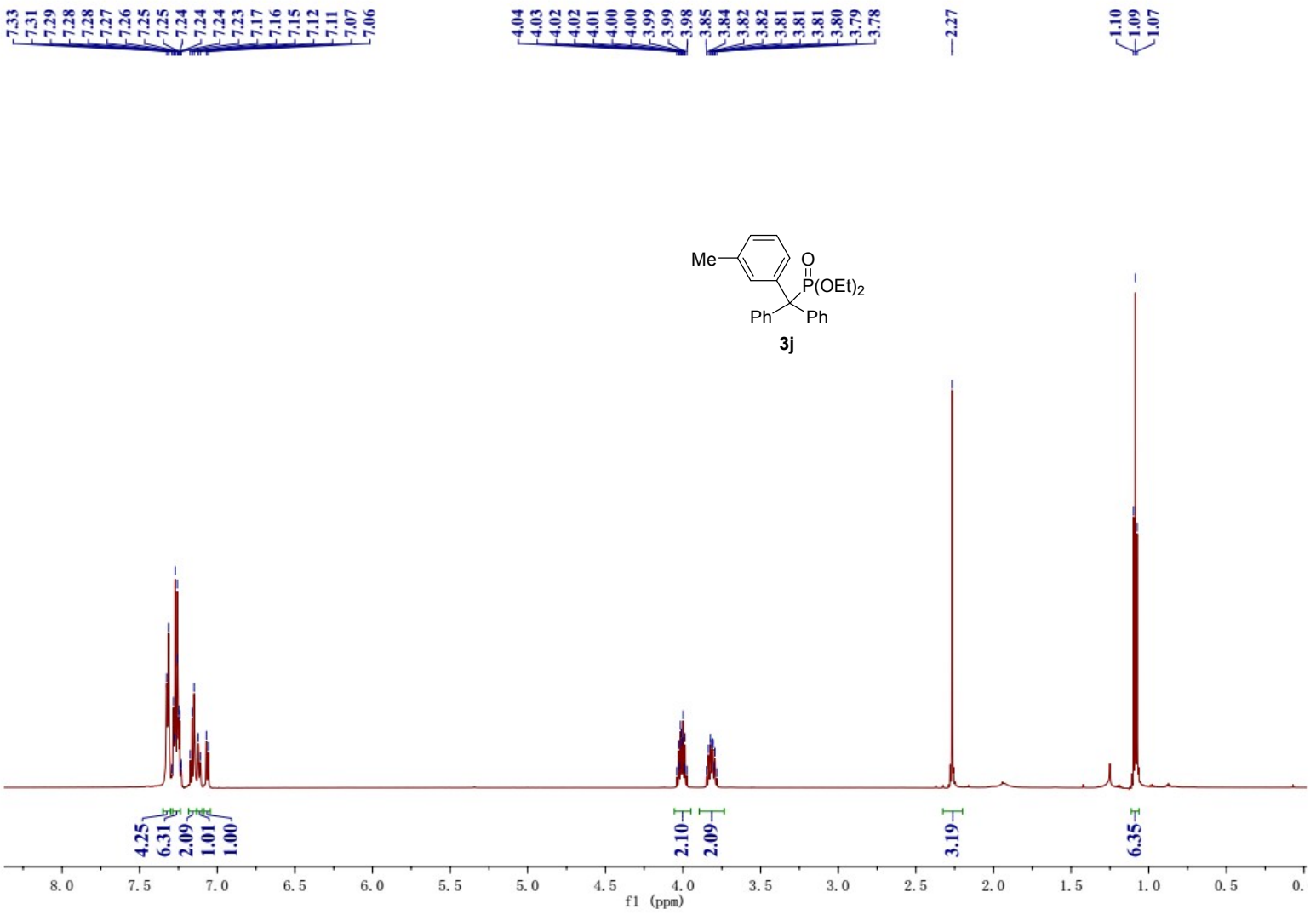

25.38
MeO
O
P(OEt)2
Ph
Ph
3h
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

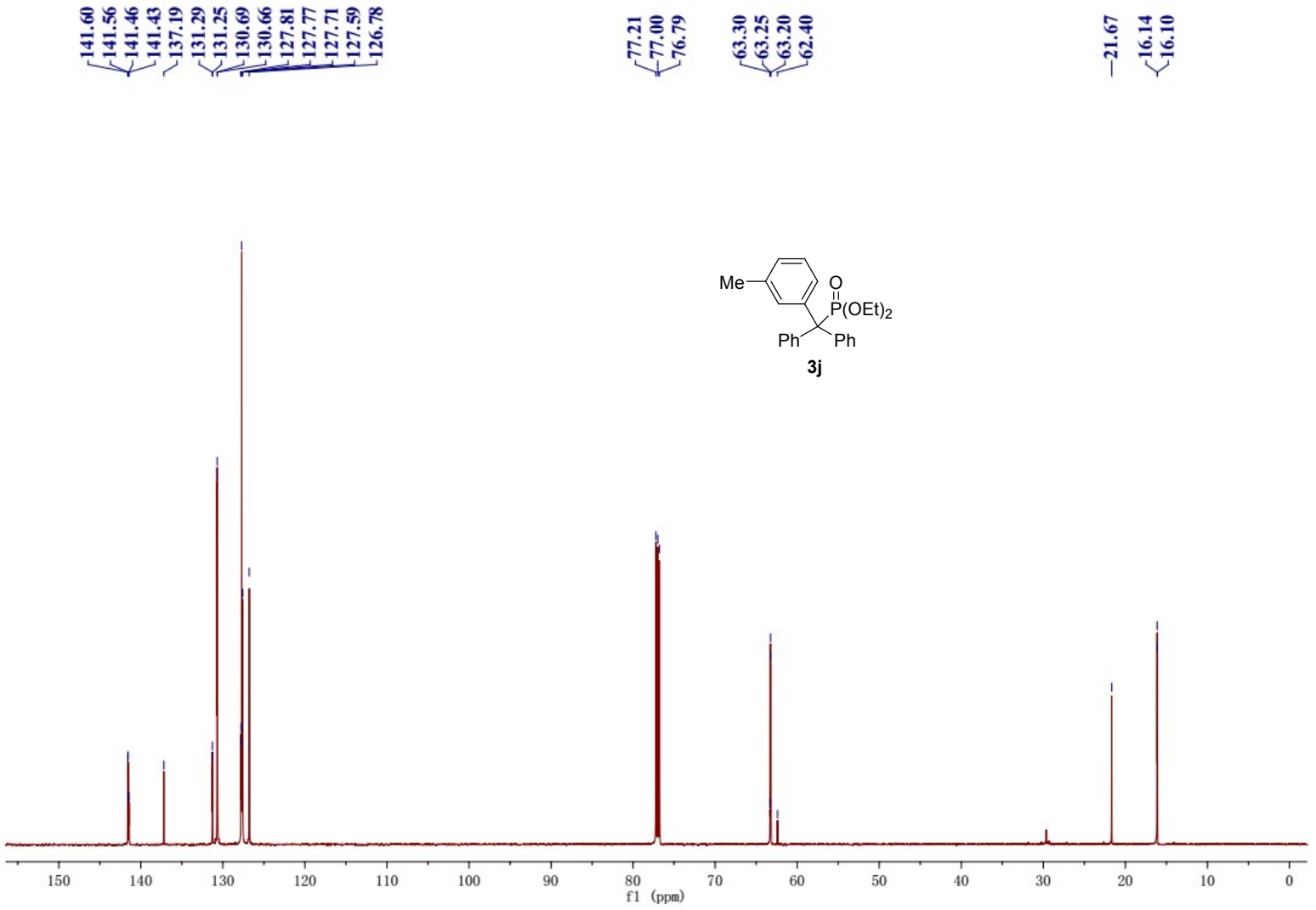

7.768
7.765
7.746
7.744
7.503
7.498
7.484
7.255
7.235
7.215
7.202
7.198
7.185
7.181
7.166
7.163
6.543
6.537
6.521
6.515
6.380
6.377
3.899
3.892
3.882
3.874
3.864
3.856
3.846
3.838
3.821
3.801
3.726
3.706
3.701
3.688
3.683
3.670
3.662
3.120
1.040
1.023
1.005
MeO
MeO
O
P(OEt)2
Ph
Ph
3i
chl-cc-9-2,4-OMe H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.04
4.17
6.00
1.00
1.03
2.03
3.00
2.12
3.16
6.10

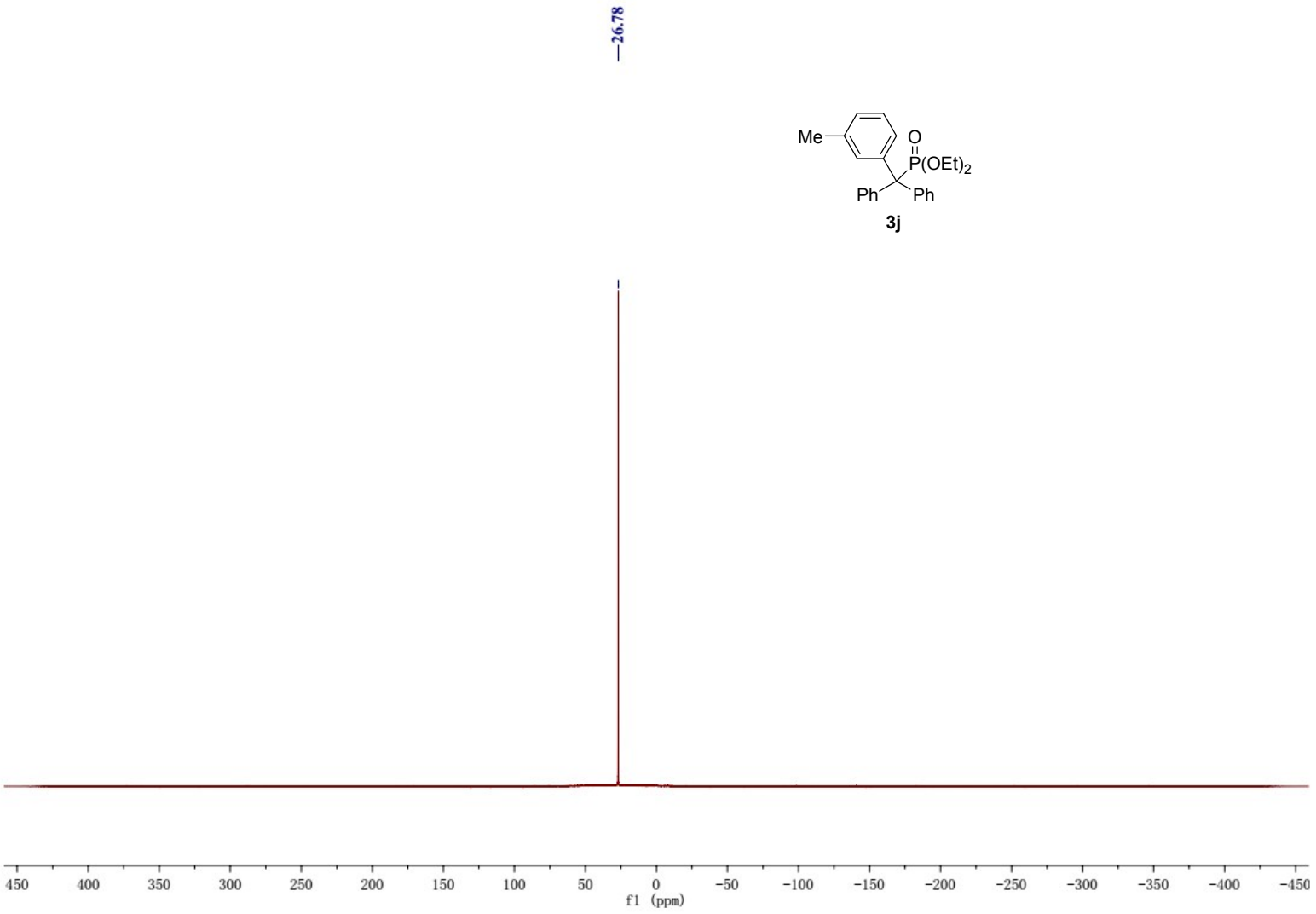

159.96
159.02
158.90
139.83
139.76
131.97
131.91
130.14
130.08
126.93
126.91
126.12
126.10
123.84
123.81
103.74
100.47
77.32
77.00
76.68
63.00
62.92
61.43
60.09
55.06
54.76
16.00
15.95
chl-cc-9-2,4-OMe C
MeO
MeO
O
P(OEt)2
Ph
Ph
3i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

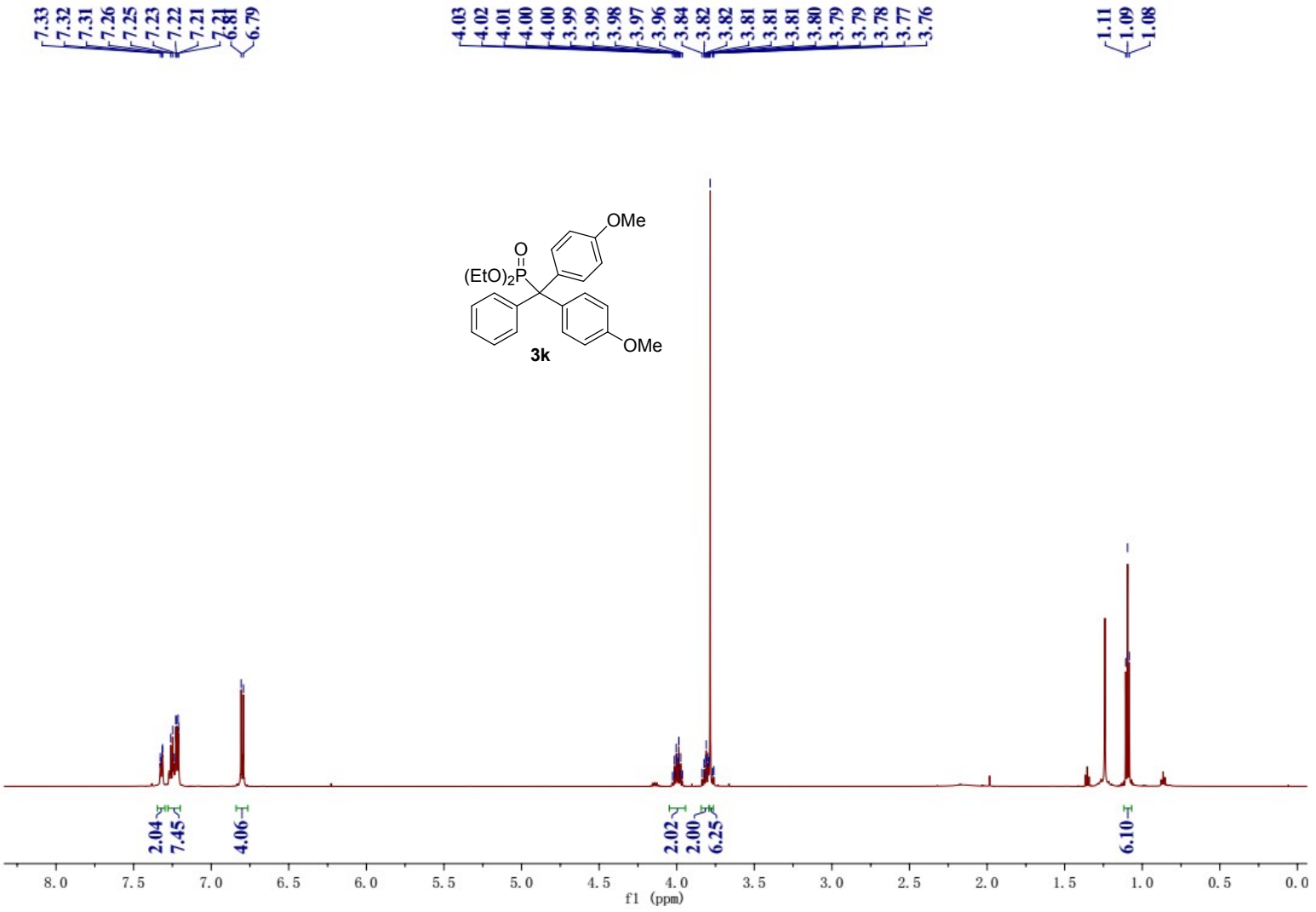

25.70
MeO
MeO
O
P(OEt)2
Ph
Ph
130
110
90
80
70
60
50
40
30
20
10
0
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
f1 (ppm)

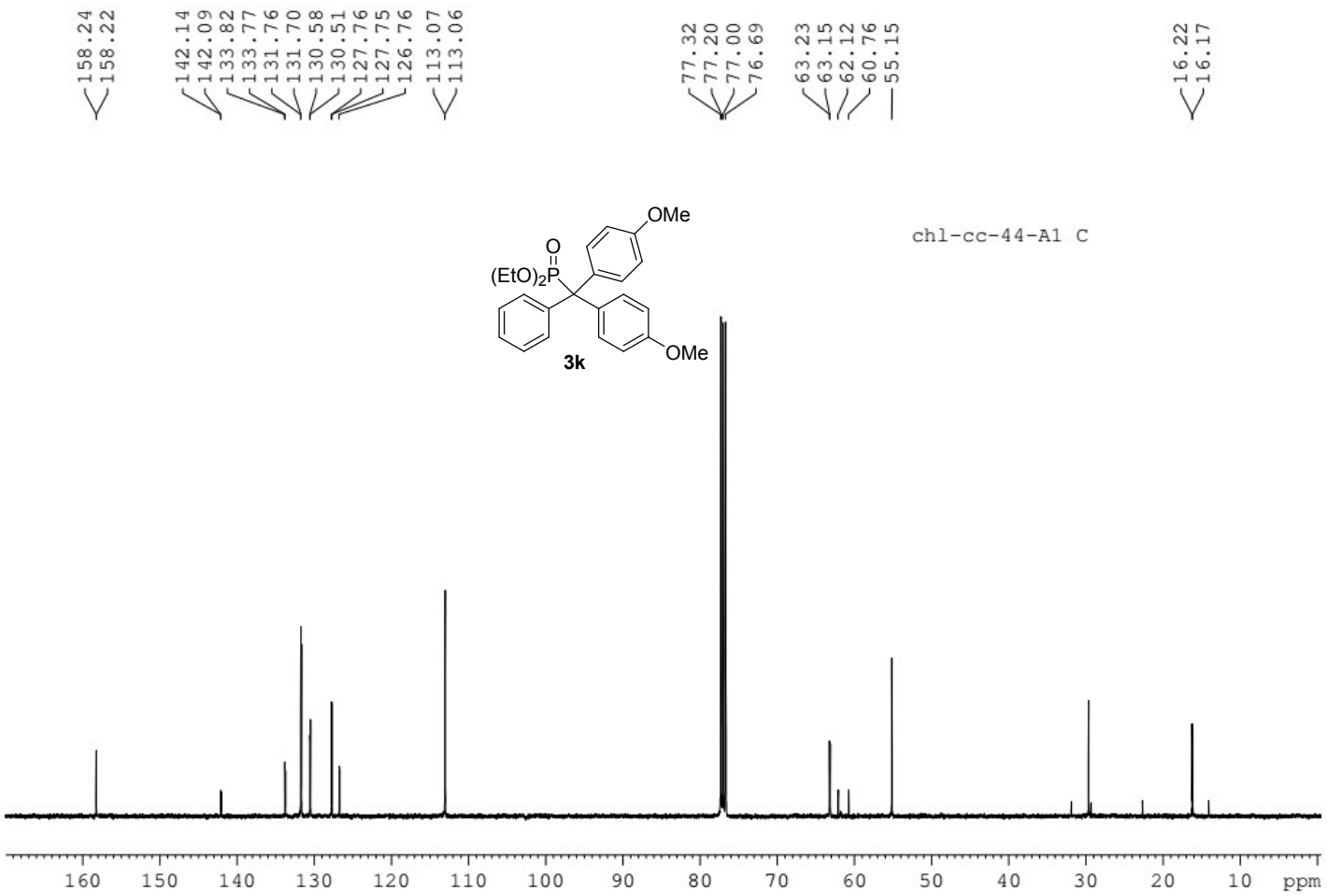
3i

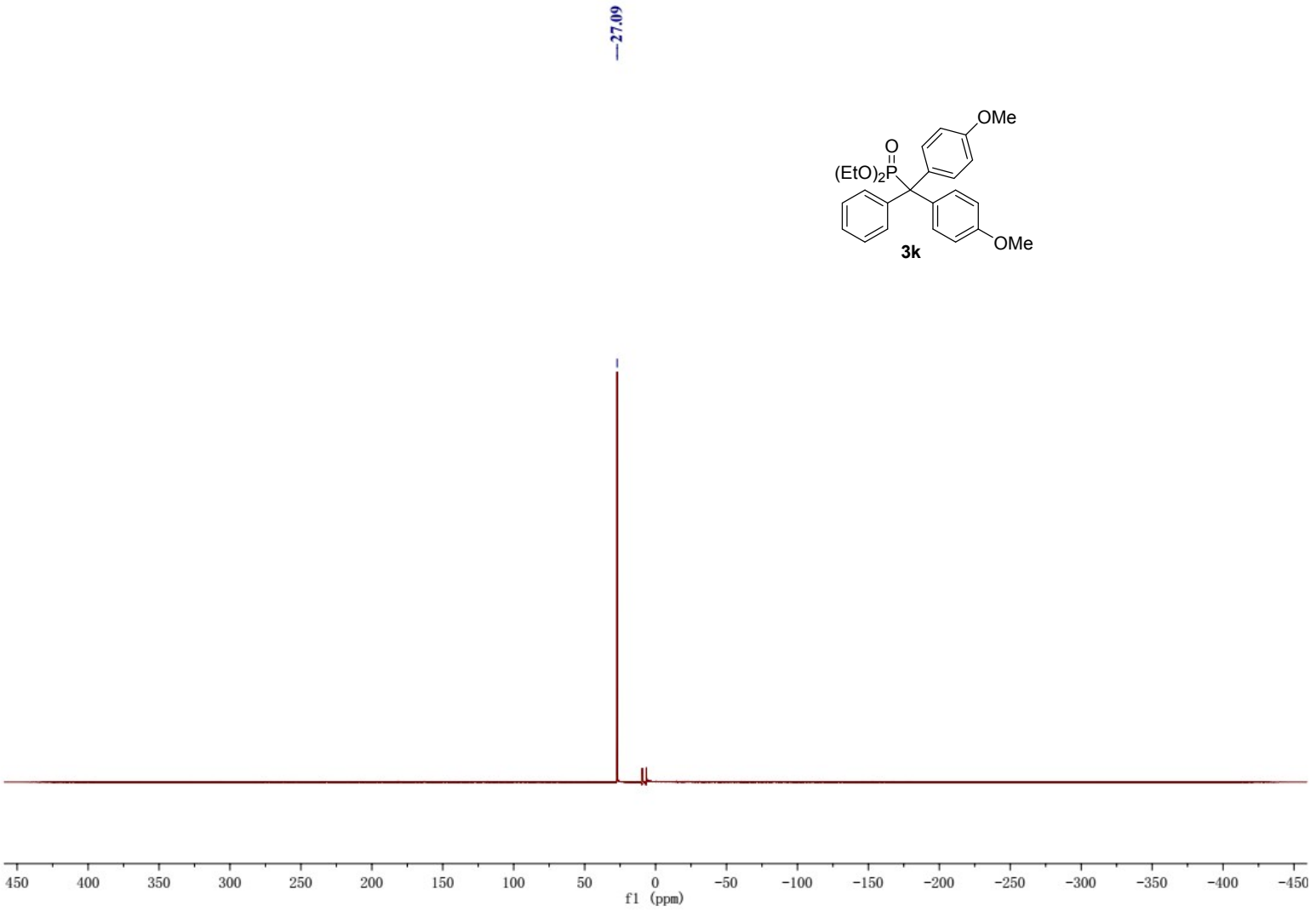

7.33
7.31
7.29
7.28
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.17
7.16
7.15
7.12
7.11
7.07
7.06
4.04
4.03
4.02
4.02
4.01
4.00
4.00
3.99
3.99
3.98
3.85
3.84
3.82
3.82
3.81
3.81
3.81
3.80
3.79
3.78
2.27
1.10
1.09
1.07
Me
O
P(OEt)2
Ph
Ph
3j
4.25
6.31
2.09
1.01
1.00
2.10
2.09
3.19
6.35
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

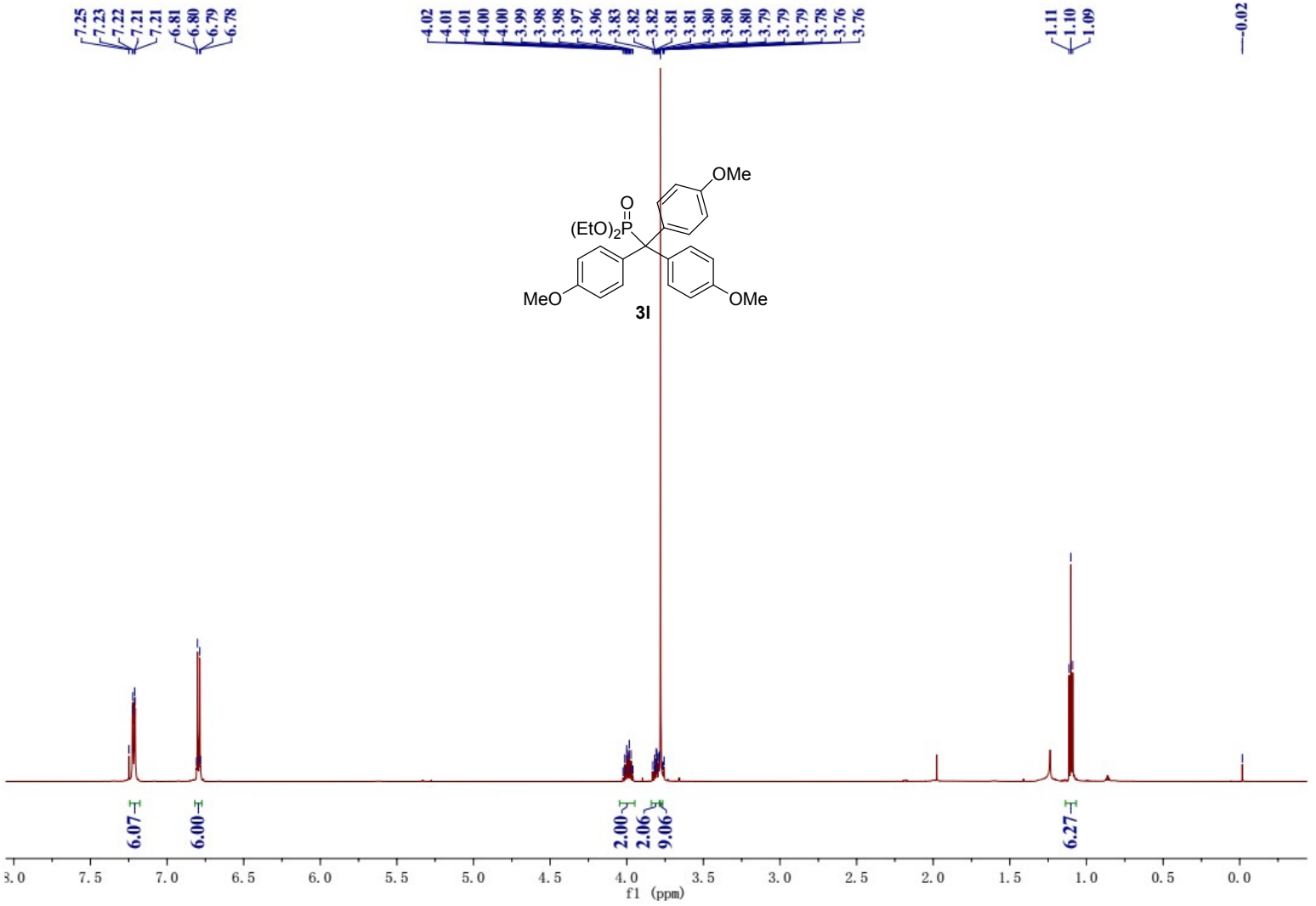

141.60
141.56
141.46
141.43
137.19
131.29
131.25
130.69
130.66
127.81
127.77
127.71
127.59
126.78
77.21
77.00
76.79
63.30
63.25
63.20
62.40
21.67
16.14
16.10
Me
O
P(OEt)2
Ph
Ph
3j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

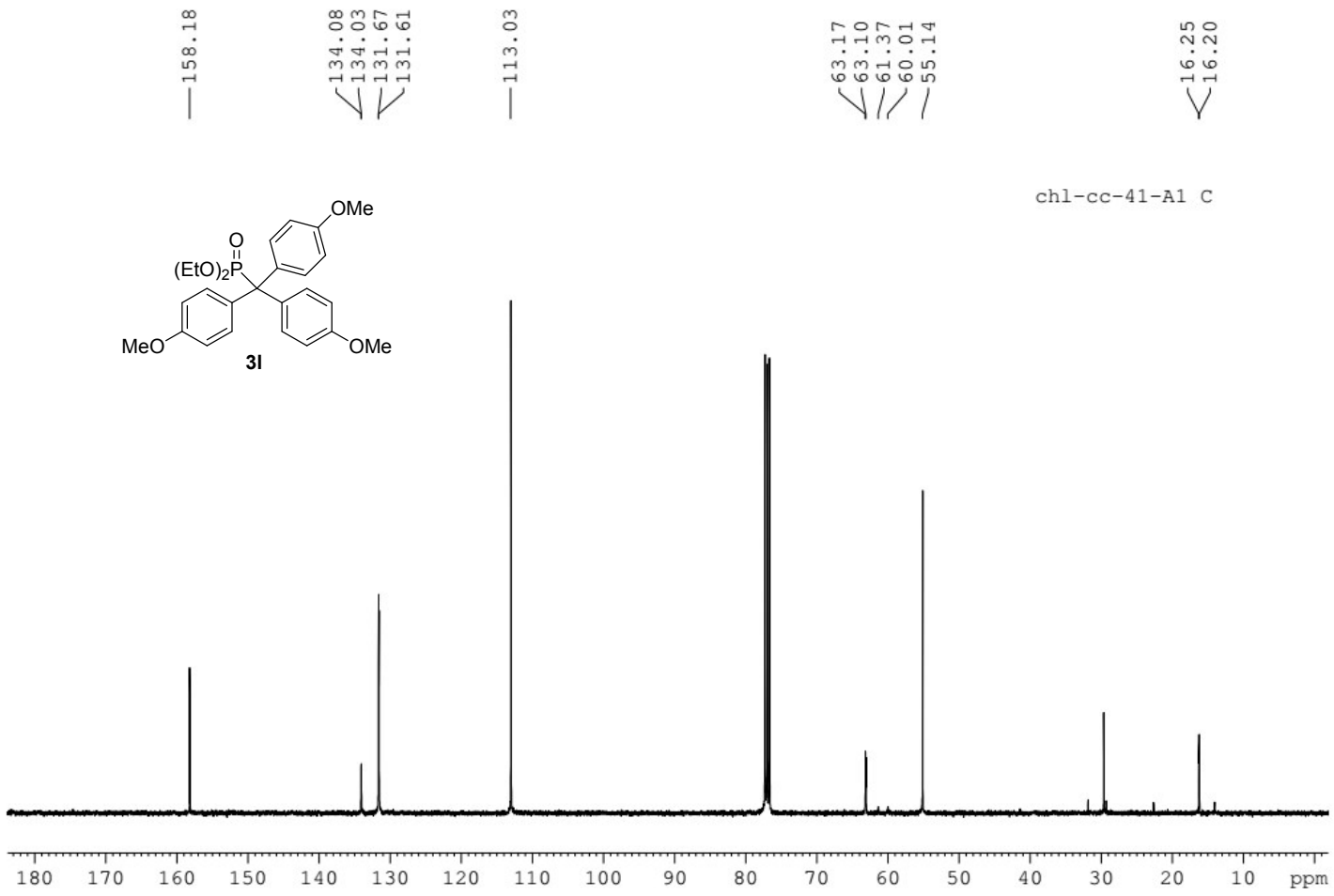

26.78
Me
O
P(OEt)2
Ph
Ph
3j
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

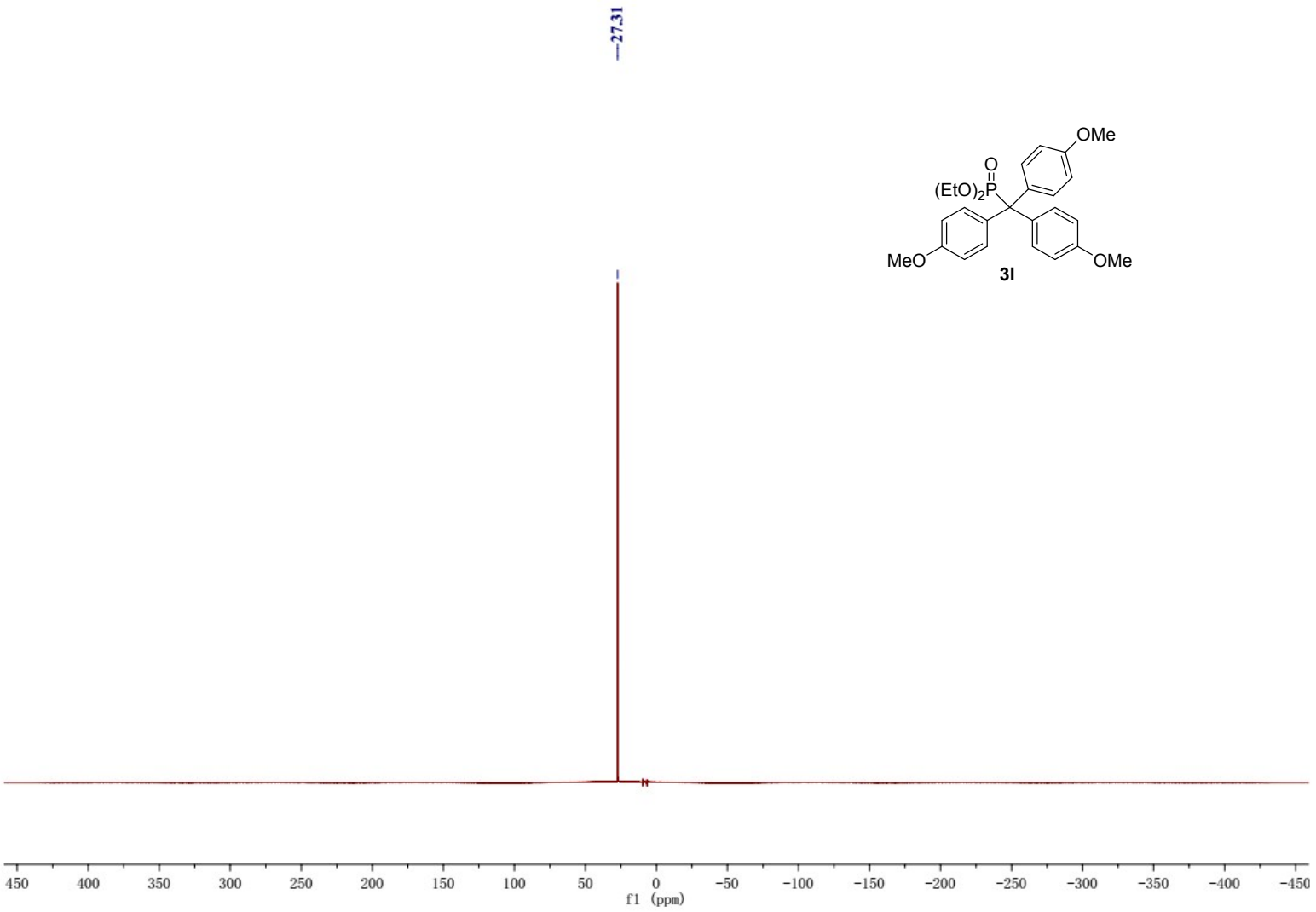

7.33
7.32
7.31
7.26
7.25
7.23
7.22
7.21
7.21
6.81
6.79
4.03
4.02
4.01
4.00
4.00
3.99
3.99
3.98
3.97
3.96
3.84
3.82
3.82
3.81
3.81
3.81
3.80
3.79
3.79
3.78
3.77
3.76
1.11
1.09
1.08
OMe
O
(EtO)2P
OMe
3k
2.04
7.45
4.06
2.02
2.00
6.25
6.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

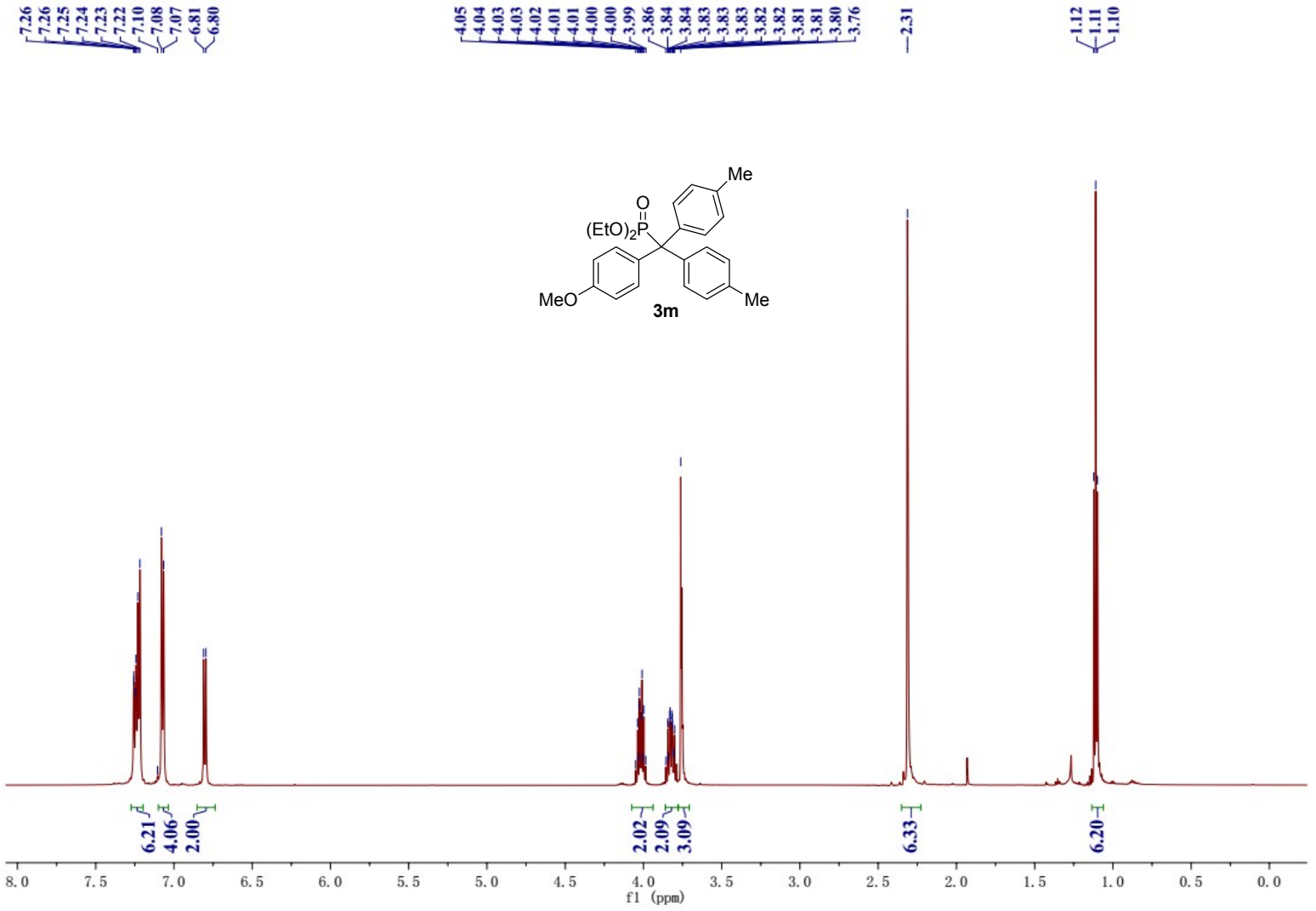

158.24
158.22
142.14
142.09
133.82
133.77
131.76
131.70
130.58
130.51
127.76
127.75
126.76
113.07
113.06
77.32
77.20
77.00
76.69
63.23
63.15
62.12
60.76
55.15
16.22
16.17
OMe
O
(EtO)2P
OMe
3k
chl-cc-44-A1 C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

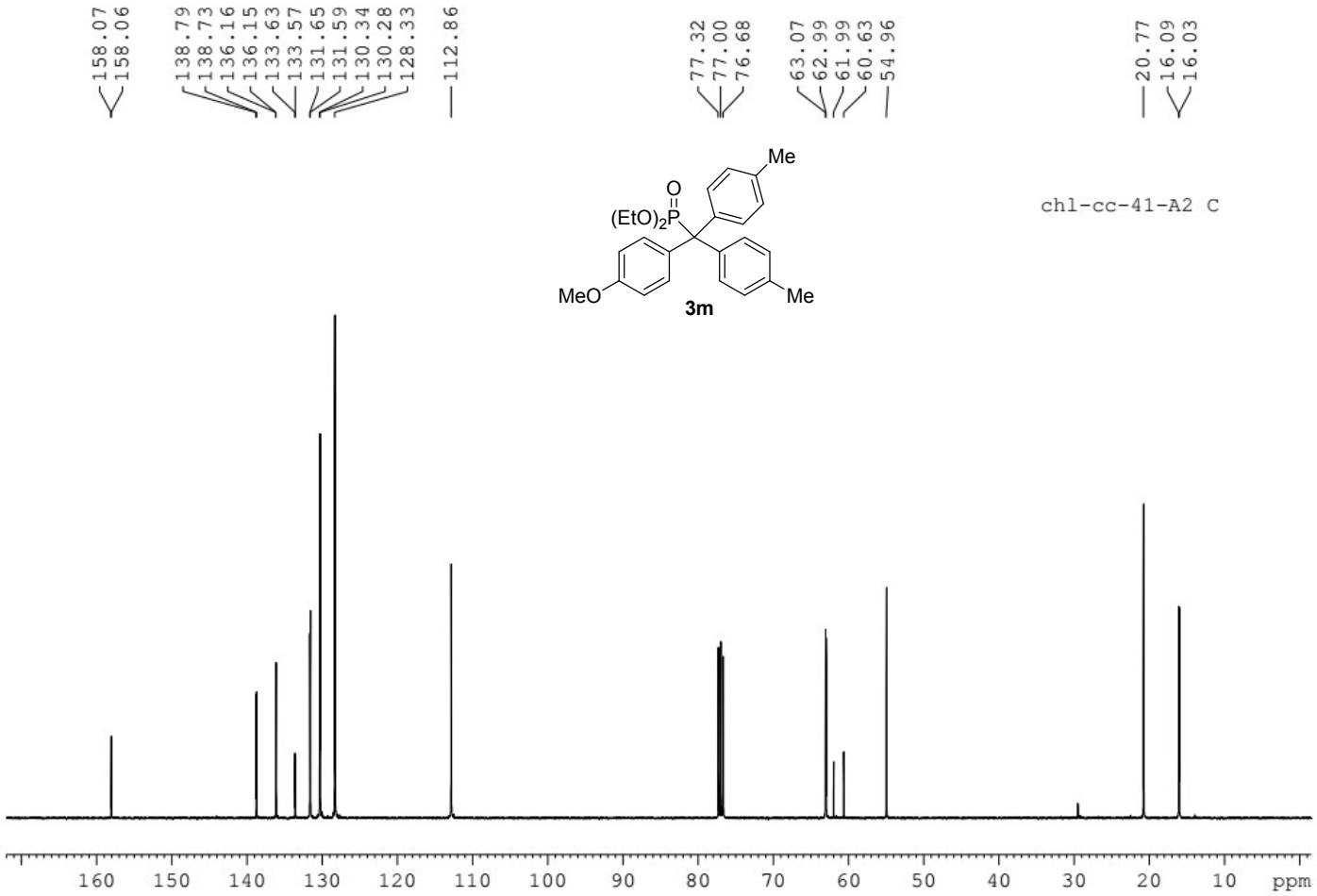

27.09
OMe
O
(EtO)2P
OMe
3k
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

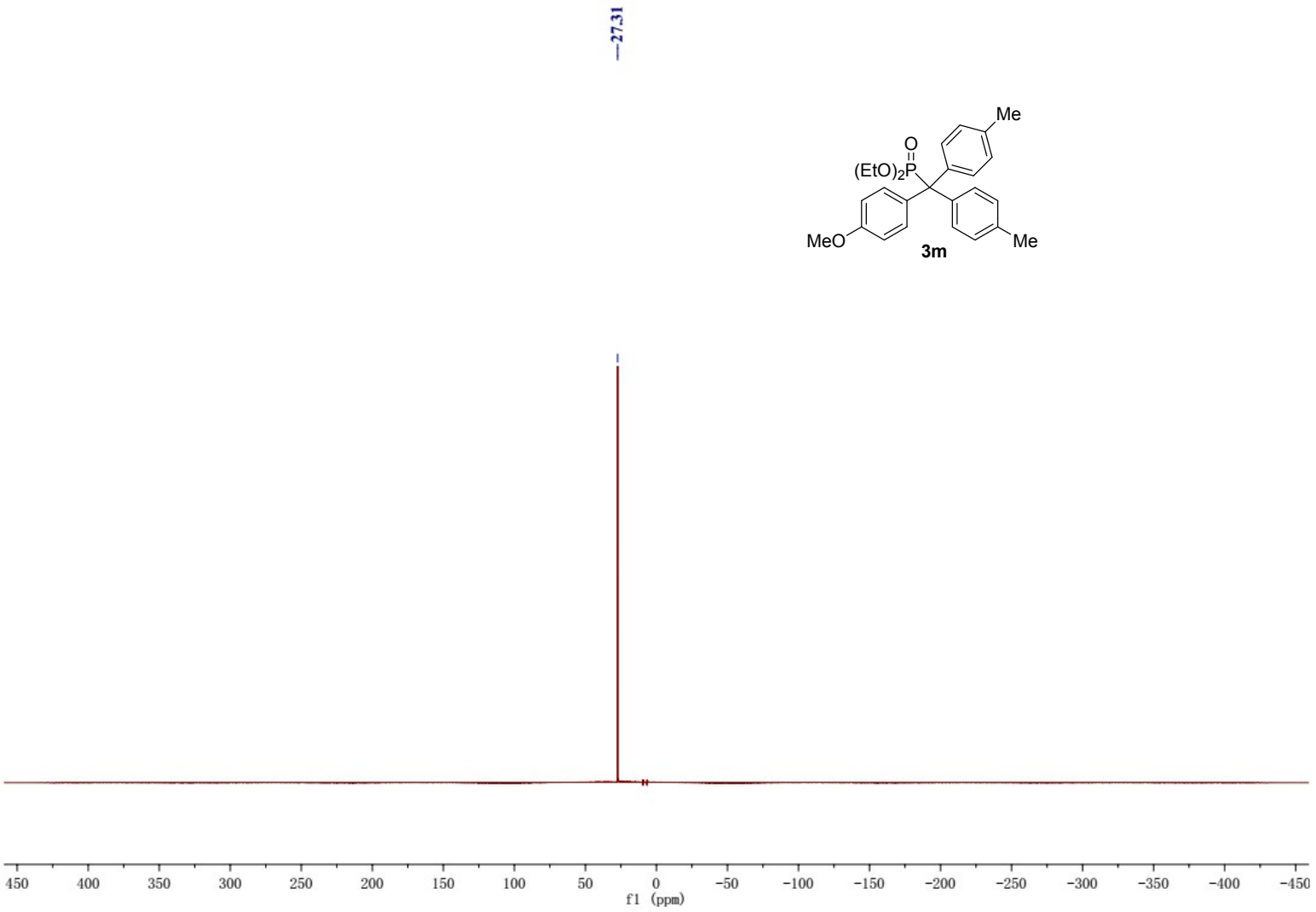

7.25
7.23
7.22
7.21
7.21
6.81
6.80
6.79
6.78
4.02
4.01
4.01
4.00
4.00
3.99
3.98
3.98
3.97
3.96
3.83
3.82
3.82
3.81
3.81
3.80
3.80
3.80
3.79
3.79
3.79
3.78
3.76
3.76
1.11
1.10
1.09
0.02
OMe
O
(EtO)2P
MeO
OMe
3l
6.07
6.00
2.00
2.06
9.06
6.27
f1 (ppm)

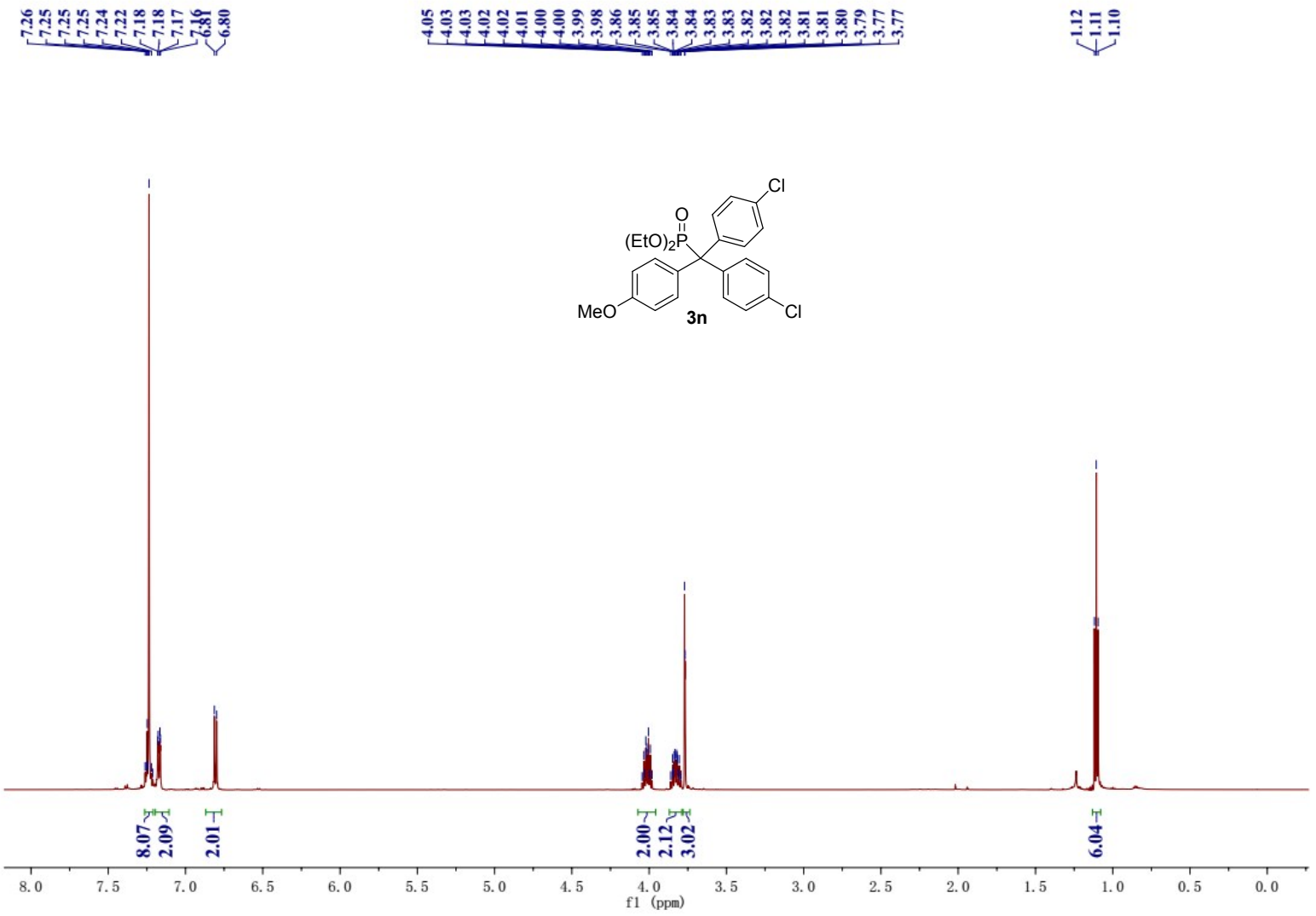

158.18
134.08
134.03
131.67
131.61
113.03
63.17
63.10
61.37
60.01
55.14
16.25
16.20
chl-cc-41-A1 C
OMe
O
(EtO)2P
MeO
OMe
3l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

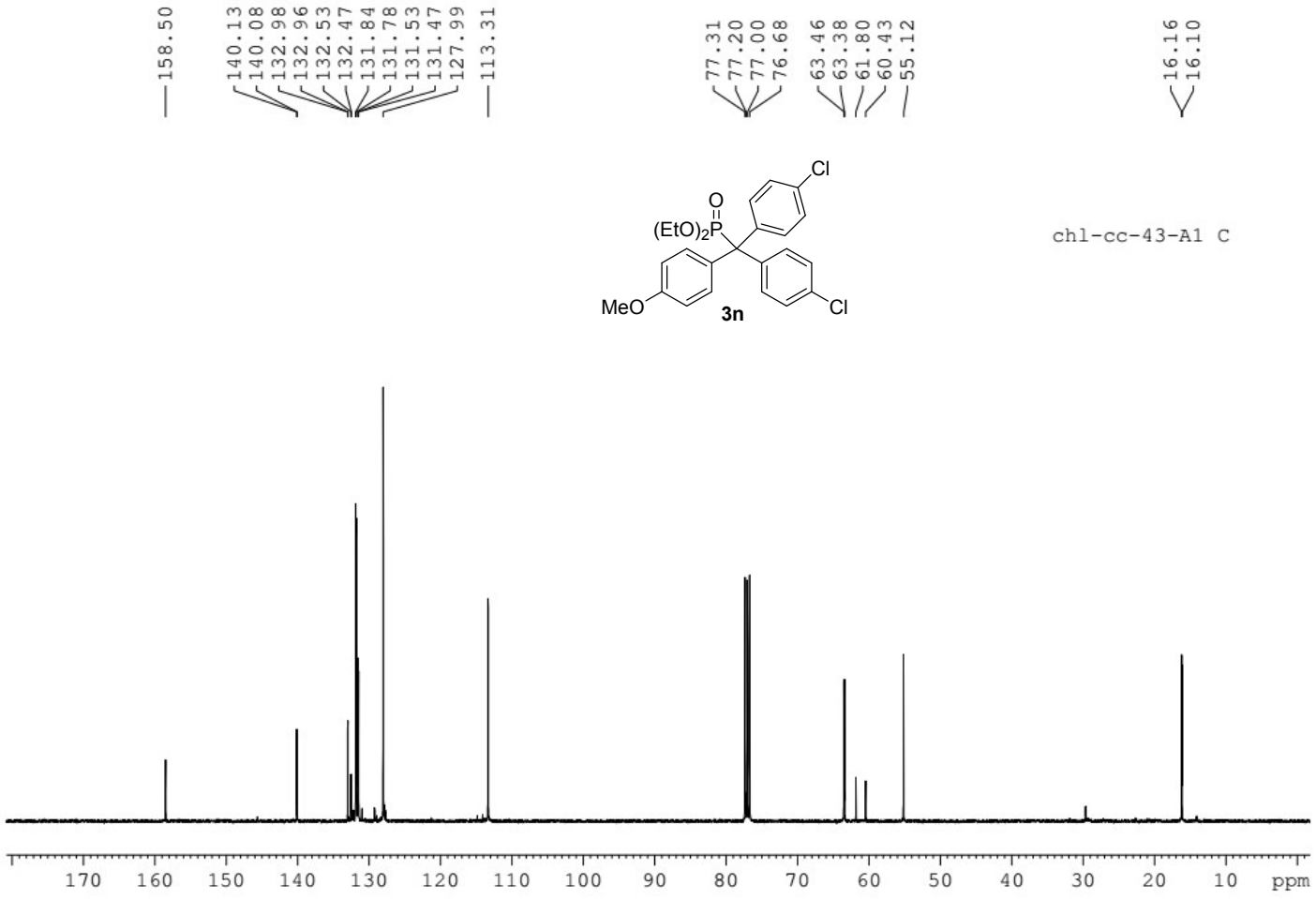

27.31
OMe
O
(EtO)2P
MeO
OMe
3l
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

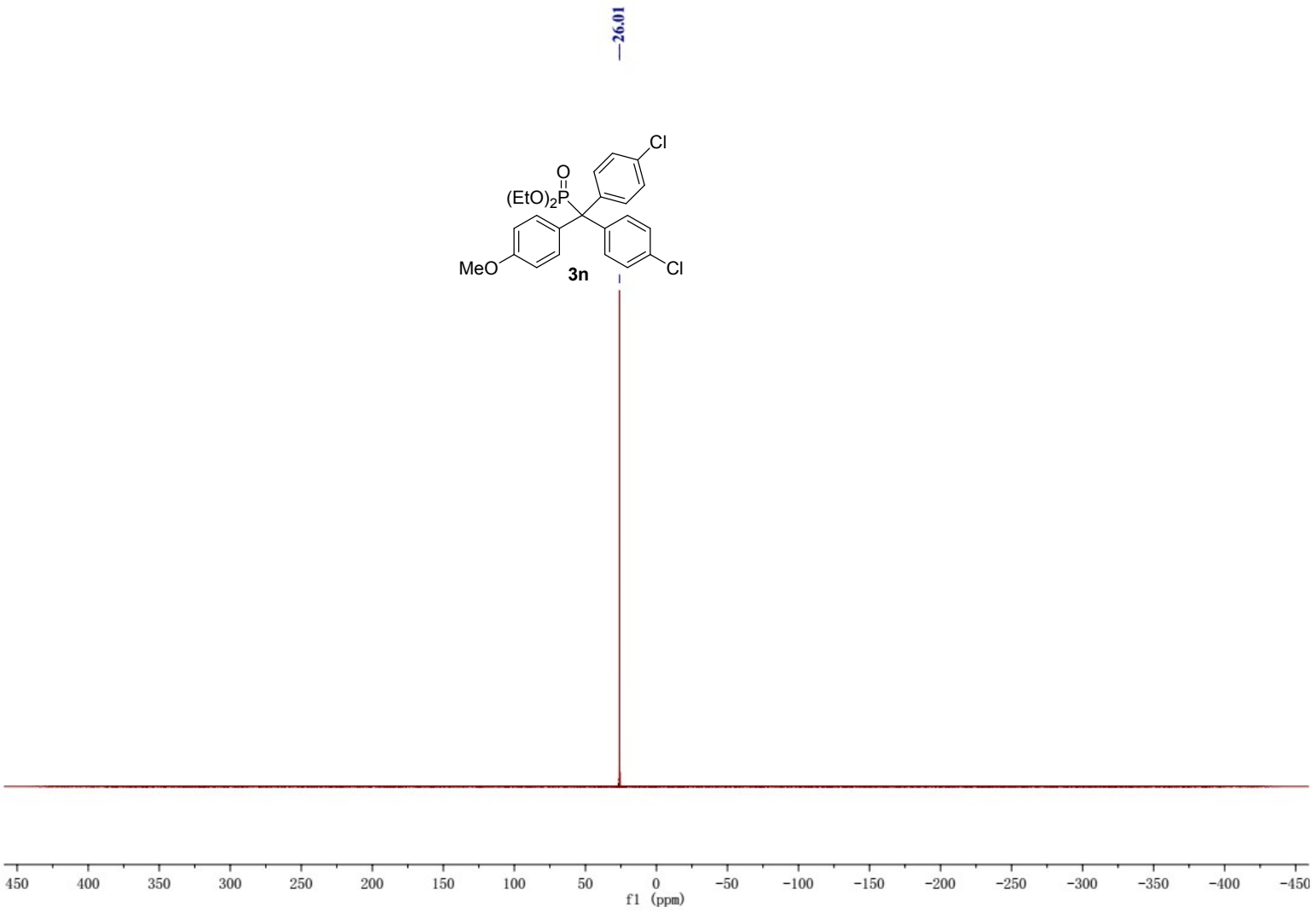

7.26
7.26
7.25
7.24
7.23
7.22
7.10
7.08
7.07
6.81
6.80
4.05
4.04
4.03
4.03
4.02
4.01
4.01
4.00
4.00
3.99
3.86
3.84
3.84
3.83
3.83
3.83
3.82
3.82
3.81
3.81
3.80
3.76
2.31
1.12
1.11
1.10
Me
O
(EtO)2P
MeO
Me
3m
6.21
4.06
2.00
2.02
2.09
3.09
6.33
6.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

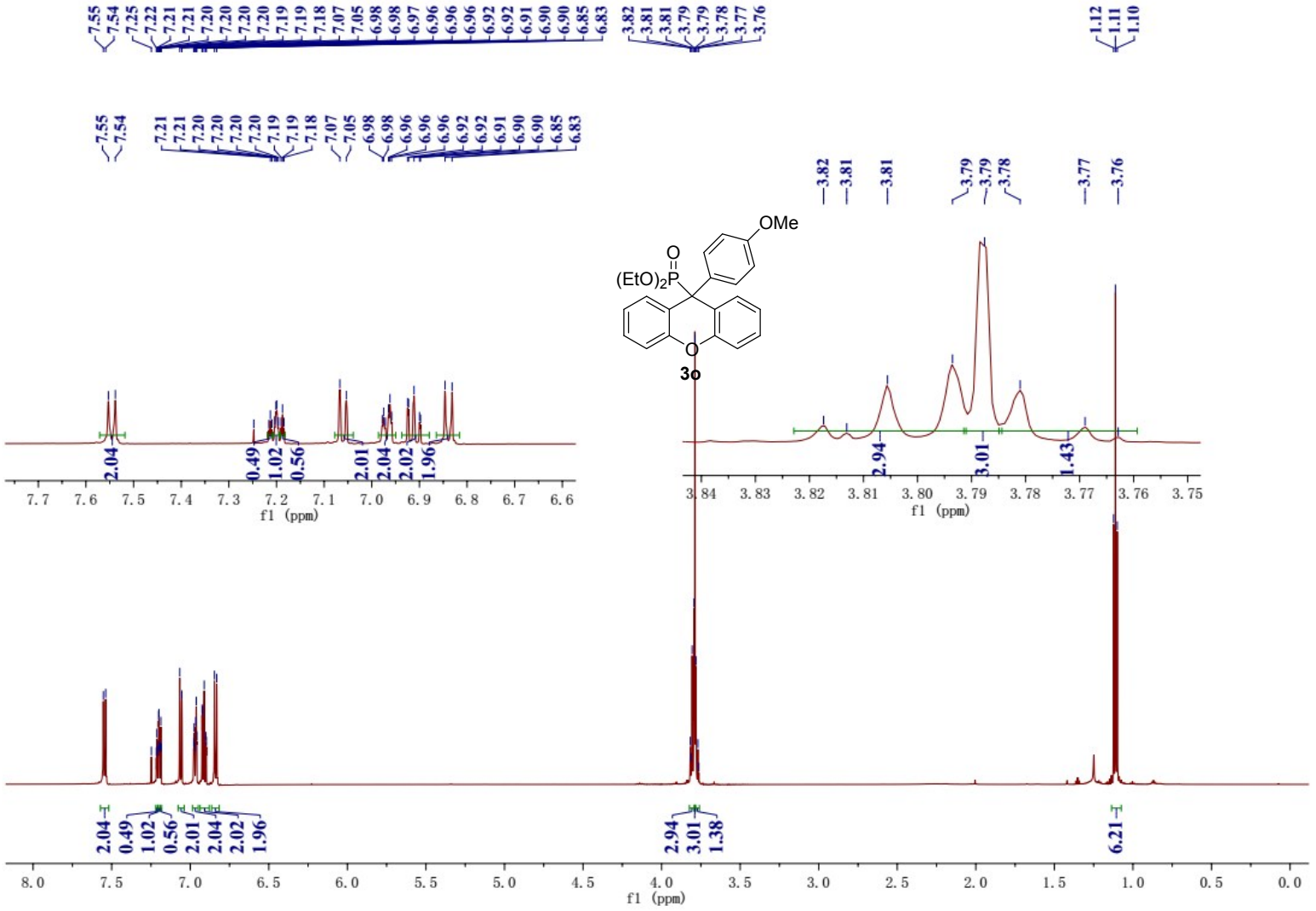

158.07
158.06
138.79
138.73
136.16
136.15
133.63
133.57
131.65
131.59
130.34
130.28
128.33
112.86
77.32
77.00
76.68
63.07
62.99
61.99
60.63
54.96
20.77
16.09
16.03
chl-cc-41-A2 C
Me
O
(EtO)2P
MeO
Me
3m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

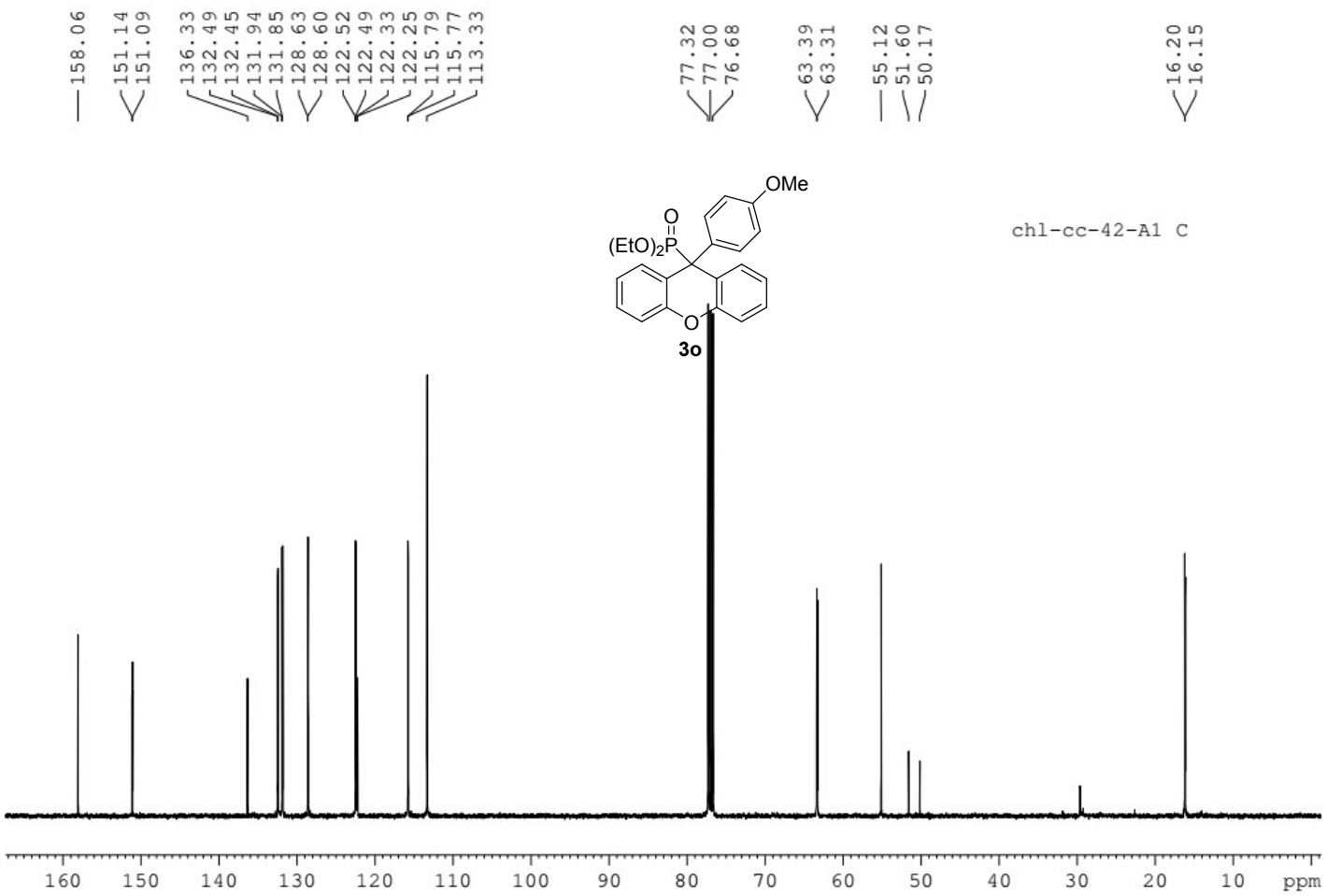

27.31
Me
O
(EtO)2P
MeO
Me
3m
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

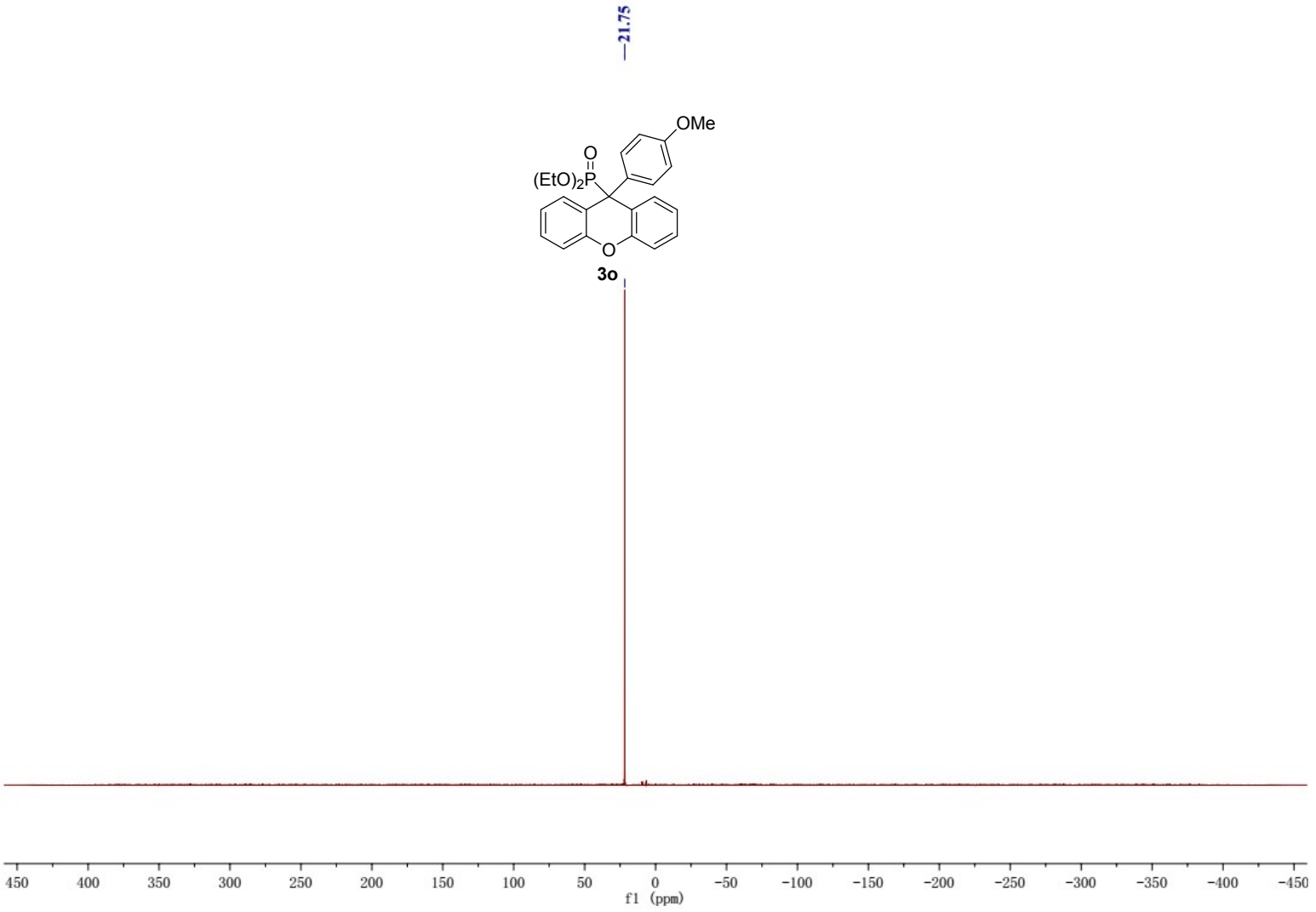

7.26
7.25
7.25
7.25
7.24
7.22
7.18
7.18
7.17
7.16
6.81
6.80
4.05
4.03
4.03
4.02
4.02
4.01
4.00
4.00
3.99
3.98
3.86
3.85
3.85
3.84
3.84
3.83
3.83
3.82
3.82
3.82
3.81
3.81
3.80
3.79
3.77
3.77
1.12
1.11
1.10
Cl
O
(EtO)2P
MeO
Cl
3n
8.07
2.09
2.01
2.00
2.12
3.02
6.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

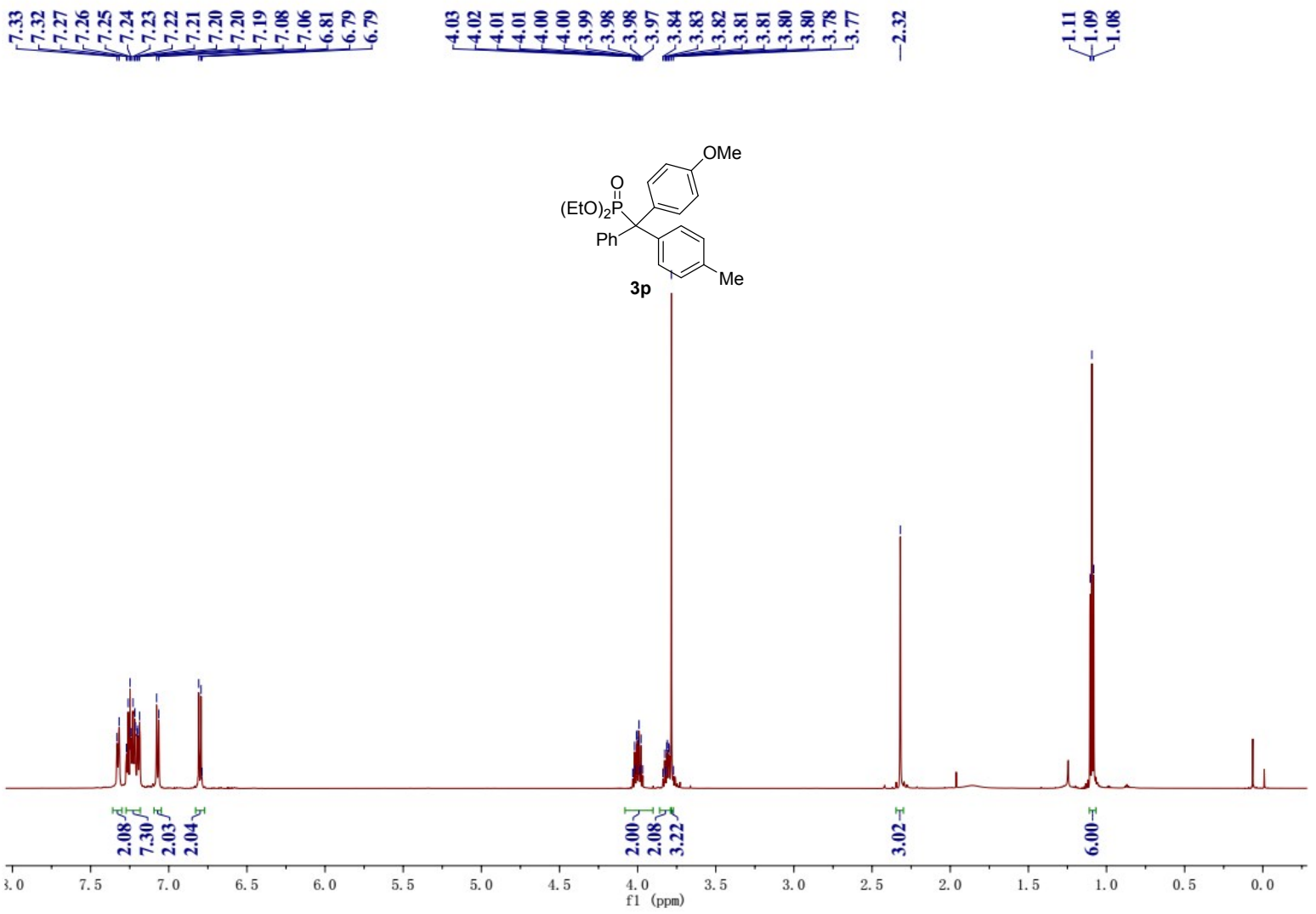

158.50
140.13
140.08
132.98
132.96
132.53
132.47
131.84
131.78
131.53
131.47
127.99
113.31
77.31
77.20
77.00
76.68
63.46
63.38
61.80
60.43
55.12
16.16
16.10
Cl
O
(EtO)2P
MeO
Cl
3n
chl-cc-43-A1 C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

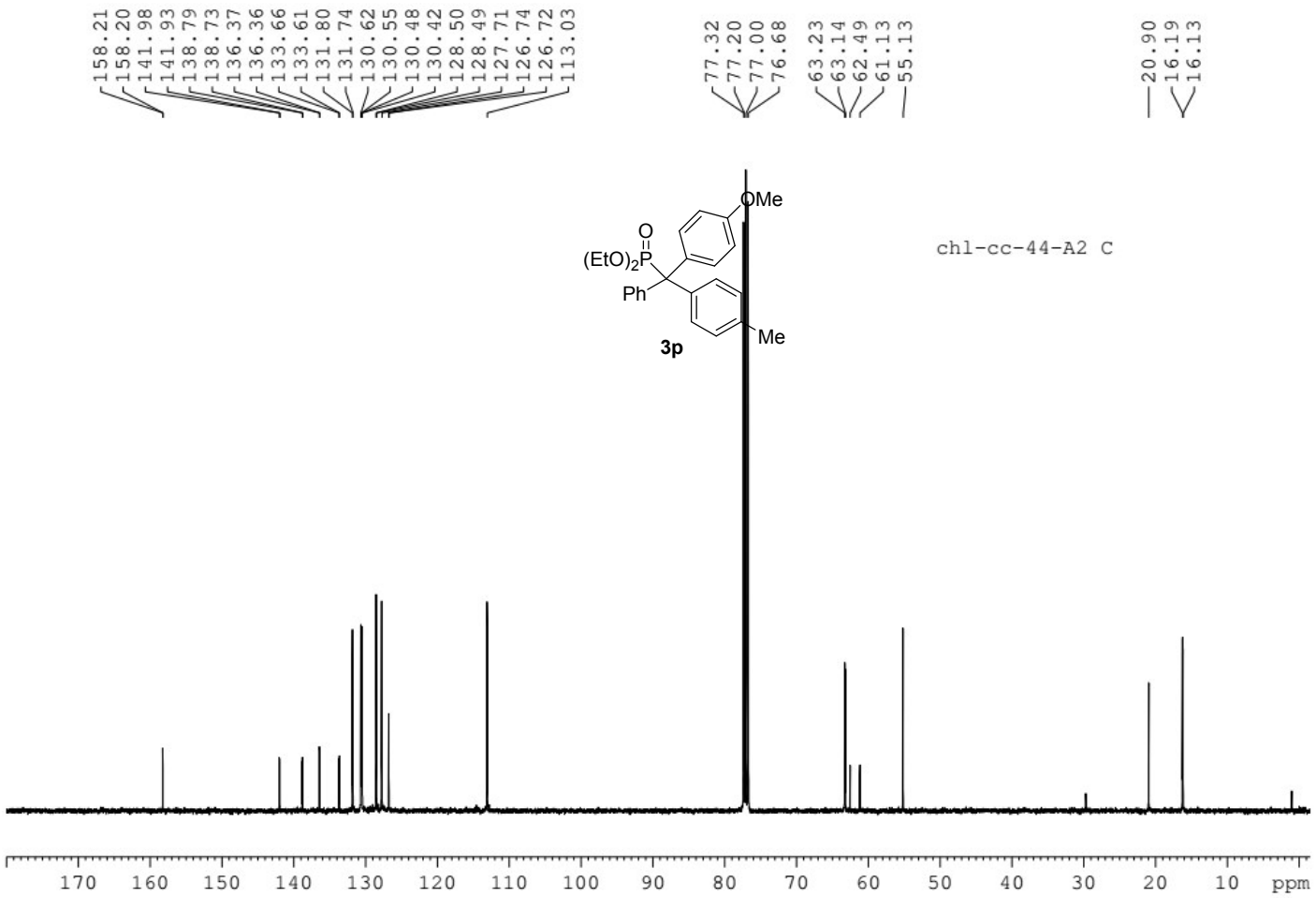

26.01
Cl
O
(EtO)2P
MeO
Cl
3n
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

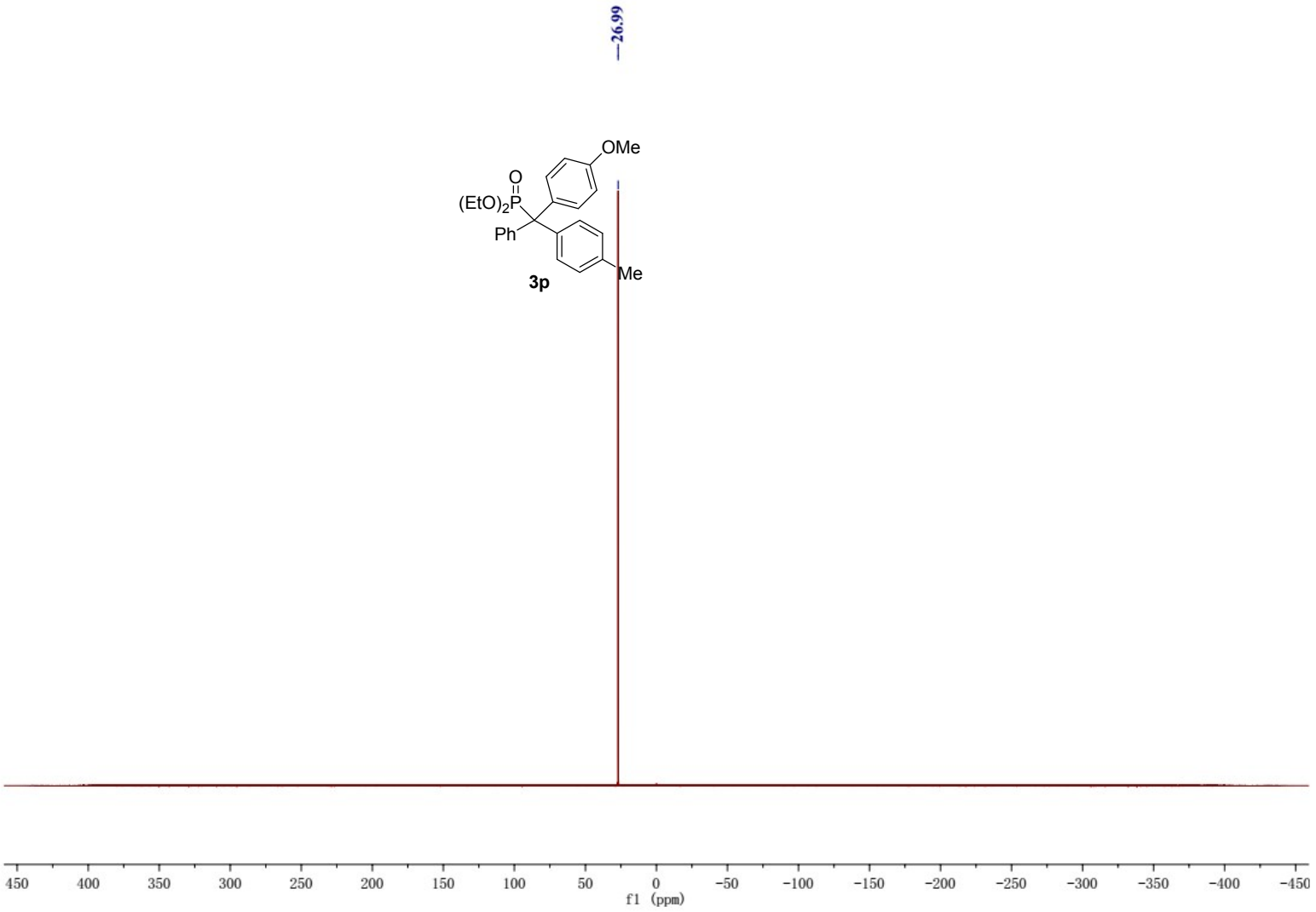

7.55 7.54 7.25 7.22 7.21 7.21 7.20 7.20 7.20 7.20 7.19 7.19 7.18 7.07 7.05 6.98 6.98 6.97 6.96 6.96 6.96 6.96 6.92 6.92 6.91 6.90 6.90 6.85 6.83
3.82 3.81 3.81 3.79 3.79 3.78 3.77 3.76
1.12 1.11 1.10
OMe
O
(EtO)2P
O
3o
2.04 0.49 1.02 0.56 2.01 2.04 2.02 1.96
2.94 3.01 1.43
2.04 0.49 1.02 0.56 2.01 2.04 2.02 1.96 2.94 3.01 1.38 6.21
f1 (ppm)

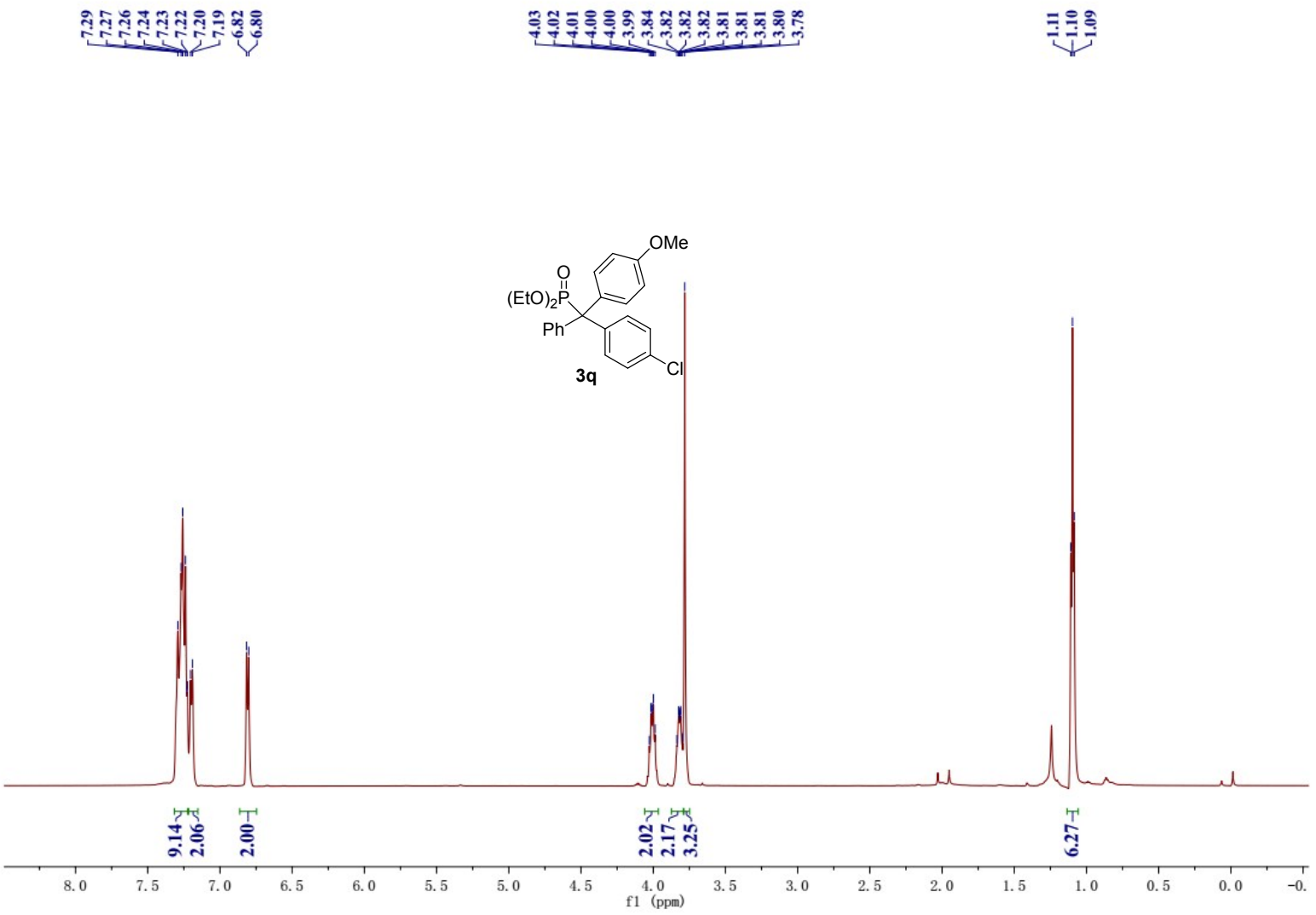

158.06
151.14
151.09
136.33
132.49
132.45
131.94
131.85
128.63
128.60
122.52
122.49
122.33
122.25
115.79
115.77
113.33
77.32
77.00
76.68
63.39
63.31
55.12
51.60
50.17
16.20
16.15
OMe
O
(EtO)2P
O
3o
chl-cc-42-A1 C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

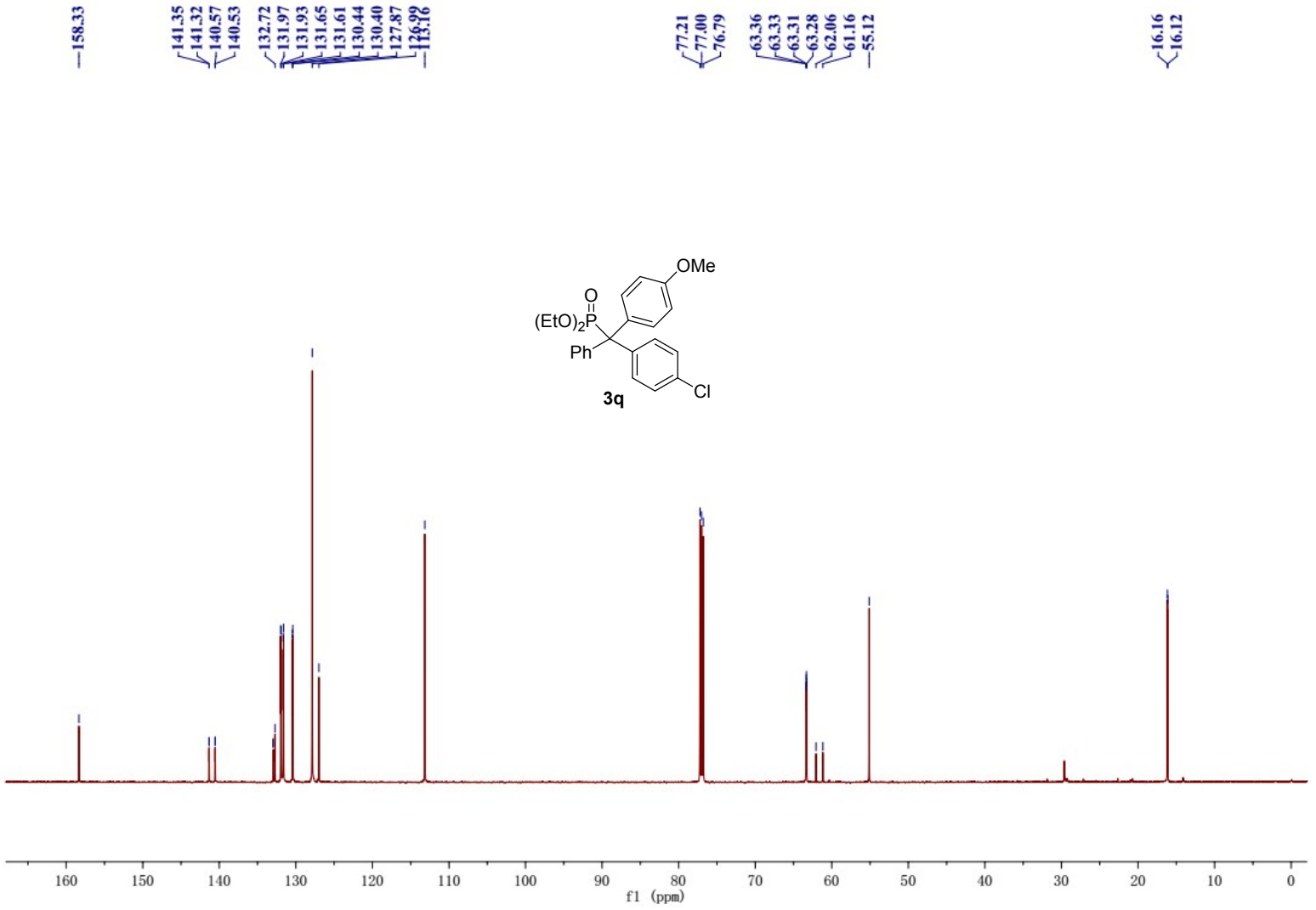

21.75
OMe
O
(EtO)2P
O
3o
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

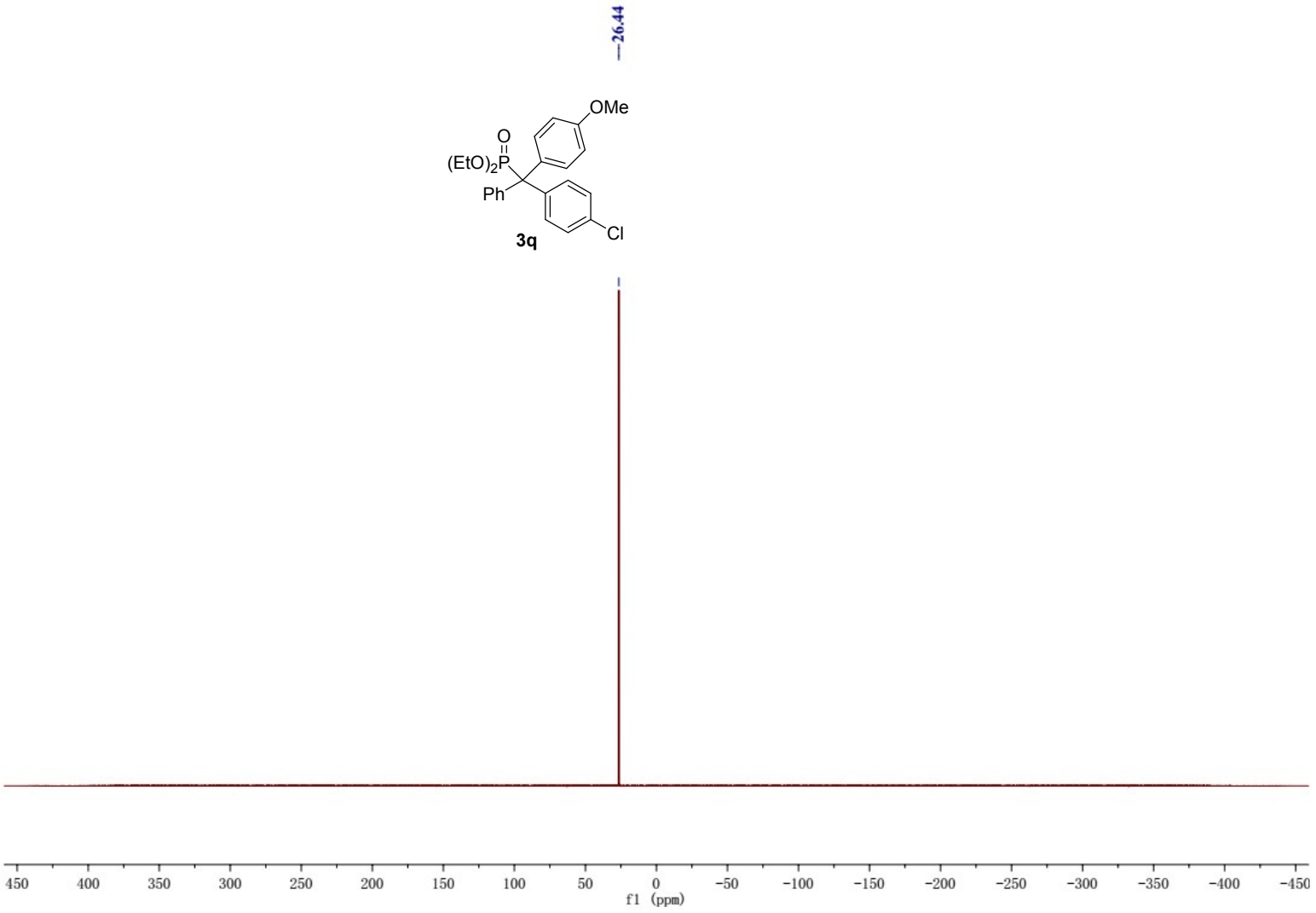

7.33
7.32
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.08
7.06
6.81
6.79
6.79
4.03
4.02
4.01
4.01
4.00
4.00
3.99
3.98
3.98
3.97
3.84
3.83
3.82
3.81
3.81
3.80
3.80
3.78
3.77
2.32
1.11
1.09
1.08
OMe
O
(EtO)2P
Ph
Me
3p
2.08
7.30
2.03
2.04
2.00
2.08
3.22
3.02
6.00
f1 (ppm)

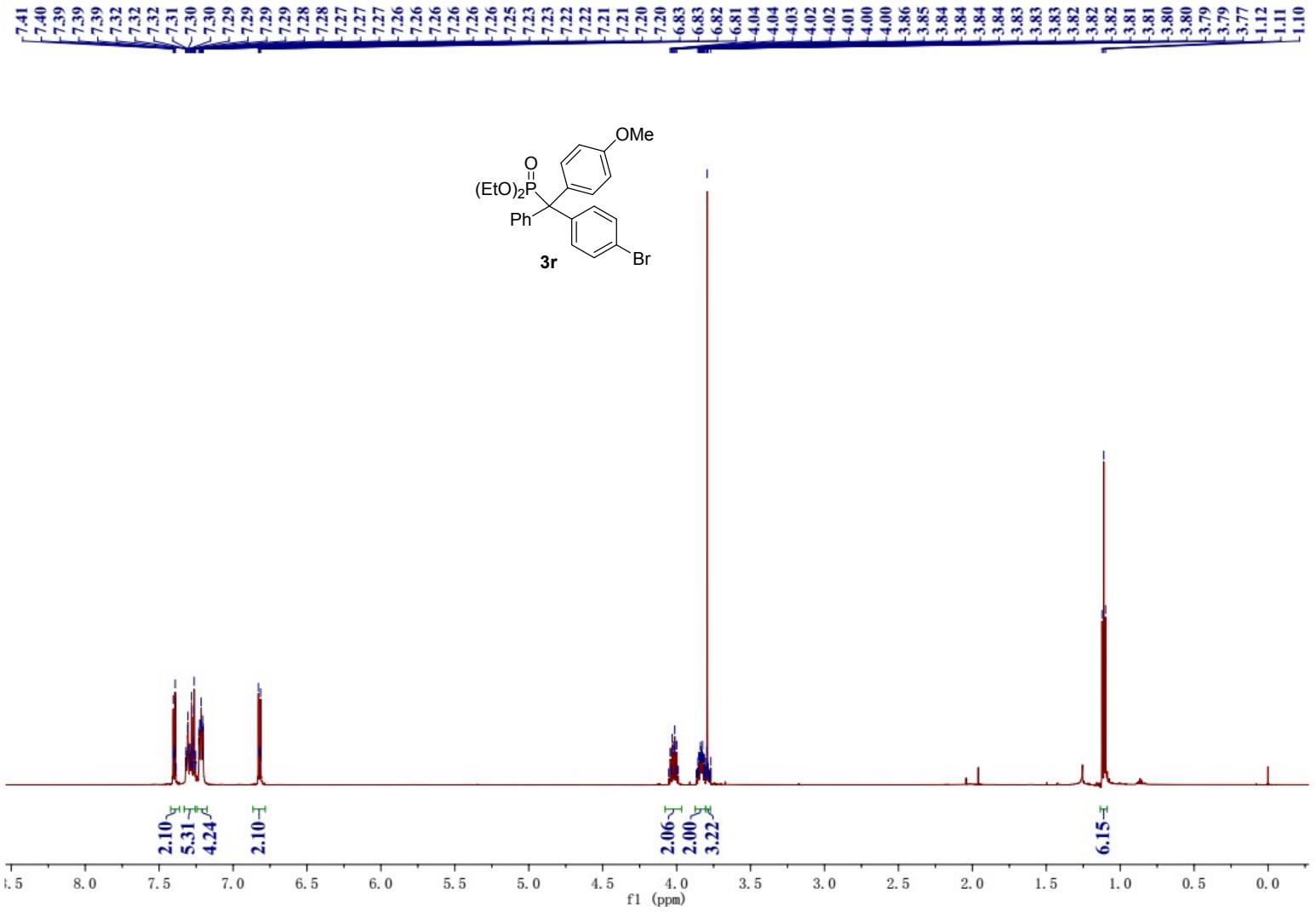

158.21
158.20
141.98
141.93
138.79
138.73
136.37
136.36
133.66
133.61
131.80
131.74
130.62
130.55
130.48
130.42
128.50
128.49
127.71
126.74
126.72
113.03
77.32
77.20
77.00
76.68
63.23
63.14
62.49
61.13
55.13
20.90
16.19
16.13
OMe
O
(EtO)2P
Ph
Me
3p
chl-cc-44-A2 C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

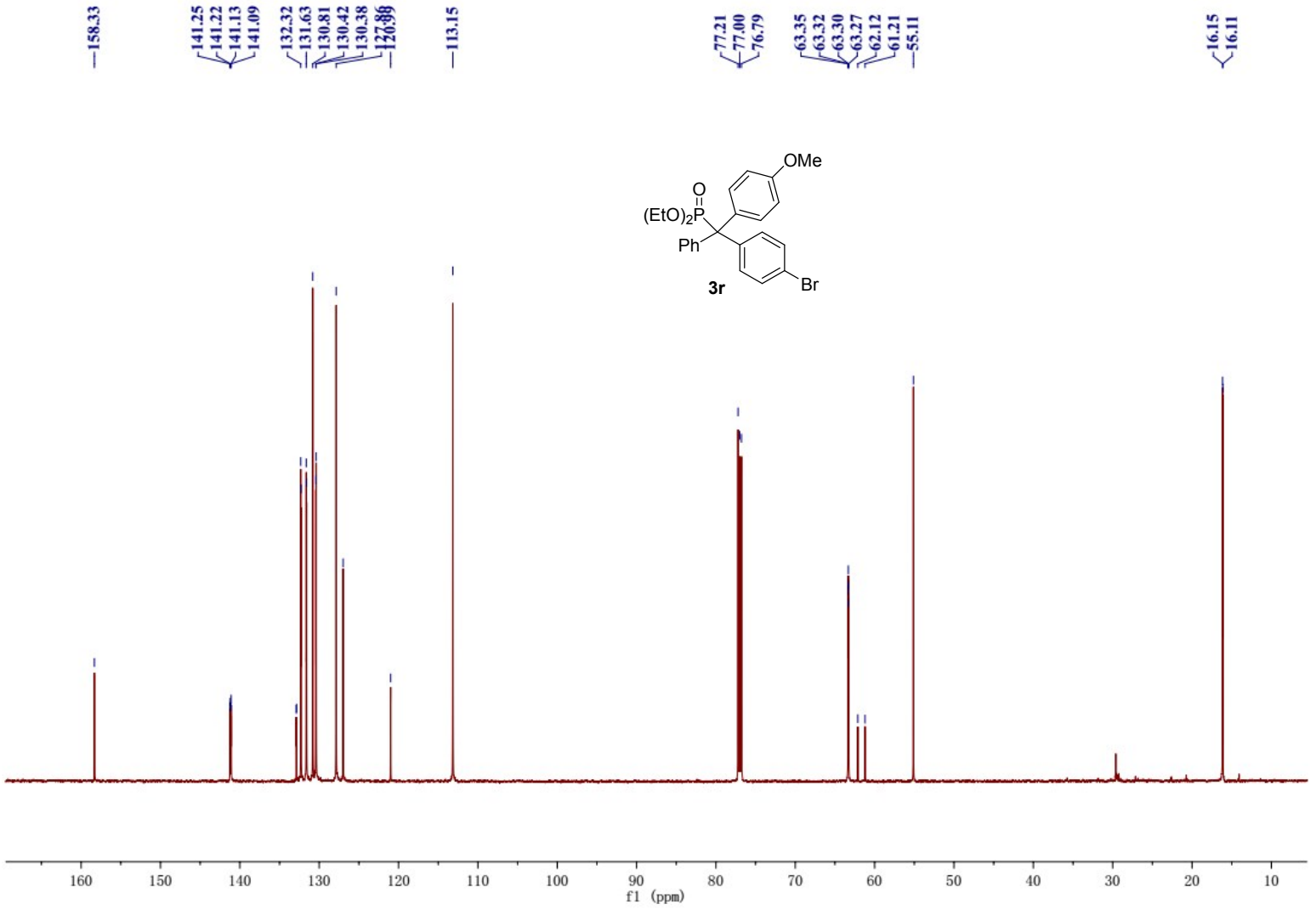

26.99
OMe
O
(EtO)2P
Ph
Me
3p
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

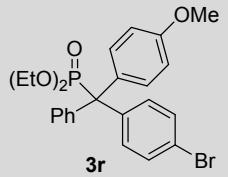

7.29
7.27
7.26
7.24
7.23
7.22
7.20
7.19
6.82
6.80
4.03
4.02
4.01
4.00
4.00
3.99
3.84
3.82
3.82
3.82
3.81
3.81
3.81
3.80
3.78
1.11
1.10
1.09
OMe
O
(EtO)2P
Ph
Cl
3q
9.14
2.06
2.00
2.02
2.17
3.25
6.27
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


158.33
141.35
141.32
140.57
140.53
132.72
131.97
131.93
131.65
131.61
130.44
130.40
127.87
77.21
77.00
76.79
63.36
63.33
63.31
63.28
62.06
61.16
55.12
16.16
16.12
OMe
O
(EtO)2P
Ph
Cl
3q
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

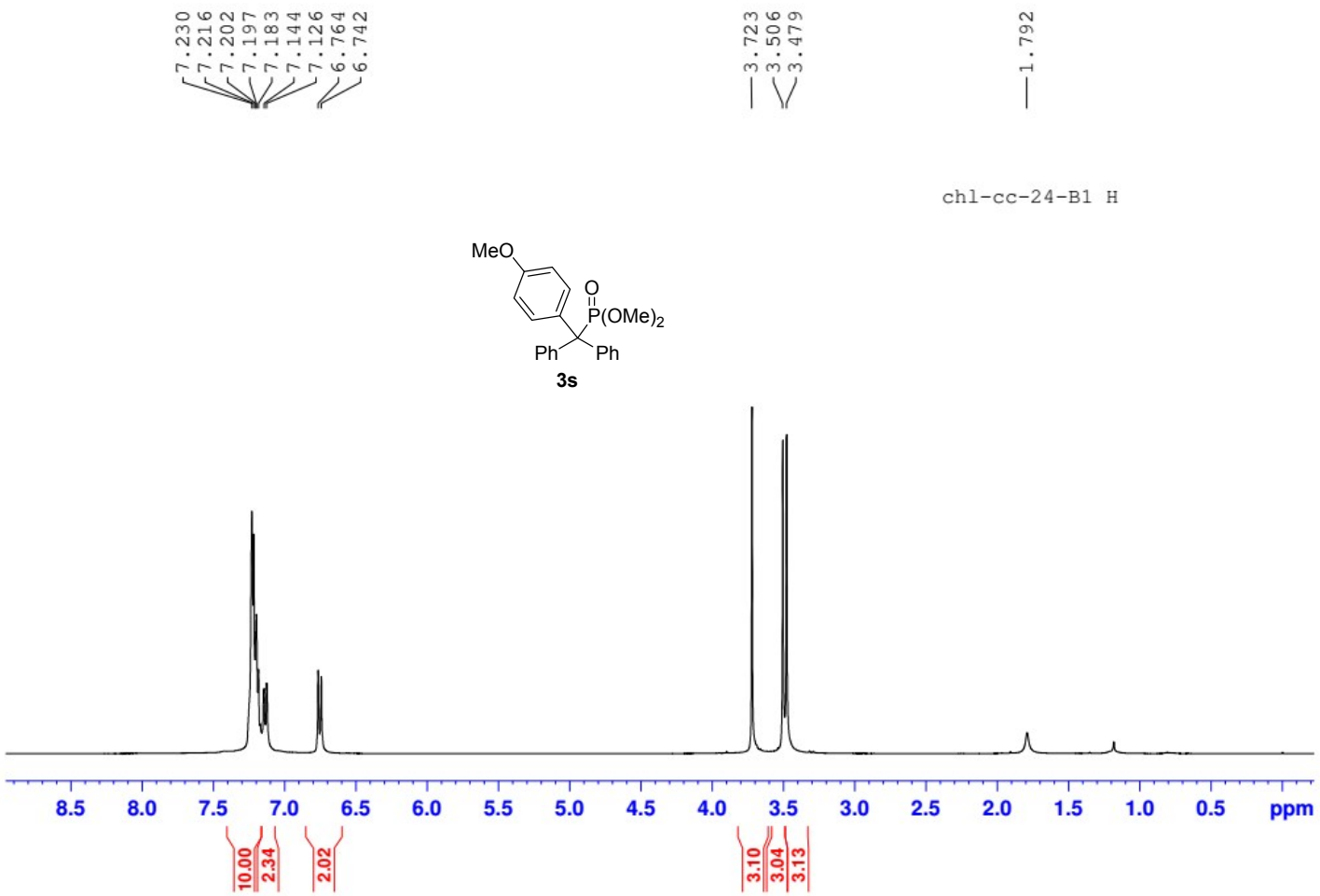

26.44
OMe
O
(EtO)2P
Ph
Cl
3q
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

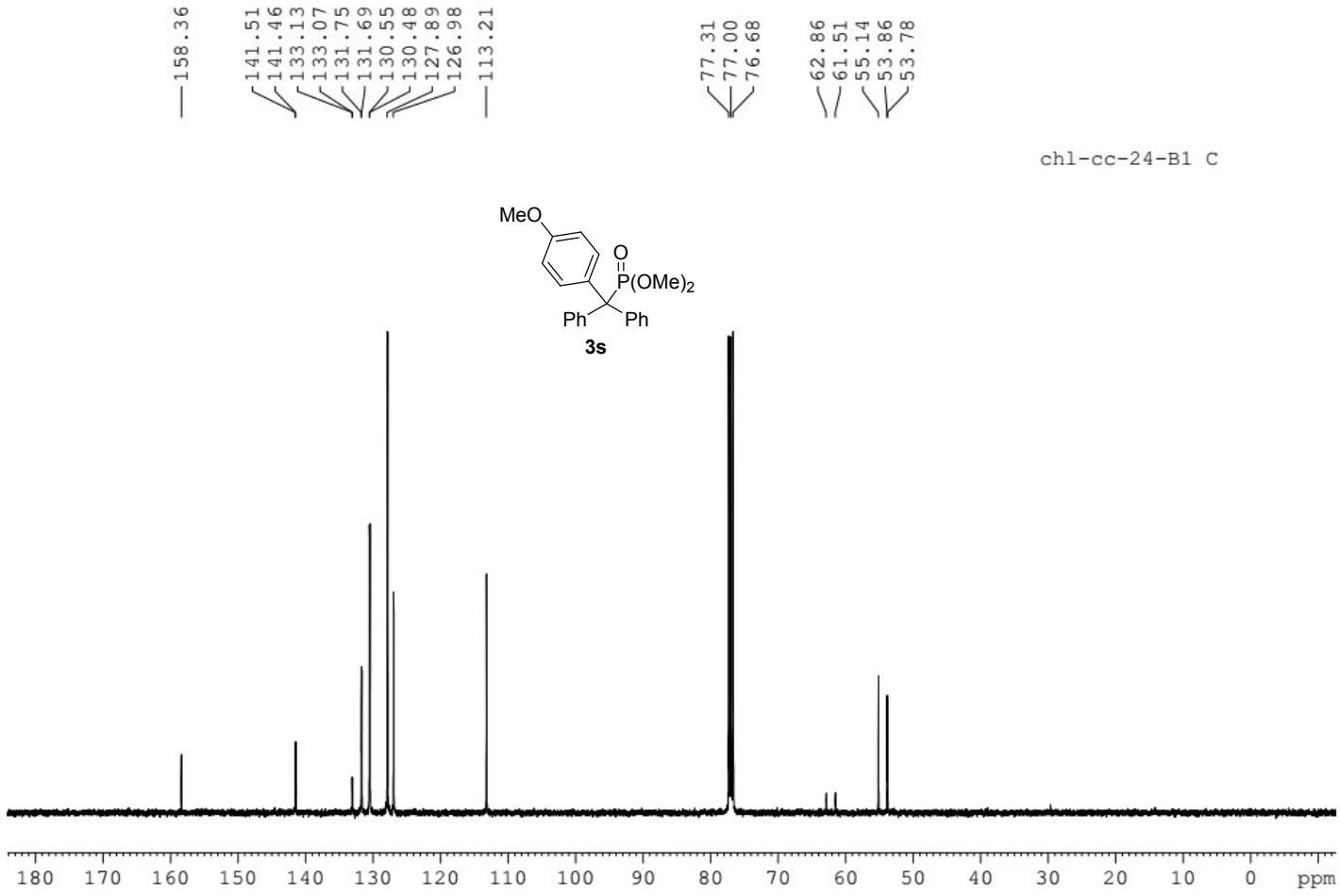

7.41 7.40 7.39 7.39 7.39 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.26 7.26 7.26 7.25 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 6.83 6.83 6.82 6.81 4.04 4.04 4.03 4.02 4.02 4.01 4.00 4.00 3.86 3.85 3.84 3.84 3.84 3.84 3.83 3.83 3.83 3.82 3.82 3.81 3.81 3.80 3.80 3.79 3.79 3.77 1.12 1.11 1.10
OMe
O
(EtO)2P
Ph
Br
3r
2.10
5.31
4.24
2.10
2.06
2.00
3.22
6.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

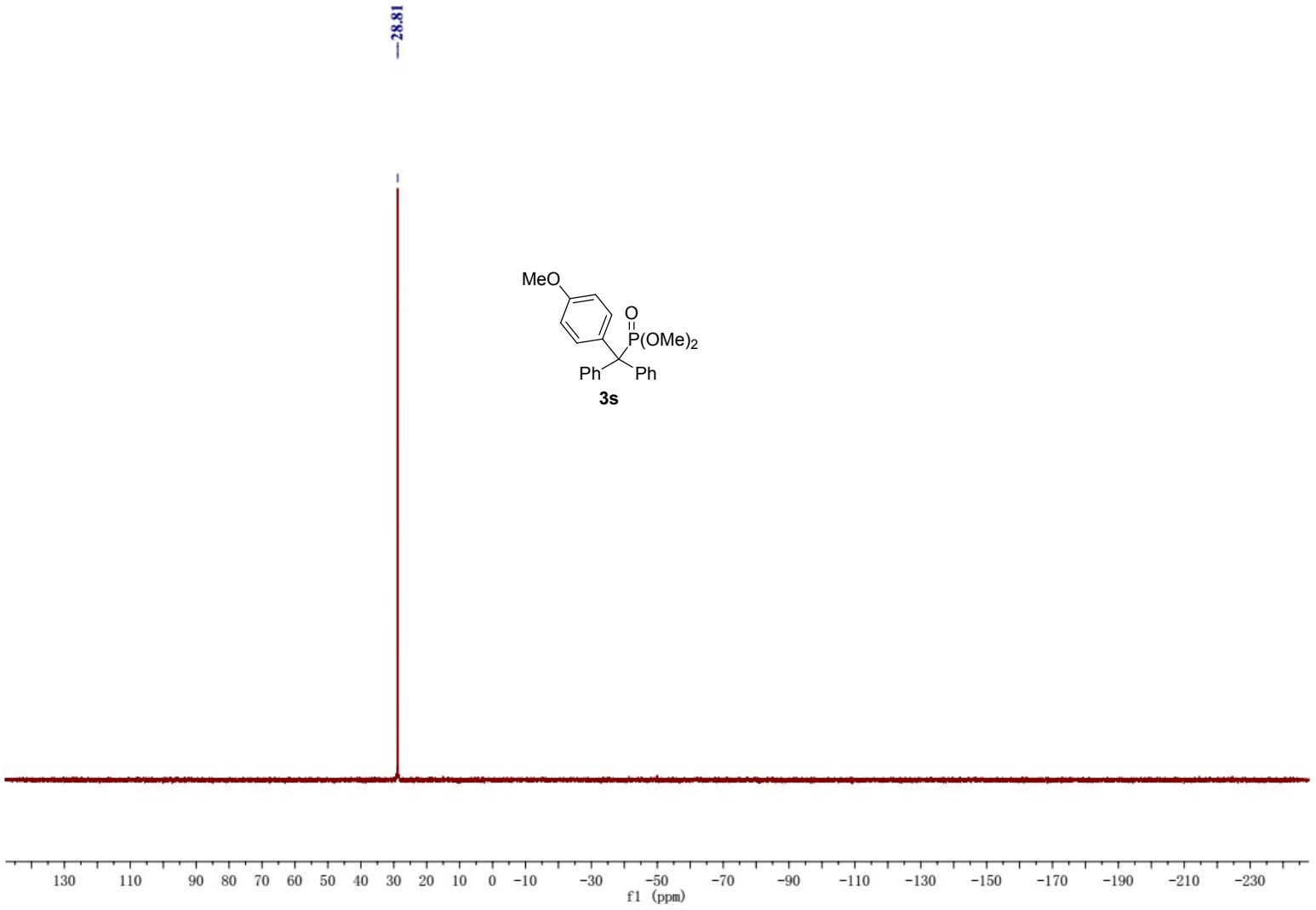

158.33
141.25
141.22
141.13
141.09
132.32
131.63
130.81
130.42
130.38
113.15
77.21
77.00
76.79
63.35
63.32
63.30
63.27
62.12
61.21
55.11
16.15
16.11
OMe
O
(EtO)2P
Ph
Br
3r
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

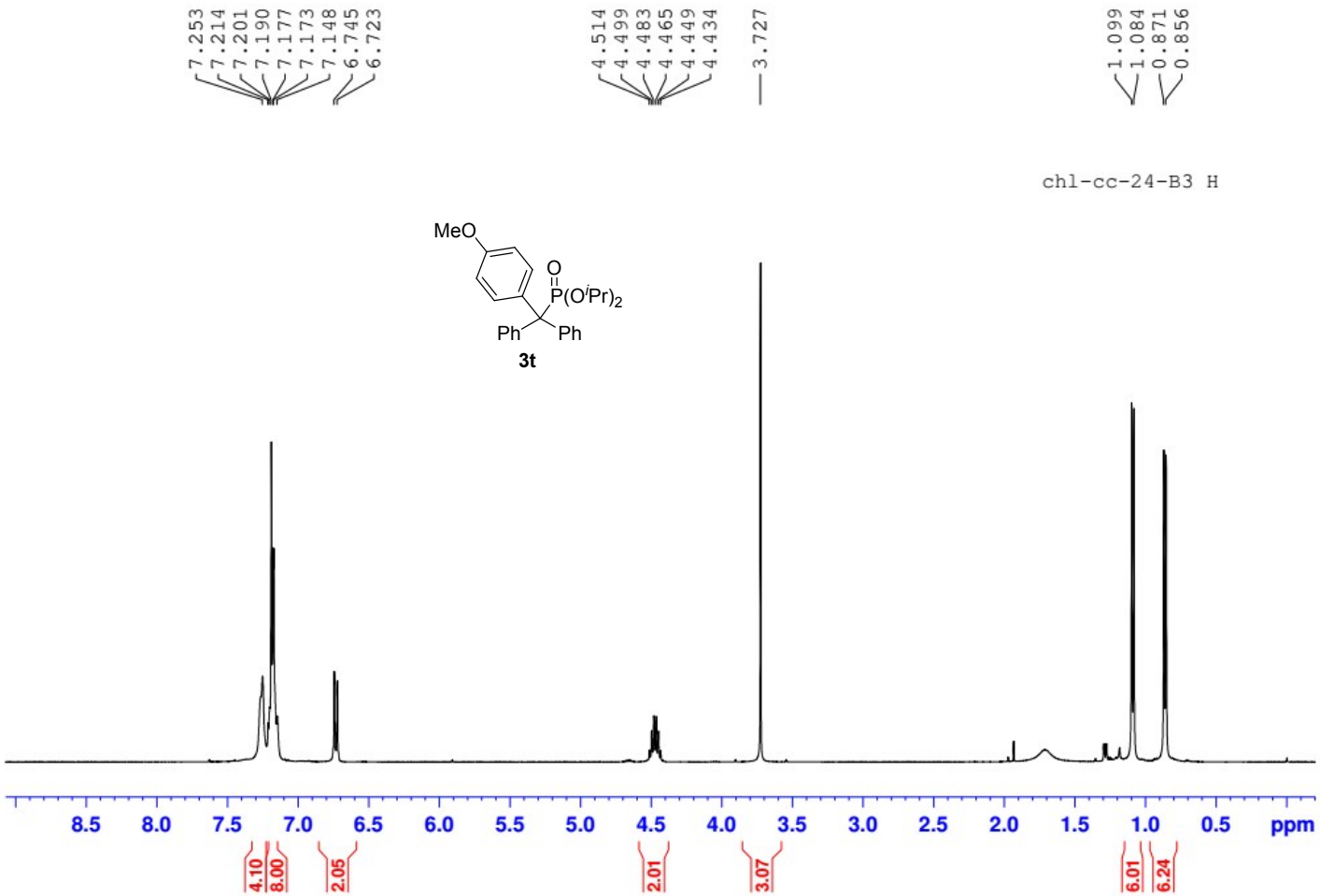


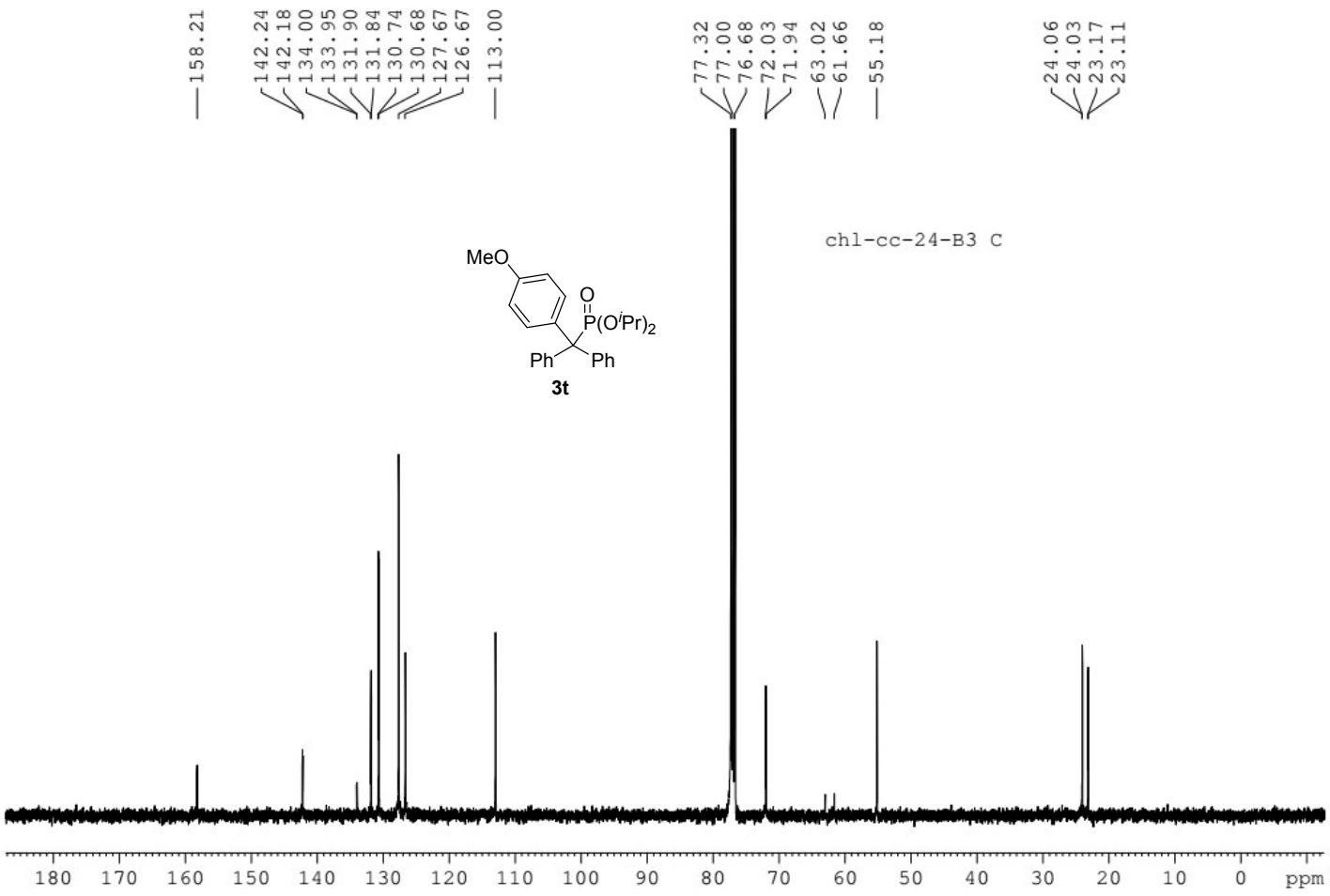
3r

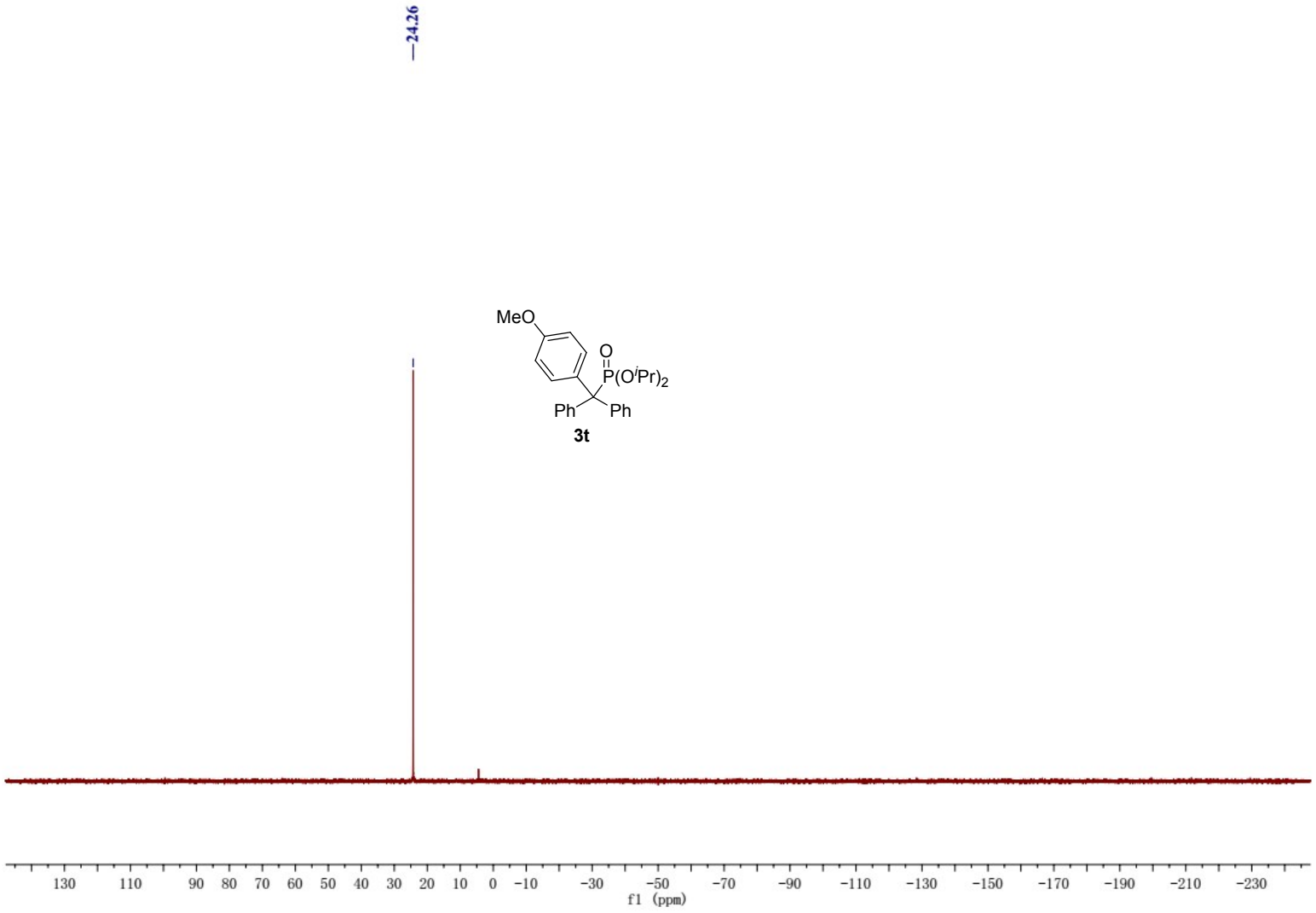

7.230
7.216
7.202
7.197
7.183
7.144
7.126
6.764
6.742
3.723
3.506
3.479
1.792
chl-cc-24-B1 H
MeO
O
P(OMe)2
Ph
Ph
3s
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
10.00
2.34
2.02
3.10
3.04
3.13

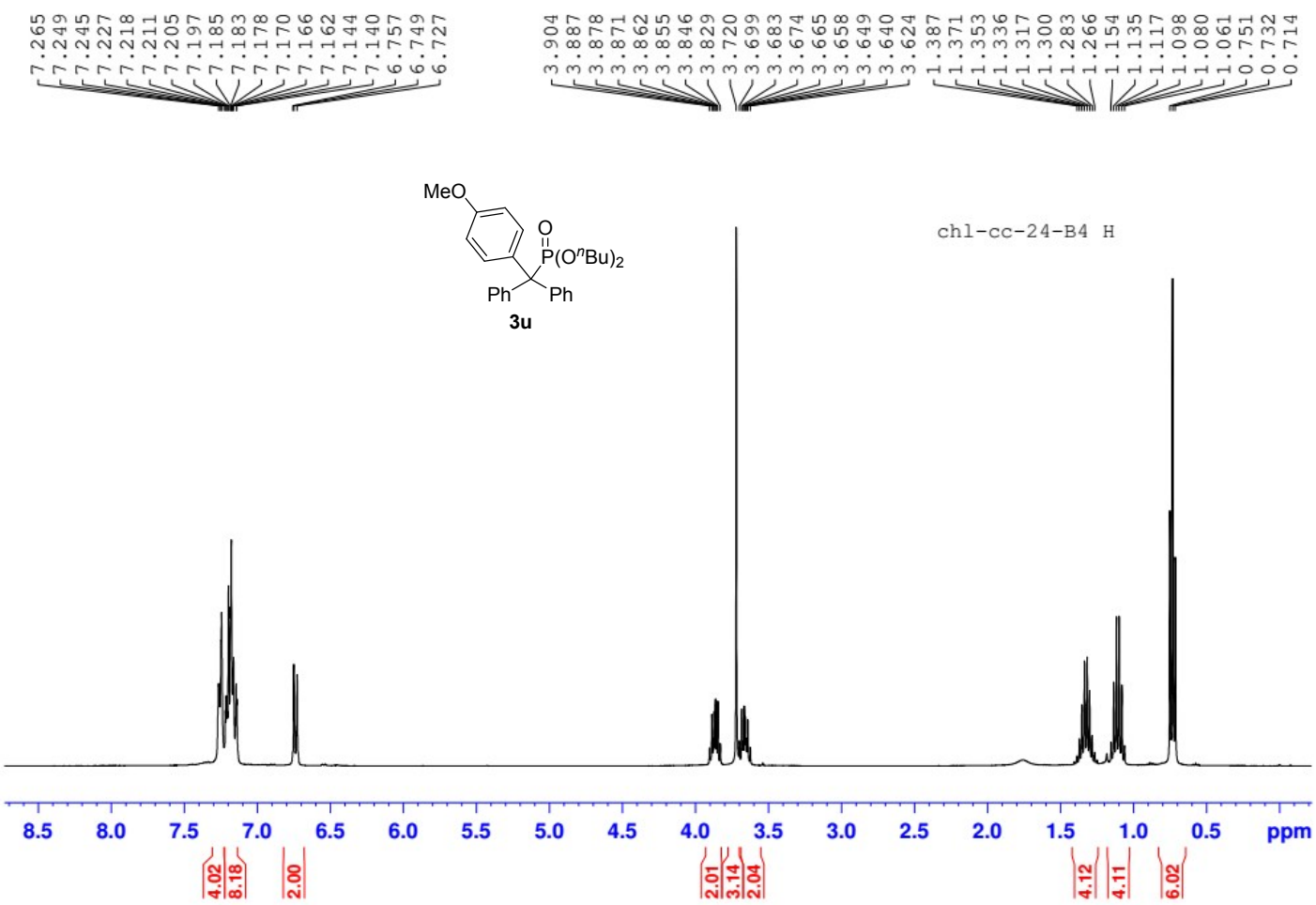

158.36
141.51
141.46
133.13
133.07
131.75
131.69
130.55
130.48
127.89
126.98
113.21
77.31
77.00
76.68
62.86
61.51
55.14
53.86
53.78
chl-cc-24-B1 C
MeO
O
P(OMe)2
Ph
Ph
3s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

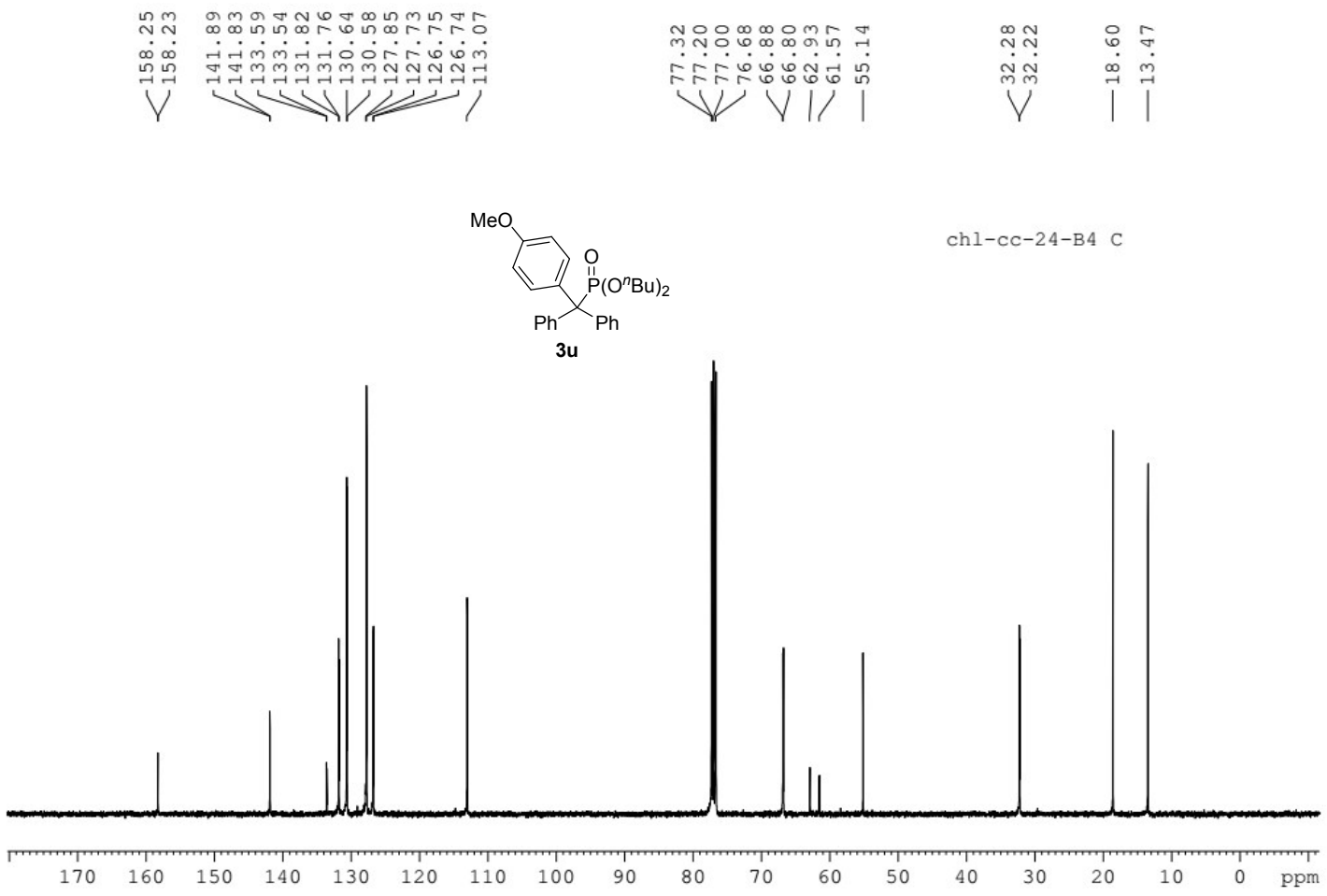

28.81
MeO
O
P(OMe)2
Ph
Ph
3s
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

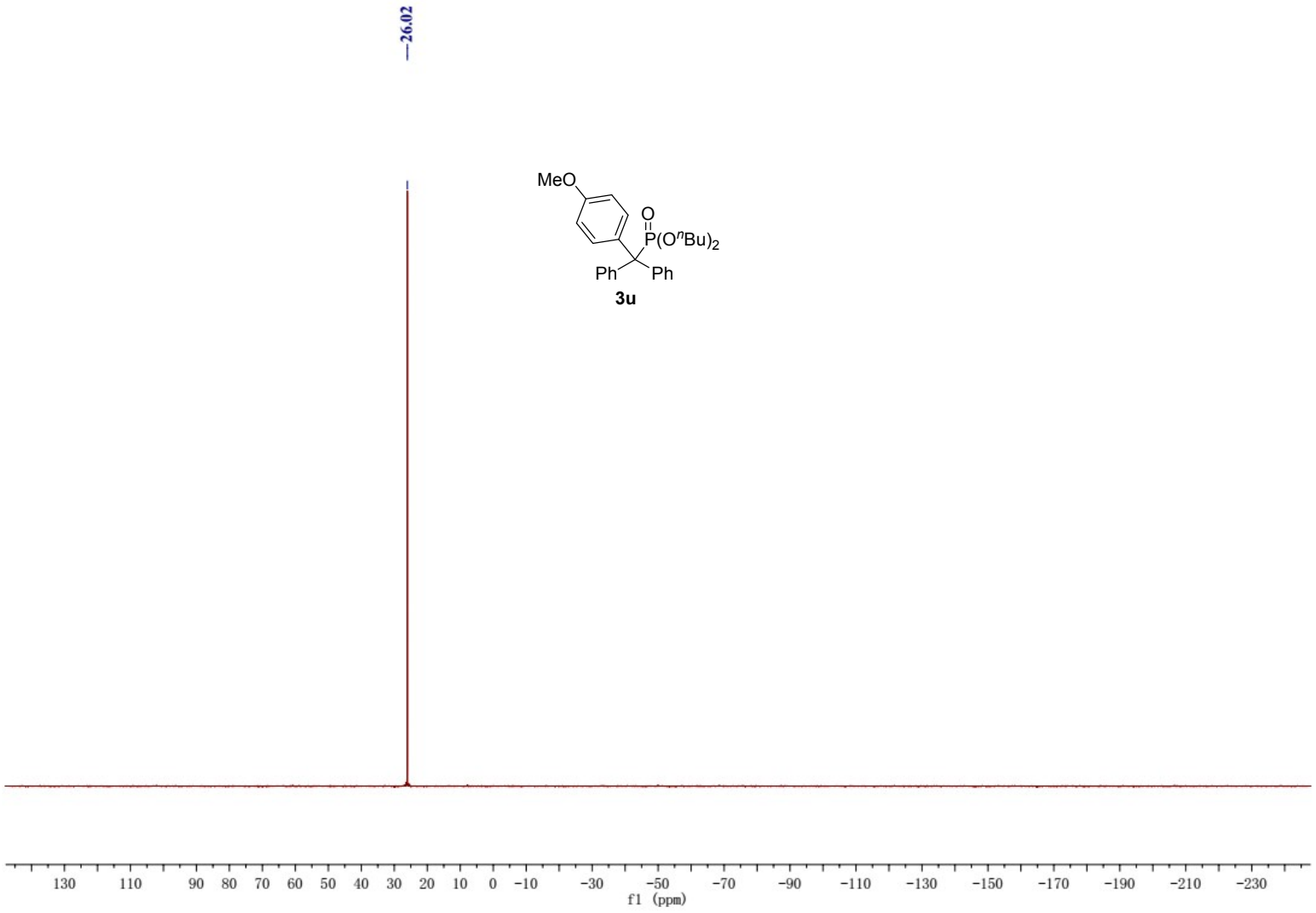

7.253
7.214
7.201
7.190
7.177
7.173
7.148
6.745
6.723
4.514
4.499
4.483
4.465
4.449
4.434
3.727
1.099
1.084
0.871
0.856
chl-cc-24-B3 H
MeO
O
P(O^{i}Pr)$_2$
Ph
Ph
3t
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.10
8.00
2.05
2.01
3.07
6.01
6.24

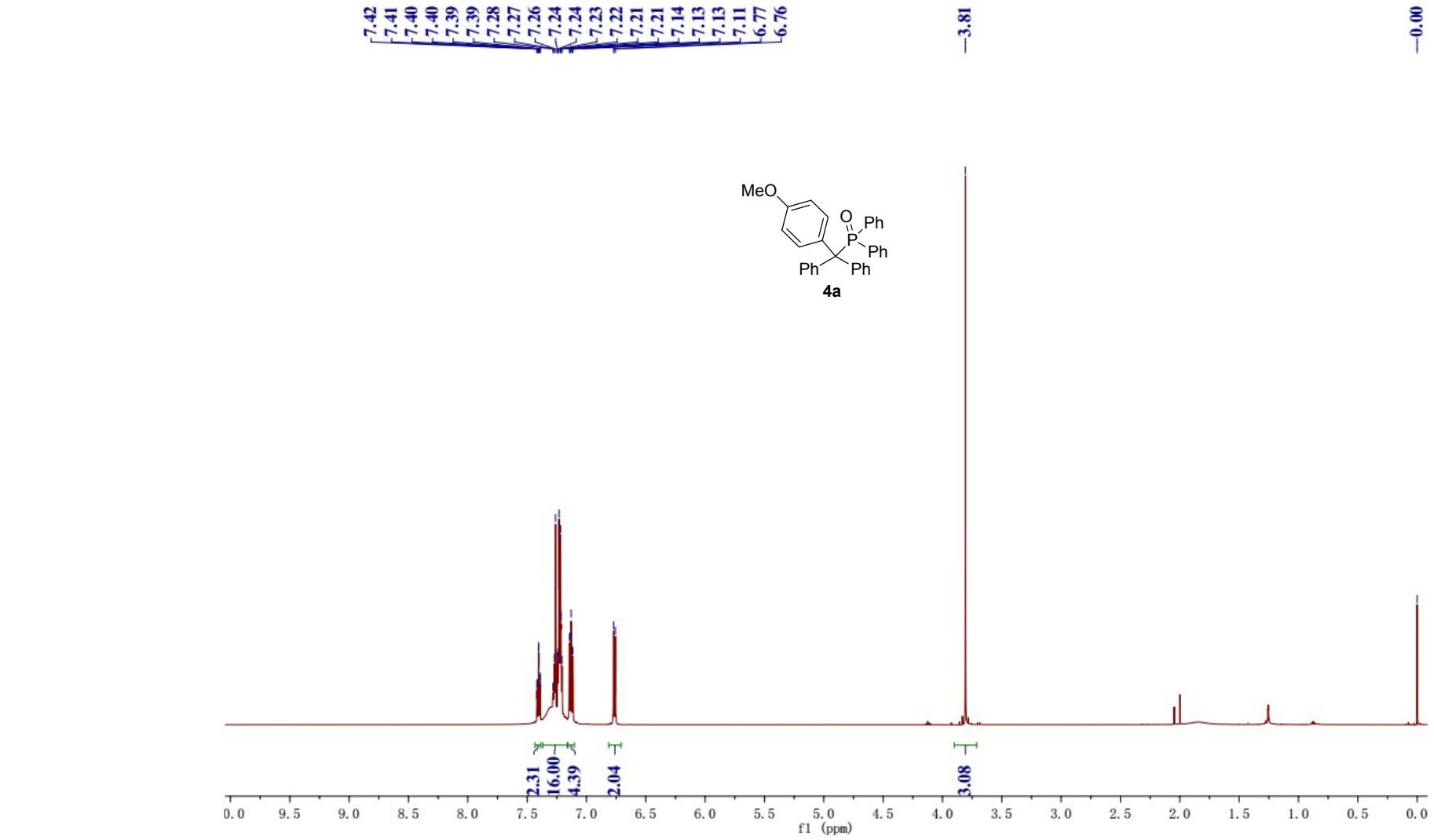

158.21
142.24
142.18
134.00
133.95
131.90
131.84
130.74
130.68
127.67
126.67
113.00
77.32
77.00
76.68
72.03
71.94
63.02
61.66
55.18
24.06
24.03
23.17
23.11
chl-cc-24-B3 C
MeO
O
P(O^{i}Pr)$_2$
Ph
Ph
3t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

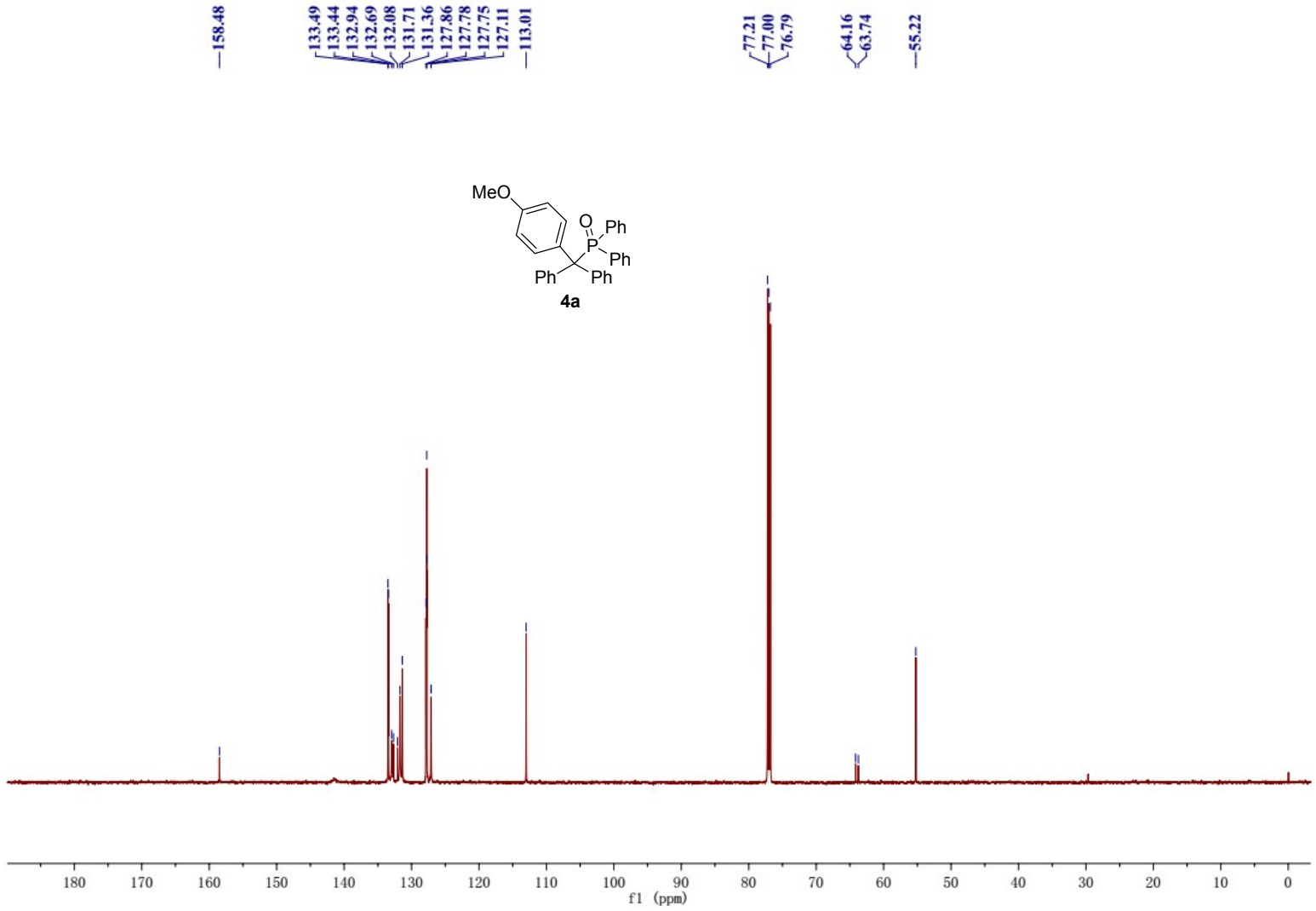

24.26
MeO
O
P(O^{i}Pr)$_2$
Ph
Ph
3t
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

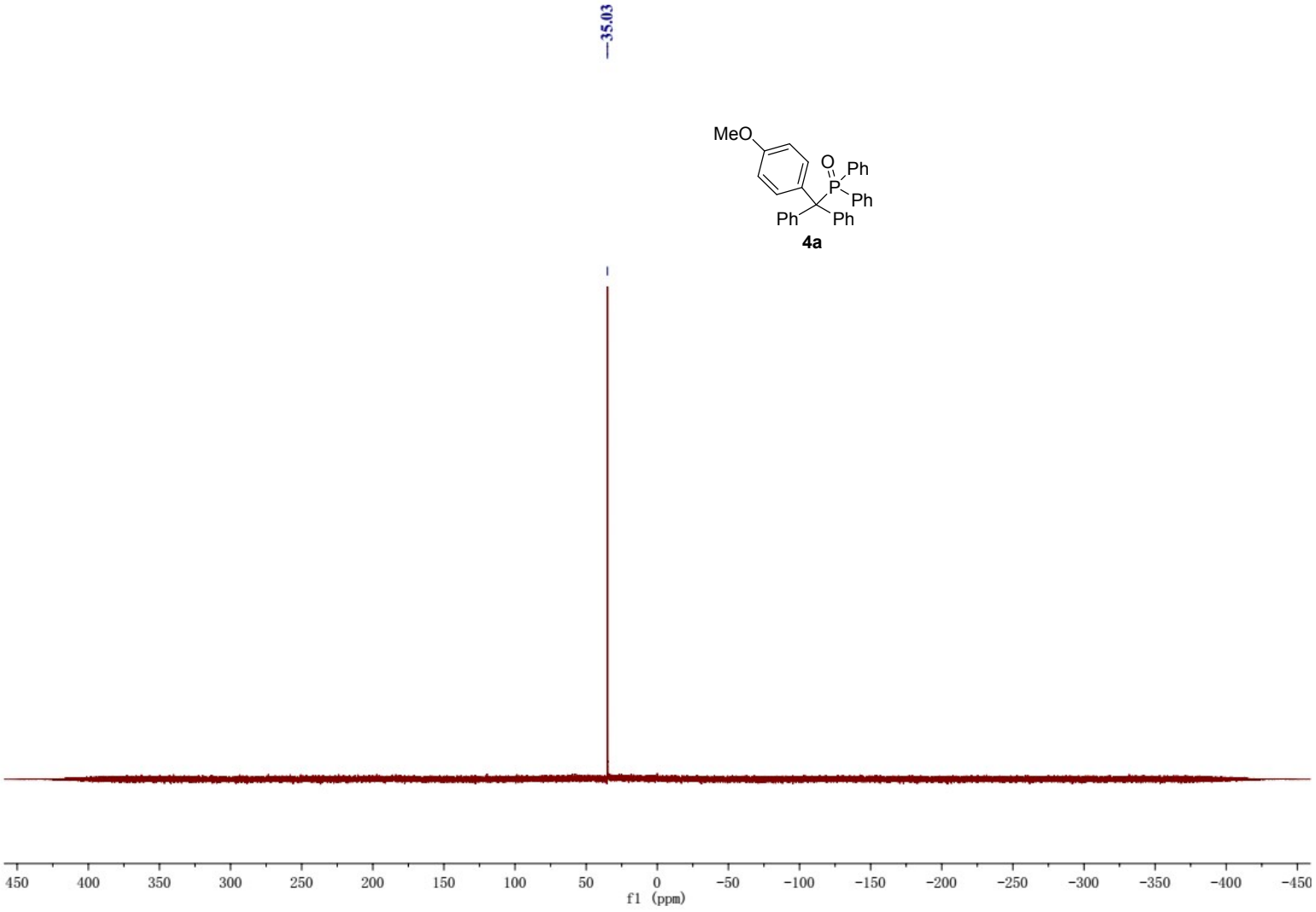

7.265
7.249
7.245
7.227
7.218
7.211
7.205
7.197
7.185
7.183
7.178
7.170
7.166
7.162
7.144
7.140
6.757
6.749
6.727
3.904
3.887
3.878
3.871
3.862
3.855
3.846
3.829
3.720
3.699
3.683
3.674
3.665
3.658
3.649
3.640
3.624
1.387
1.371
1.353
1.336
1.317
1.300
1.283
1.266
1.154
1.135
1.117
1.098
1.080
1.061
0.751
0.732
0.714
MeO
O
P(O^{n}Bu)$_2$
Ph
Ph
3u
chl-cc-24-B4 H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.02
8.18
2.00
2.01
3.14
2.04
4.12
4.11
6.02

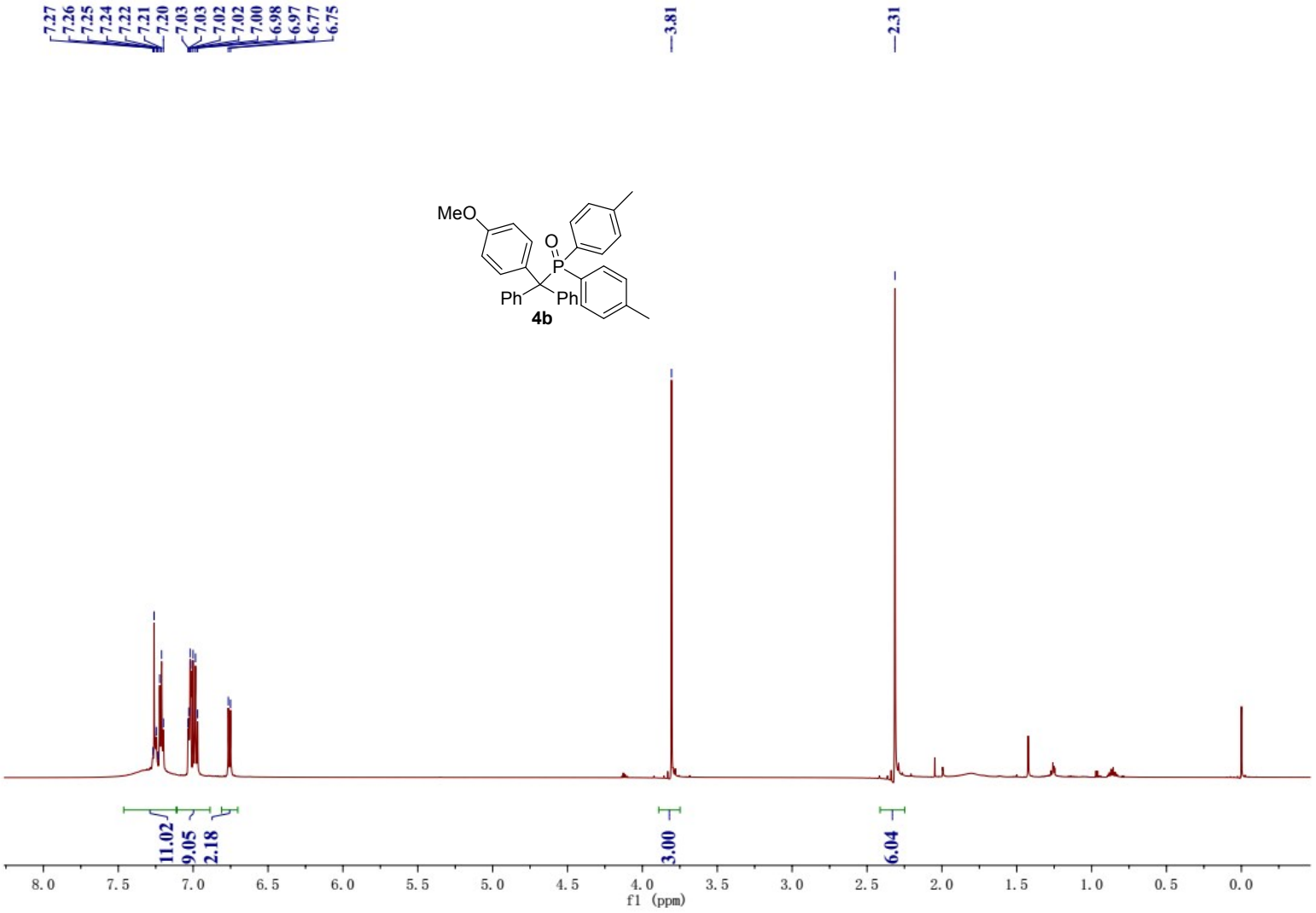

158.25
158.23
141.89
141.83
133.59
133.54
131.82
131.76
130.64
130.58
127.85
127.73
126.75
126.74
113.07
77.32
77.20
77.00
76.68
66.88
66.80
62.93
61.57
55.14
32.28
32.22
18.60
13.47
MeO
O
P(O^{n}Bu)$_2$
Ph
Ph
3u
chl-cc-24-B4 C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

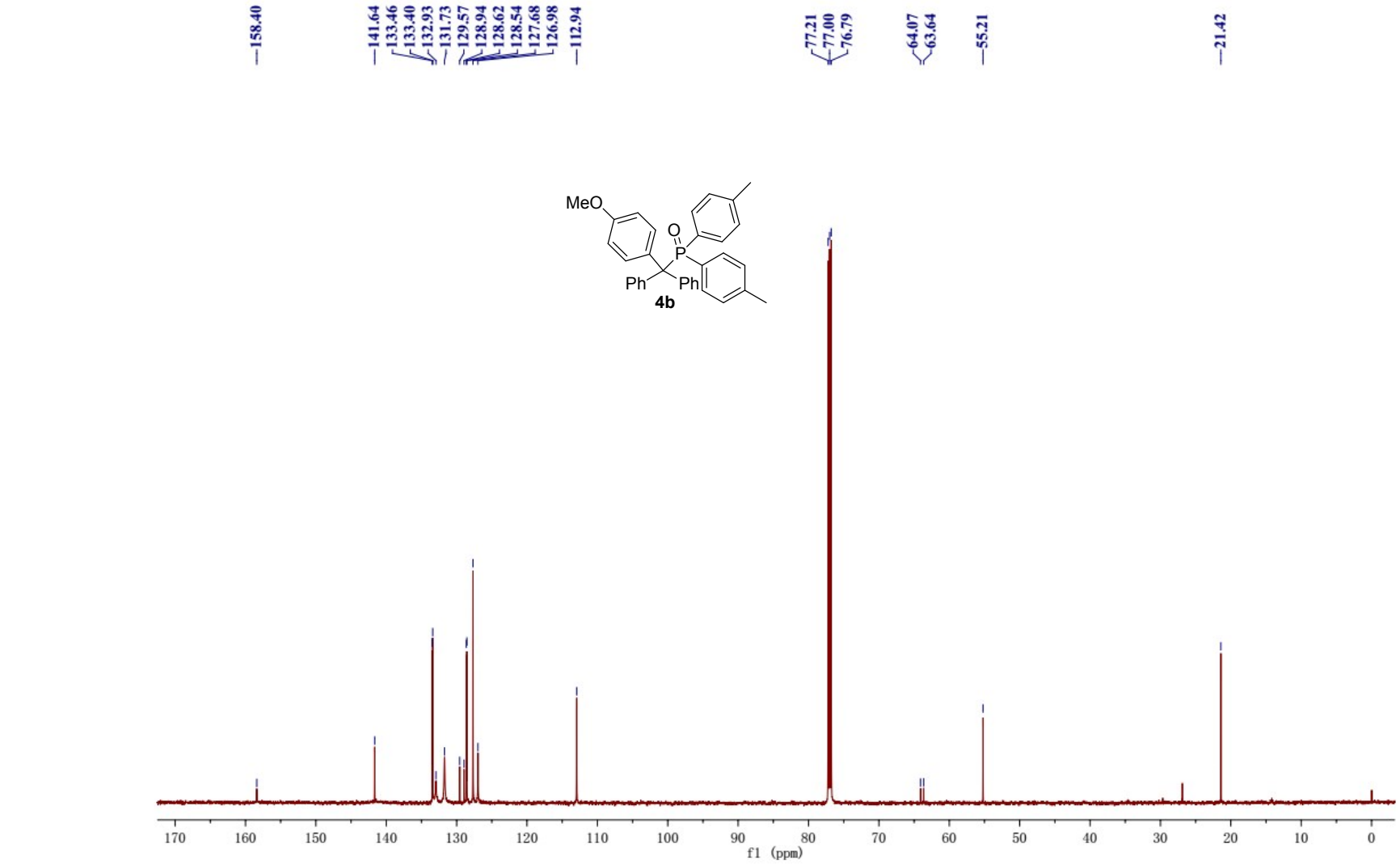

26.02
MeO
O
P(O^{n}Bu)$_2$
Ph
Ph
3u
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

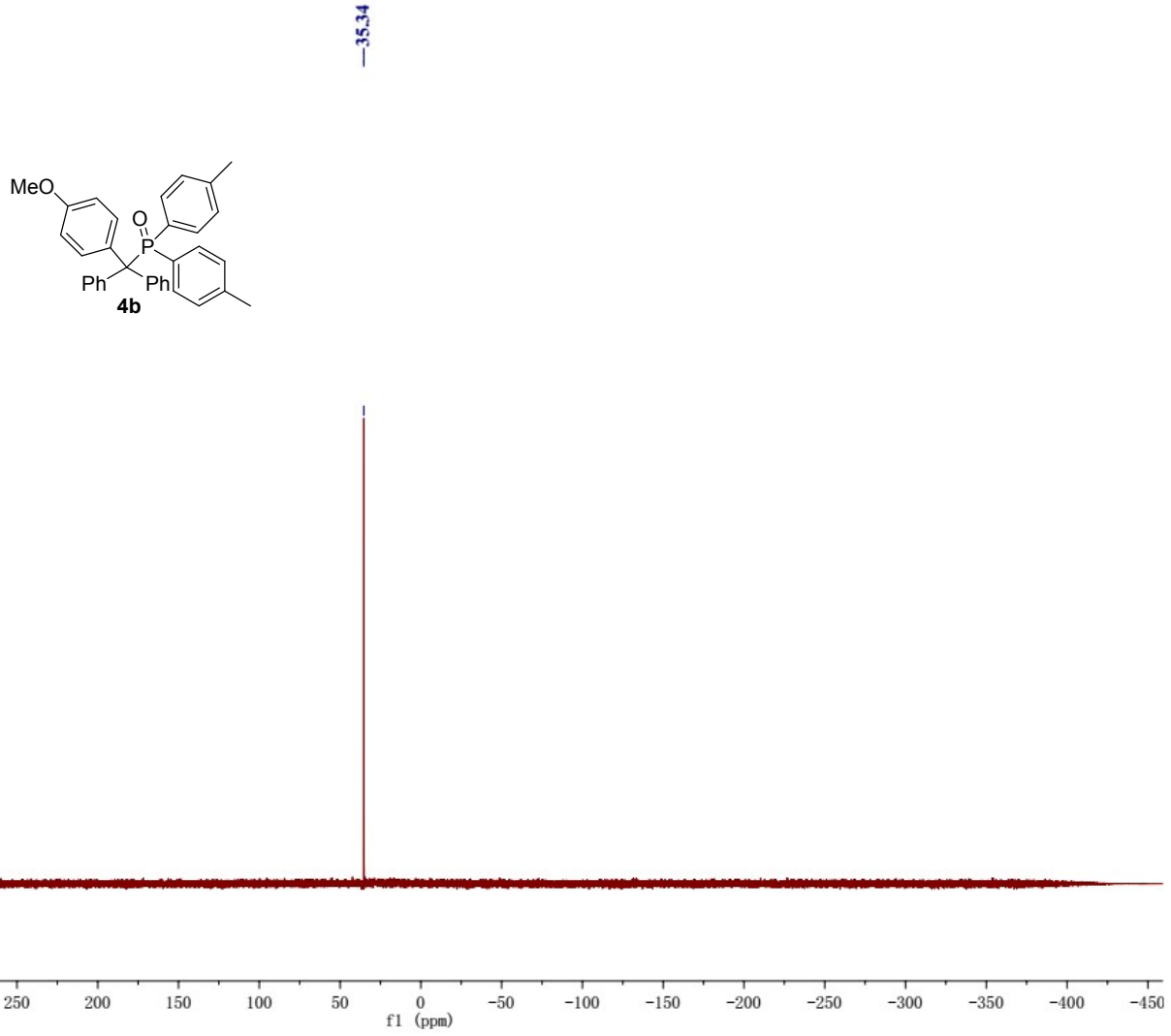

7.42
7.41
7.40
7.40
7.39
7.39
7.28
7.27
7.26
7.24
7.24
7.23
7.22
7.21
7.21
7.14
7.13
7.13
7.11
6.77
6.76
3.81
0.00
MeO
O
P
Ph
Ph
Ph
Ph
4a
2.31
16.00
4.39
2.04
3.08
f1 (ppm)

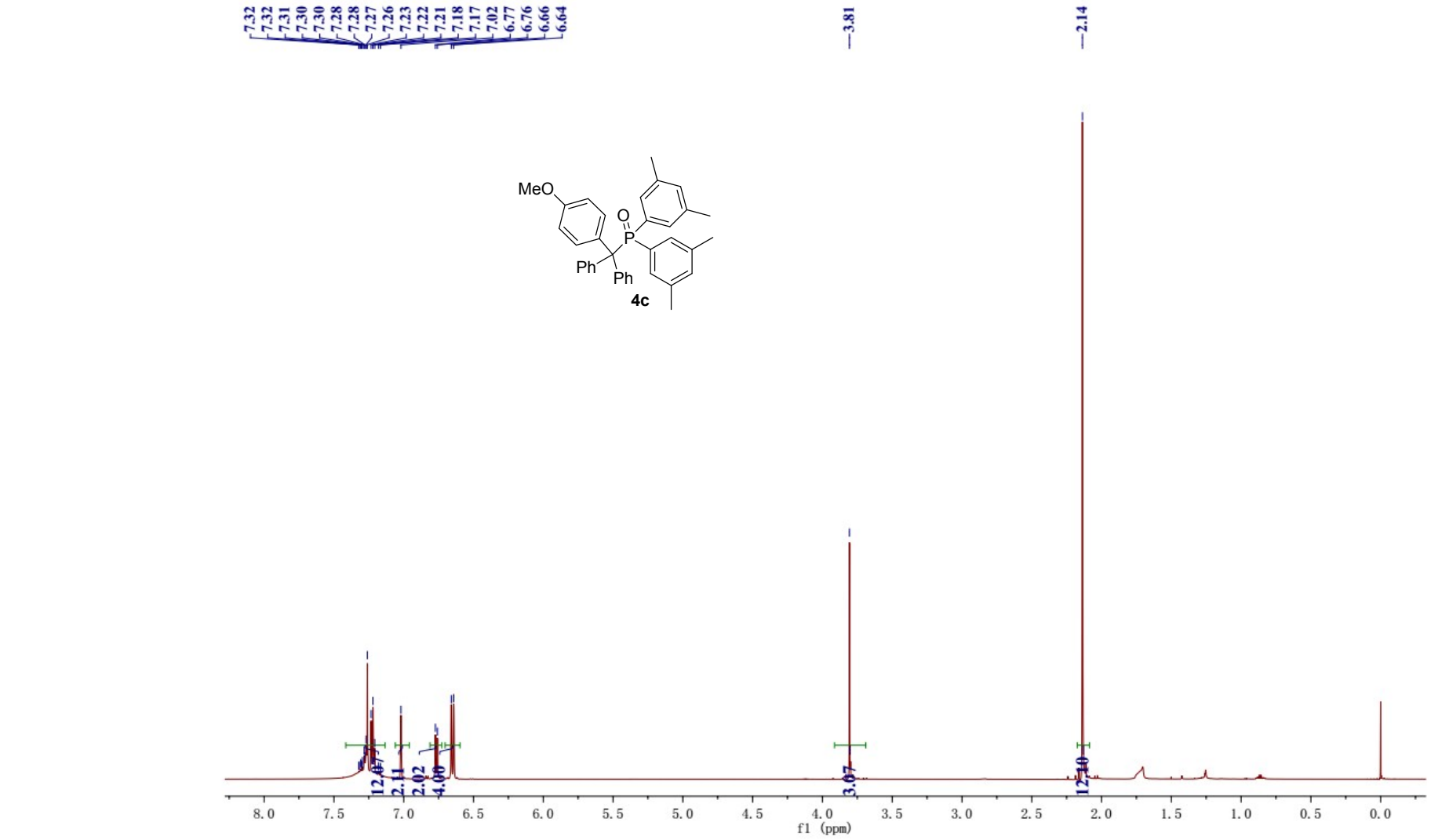

158.48
133.49
133.44
132.94
132.69
132.08
131.71
131.36
127.86
127.78
127.75
127.11
113.01
77.21
77.00
76.79
64.16
63.74
55.22
MeO
O
P
Ph
Ph
Ph
Ph
4a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

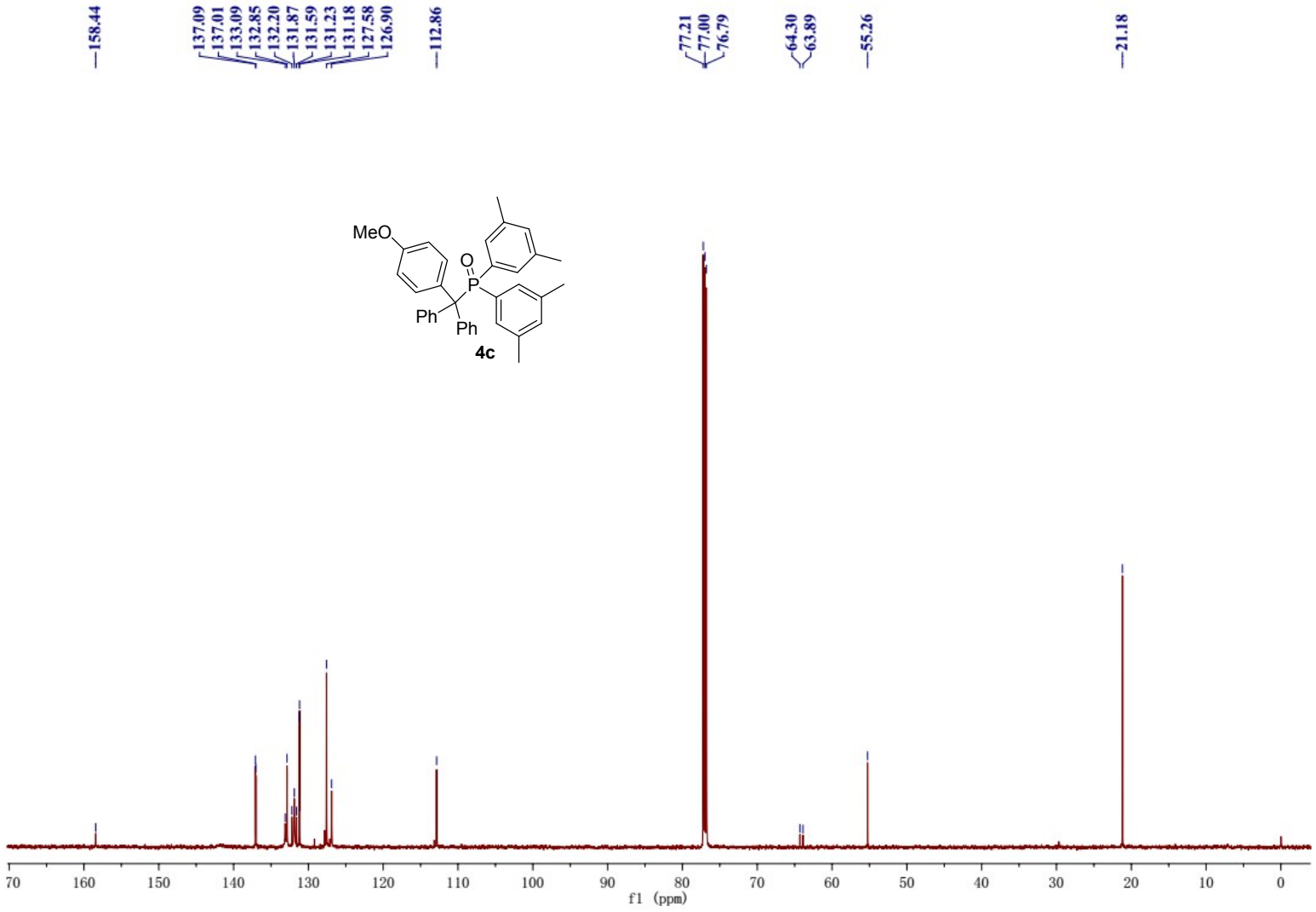

35.03
MeO
O
Ph
P
Ph
Ph
Ph
4a
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

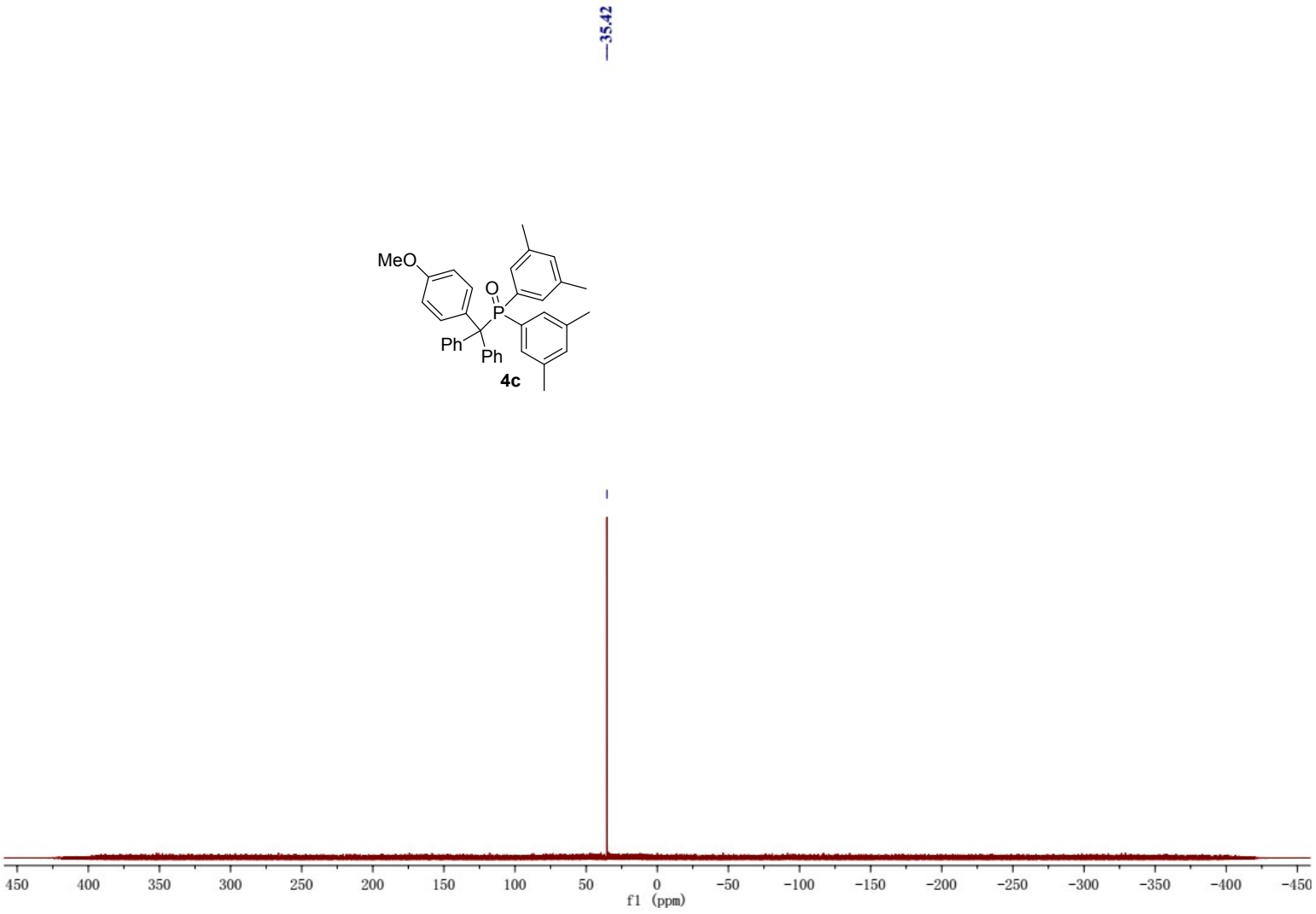

7.27
7.26
7.25
7.24
7.22
7.21
7.20
7.03
7.03
7.02
7.02
7.00
6.98
6.97
6.77
6.75
3.81
2.31
MeO
O
P
Ph
Ph
4b
11.02
9.05
2.18
3.00
6.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

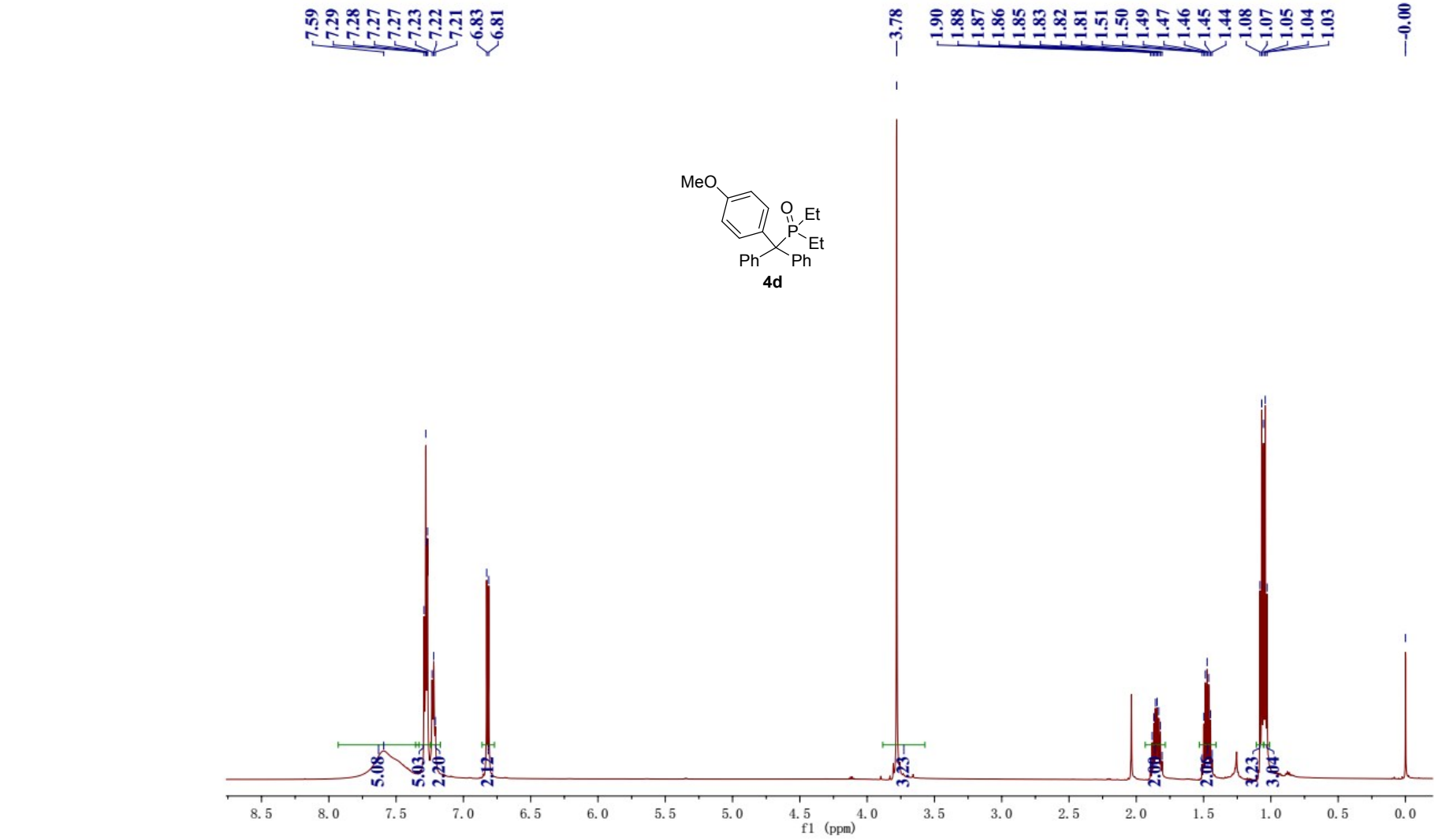

158.40
141.64
133.46
133.40
132.93
131.73
129.57
128.94
128.62
128.54
127.68
126.98
112.94
77.21
77.00
76.79
64.07
63.64
55.21
21.42
MeO
O
P
Ph
Ph
4b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

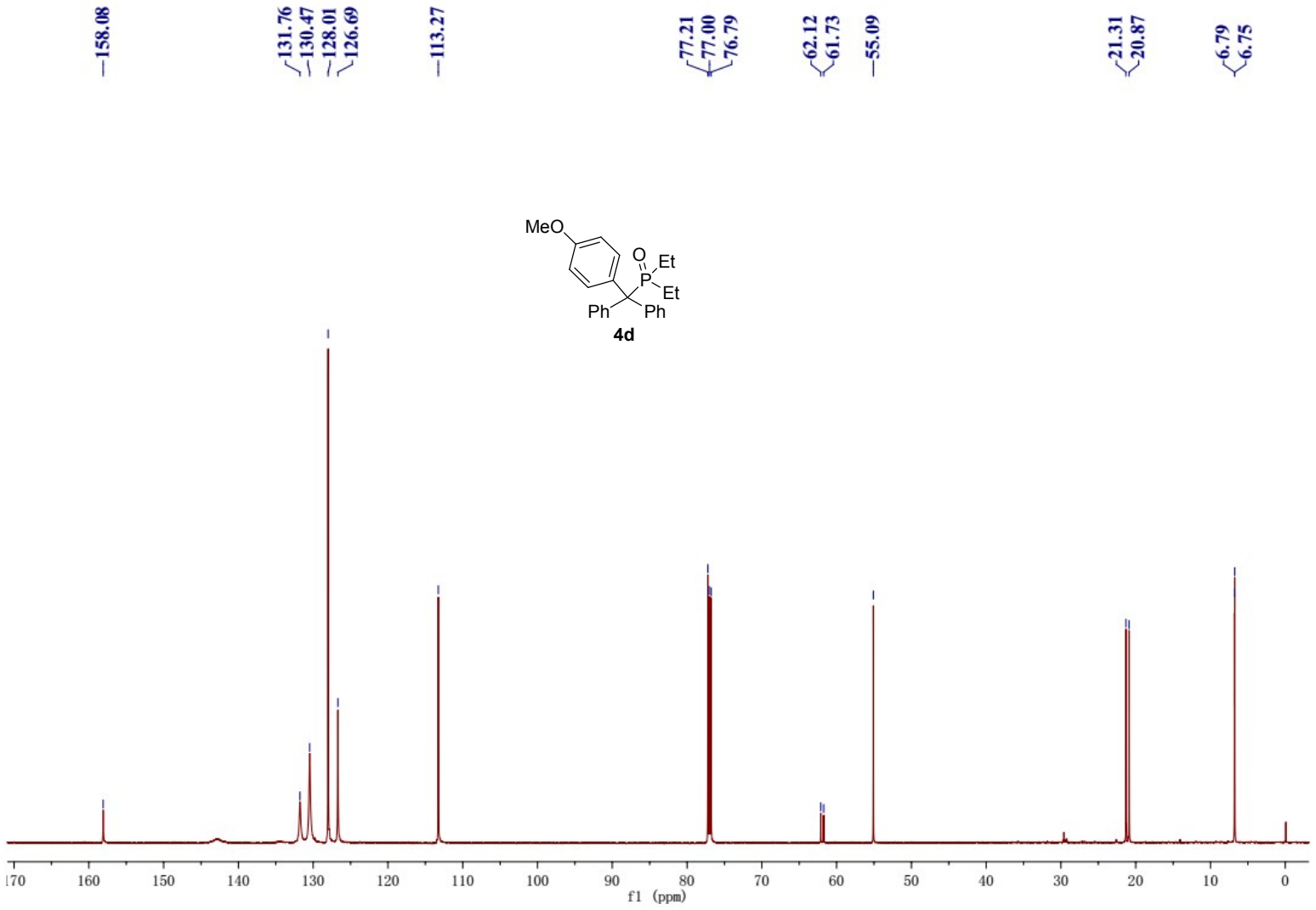

35.34
MeO
O
P
Ph
Ph
4b
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

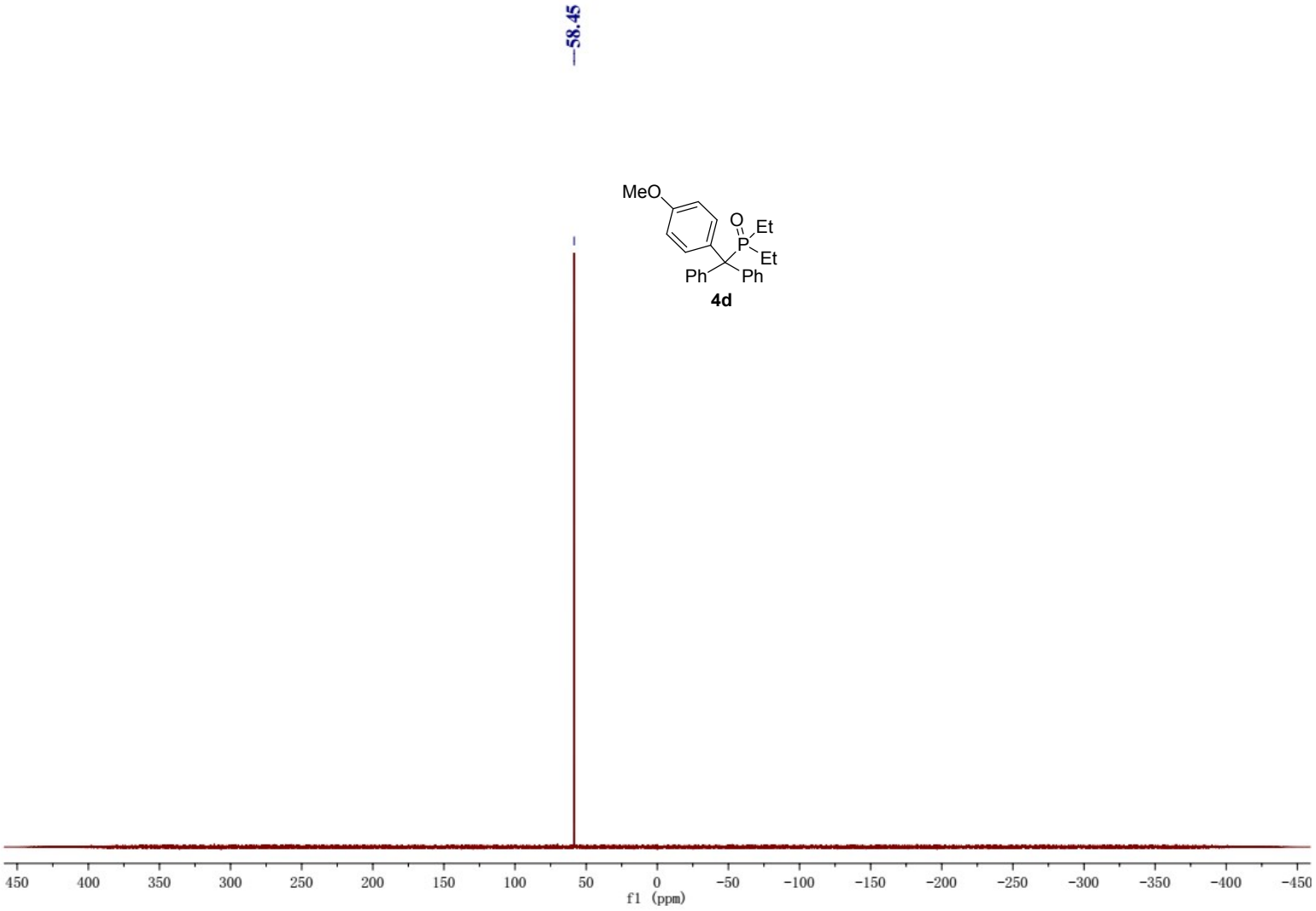

7.32
7.32
7.31
7.30
7.30
7.28
7.28
7.27
7.26
7.23
7.22
7.21
7.18
7.17
7.02
6.77
6.76
6.66
6.64
3.81
2.14
MeO
O
P
Ph
Ph
4c
12.07
2.11
2.02
4.00
3.07
12.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

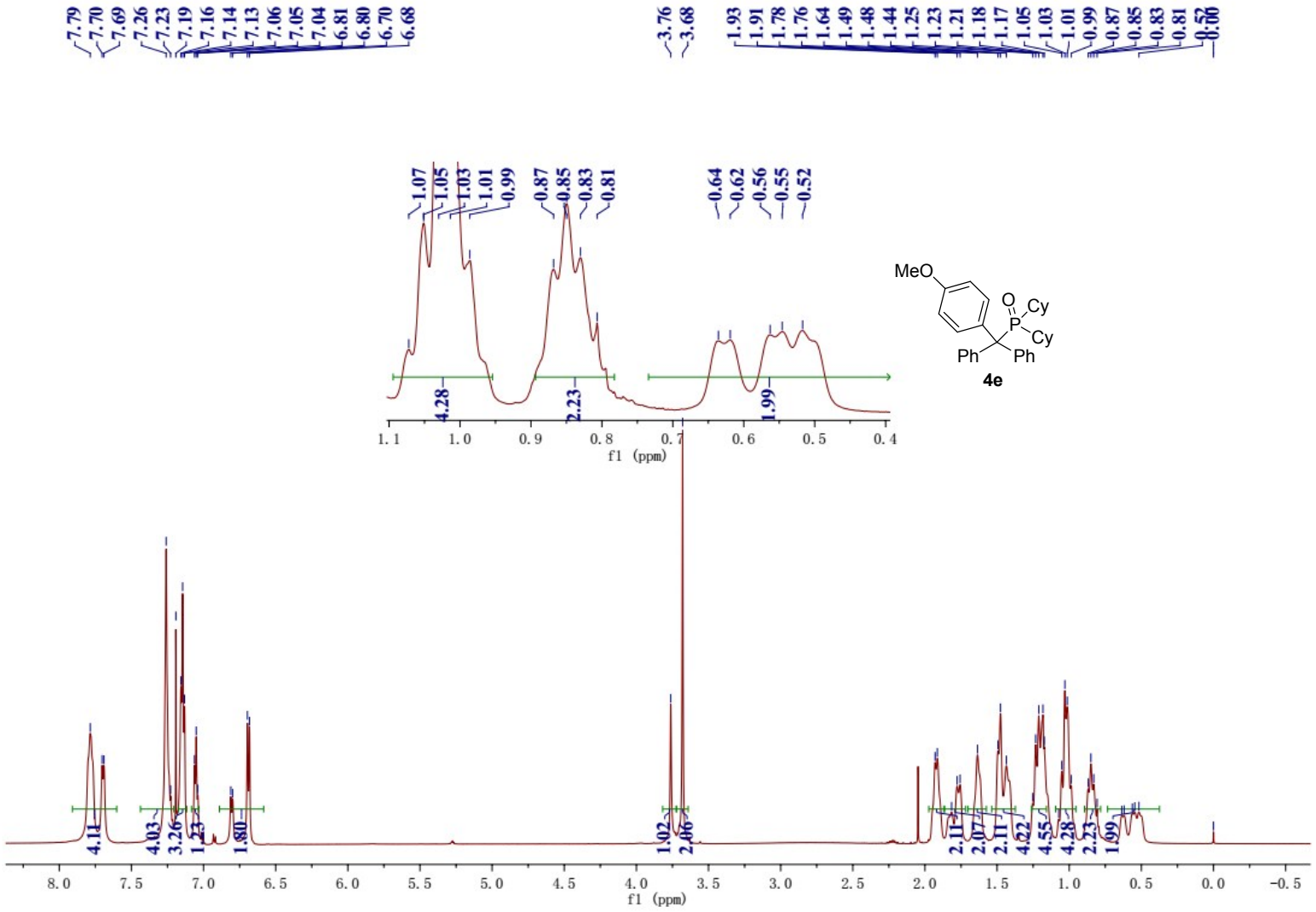

158.44
137.09
137.01
133.09
132.85
132.20
131.87
131.59
131.23
131.18
127.58
126.90
112.86
77.21
77.00
76.79
64.30
63.89
55.26
21.18
MeO
O
P
Ph
Ph
4c
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

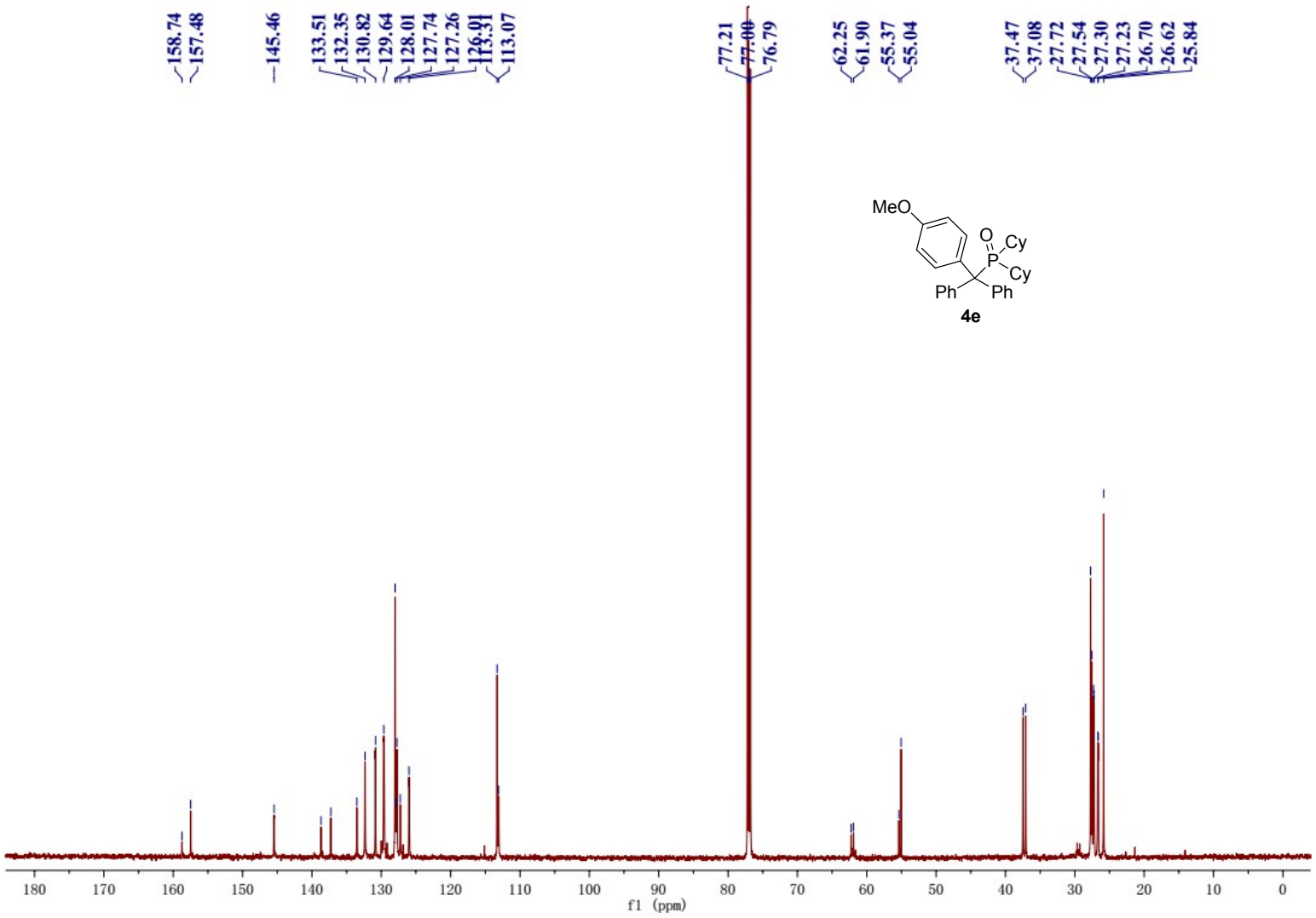

35.42
MeO
O
P
Ph
Ph
4c
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

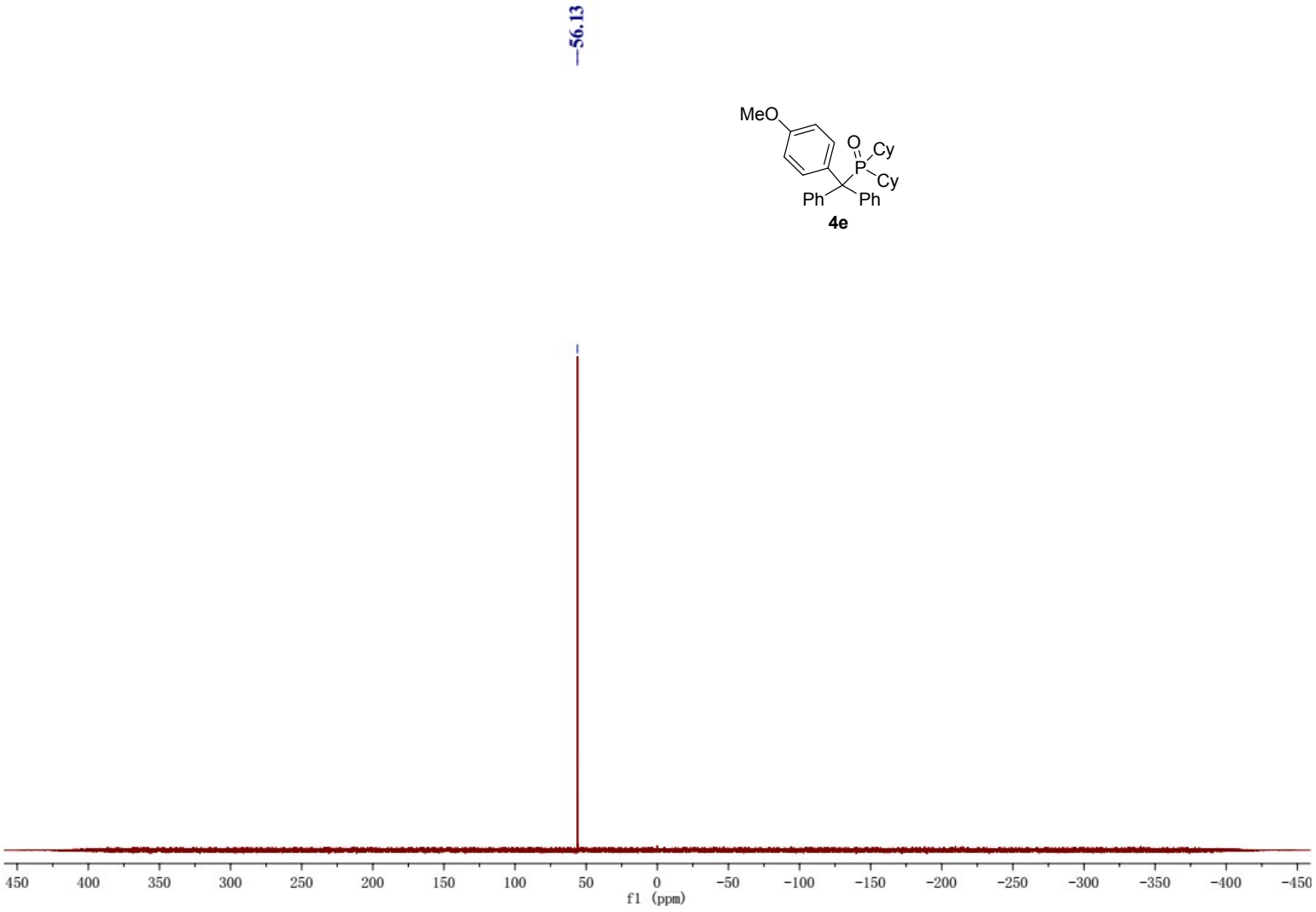

7.59
7.29
7.28
7.27
7.27
7.27
7.23
7.22
7.21
6.83
6.81
3.78
1.90
1.88
1.87
1.86
1.85
1.83
1.82
1.81
1.51
1.50
1.49
1.47
1.46
1.45
1.44
1.08
1.07
1.05
1.04
1.03
0.00
MeO
O
Et
P
Et
Ph
Ph
4d
5.08
5.03
2.20
2.12
3.23
2.00
2.00
3.23
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

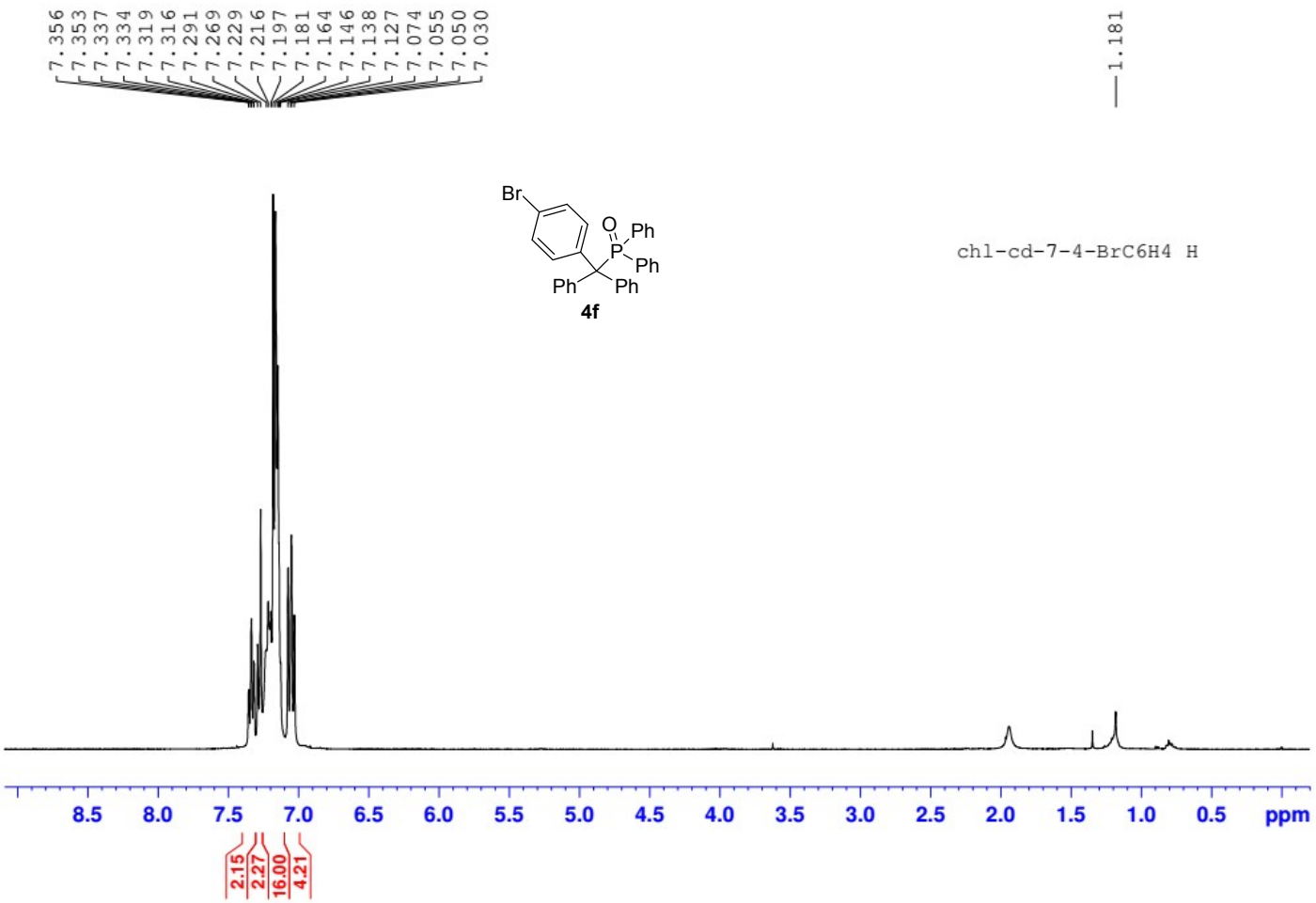

158.08
131.76
130.47
128.01
126.69
113.27
77.21
77.00
76.79
62.12
61.73
55.09
21.31
20.87
6.79
6.75
MeO
O
Et
P
Et
Ph
Ph
4d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

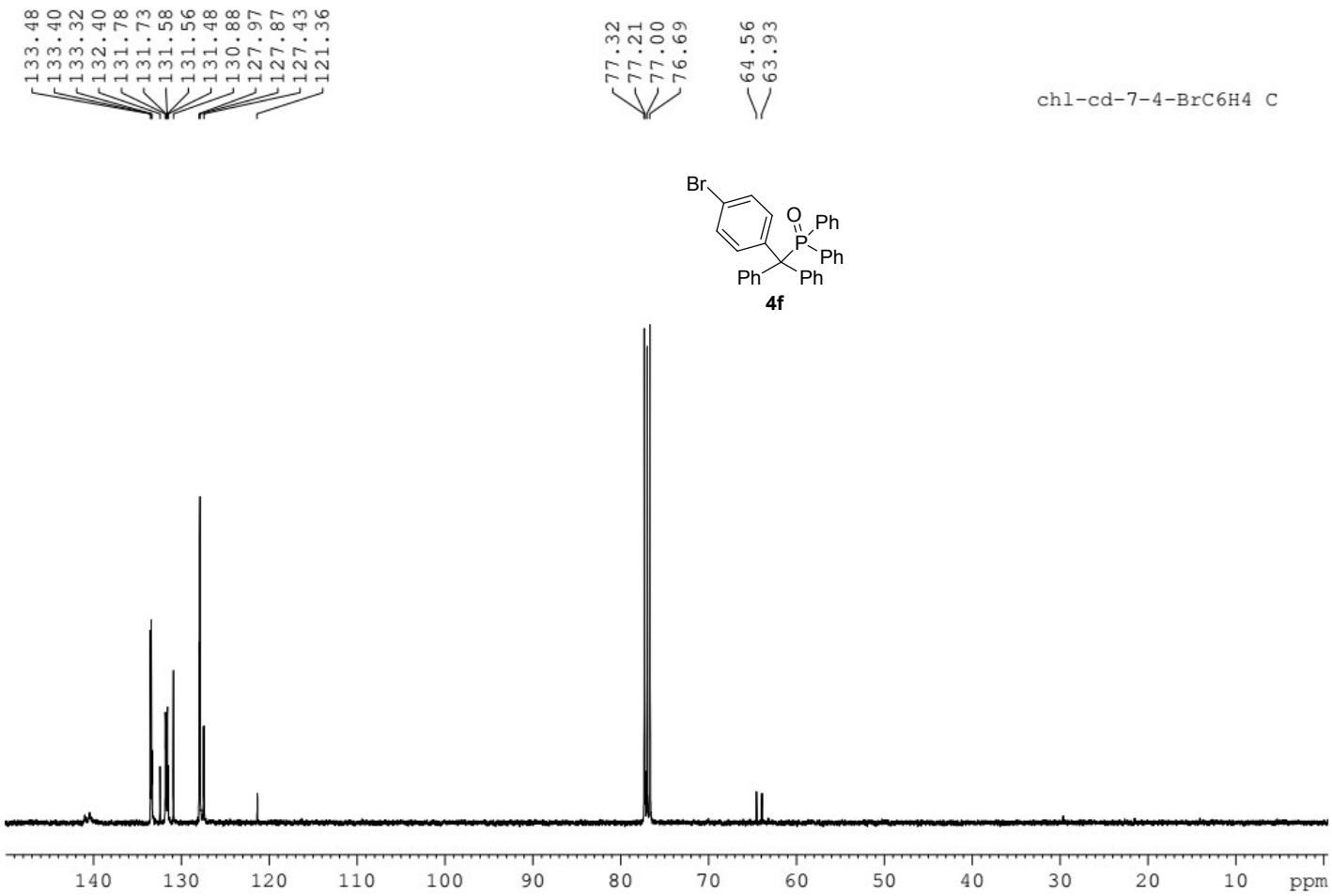

58.45
MeO
O
Et
P
Et
Ph
Ph
4d
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

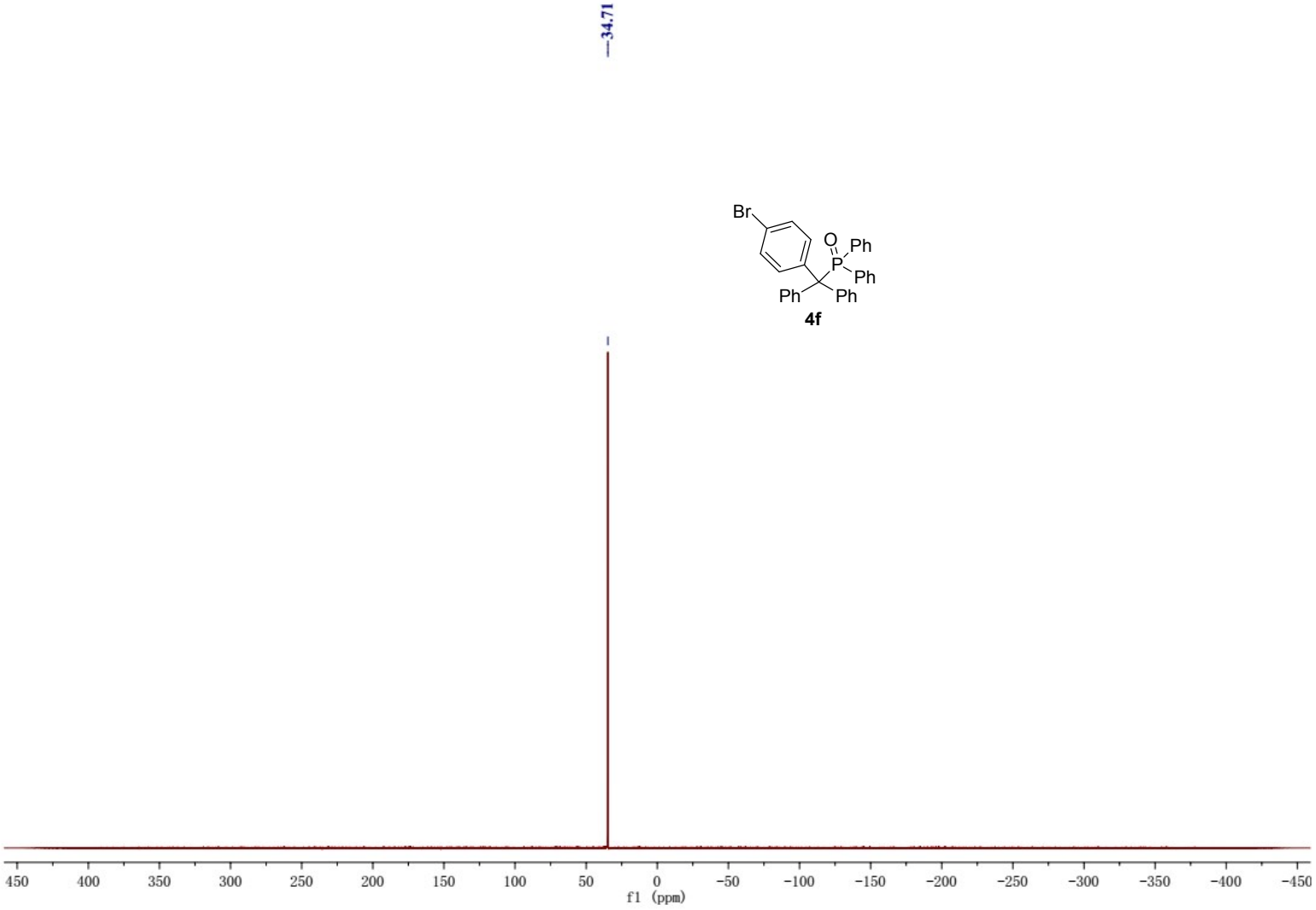

7.79
7.70
7.69
7.26
7.23
7.19
7.16
7.14
7.13
7.06
7.05
7.04
6.81
6.80
6.70
6.68
3.76
3.68
1.93
1.91
1.78
1.76
1.64
1.49
1.48
1.44
1.25
1.23
1.21
1.18
1.17
1.05
1.03
1.01
0.99
0.87
0.85
0.83
0.81
0.64
0.62
0.56
0.55
0.52
MeO
O
Cy
P
Cy
Ph
Ph
4e
4.28
2.23
1.99
f1 (ppm)
4.11
4.03
3.26
1.23
1.80
1.02
2.06
2.11
2.07
2.11
4.22
4.55
4.28
2.23
1.99
f1 (ppm)

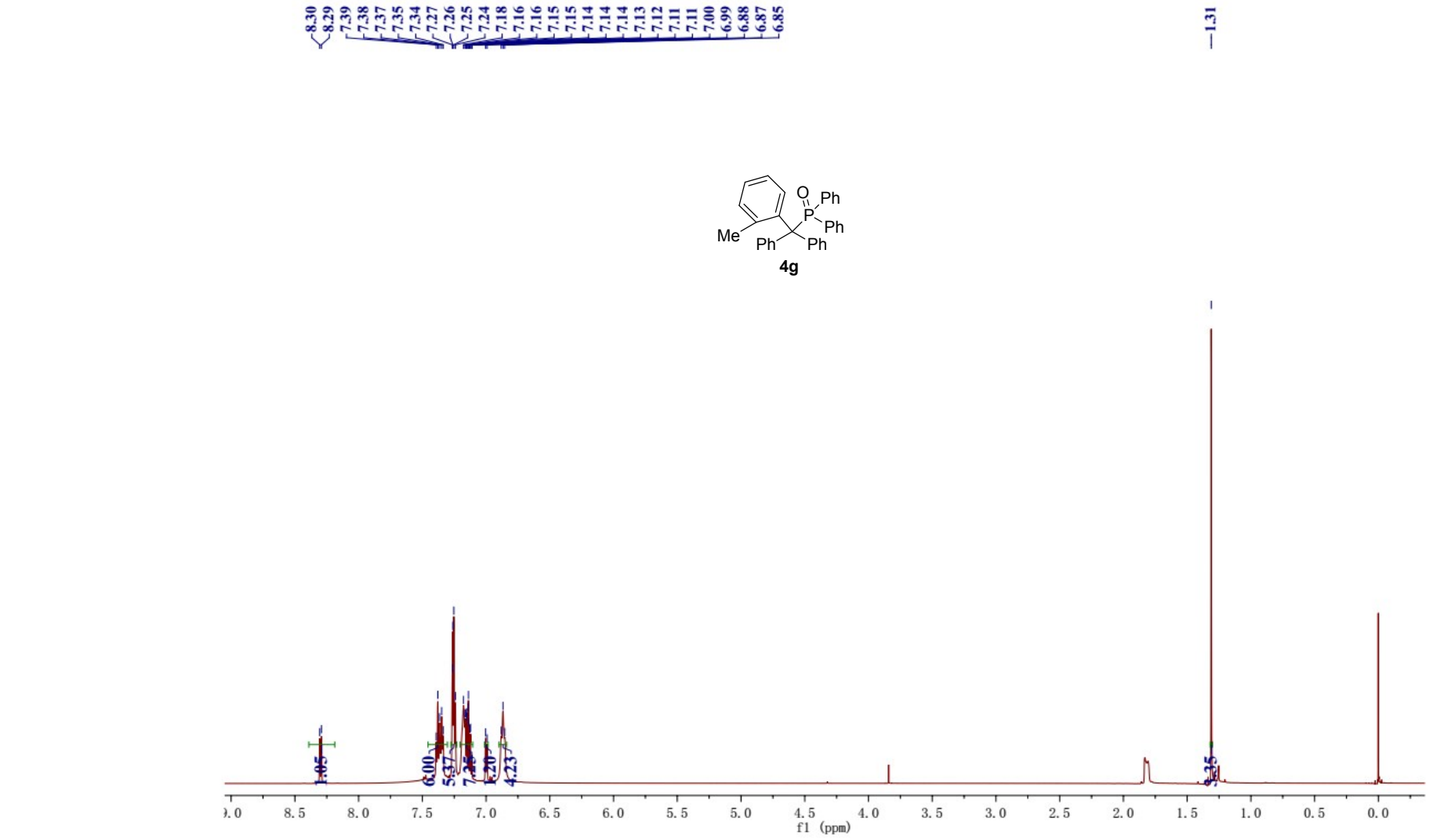

158.74
157.48
145.46
133.51
132.35
130.82
129.64
128.01
127.74
127.26
126.01
113.31
113.07
77.21
77.00
76.79
62.25
61.90
55.37
55.04
37.47
37.08
27.72
27.54
27.30
27.23
26.70
26.62
25.84
MeO
O
P
Cy
Cy
Ph
Ph
4e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


56.13
MeO
O
Cy
P
Cy
Ph
Ph
4e
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

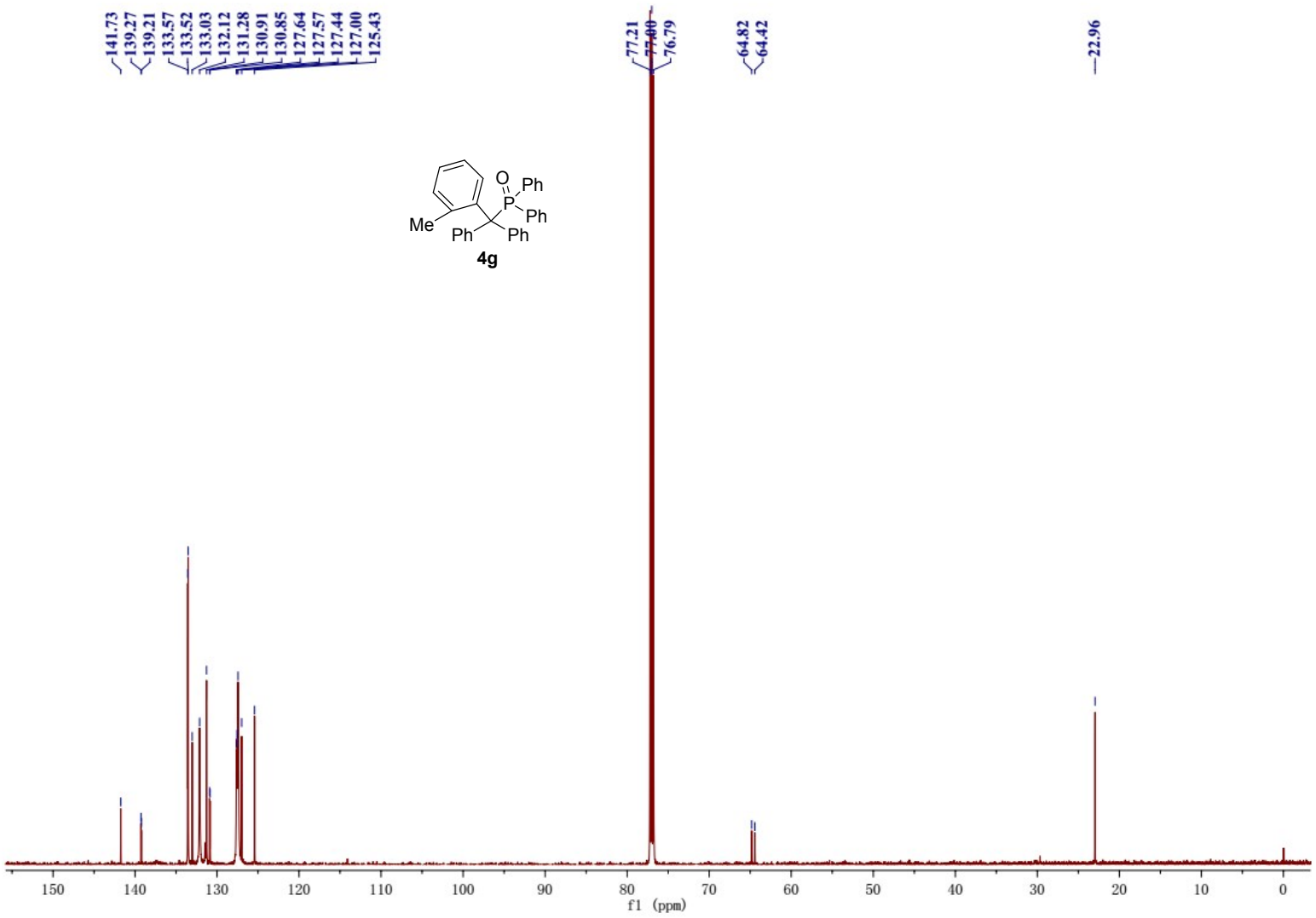

7.356
7.353
7.337
7.334
7.319
7.316
7.291
7.269
7.229
7.216
7.197
7.181
7.164
7.146
7.138
7.127
7.074
7.055
7.050
7.030
1.181
Br
O
P
Ph
Ph
Ph
Ph
4f
chl-cd-7-4-BrC6H4 H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.15
2.27
16.00
4.21

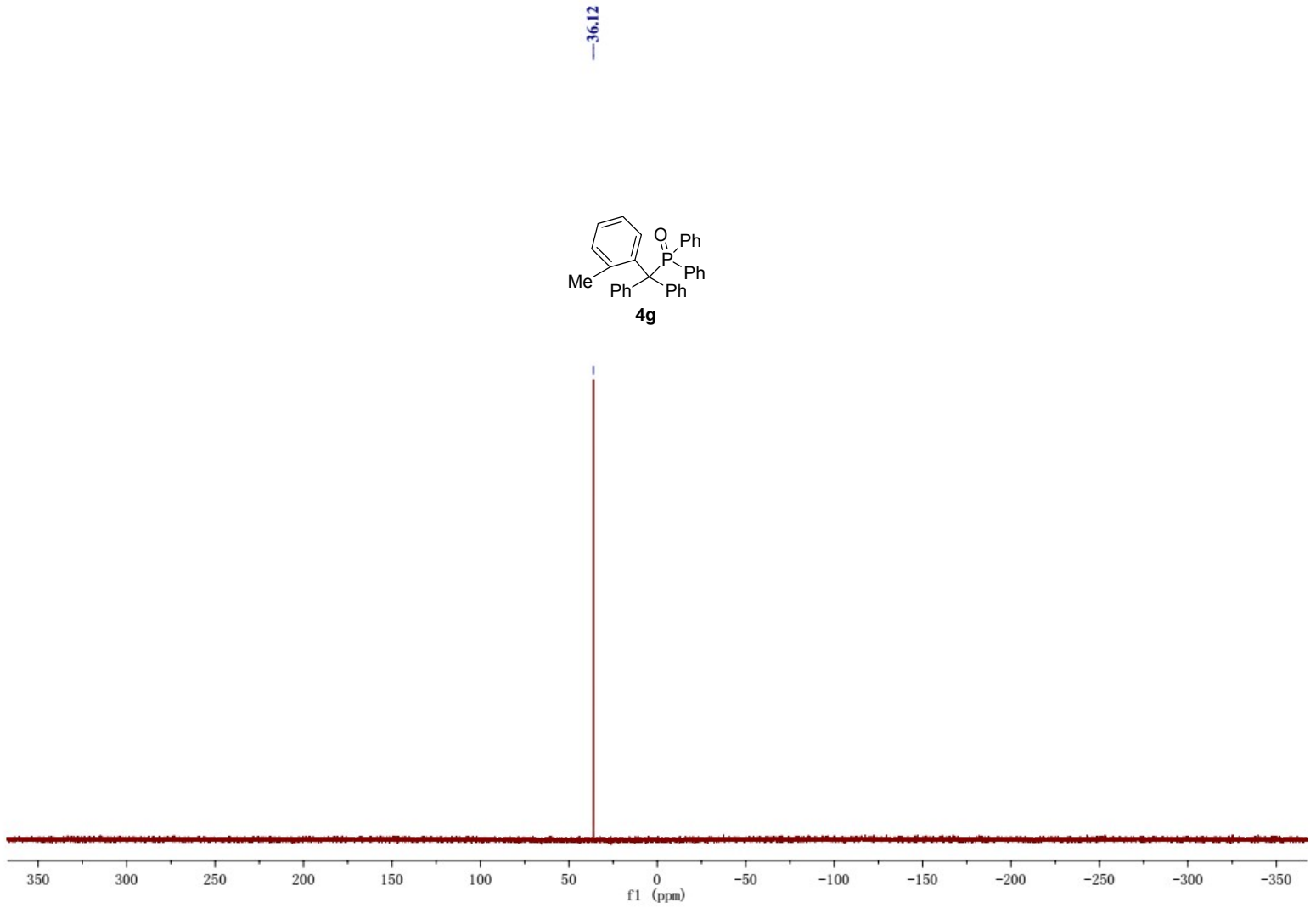

133.48
133.40
133.32
132.40
131.78
131.73
131.58
131.56
131.48
130.88
127.97
127.87
127.43
121.36
77.32
77.21
77.00
76.69
64.56
63.93
chl-cd-7-4-BrC6H4 C
Br
O
P
Ph
Ph
Ph
Ph
4f
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


34.71
Br
O
P
Ph
Ph
Ph
Ph
4f
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

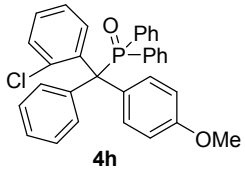

8.30
8.29
7.39
7.38
7.37
7.35
7.34
7.27
7.26
7.25
7.24
7.18
7.16
7.16
7.15
7.15
7.14
7.14
7.14
7.13
7.12
7.11
7.11
7.00
6.99
6.88
6.87
6.85
1.31
Me
Ph
Ph
O
P
Ph
Ph
1.05
6.00
5.37
7.26
2.20
4.23
9.35
f1 (ppm)

4g

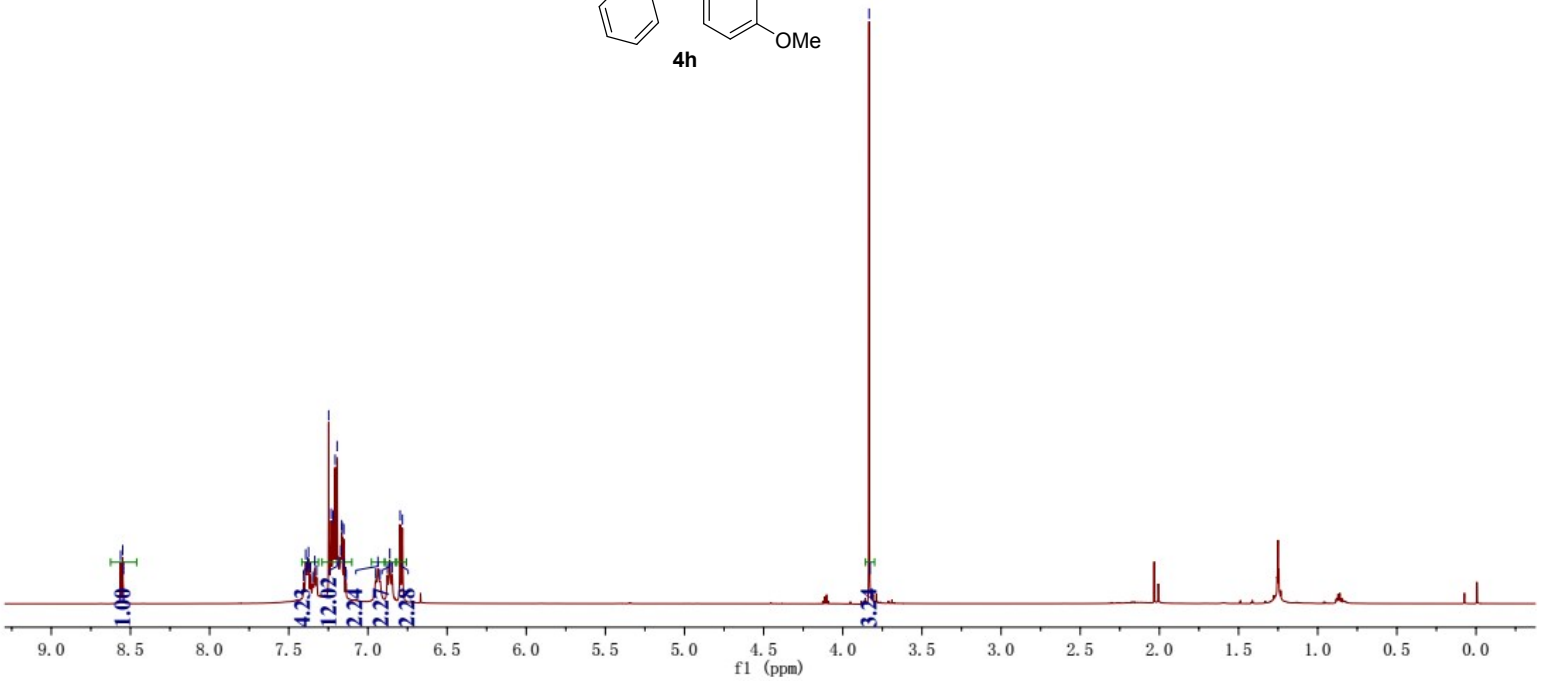

141.73
139.27
139.21
133.57
133.52
133.03
132.12
131.28
130.91
130.85
127.64
127.57
127.44
127.00
125.43
77.21
77.00
76.79
64.82
64.42
22.96
O
P
Ph
Ph
Me
Ph
Ph
4g
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

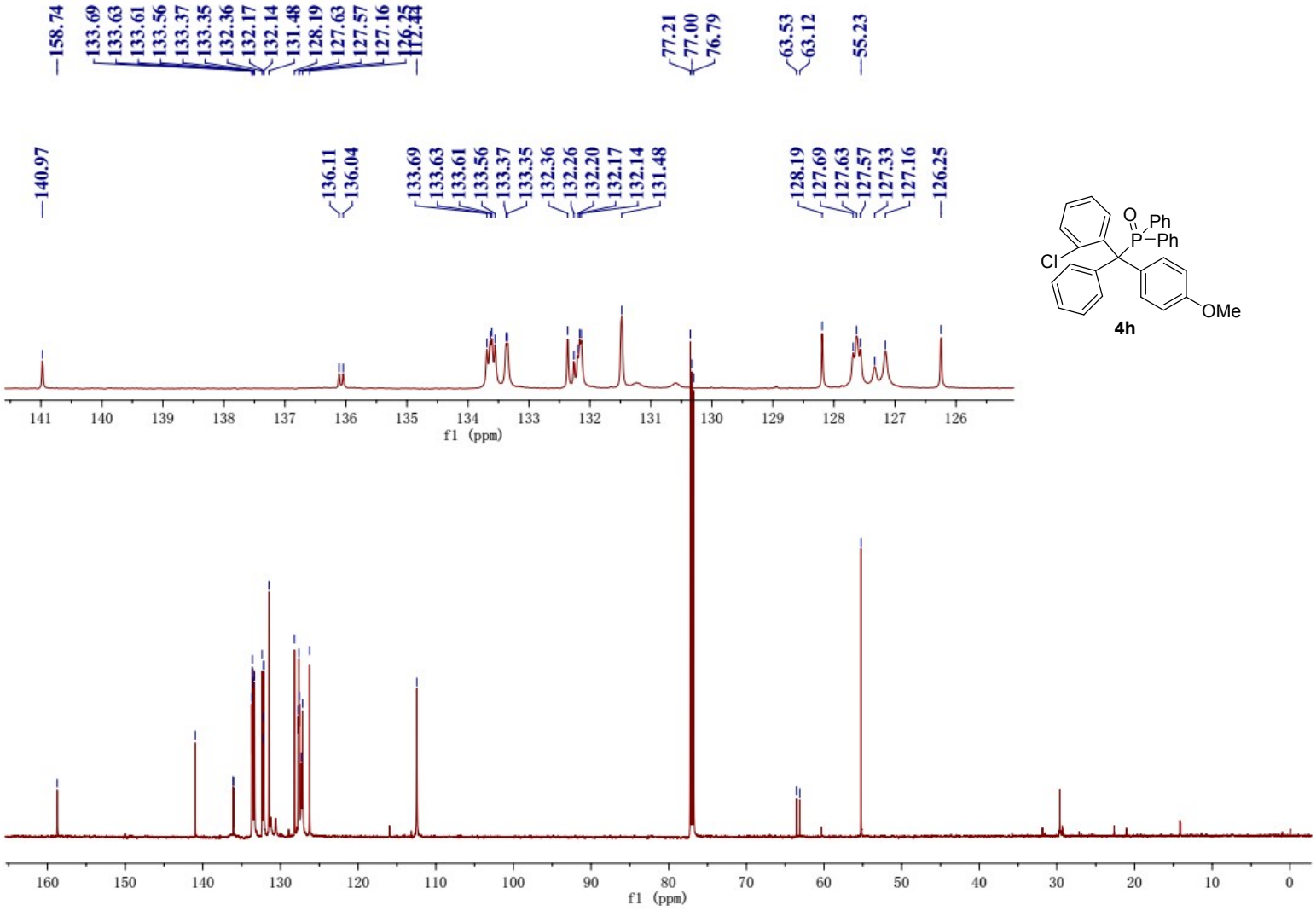

36.12
O
Ph
P
Ph
Me
Ph
Ph
4g
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)


8.56
8.55
7.41
7.39
7.39
7.38
7.38
7.36
7.35
7.34
7.32
7.25
7.23
7.22
7.22
7.21
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
6.95
6.94
6.92
6.88
6.86
6.85
6.80
6.78
3.83


O
Ph
P
Ph
Cl
OMe

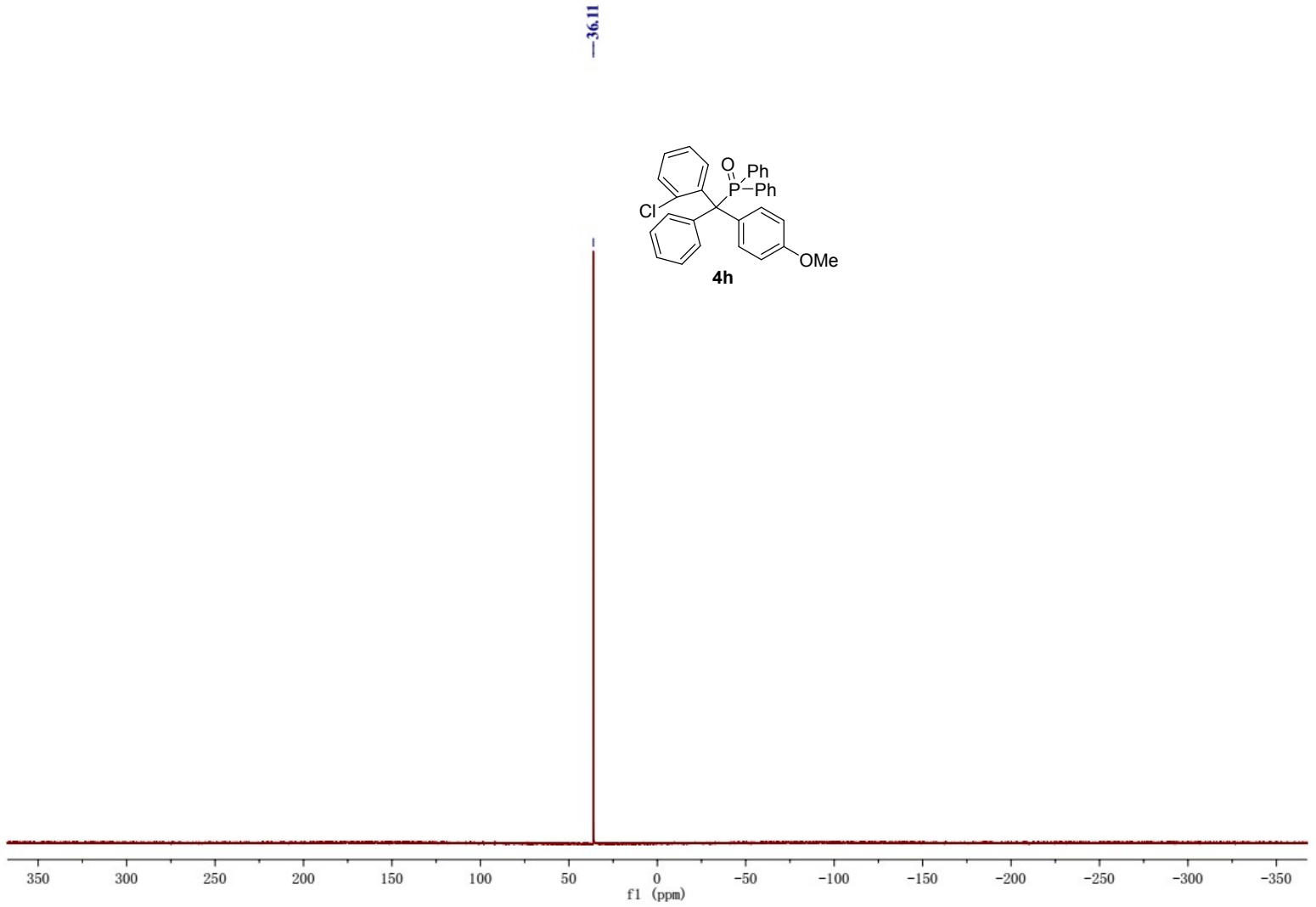
4h

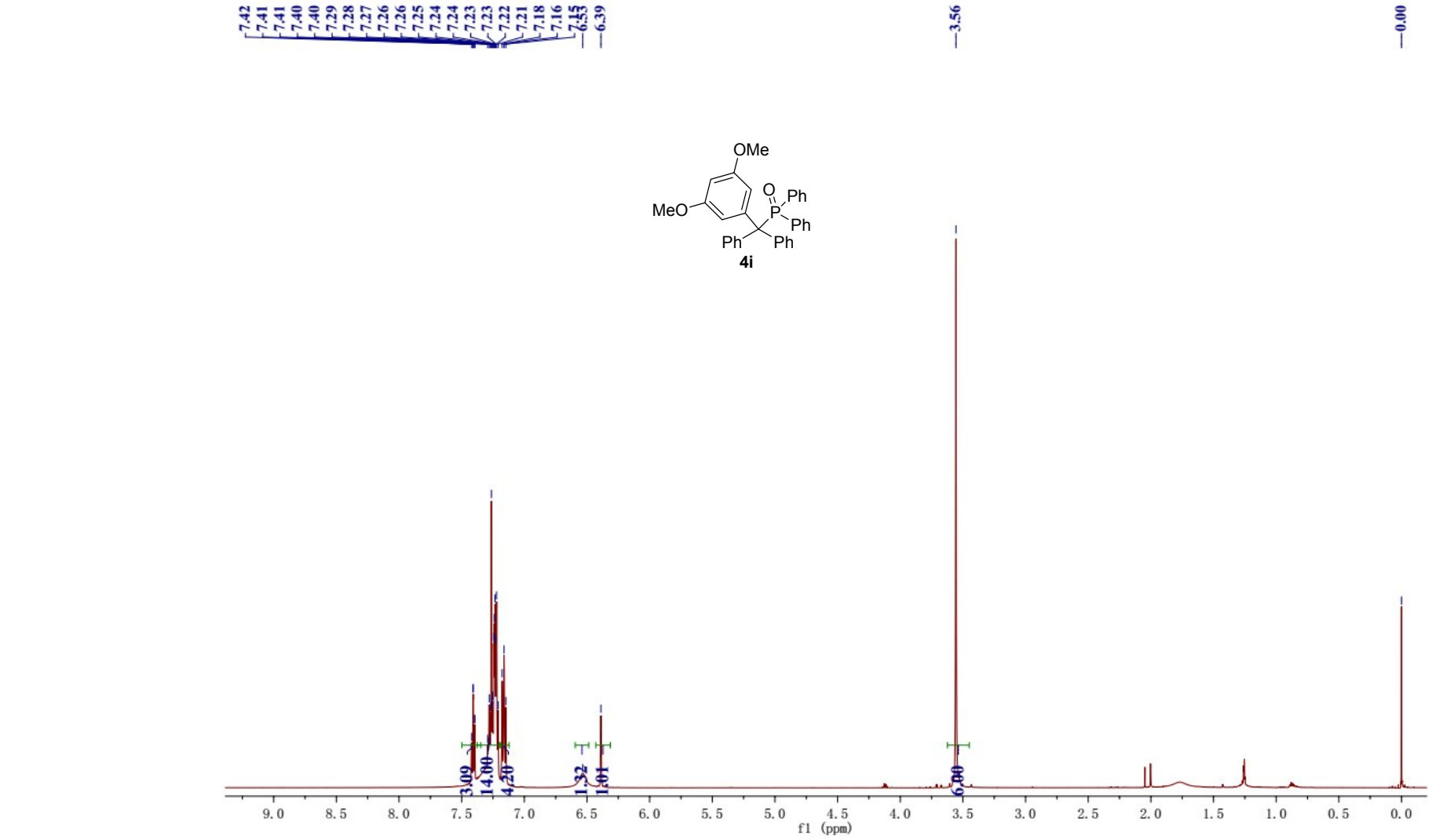

1.00
4.23
12.02
2.24
2.22
2.28
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

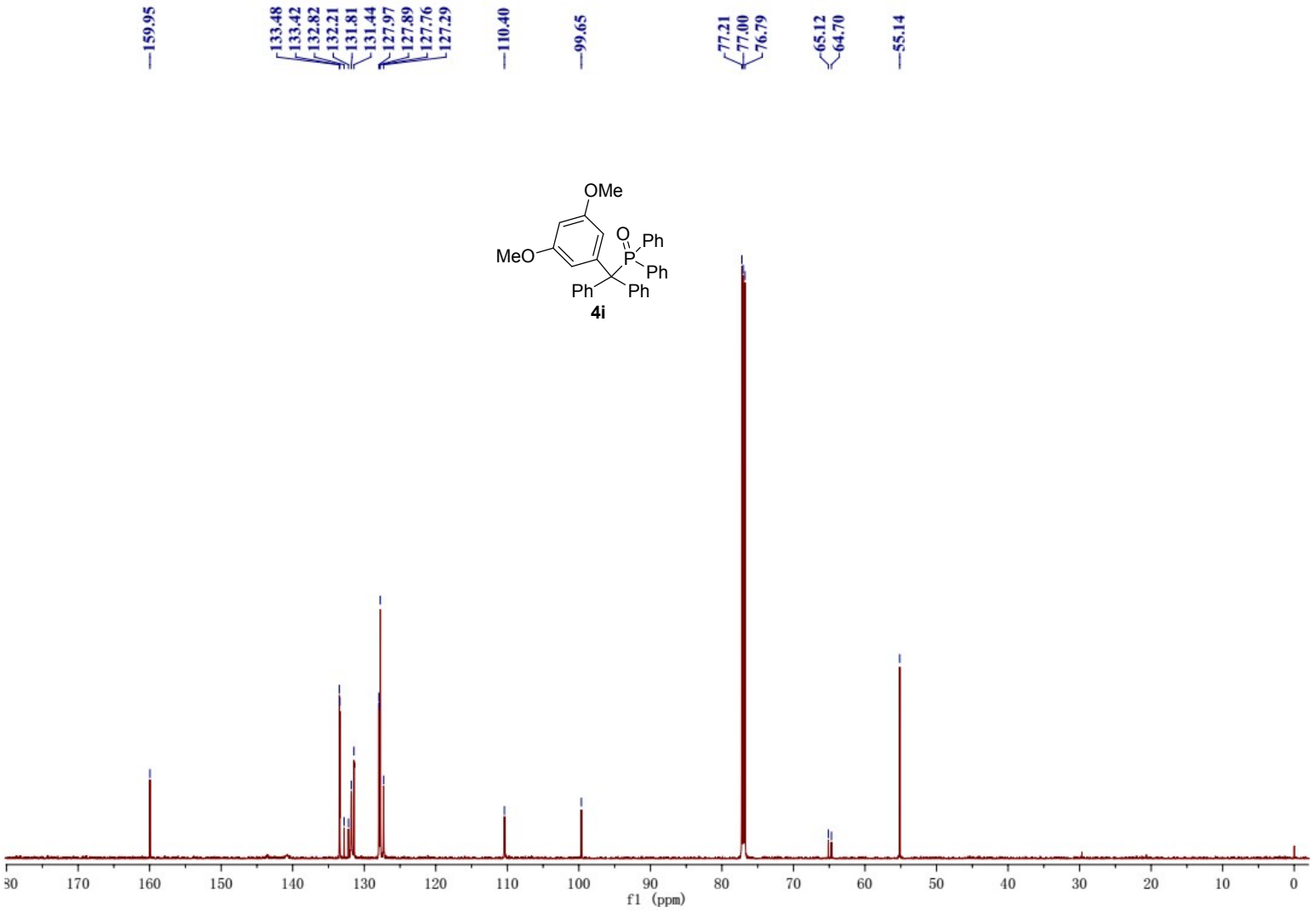

158.74
133.69
133.63
133.61
133.56
133.37
133.35
132.36
132.17
132.14
131.48
128.19
127.63
127.57
127.16
126.25
126.21
77.21
77.00
76.79
63.53
63.12
55.23
140.97
136.11
136.04
133.69
133.63
133.61
133.56
133.37
133.35
132.36
132.26
132.20
132.17
132.14
131.48
128.19
127.69
127.63
127.57
127.33
127.16
126.25
f1 (ppm)
f1 (ppm)

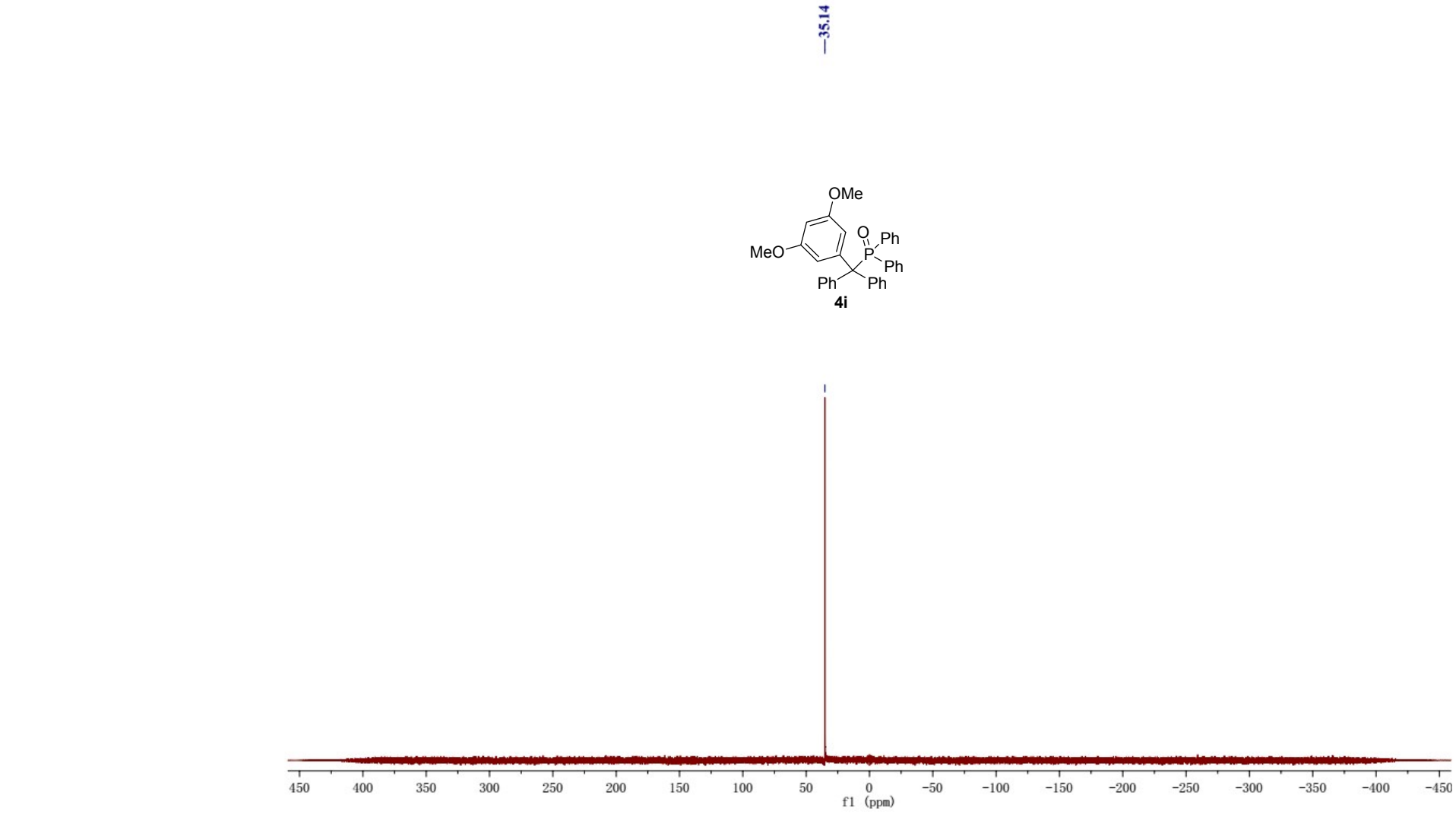
O
Ph
P
Ph
Cl
OMe

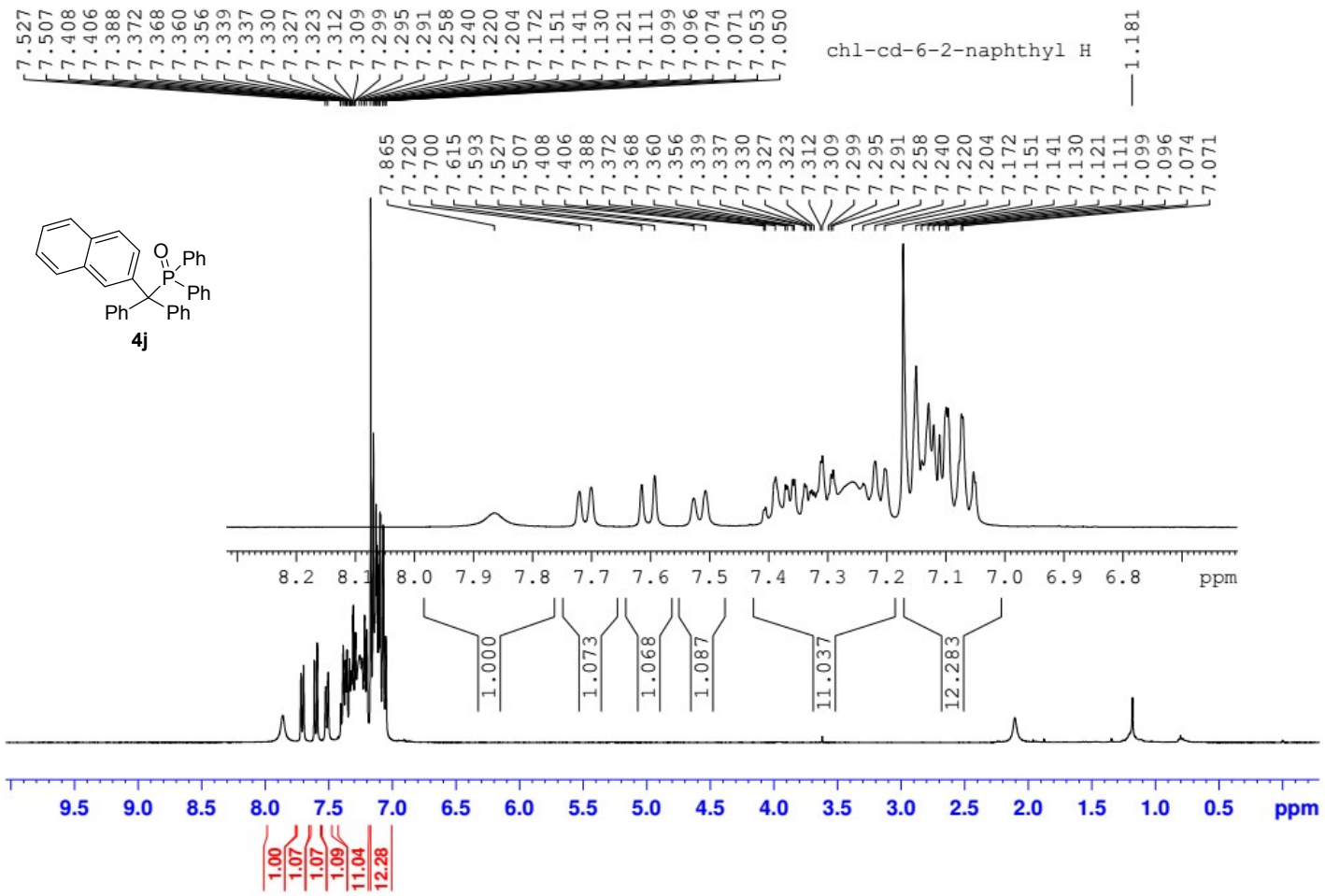
4h

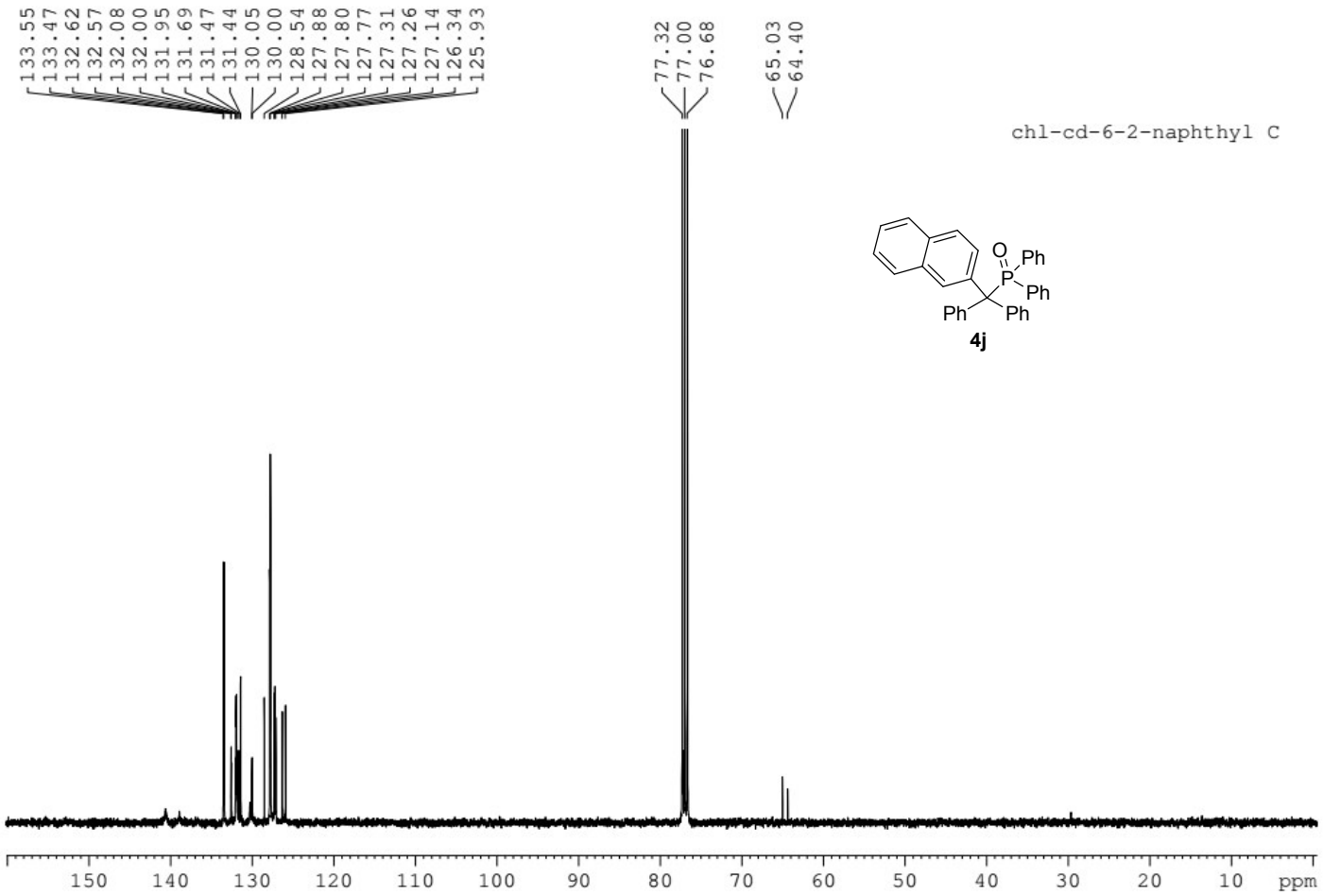

36.11
O
Ph
P
Ph
Cl
OMe
4h
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

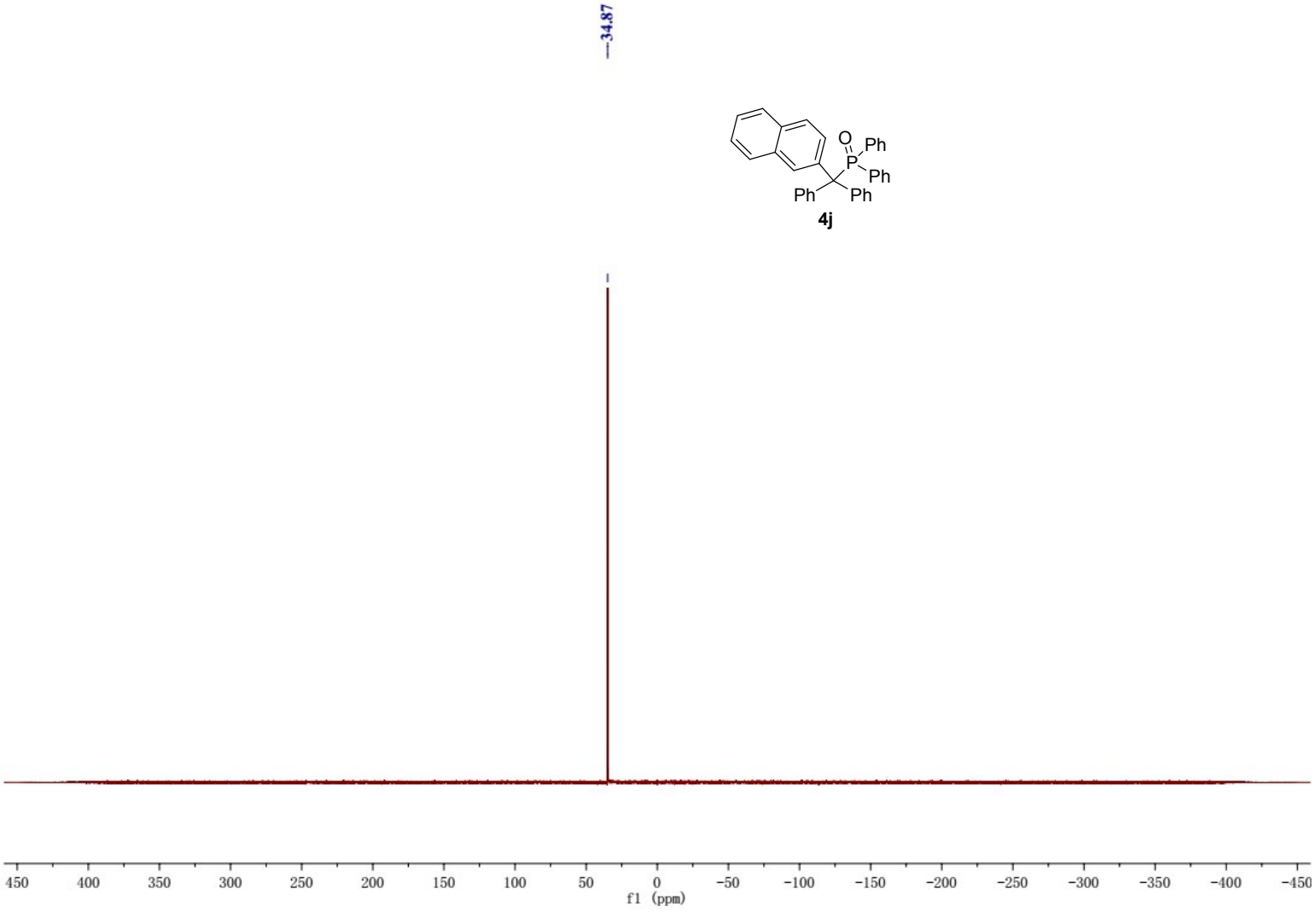

7.42
7.41
7.41
7.40
7.40
7.29
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.18
7.16
7.15
6.53
6.39
3.56
0.00
OMe
MeO
O
P
Ph
Ph
Ph
Ph
4i
3.09
14.00
4.20
1.32
1.01
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

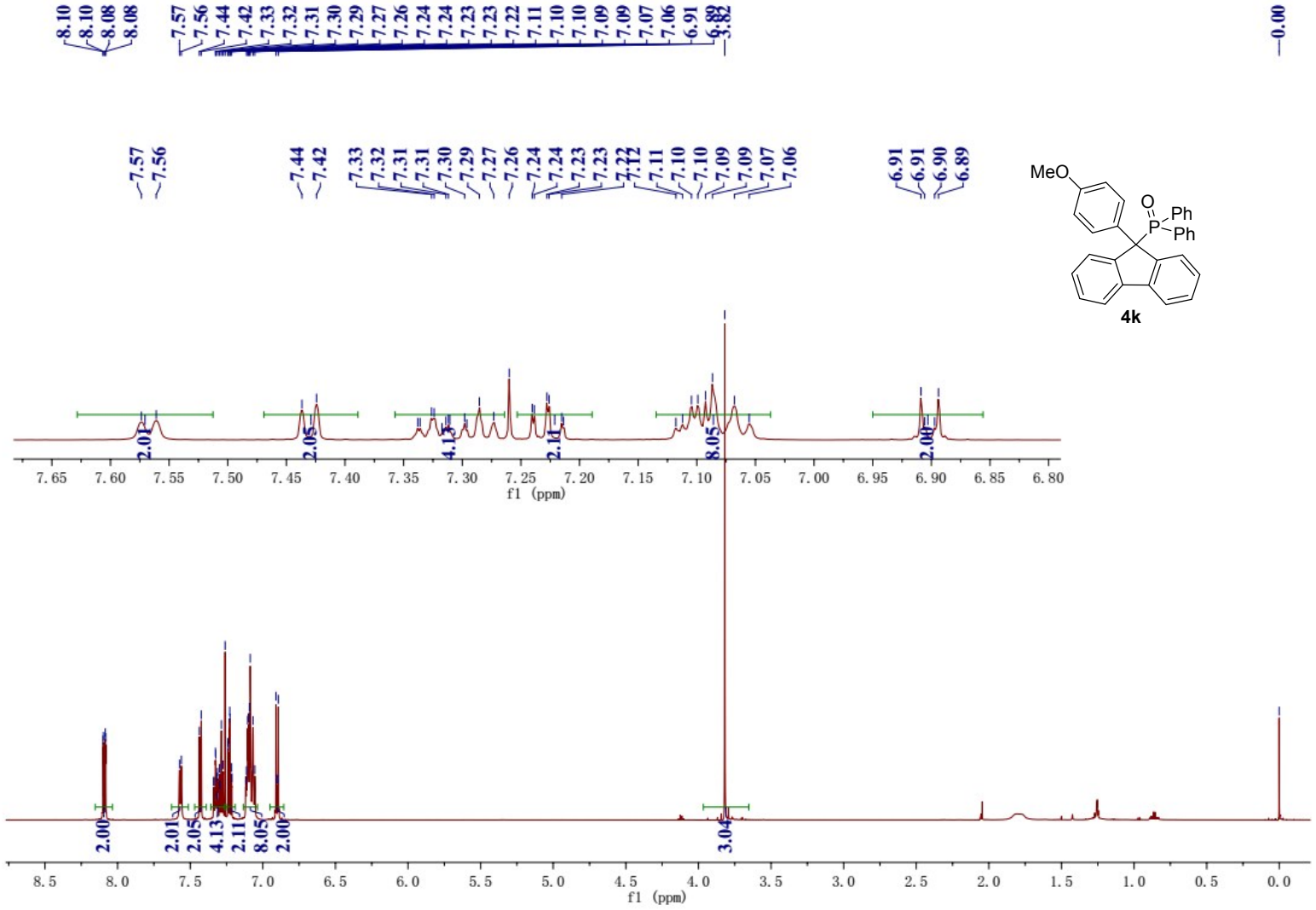

159.95
133.48
133.42
132.82
132.21
131.81
131.44
127.97
127.89
127.76
127.29
110.40
99.65
77.21
77.00
76.79
65.12
64.70
55.14
OMe
MeO
O
P
Ph
Ph
Ph
Ph
4i
f1 (ppm)

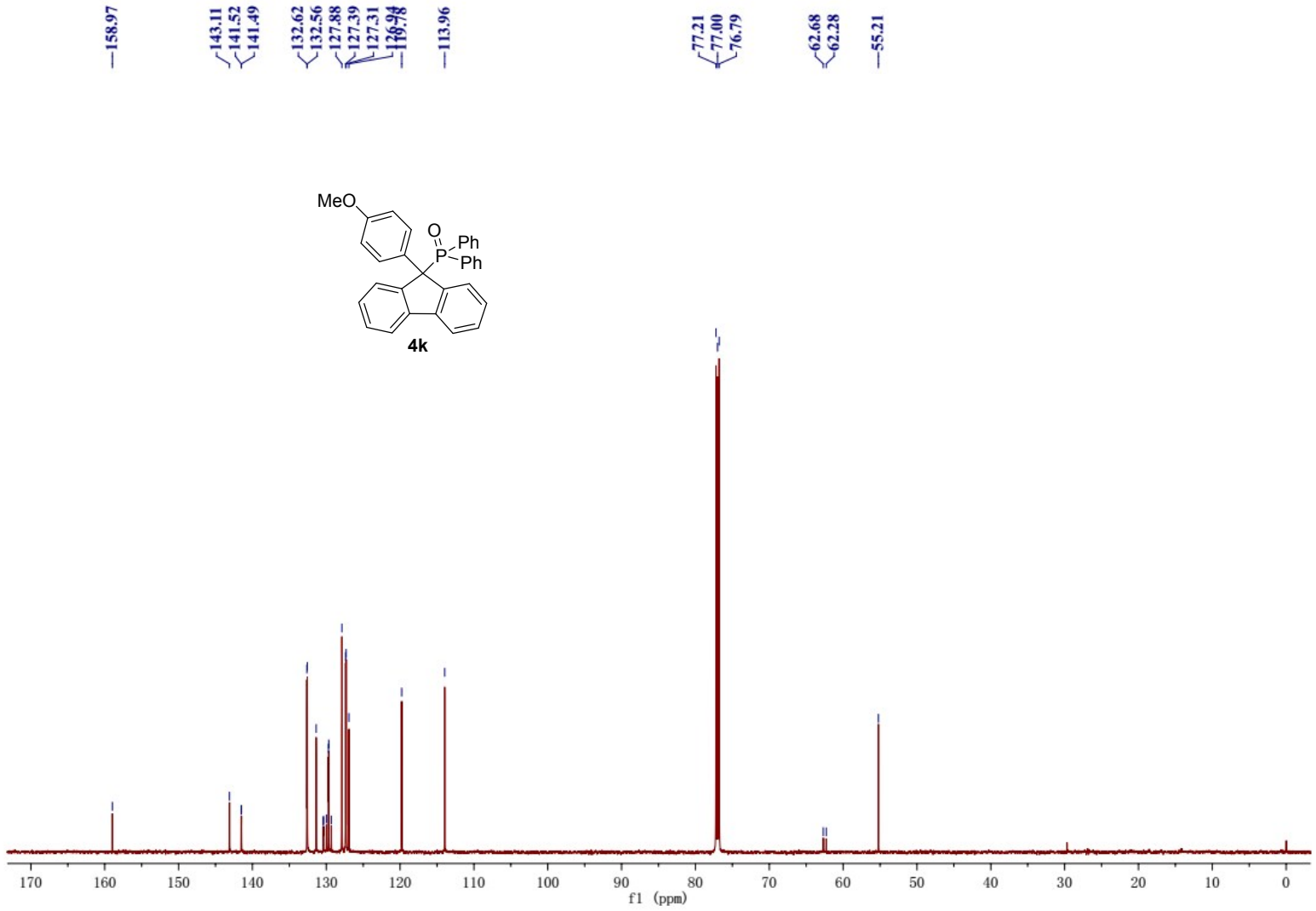

35.14
OMe
MeO
O
P
Ph
Ph
Ph
Ph
4i
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

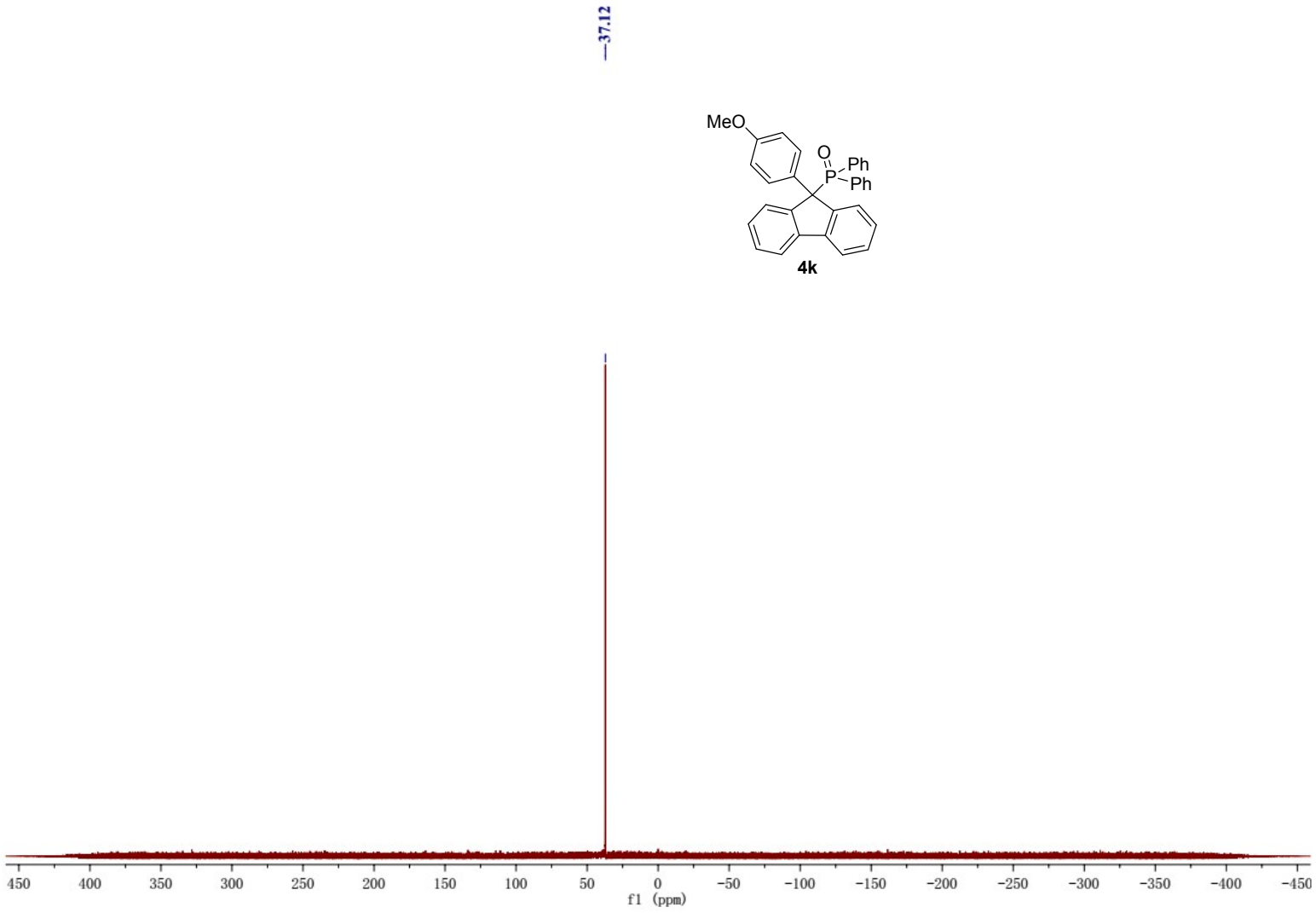

7.527
7.507
7.408
7.406
7.388
7.372
7.368
7.360
7.356
7.339
7.337
7.330
7.327
7.323
7.312
7.309
7.299
7.295
7.291
7.258
7.240
7.220
7.204
7.172
7.151
7.141
7.130
7.121
7.111
7.099
7.096
7.074
7.071
7.053
7.050
chl-cd-6-2-naphthyl H
1.181
7.865
7.720
7.700
7.615
7.593
7.527
7.507
7.408
7.406
7.388
7.372
7.368
7.360
7.356
7.339
7.337
7.330
7.327
7.323
7.312
7.309
7.299
7.295
7.291
7.258
7.240
7.220
7.204
7.172
7.151
7.141
7.130
7.121
7.111
7.099
7.096
7.074
7.071
O
P
Ph
Ph
Ph
Ph
4j
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
ppm
1.000
1.073
1.068
1.087
11.037
12.283
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.07
1.07
1.09
11.04
12.28

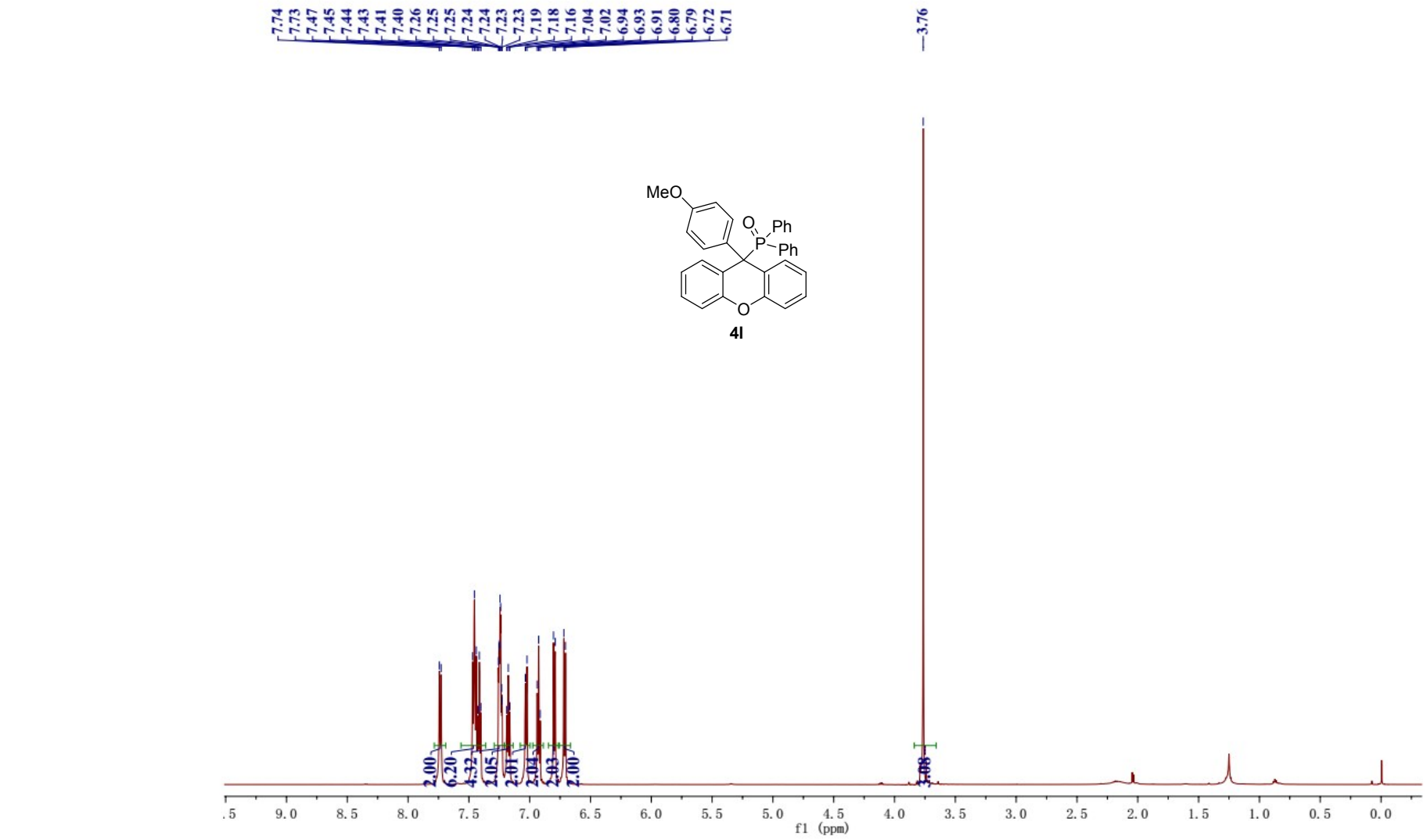

133.55
133.47
132.62
132.57
132.08
132.00
131.95
131.69
131.47
131.44
130.05
130.00
128.54
127.88
127.80
127.77
127.31
127.26
127.14
126.34
125.93
77.32
77.00
76.68
65.03
64.40
chl-cd-6-2-naphthyl C
O
Ph
P
Ph
Ph
Ph
4j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

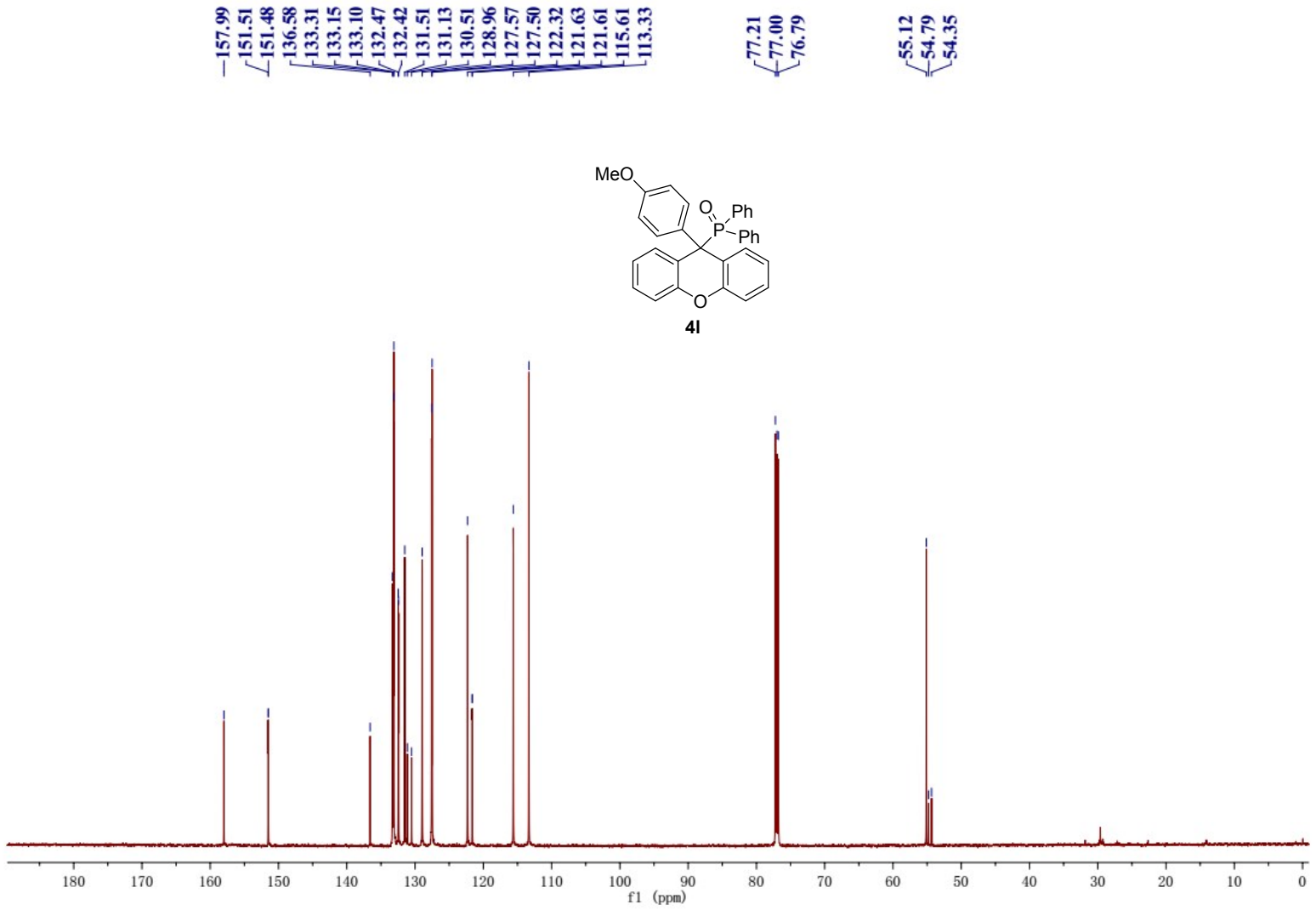

34.87
O
Ph
P
Ph
Ph
Ph
4j
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

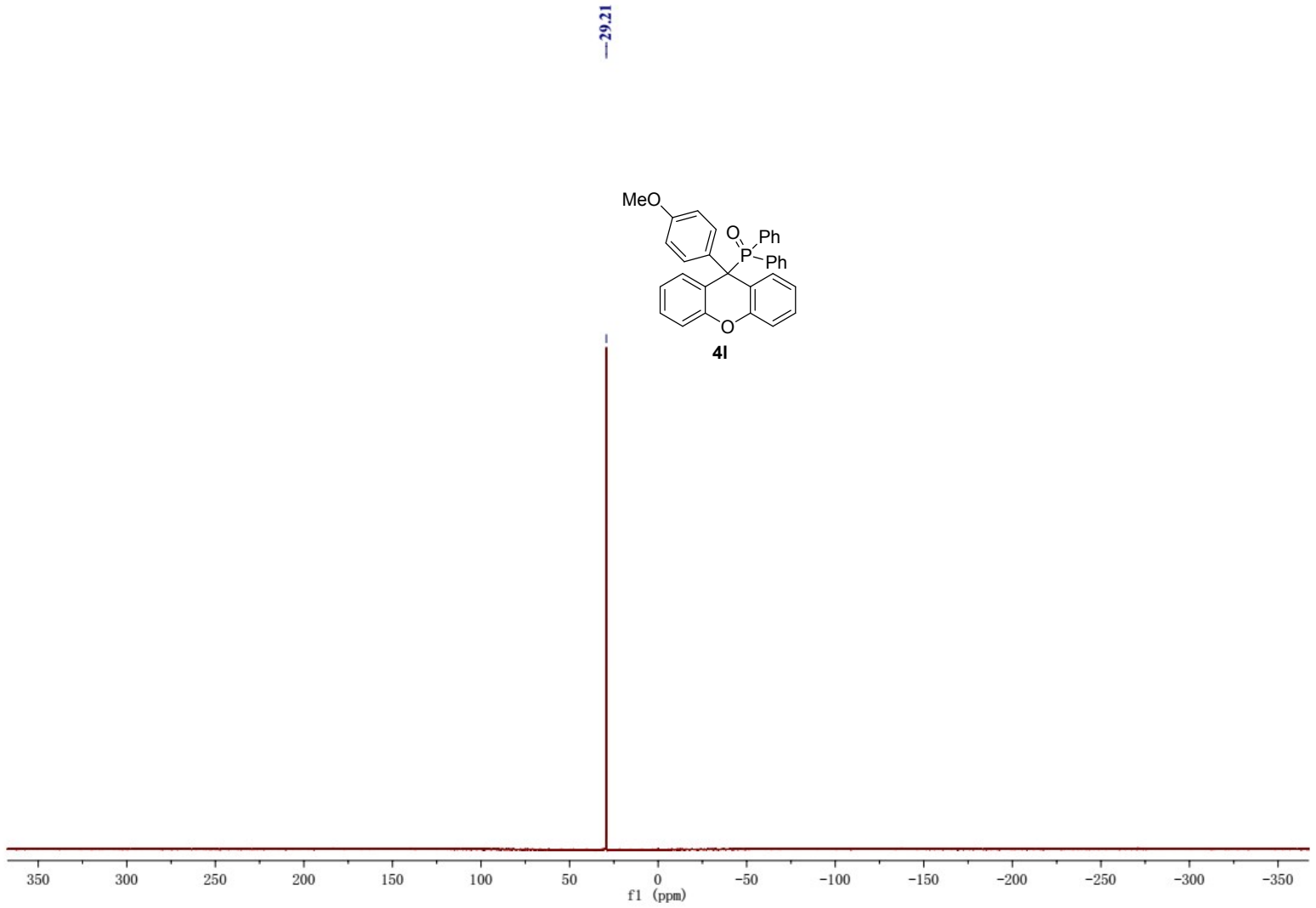

8.10
8.10
8.08
8.08
7.57
7.56
7.44
7.42
7.33
7.32
7.31
7.30
7.29
7.27
7.26
7.24
7.24
7.23
7.23
7.22
7.11
7.10
7.10
7.09
7.09
7.07
7.06
6.91
6.82
3.82
0.00
MeO
O
P
Ph
Ph
4k
f1 (ppm)
f1 (ppm)

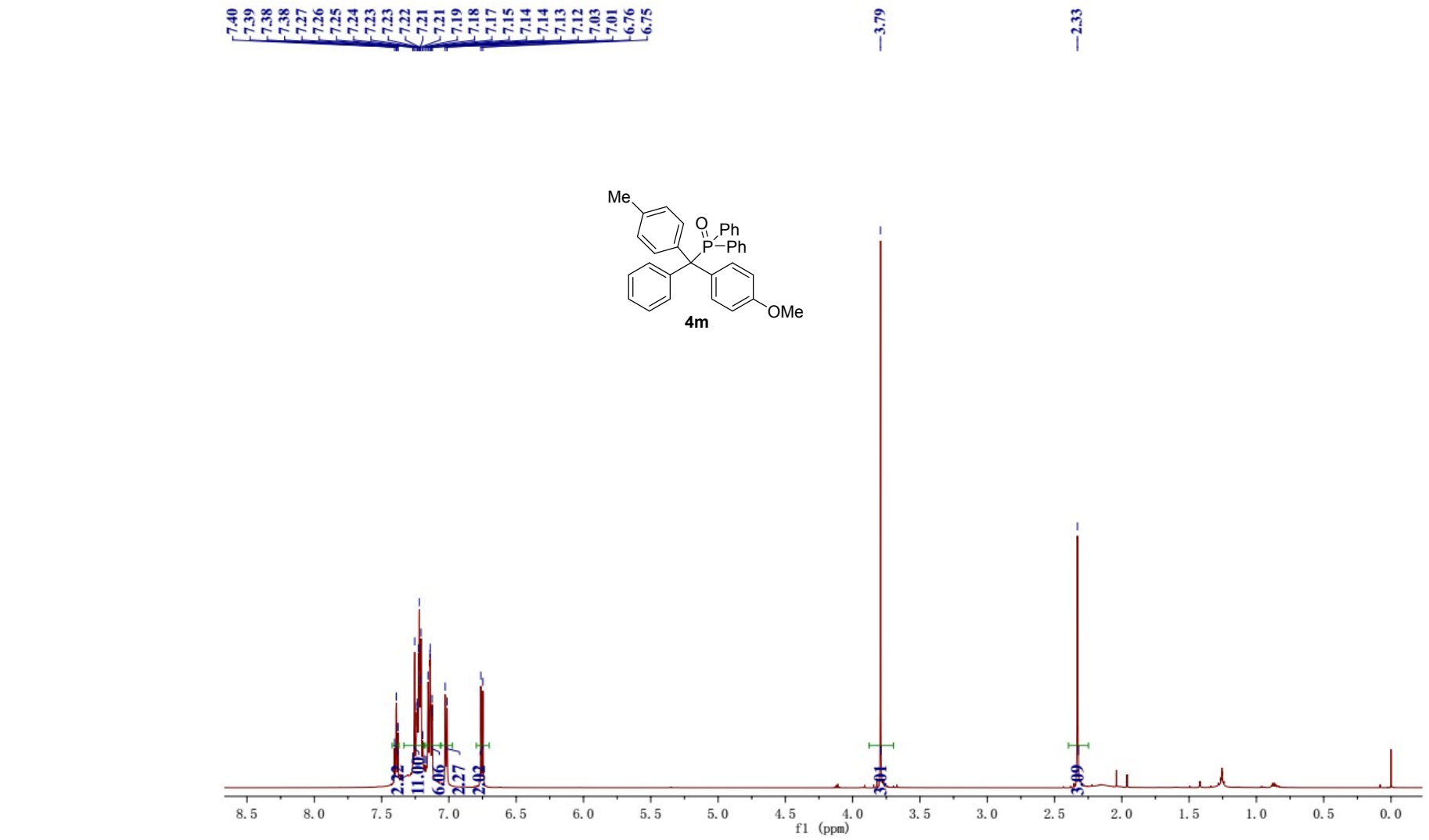

158.97
143.11
141.52
141.49
132.62
132.56
127.88
127.39
127.31
113.96
77.21
77.00
76.79
62.68
62.28
55.21
MeO
O
P
Ph
Ph
4k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

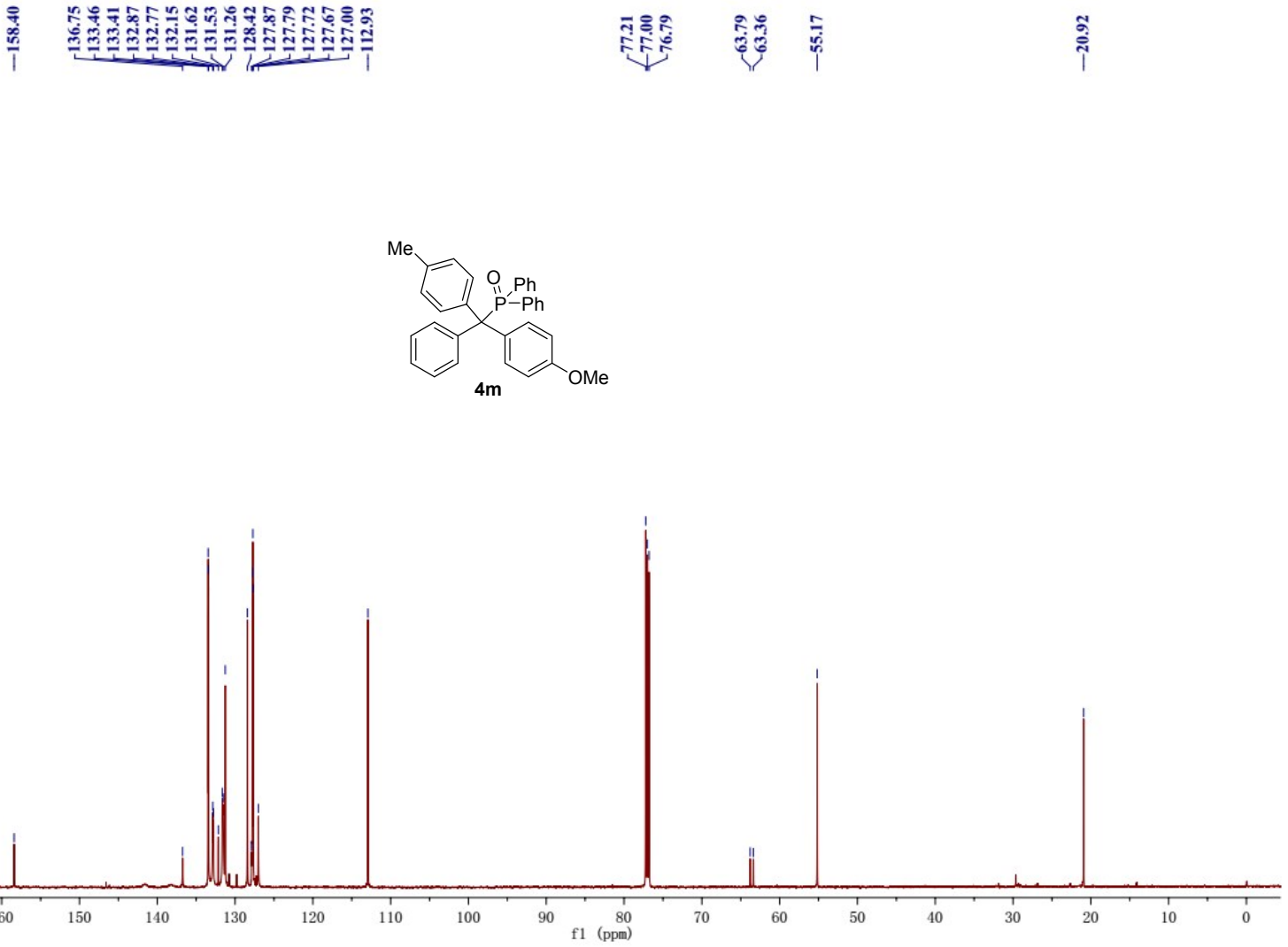

37.12
MeO
O
P
Ph
Ph
4k
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

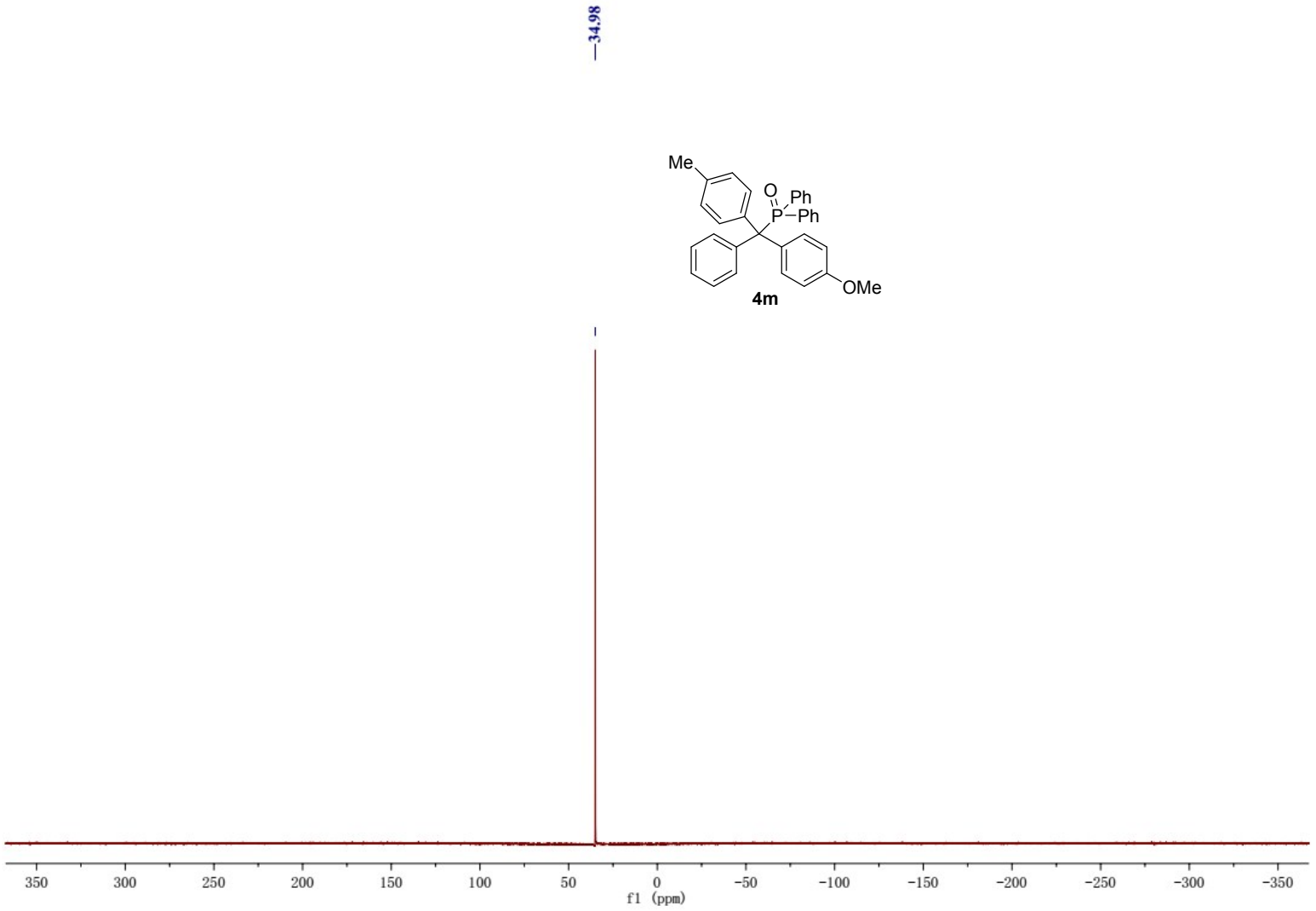

7.74
7.73
7.47
7.45
7.44
7.43
7.41
7.40
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.19
7.18
7.16
7.04
7.02
6.94
6.93
6.91
6.80
6.79
6.72
6.71
3.76
MeO
O
P
Ph
Ph
O
4l
2.00
6.20
4.32
1.05
2.01
2.04
2.03
2.00
3.08
f1 (ppm)

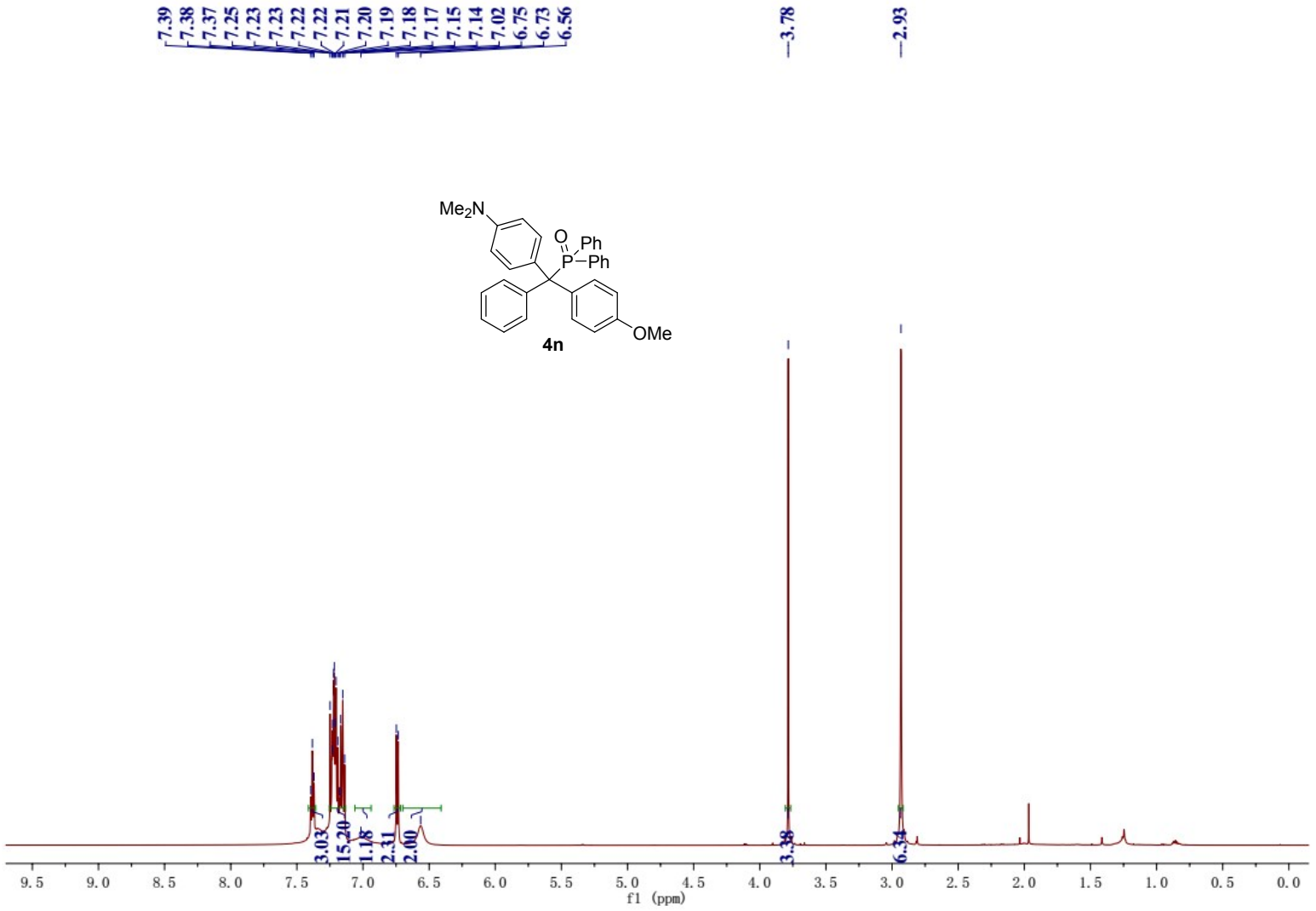

157.99
151.51
151.48
136.58
133.31
133.15
133.10
132.47
132.42
131.51
131.13
130.51
128.96
127.57
127.50
122.32
121.63
121.61
115.61
113.33
77.21
77.00
76.79
55.12
54.79
54.35
MeO
O
P
Ph
Ph
O
4l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

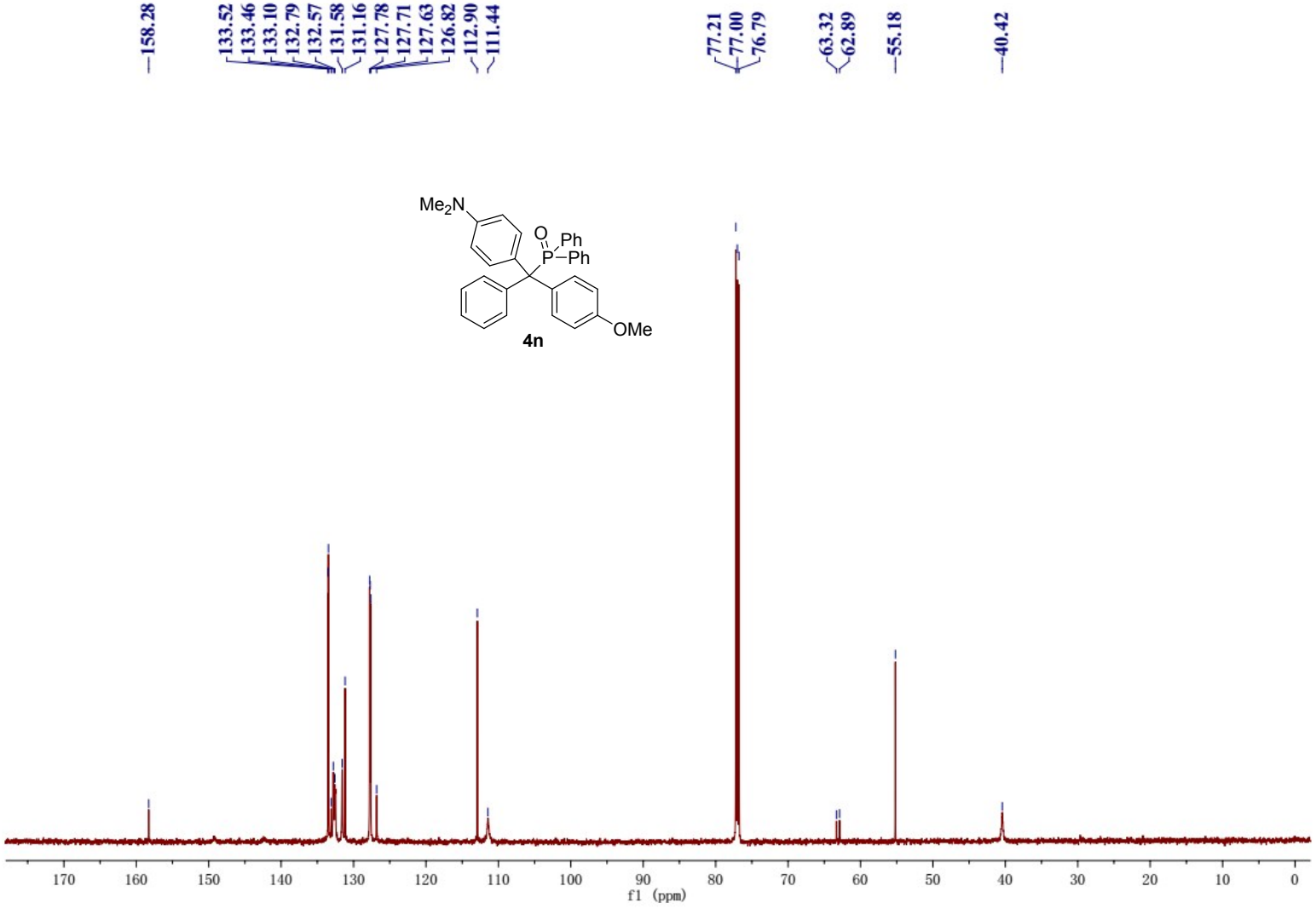

29.21
MeO
O
Ph
P
Ph
O
4l
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

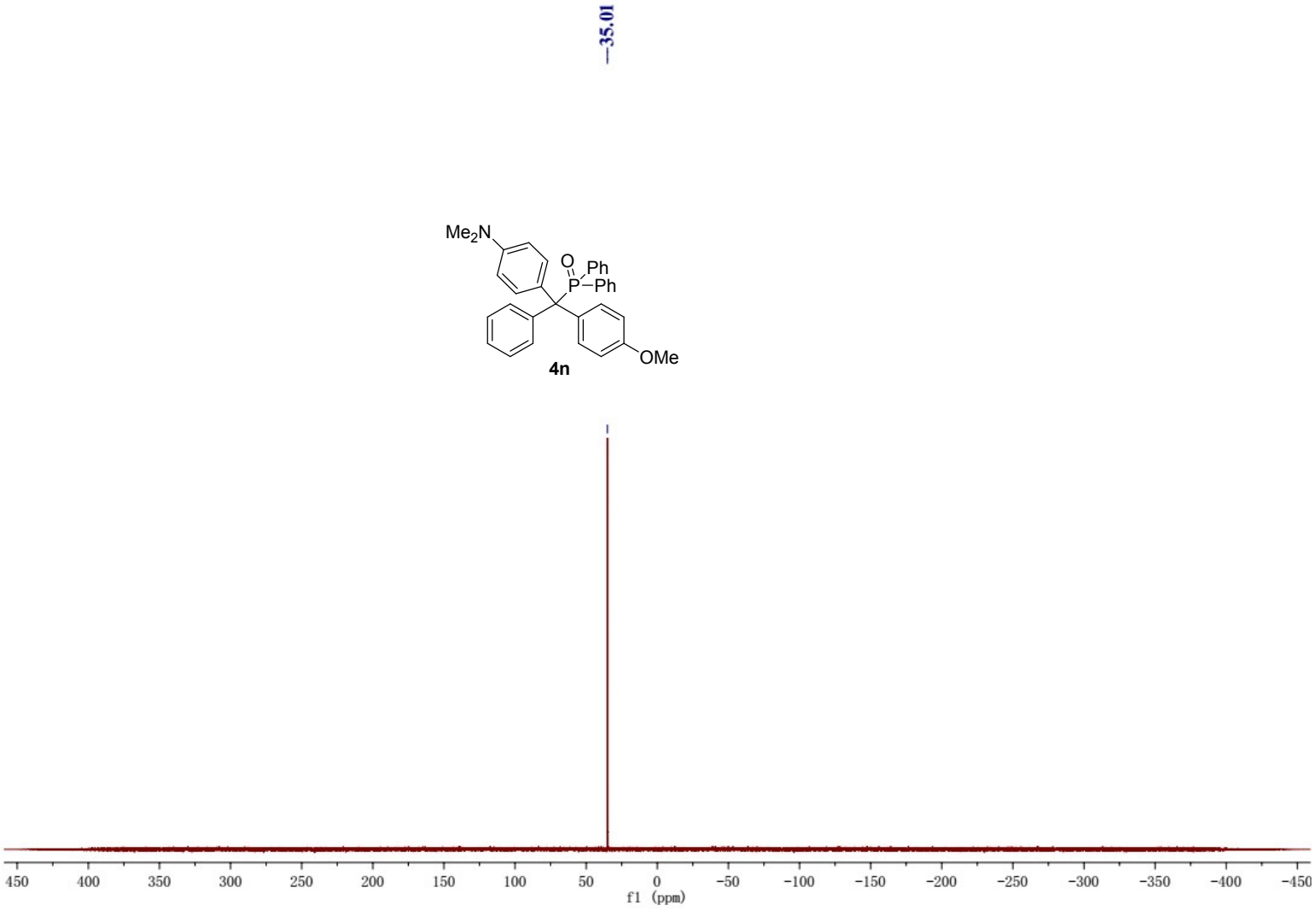

7.40
7.39
7.38
7.38
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.19
7.18
7.17
7.15
7.14
7.14
7.13
7.12
7.03
7.01
6.76
6.75
3.79
2.33
Me
O
Ph
P
Ph
OMe
4m
2.22
11.00
6.06
2.27
2.02
3.01
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

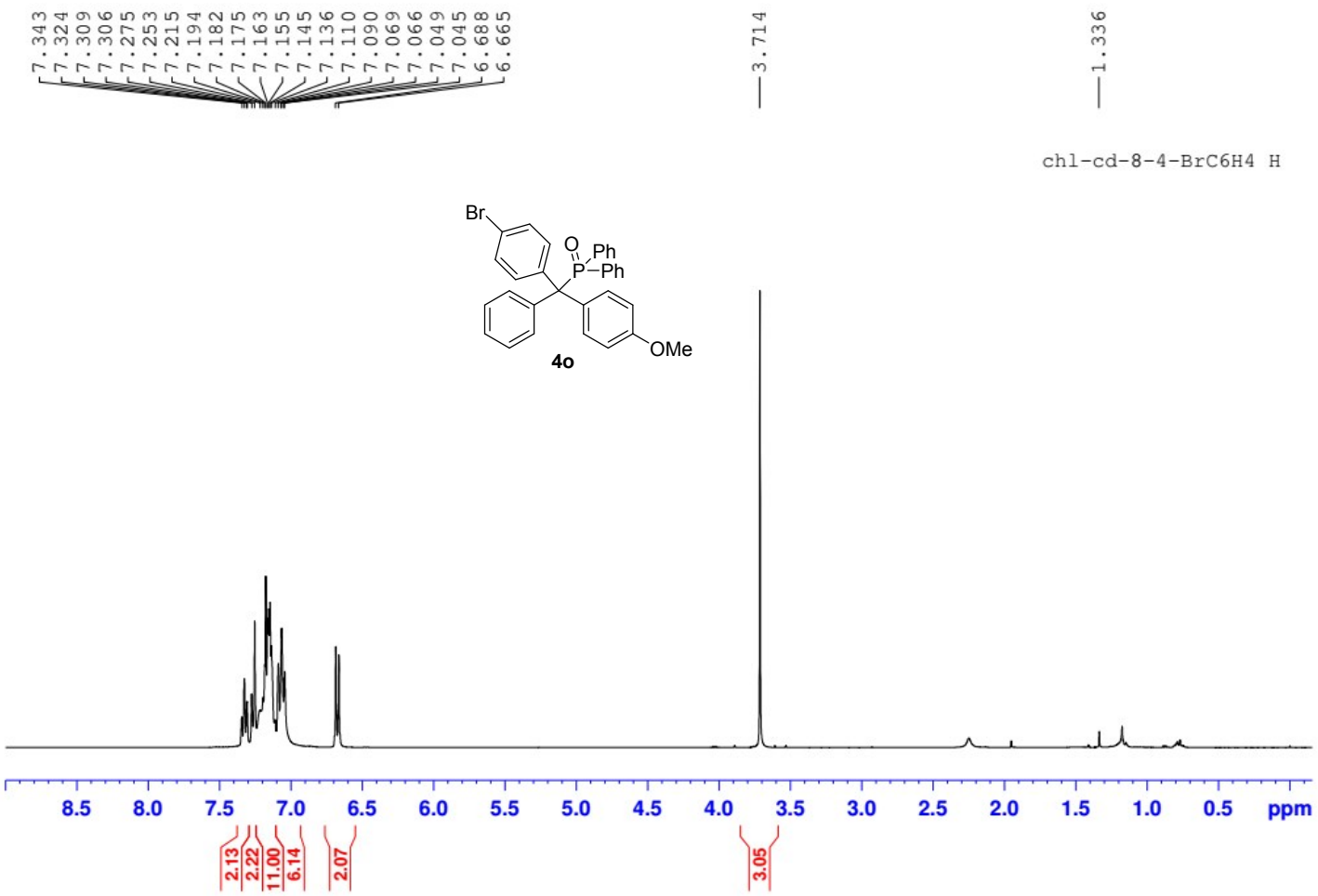

158.40
136.75
133.46
133.41
132.87
132.77
132.15
131.62
131.53
131.26
128.42
127.87
127.79
127.72
127.67
127.00
112.93
77.21
77.00
76.79
63.79
63.36
55.17
20.92
Me
O
Ph
P
Ph
OMe
4m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

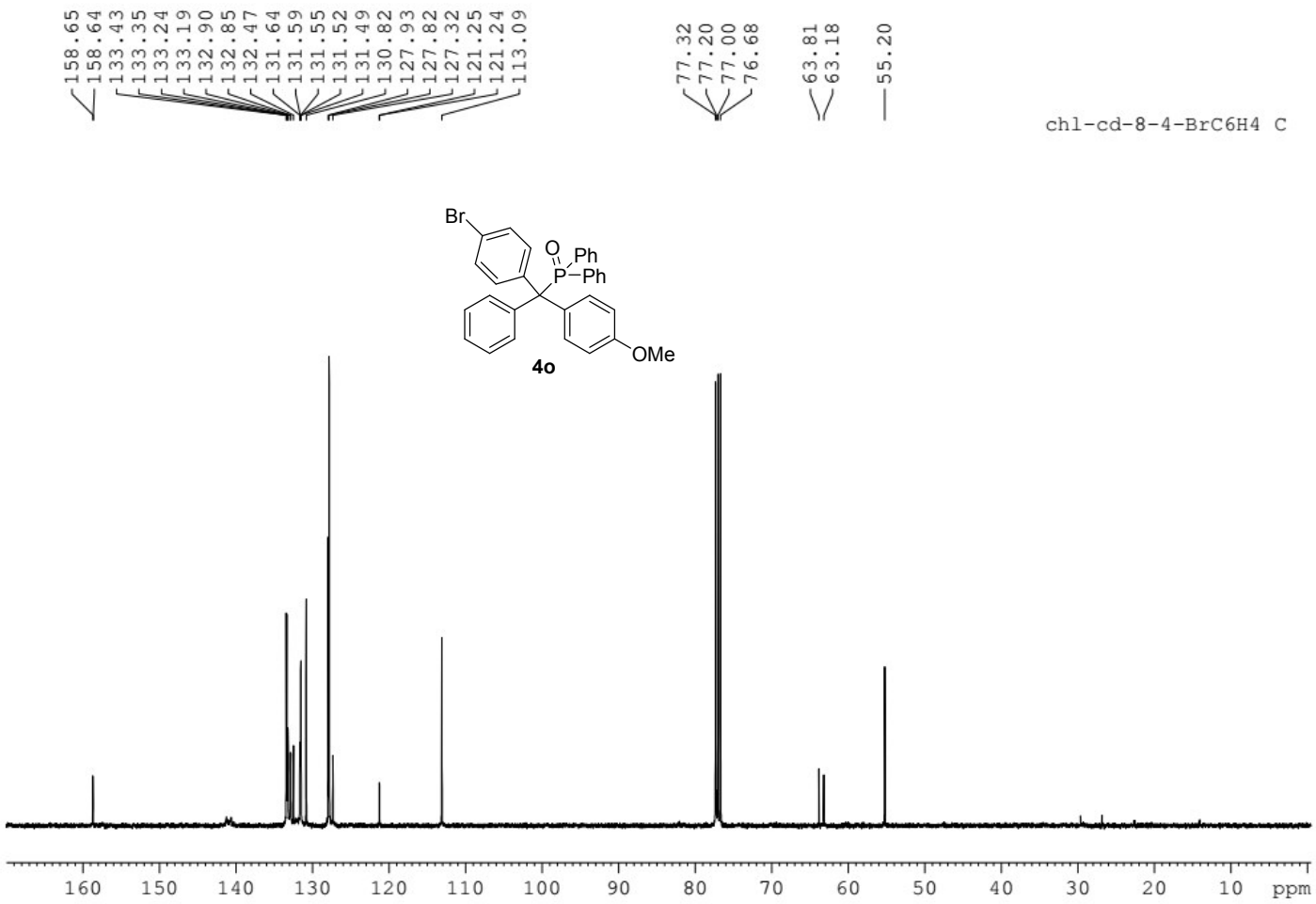

34.98
Me
O
Ph
P
Ph
OMe
4m
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

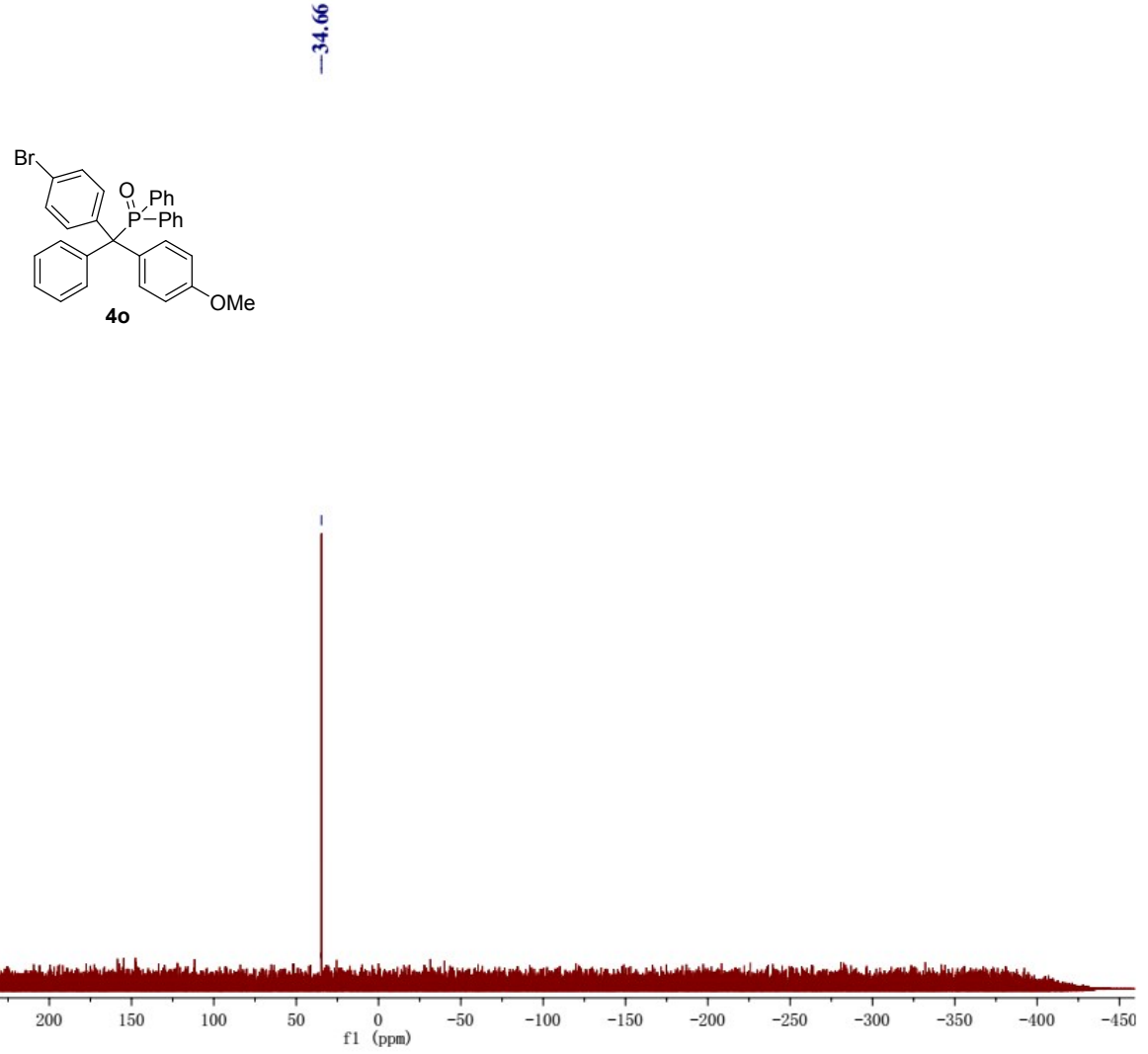

7.39
7.38
7.37
7.25
7.23
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.17
7.15
7.14
7.02
6.75
6.73
6.56
3.78
2.93
Me2N
O
Ph
P
Ph
OMe
4n
3.03
15.20
1.18
2.31
2.00
3.38
6.34
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

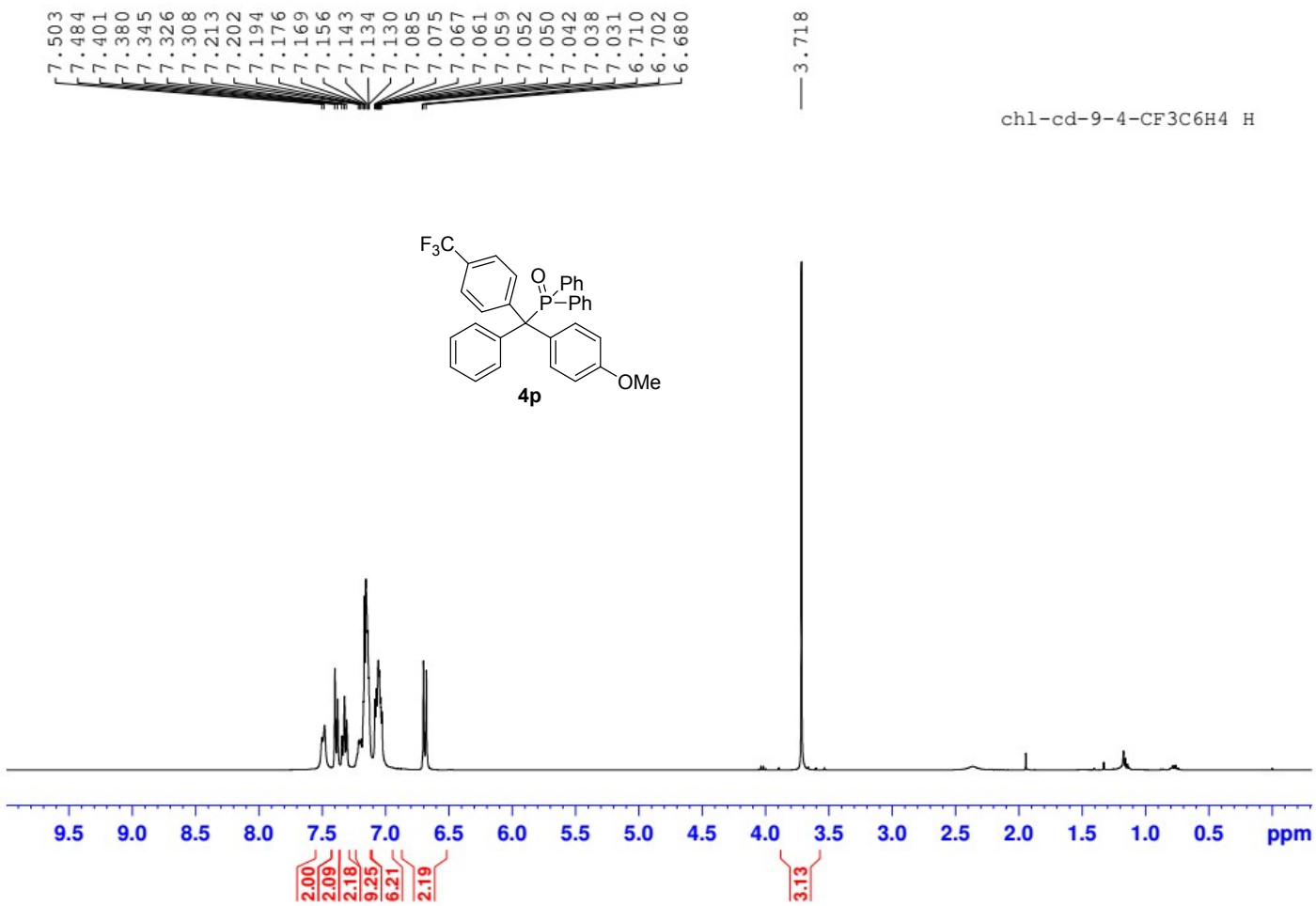

158.28
133.52
133.46
133.10
132.79
132.57
131.58
131.16
127.78
127.71
127.63
126.82
112.90
111.44
77.21
77.00
76.79
63.32
62.89
55.18
40.42
Me2N
O
Ph
P
Ph
OMe
4n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

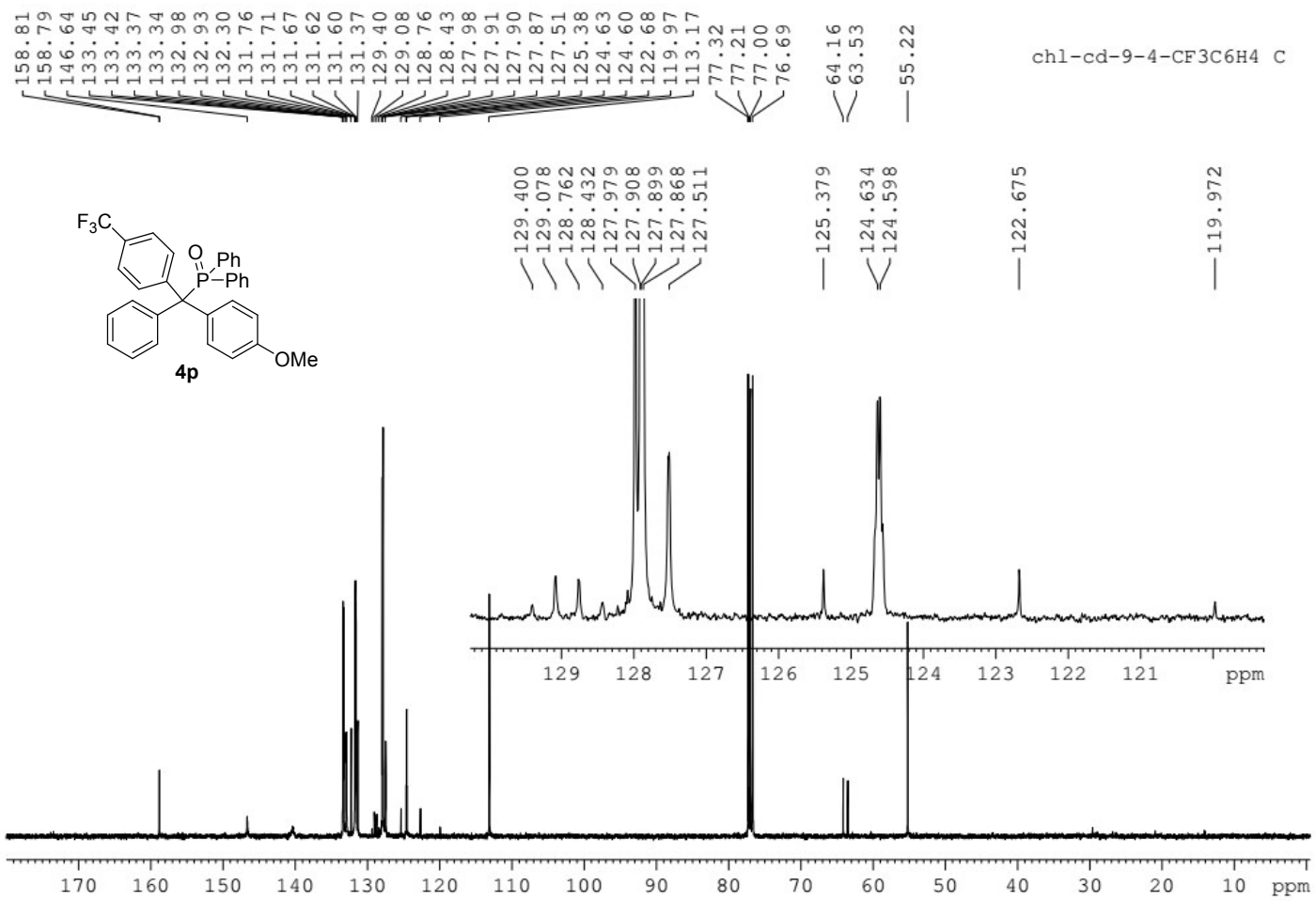

35.01
Me2N
O
Ph
P
Ph
OMe
4n
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)

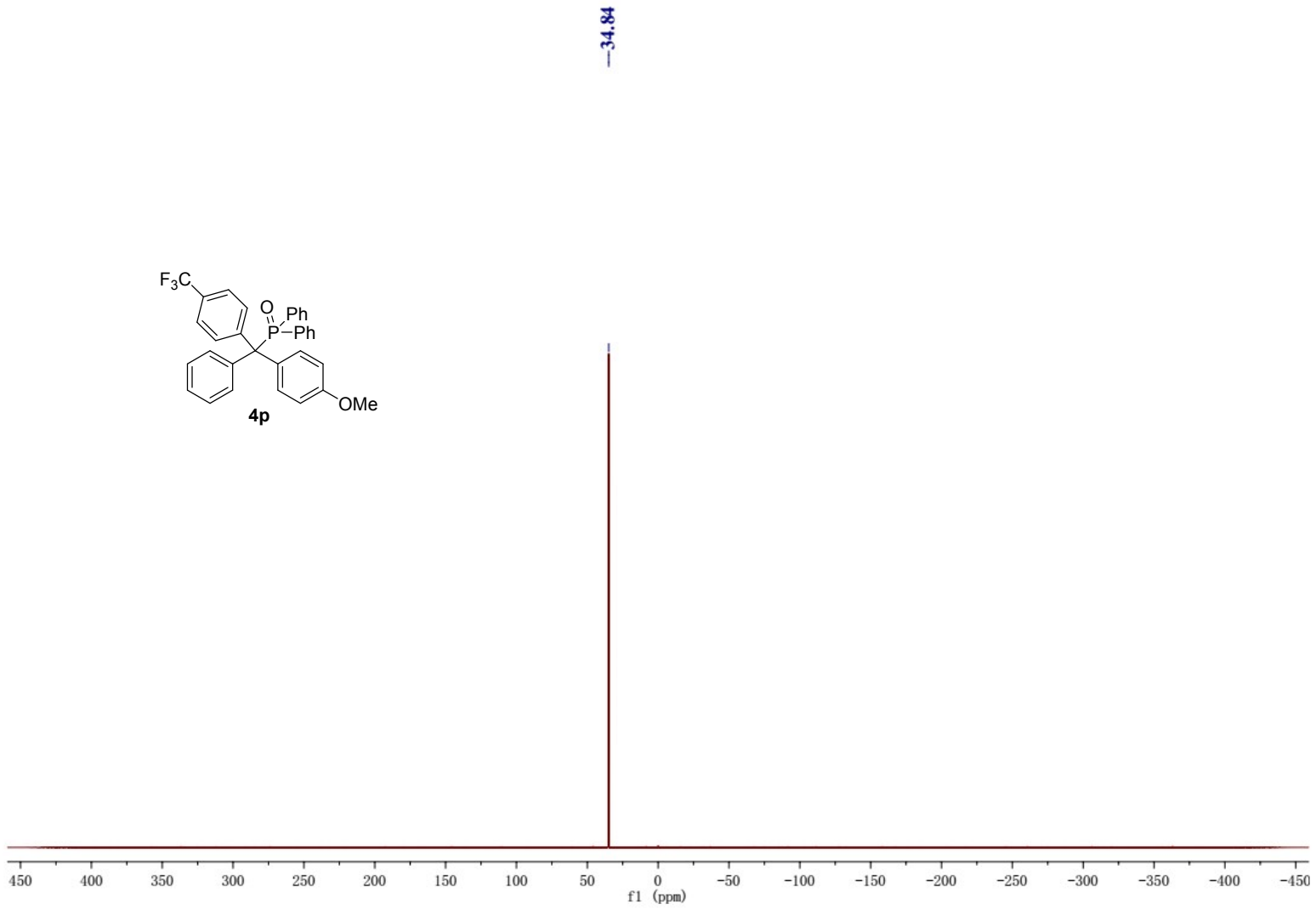

7.343
7.324
7.309
7.306
7.275
7.253
7.215
7.194
7.182
7.175
7.163
7.155
7.145
7.136
7.110
7.090
7.069
7.066
7.049
7.045
6.688
6.665
3.714
1.336
chl-cd-8-4-BrC6H4 H
Br
O
Ph
P
Ph
OMe
4o
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.13
2.22
11.00
6.14
2.07
3.05

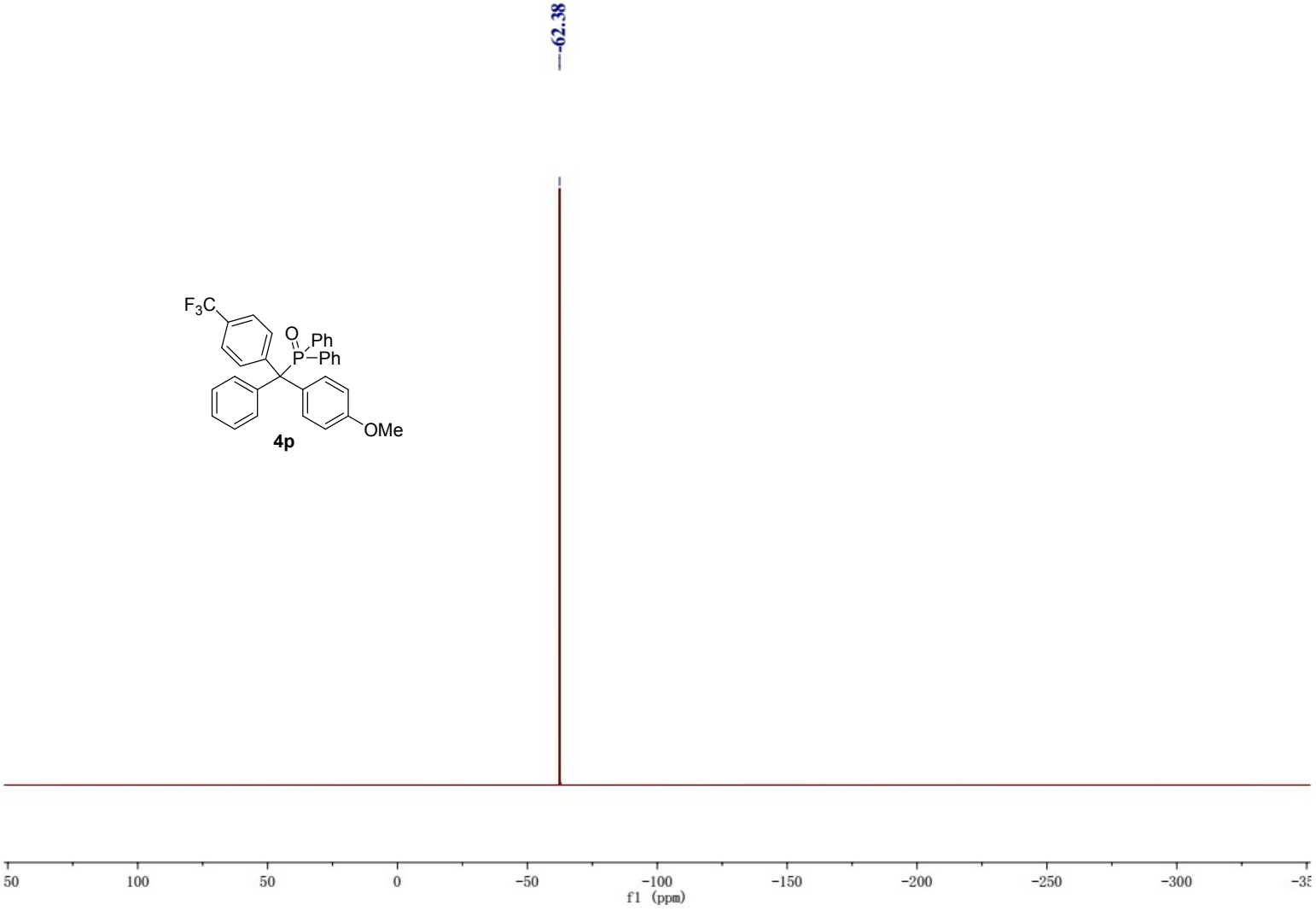

158.65
158.64
133.43
133.35
133.24
133.19
132.90
132.85
132.47
131.64
131.59
131.55
131.52
131.49
130.82
127.93
127.82
127.32
121.25
121.24
113.09
77.32
77.20
77.00
76.68
63.81
63.18
55.20
chl-cd-8-4-BrC6H4 C
Br
O
Ph
P
Ph
OMe
4o
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

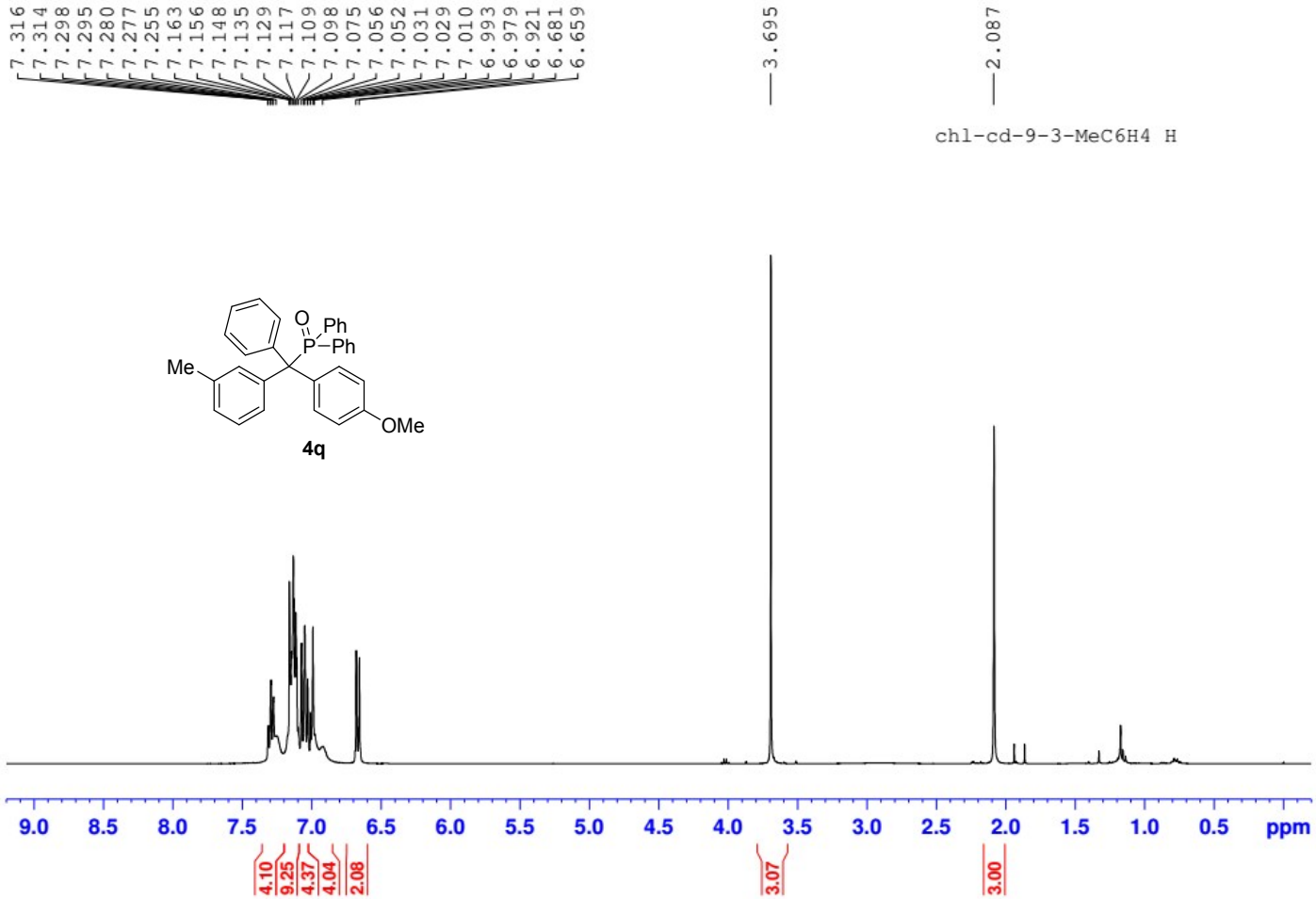

34.66
Br
O
Ph
P
Ph
OMe
4o
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
−250
−300
−350
−400
−450
f1 (ppm)

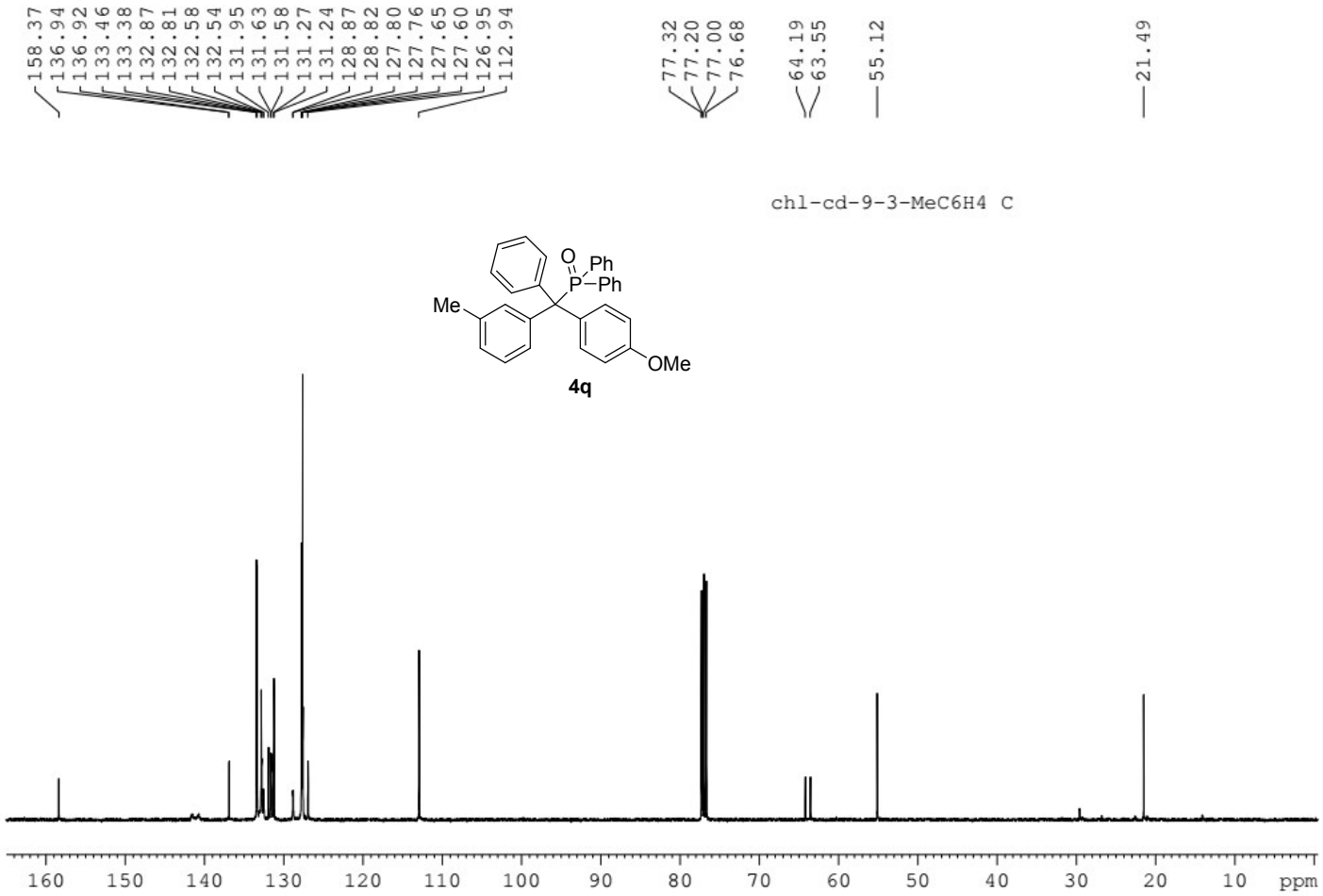

7.503
7.484
7.401
7.380
7.345
7.326
7.308
7.213
7.202
7.194
7.176
7.169
7.156
7.143
7.134
7.130
7.085
7.075
7.067
7.061
7.059
7.052
7.050
7.042
7.038
7.031
6.710
6.702
6.680
3.718
chl-cd-9-4-CF3C6H4 H
F3C
O
Ph
P
Ph
OMe
4p
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.09
2.18
9.25
6.21
2.19
3.13

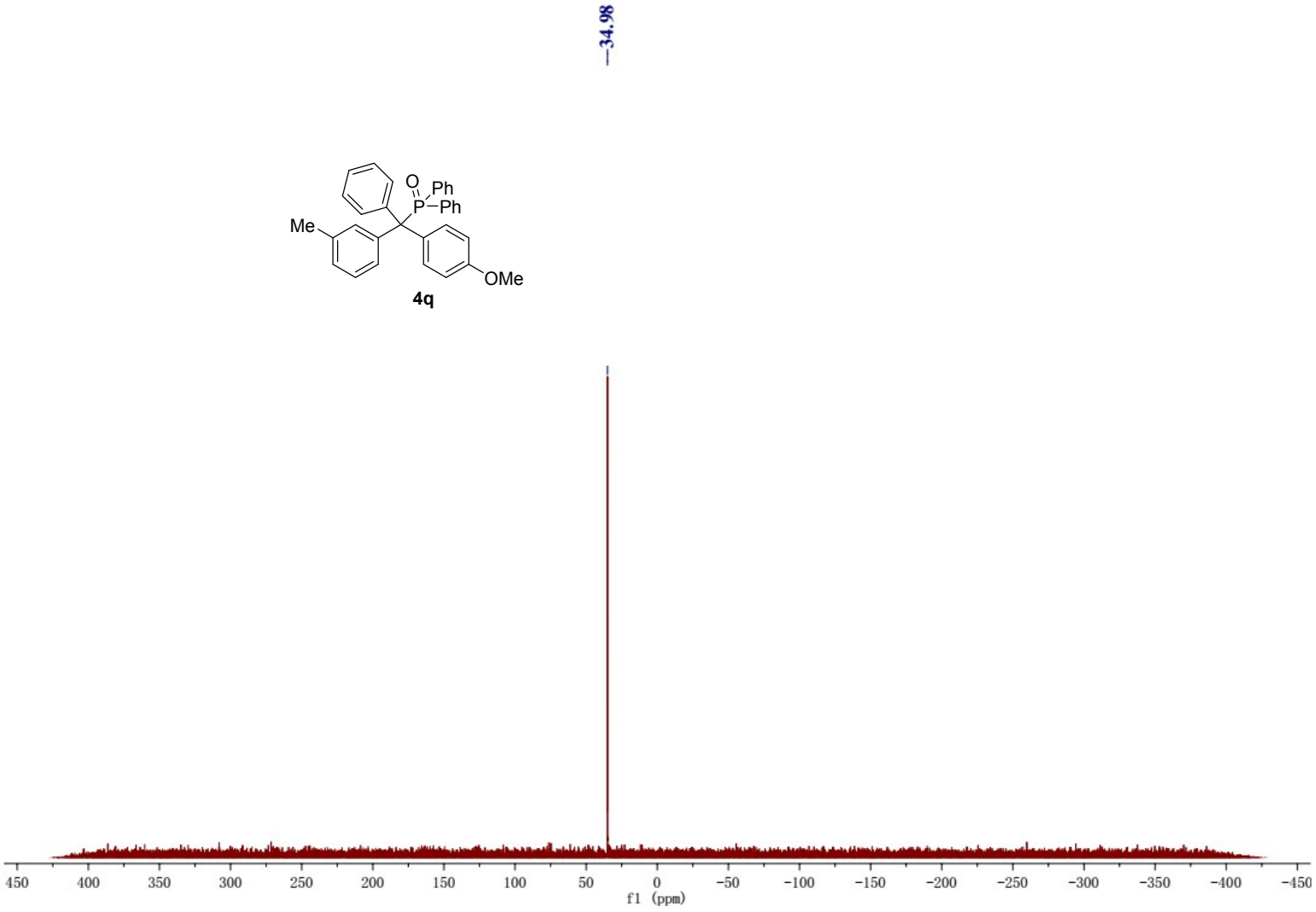

158.81
158.79
146.64
133.45
133.42
133.37
133.34
132.98
132.93
132.30
131.76
131.71
131.67
131.62
131.60
131.37
129.40
129.08
128.76
128.43
127.98
127.91
127.90
127.87
127.51
125.38
124.63
124.60
122.68
119.97
113.17
77.32
77.21
77.00
76.69
64.16
63.53
55.22
chl-cd-9-4-CF3C6H4 C
129.400
129.078
128.762
128.432
127.979
127.908
127.899
127.868
127.511
125.379
124.634
124.598
122.675
119.972
F3C
O
Ph
P
Ph
OMe
4p
129
128
127
126
125
124
123
122
121
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


34.84
F3C
O
Ph
P
Ph
OMe
4p
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)


-62.38
F3C
O
Ph
P
Ph
OMe
4p
50
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


7.316
7.314
7.298
7.295
7.280
7.277
7.255
7.163
7.156
7.148
7.135
7.129
7.117
7.109
7.098
7.075
7.056
7.052
7.031
7.029
7.010
6.993
6.979
6.921
6.681
6.659
3.695
2.087
ch1-cd-9-3-MeC6H4 H
O
Ph
P
Ph
Me
OMe
4q
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.10
9.25
4.37
4.04
2.08
3.07
3.00


158.37
136.94
136.92
133.46
133.38
132.87
132.81
132.58
132.54
131.95
131.63
131.58
131.27
131.24
128.87
128.82
127.80
127.76
127.65
127.60
126.95
112.94
77.32
77.20
77.00
76.68
64.19
63.55
55.12
21.49
chl-cd-9-3-MeC6H4 C
O
Ph
P
Ph
Me
OMe
4q
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


34.98
O
Ph
P
Ph
Me
OMe
4q
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
f1 (ppm)