Phosphoryl radical-initiated Atherton–Todd-type reaction under open air

Yingcong Ou,[a] Yuanting Huang,[a] Zhenlin He,[a] Guodian Yu,[a] Yanping Huo,[a] Xianwei Li,[a] Yang Gao,[a] and Qian Chen*[a,b]

[a]School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China

[b]Key Laboratory of Functional Molecular Engineering of Guangdong Province, South China University of Technology, Guangzhou 510640, China

*qianchen@gdut.edu.cn

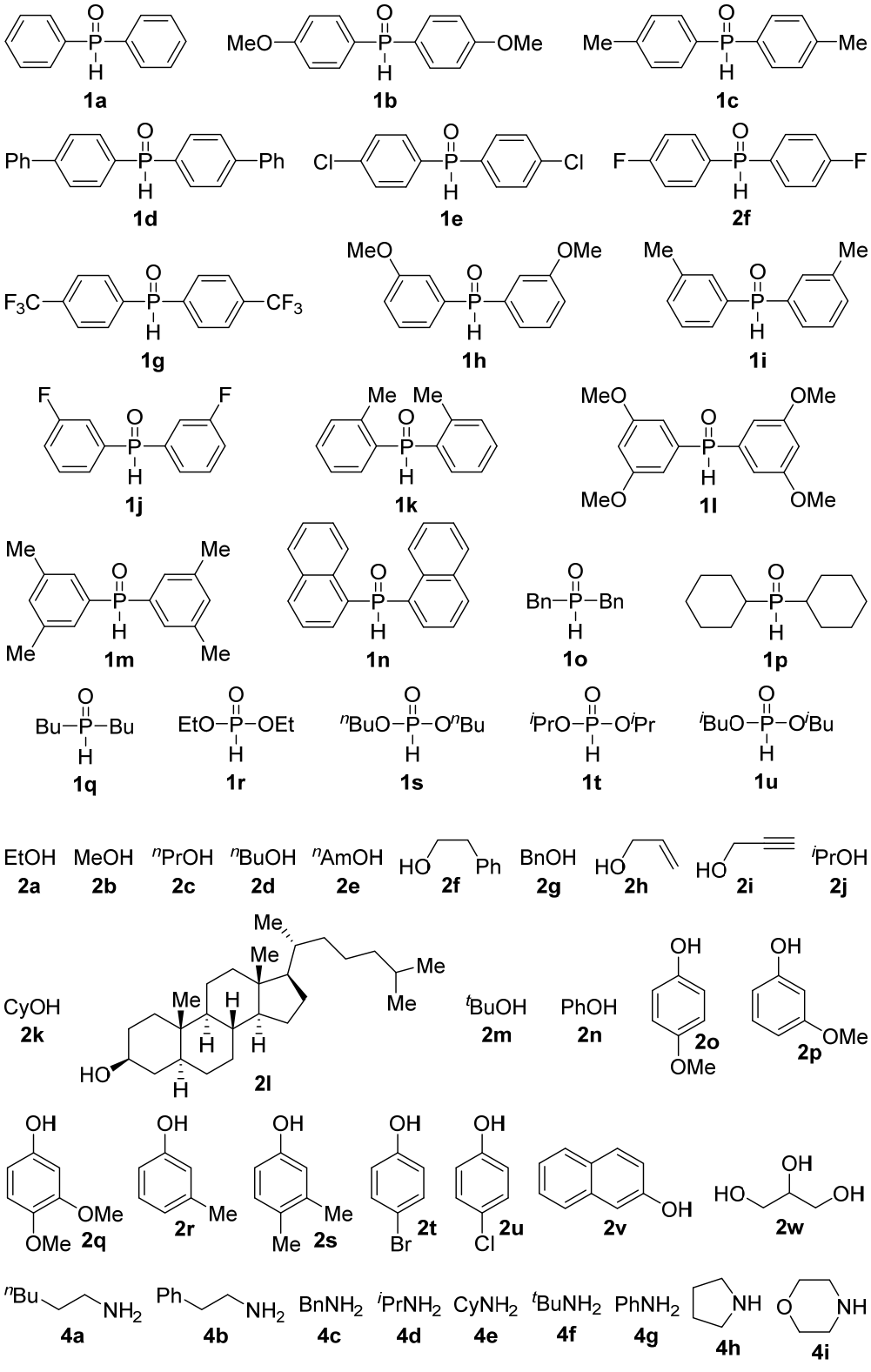
SUPPORTING INFORMATION

Content:

1. General Information

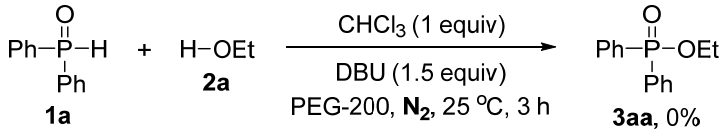
Unless otherwise stated, commercially available reagents including dry solvents were used without additional purification. Petroleum ether refers to the petroleum fraction b.p. 60−90 °C. Secondary phosphine oxides which were not commercially available were prepared according to the literature.[1] All reactions were carried out in oven-dried thick-walled glassware. Flash chromatography was performed using the indicated solvent system on silica gel standard grade (200−300 mesh). ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (100 MHz) spectrometer. ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (162 MHz) spectrometer. ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (376 MHz) spectrometer. Chemical shifts were reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.16 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on an Q-Exactive Orbitrap mass spectrometer (Thermo, CA). Abbreviations for signal coupling are as follows: s = singlet, d = doublet; t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad.

2. Overview of Substrates Numbering



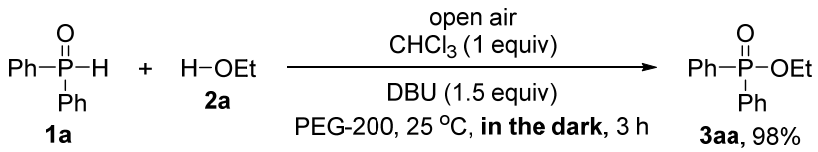
3. Mechanistic Studies

1) The Investigation of the Effect of Air Atmosphere



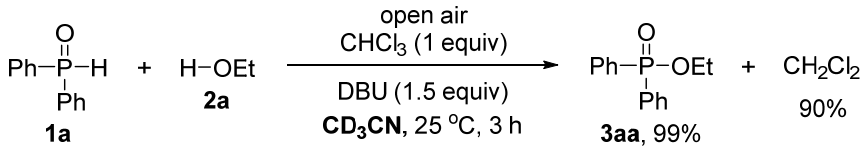
To a solution of diphenylphosphine oxide **1a** (40 mg, 0.2 mmol) and ethanol **2a** (46 mg, 1 mmol) in PEG-200 (2 mL) were added $CHCl_3$ (24 mg, 0.2 mmol) and DBU (46 mg, 0.3 mmol). The mixture was stirred at 25 ^oC under N_2 for 3 h. The reaction mixture was quenched with saturated aqueous NaCl solution (20 mL), and the resulting mixture was then extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The desired ethyl diphenylphosphinate **3aa** was not detected from ^1H NMR spectrum of the crude mixture.

2) The Investigation of the Effect of Visible Light

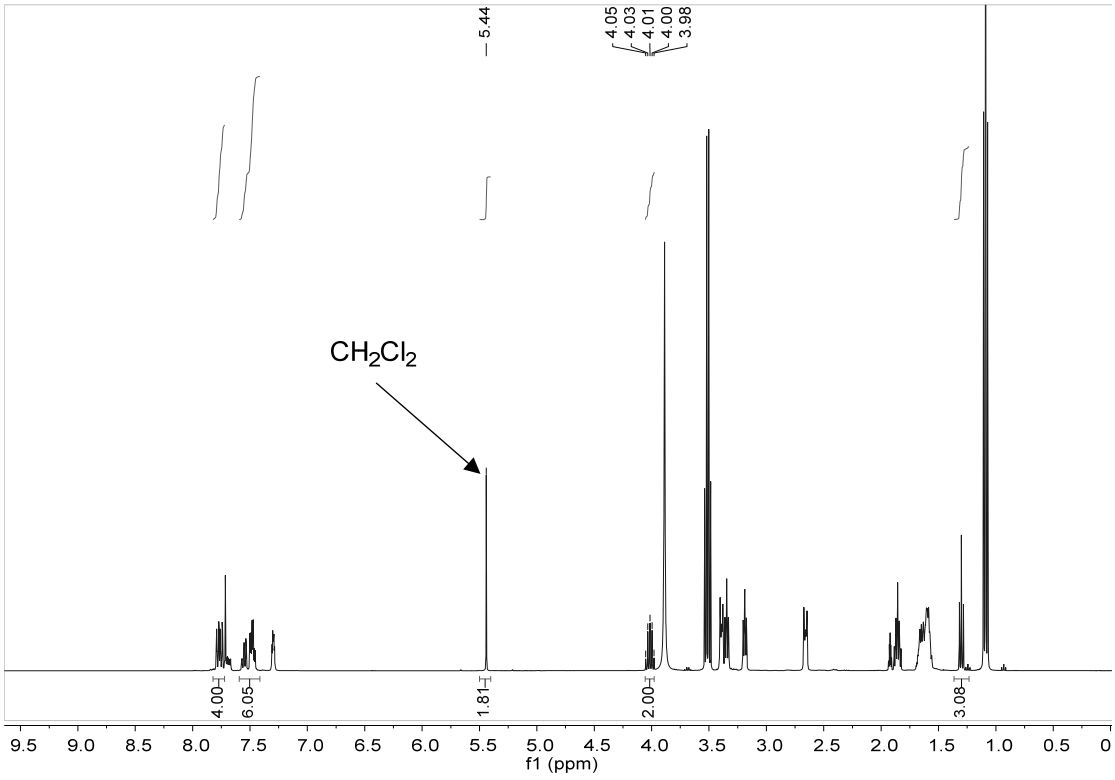


To a solution of diphenylphosphine oxide **1a** (40 mg, 0.2 mmol) and ethanol **2a** (46 mg, 1 mmol) in PEG-200 (2 mL) were added $CHCl_3$ (24 mg, 0.2 mmol) and DBU (46 mg, 0.3 mmol). The mixture was stirred at 25 ^oC under air atmosphere in the dark for 3 h. The reaction mixture was quenched with saturated aqueous NaCl solution (20 mL), and the resulting mixture was then extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to afford ethyl diphenylphosphinate **3aa** (48 mg, 98%) as a colorless oil.

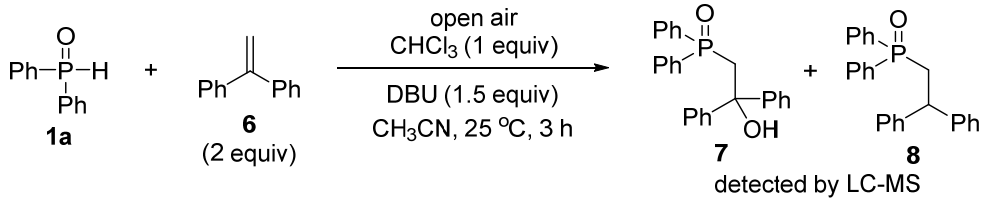
3) The Investigation of By-Products



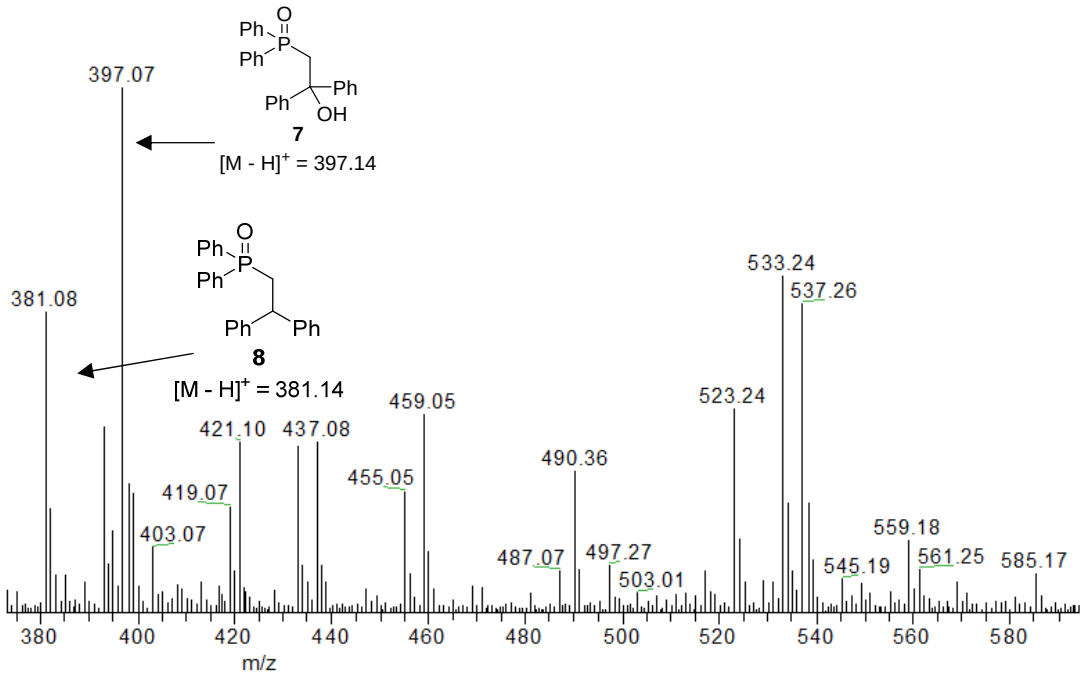
To a solution of diphenylphosphine oxide **1a** (10 mg, 0.05 mmol) and ethanol **2a** (12 mg, 0.25 mmol) in CD_3CN (0.5 mL) were added $CHCl_3$ (6 mg, 0.05 mmol) and DBU (12 mg, 0.075 mmol). The mixture was stirred at 25 ^oC under air atmosphere for 3 h. The by-product CH_2Cl_2 with 90% yield was detected from ^1H NMR spectrum of the resulting mixture according to the yield of **3aa** (99%).

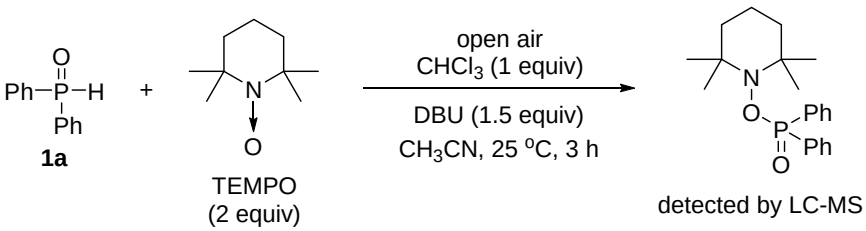


4) Radical-Trapping Experiment



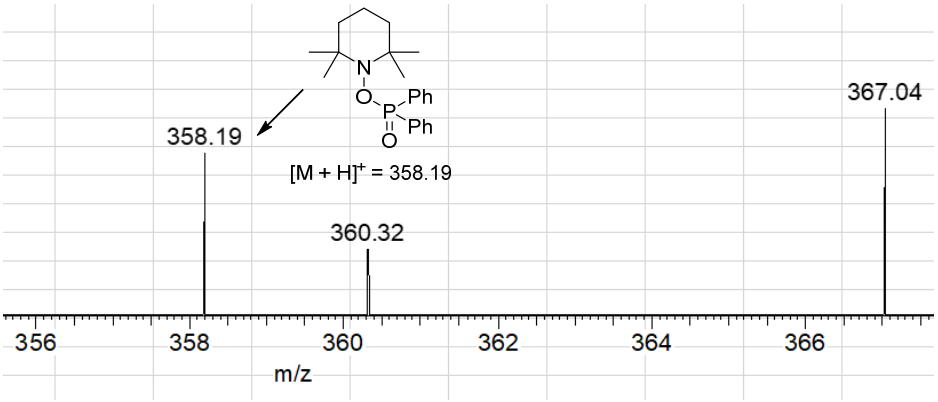
To a solution of diphenylphosphine oxide **1a** (40 mg, 0.2 mmol) and the radical scavenger diphenylethene **6** (72 mg, 0.4 mmol) in CH_3CN (2 mL) were added $CHCl_3$ (24 mg, 0.2 mmol) and DBU (46 mg, 0.3 mmol). The mixture was stirred at 25 °C under air atmosphere for 3 h. The reaction mixture was then concentrated under reduced pressure. The adducts **7** and **8**, which should be generated via a phosphoryl radical pathway, were detected by LC-MS spectrum of the crude mixture.

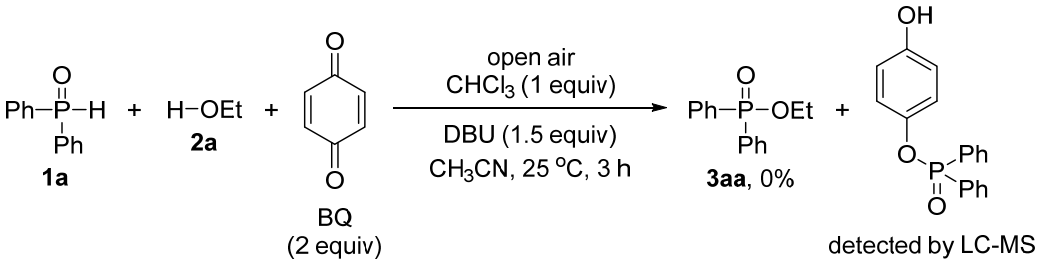




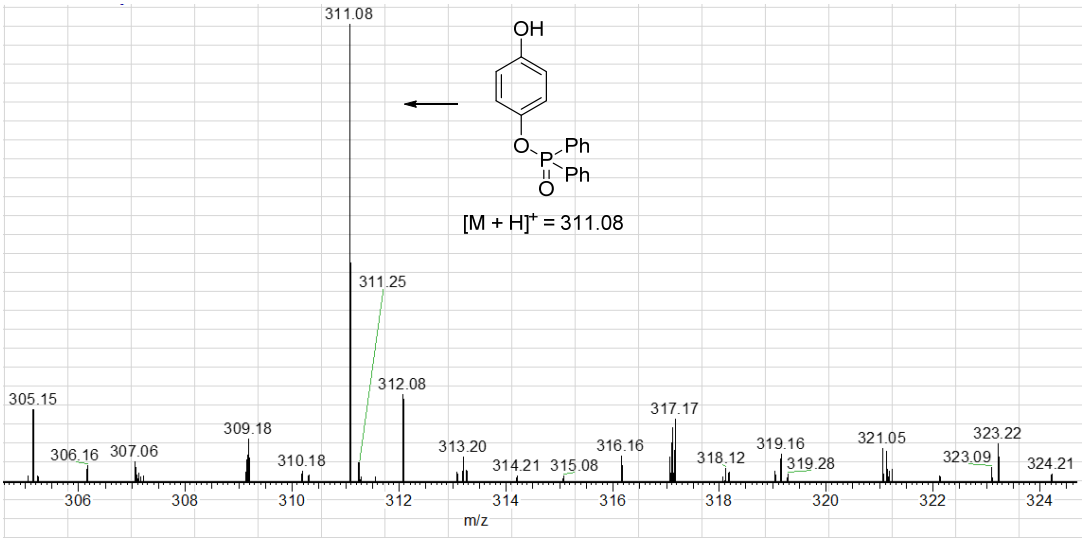
To a solution of diphenylphosphine oxide **1a** (40 mg, 0.2 mmol) and the radical scavenger TEMPO (62 mg, 0.4 mmol) in CH_3CN (2 mL) were added $CHCl_3$ (24 mg, 0.2 mmol) and DBU (46 mg, 0.3 mmol). The mixture was stirred at 25 °C under air atmosphere for 3 h. The reaction mixture was then concentrated under reduced

pressure. The TEMPO-P(O)Ph_2 adduct was detected by LC-MS spectrum of the crude mixture, suggesting that a phosphoryl radical reaction pathway might be involved.

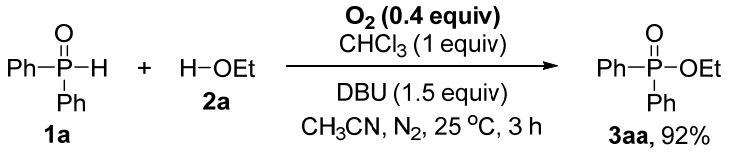




To a solution of diphenylphosphine oxide **1a** (40 mg, 0.2 mmol), ethanol **2a** (46 mg, 1 mmol) and the radical scavenger BQ (43 mg, 0.4 mmol) in CH_3CN (2 mL) were added $CHCl_3$ (24 mg, 0.2 mmol) and DBU (46 mg, 0.3 mmol). The mixture was stirred at 25 °C under air atmosphere for 3 h. The reaction mixture was then concentrated under reduced pressure. The desired reaction of **1a** with **2a** was completely inhibited, and the BQ-P(O)Ph_2 adduct was detected by LC-MS spectrum of the crude mixture, suggesting that a radical reaction pathway might be involved.



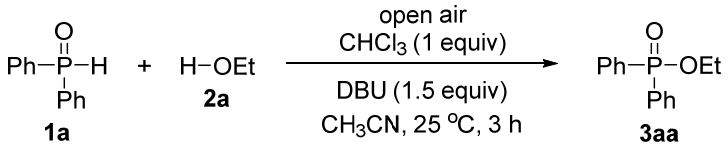
5) The Investigation of the Effect of Catalytic Amounts of O_2



To a solution of diphenylphosphine oxide **1a** (40 mg, 0.2 mmol) and ethanol **2a** (46 mg, 1 mmol) in CH_3CN (2 mL) were added $CHCl_3$ (24 mg, 0.2 mmol), DBU (46 mg, 0.3 mmol), and O_2 (1.8 mL, 0.08 mmol) under N_2. The mixture was stirred at 25 ^oC for 3 h. The reaction mixture was then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to afford ethyl diphenylphosphinate **3aa** (45 mg, 92%) as a colorless oil.

4. Experimental Section

1) General Procedure for the Atherton–Todd-Type Reaction in CH_3CN



To a solution of diphenylphosphine oxide **1a** (40 mg, 0.2 mmol) and ethanol **2a** (46 mg, 1 mmol) in CH_3CN (2 mL) were added $CHCl_3$ (24 mg, 0.2 mmol) and DBU (46 mg, 0.3 mmol). The mixture was stirred at 25 °C under air atmosphere for 3 h (Figure S1). The reaction mixture was then concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to afford ethyl diphenylphosphinate **3aa** (48 mg, 98%) as a colorless oil.

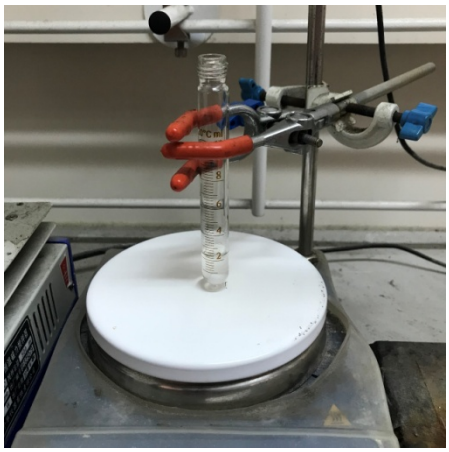
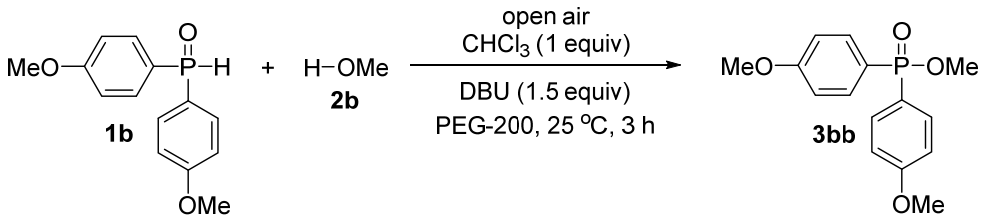


Figure S1 The reaction setup for the general procedure.

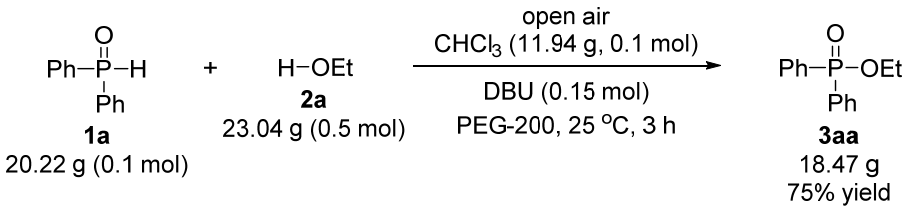
2) General Procedure for the Atherton–Todd-Type Reaction in PEG-200



To a solution of bis(4-methoxyphenyl)phosphine oxide **1b** (52 mg, 0.2 mmol) and methanol **2b** (32 mg, 1 mmol) in PEG-200 (2 mL) were added $CHCl_3$ (24 mg, 0.2

mmol) and DBU (46 mg, 0.3 mmol). The mixture was stirred at 25 °C under air atmosphere for 3 h (Figure S1). The reaction mixture was quenched with saturated aqueous NaCl solution (20 mL), and the resulting mixture was then extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to afford methyl bis(4-methoxyphenyl)phosphinate **3bb** (58 mg, 99%) as a colorless oil.

3) Large-Scale Synthesis

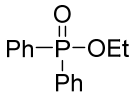


To a solution of diphenylphosphine oxide **1a** (20.22 g, 0.10 mol) and ethanol **2a** (23.04 g, 0.50 mol) in PEG-200 (100 mL) were added $CHCl_3$ (11.94 g, 0.10 mol) and DBU (22.84 g, 0.15 mol). The mixture was stirred at 25 °C under air atmosphere for 3 h. The reaction mixture was quenched with saturated aqueous NaCl solution (1 L), and the resulting mixture was then extracted with ethyl acetate (3×1 L). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to afford ethyl diphenylphosphinate **3aa** (18.47 g, 75%) as a colorless oil.

5. Analytic Data for Products

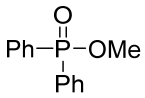
The known compounds **3aa**,[2] **3ab**,[2] **3ac**,[2] **3ad**,[2] **3ae**,[2] **3af**,[3] **3ag**,[3] **3ah**,[3] **3ai**,[4] **3aj**,[2] **3ak**,[3] **3an**,[5] **3ao**,[5] **3ap**,[6] **3ar**,[6] **3as**,[7] **3at**,[7] **3au**,[7] **3av**,[6] **3bb**,[2] **3cb**,[2] **3eb**,[2] **3fb**,[2] **3gb**,[2] **3hb**,[8] **3ib**,[2] **3kb**,[2] **3mb**,[2] **3ob**,[2] **5a**,[9] **5b**,[10] **5c**,[11] **5d**,[12] **5e**,[13] **5f**,[14] **5h**,[15] **5i**,[15] **5j**,[16] and **5l**[16] showed characterization data in full agreement with previously reported data.

Ethyl Diphenylphosphinate (3aa)[2].



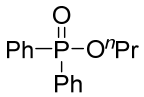
Colorless oil (48 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.77 (m, 4H), 7.53−7.47 (m, 2H), 7.46−7.40 (m, 4H), 4.14−4.05 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J = 2.8 Hz), 131.7 (d, J = 136 Hz), 131.6 (d, J = 10.1 Hz), 128.5 (d, J = 13.1 Hz), 61.1 (d, J = 5.9 Hz), 16.5 (d, J = 6.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.4.

Methyl Diphenylphosphinate (3ab)[2].



Colorless oil (46 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.77 (m, 4H), 7.55−7.49 (m, 2H), 7.48−7.41 (m, 4H), 3.76 (d, J = 11.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (d, J = 2.8 Hz), 131.7 (d, J = 10.1 Hz), 131.1 (d, J = 136 Hz), 128.6 (d, J = 13.1 Hz), 51.5 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.3.

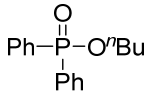
Propyl Diphenylphosphinate (3ac)[2].



Colorless oil (48 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.76 (m, 4H), 7.55−7.48 (m, 2H), 7.47−7.42 (m, 4H), 3.99 (q, J = 6.7 Hz, 2H), 1.79−1.70 (m, 2H),

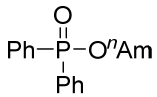
0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J = 2.8 Hz), 131.7 (d, J = 137 Hz), 131.6 (d, J = 10.1 Hz), 128.5 (d, J = 13.1 Hz), 66.5 (d, J = 6.1 Hz), 23.9 (d, J = 6.7 Hz), 10.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1.

Butyl Diphenylphosphinate (3ad)[2].



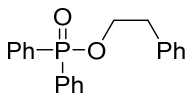
Colorless oil (53 mg, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.77 (m, 4H), 7.53−7.38 (m, 6H), 4.01 (q, J = 6.6 Hz, 2H), 1.79−1.62 (m, 2H), 1.47−1.37 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0 (d, J = 2.8 Hz), 131.7 (d, J = 137 Hz), 131.6 (d, J = 10.1 Hz), 128.5 (d, J = 13.1 Hz), 64.7 (d, J = 6.0 Hz), 32.6 (d, J = 6.7 Hz), 18.9, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1.

Pentyl Diphenylphosphinate (3ae)[2].



Colorless oil (51 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.74 (m, 4H), 7.56−7.38 (m, 6H), 4.01 (q, J = 6.7 Hz, 2H), 1.75−1.68 (m, 2H), 1.44−1.25 (m, 4H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J = 2.8 Hz), 131.7 (d, J = 137 Hz), 131.6 (d, J = 10.1 Hz), 128.5 (d, J = 13.1 Hz), 65.0 (d, J = 6.1 Hz), 30.2 (d, J = 6.6 Hz), 27.8, 22.2, 13.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2.

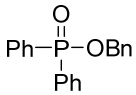
Phenethyl Diphenylphosphinate (3af)[3].



Colorless oil (63 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.62 (m, 4H), 7.51−7.44 (m, 2H), 7.42−7.34 (m, 4H), 7.30−7.15 (m, 5H), 4.20 (q, J = 6.8 Hz, 2H), 3.02 (t, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 132.1 (d, J = 2.8 Hz), 131.6 (d, J = 10.2 Hz), 131.3 (d, J = 136 Hz), 129.1, 128.6, 128.5 (d, J = 4.9 Hz),

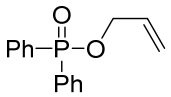
126.6, 65.4 (d, J = 6.0 Hz), 37.1 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.6.

Benzyl Diphenylphosphinate (3ag)[3].



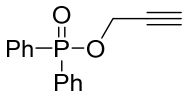
Colorless oil (55 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.78 (m, 4H), 7.54−7.50 (m, 2H), 7.47−7.42 (m, 4H), 7.39−7.28 (m, 5H), 5.07 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4 (d, J = 7.5 Hz), 132.2 (d, J = 2.8 Hz), 131.7 (d, J = 10.2 Hz), 131.3 (d, J = 137 Hz), 128.6 (d, J = 13.1 Hz), 128.5, 128.2, 127.8, 66.3 (d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4.

Allyl Diphenylphosphinate (3ah)[3].



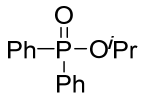
Colorless oil (51 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.73 (m, 4H), 7.54−7.47 (m, 2H), 7.47−7.36 (m, 4H), 6.03−5.88 (m, 1H), 5.37−5.32 (m, 1H), 5.23−5.19 (m, 1H), 4.54−4.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0 (d, J = 7.3 Hz), 132.2 (d, J = 2.8 Hz), 131.6 (d, J = 10.2 Hz), 131.4 (d, J = 137 Hz), 128.6 (d, J = 13.2 Hz), 117.9, 65.3 (d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2.

Prop-2-yn-1-yl Diphenylphosphinate (3ai)[4].



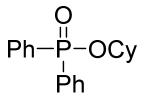
Colorless oil (50 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.73 (m, 4H), 7.53−7.46 (m, 2H), 7.44−7.40 (m, 4H), 4.66 (dd, J = 6.8, 2.4 Hz, 2H), 2.47 (t, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5 (d, J = 2.8 Hz), 131.7 (d, J = 10.4 Hz), 130.7 (d, J = 137 Hz), 128.6 (d, J = 13.3 Hz), 78.0 (d, J = 8.9 Hz), 75.8, 52.4 (d, J = 4.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.1.

Isopropyl Diphenylphosphinate (3aj)[2].



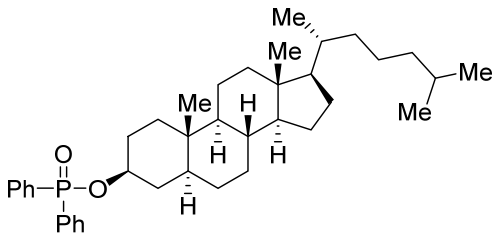
Colorless oil (21 mg, 41%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.77 (m, 4H), 7.53−7.46 (m, 2H), 7.46−7.39 (m, 4H), 4.73−4.60 (m, 1H), 1.34 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4 (d, J = 136 Hz), 131.9 (d, J = 2.7 Hz), 131.6 (d, J = 10.1 Hz), 128.4 (d, J = 13.1 Hz), 70.2 (d, J = 6.0 Hz), 24.3 (d, J = 4.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8.

Cyclohexyl Diphenylphosphinate (3ak)[3].



Colorless oil (19 mg, 31%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.74 (m, 4H), 7.53−7.38 (m, 6H), 4.46−4.37 (m, 1H), 1.90−1.87 (m, 2H), 1.77−1.67 (m, 2H), 1.67−1.54 (m, 2H), 1.51−1.40 (m, 1H), 1.35−1.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, J = 137 Hz), 131.9 (d, J = 2.8 Hz), 131.6 (d, J = 10.1 Hz), 128.4 (d, J = 13.1 Hz), 75.0 (d, J = 6.1 Hz), 33.9 (d, J = 3.6 Hz), 25.2, 23.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7.

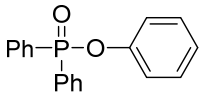
(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl Diphenylphosphinate (3al).



White amorphous solid (47 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.75 (m, 4H), 7.53−7.39 (m, 6H), 4.37−4.27 (m, 1H), 1.98−1.85 (m, 3H), 1.84−0.93 (m, 28H), 0.88 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 1.8 Hz, 3H), 0.84 (d, J = 1.8 Hz, 3H), 0.82 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, J = 135 Hz), 132.5 (d, J =

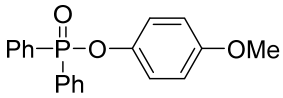
135 Hz), 131.9 (d, J = 2.6 Hz), 131.6 (d, J = 10.0 Hz), 131.6 (d, J = 10.0 Hz), 128.4 (d, J = 13.0 Hz), 76.2 (d, J = 6.3 Hz), 56.3 (d, J = 13.9 Hz), 54.2, 44.7, 42.6, 40.0, 39.5, 36.8, 36.6 (d, J = 3.5 Hz), 36.2, 35.8, 35.4, 35.3, 31.9, 30.1 (d, J = 3.8 Hz), 28.5, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 12.3, 12.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9; HRMS (ESI-Orbitrap) m/z: $[M + Na]^+$ calcd for $C_{39}H_{57}O_2PNa$ 611.3981, found 611.3989.

Phenyl Diphenylphosphinate (3an)[5].



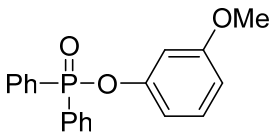
White amorphous solid (57 mg, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.87 (m, 4H), 7.60−7.43 (m, 6H), 7.29−7.22 (m, 4H), 7.15−7.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (d, J = 8.2 Hz), 132.4 (d, J = 2.9 Hz), 131.8 (d, J = 10.4 Hz), 131.0 (d, J = 138 Hz), 129.6, 128.6 (d, J = 13.5 Hz), 124.6, 120.7 (d, J = 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.4.

4-Methoxyphenyl Diphenylphosphinate (3ao)[5].



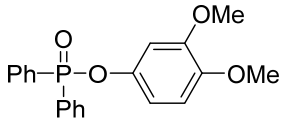
White amorphous solid (64 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.85 (m, 4H), 7.55−7.47 (m, 2H), 7.47−7.40 (m, 4H), 7.10 (dd, J = 9.1, 1.2 Hz, 2H), 6.73 (d, J = 9.0 Hz, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 144.3 (d, J = 8.4 Hz), 132.5 (d, J = 2.8 Hz), 131.8 (d, J = 10.4 Hz), 130.9 (d, J = 138 Hz), 128.6 (d, J = 13.4 Hz), 121.7 (d, J = 4.5 Hz), 114.6, 55.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7.

3-Methoxyphenyl Diphenylphosphinate (3ap)[6].



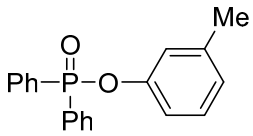
Colorless oil (64 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.83 (m, 4H), 7.58−7.50 (m, 2H), 7.50−7.41 (m, 4H), 7.11 (dd, J = 8.4, 8.0 Hz, 1H), 6.82−6.73 (m, 2H), 6.66−6.59 (m, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 151.8 (d, J = 8.0 Hz), 132.5 (d, J = 2.8 Hz), 131.8 (d, J = 10.4 Hz), 131.0 (d, J = 138 Hz), 129.9, 128.6 (d, J = 13.5 Hz), 112.9 (d, J = 4.7 Hz), 110.7, 106.7 (d, J = 5.1 Hz), 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0.

3,4-Dimethoxyphenyl Diphenylphosphinate (3aq).



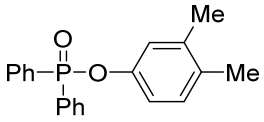
Colorless oil (67 mg, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.88 (m, 4H), 7.58−7.40 (m, 6H), 6.75 (s, 1H), 6.70−6.66 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 146.0, 144.5 (d, J = 8.4 Hz), 132.4 (d, J = 2.9 Hz), 131.8 (d, J = 10.3 Hz), 130.9 (d, J = 138 Hz), 128.6 (d, J = 13.4 Hz), 112.0 (d, J = 4.7 Hz), 111.4, 105.4 (d, J = 4.5 Hz), 56.1, 55.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{19}O_4PNa$ 377.0913, found 377.0908.

***m*-Tolyl Diphenylphosphinate (3ar)[6].**



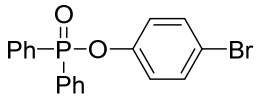
Yellow oil (61 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.82 (m, 4H), 7.54−7.48 (m, 2H), 7.48−7.40 (m, 4H), 7.11−7.07 (m, 1H), 7.05 (s, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, J = 8.3 Hz), 139.9, 132.4 (d, J = 2.8 Hz), 131.8 (d, J = 10.3 Hz), 131.1 (d, J = 138 Hz), 129.3, 128.6 (d, J = 13.4 Hz), 125.4, 121.4 (d, J = 4.8 Hz), 117.6 (d, J = 4.8 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1.

3,4-Dimethylphenyl Diphenylphosphinate (3as)[7].



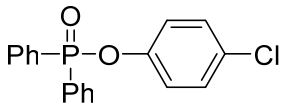
White amorphous solid (64 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.87 (m, 4H), 7.54−7.38 (m, 6H), 7.02 (s, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8 (d, J = 8.3 Hz), 138.1, 132.8, 132.3 (d, J = 2.8 Hz), 131.8 (d, J = 10.3 Hz), 131.3 (d, J = 138 Hz), 130.4, 128.5 (d, J = 13.4 Hz), 121.8 (d, J = 4.7 Hz), 117.7 (d, J = 4.7 Hz), 19.8, 19.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9.

4-Bromophenyl Diphenylphosphinate (3at)[7].



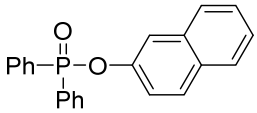
White amorphous solid (35 mg, 47%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.81 (m, 4H), 7.59−7.51 (m, 2H), 7.50−7.42 (m, 4H), 7.37−7.30 (m, 2H), 7.13−7.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0 (d, J = 8.2 Hz), 132.7, 132.6, 131.8 (d, J = 10.4 Hz), 130.5 (d, J = 138 Hz), 128.7 (d, J = 13.5 Hz), 122.5 (d, J = 4.8 Hz), 117.6 (d, J = 1.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3.

4-Chlorophenyl Diphenylphosphinate(3au)[7].



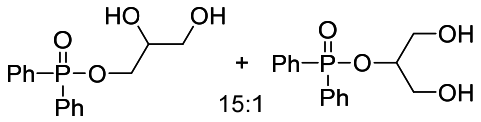
White amorphous solid (20 mg, 30%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.80 (m, 4H), 7.62−7.41 (m, 6H), 7.23−7.17 (m, 2H), 7.15−7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (d, J = 8.2 Hz), 132.7 (d, J = 2.8 Hz), 131.8 (d, J = 10.4 Hz), 130.5 (d, J = 138 Hz), 129.7, 128.7 (d, J = 13.5 Hz), 122.1 (d, J = 4.8 Hz), 116.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3.

Naphthalen-2-yl Diphenylphosphinate (3av)[6].



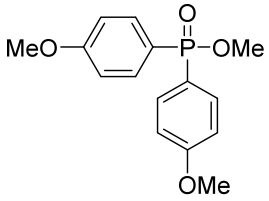
White amorphous solid (68 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.86 (m, 4H), 7.77−7.66 (m, 4H), 7.56−7.31 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6 (d, J = 8.4 Hz), 133.9, 132.5 (d, J = 2.8 Hz), 131.9, 131.8, 130.9 (d, J = 138 Hz), 130.7, 129.8, 128.7 (d, J = 13.5 Hz), 127.6 (d, J = 10.0 Hz), 126.6, 125.3, 120.7 (d, J = 4.9 Hz), 117.2 (d, J = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8.

2,3-Dihydroxypropyl Diphenylphosphinate and 1,3-Dihydroxypropan-2-yl Diphenylphosphinate (3aw).



Colorless oil (56 mg, 96%), two isomers in ~15:1 ratio: ^{1}H NMR (400 MHz, $CDCl_3$) major product: δ 7.85−7.75 (m, 4H), 7.60−7.51 (m, 2H), 7.50−7.41 (m, 4H), 4.11 (dd, J = 11.0, 5.0 Hz, 2H), 3.97−3.93 (m, 1H), 3.71 (d, J = 4.7 Hz, 2H), 2.84 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) major product: δ 132.7 (d, J = 2.7 Hz), 132.6 (d, J = 2.6 Hz), 131.7 (d, J = 10.3 Hz), 131.6 (d, J = 10.3 Hz), 130.2 (d, J = 138 Hz), 130.1 (d, J = 137 Hz), 128.8 (d, J = 13.3 Hz), 128.7 (d, J = 13.3 Hz), 70.8 (d, J = 3.4 Hz), 67.2 (d, J = 6.3 Hz), 62.7; ^{31}P NMR (162 MHz, $CDCl_3$) major product: δ 36.2; HRMS (ESI-Orbitrap) m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}O_4PNa$ 315.0757, found 315.0755.

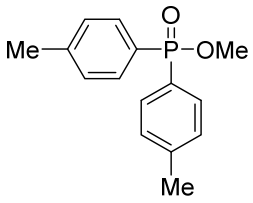
Methyl Bis(4-methoxyphenyl)phosphinate (3bb)[2].



Colorless oil (58 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 11.7, 8.5 Hz, 4H), 6.93 (dd, J = 8.7, 2.5 Hz, 4H), 3.81 (s, 6H), 3.70 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 3.1 Hz), 133.4 (d, J = 11.4 Hz), 122.7 (d, J = 145

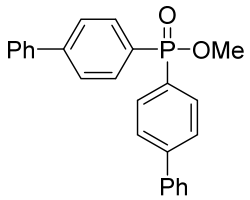
Hz), 114.0 (d, J = 14.2 Hz), 55.3, 51.2 (d, J = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.0.

Methyl Di-*p*-tolylphosphinate (3cb)[2].



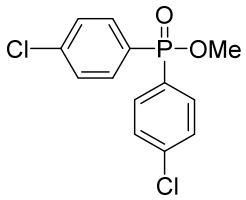
Colorless oil (48 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 12.0, 7.7 Hz, 4H), 7.25 (dd, J = 7.7, 2.4 Hz, 4H), 3.73 (d, J = 11.1 Hz, 3H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (d, J = 2.9 Hz), 131.6 (d, J = 10.5 Hz), 129.2 (d, J = 13.5 Hz), 127.9 (d, J = 140 Hz), 51.4 (d, J = 6.0 Hz), 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.3.

Methyl Di([1,1'-biphenyl]-4-yl)phosphinate (3db).



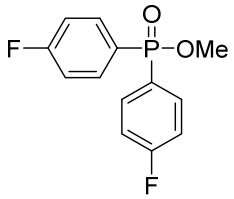
White amorphous solid (65 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 11.9, 8.3 Hz, 4H), 7.70 (dd, J = 8.3, 3.2 Hz, 4H), 7.63−7.56 (m, 4H), 7.48−7.42 (m, 4H), 7.41−7.35 (m, 2H), 3.83 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (d, J = 2.9 Hz), 139.8, 132.1 (d, J = 10.5 Hz), 129.5 (d, J = 139 Hz), 128.8, 128.0, 127.3, 127.1, 51.5 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.3; HRMS (ESI-Orbitrap) m/z: $[M + Na]^+$ calcd for $C_{25}H_{21}O_2PNa$ 407.1171, found 407.1169.

Methyl Bis(4-chlorophenyl)phosphinate (3eb)[2].



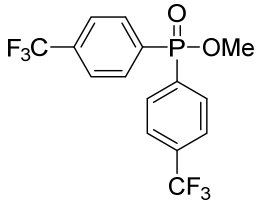
Yellow oil (57 mg, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.68 (m, 4H), 7.47−7.40 (m, 4H), 3.76 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1 (d, J = 3.5 Hz), 133.0 (d, J = 11.0 Hz), 129.2 (d, J = 139 Hz), 129.1 (d, J = 13.8 Hz), 51.7 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.2.

Methyl Bis(4-fluorophenyl)phosphinate (3fb)[2].



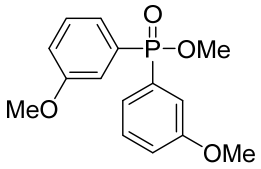
Colorless oil (50 mg, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.71 (m, 4H), 7.16−7.09 (m, 4H), 3.73 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (dd, J = 254, 3.5 Hz), 134.1 (dd, J = 11.5, 8.9 Hz), 126.8 (dd, J = 142, 3.4 Hz), 116.0 (dd, J = 21.4, 14.4 Hz), 51.5 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.9 (d, J = 1.2 Hz).

Methyl Bis(4-(trifluoromethyl)phenyl)phosphinate (3gb)[2].



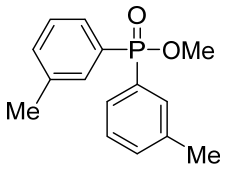
Colorless oil (55 mg, 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 11.9, 8.1 Hz, 4H), 7.73 (dd, J = 8.2, 2.6 Hz, 4H), 3.82 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6 (d, J = 137 Hz), 134.4 (dd, J = 32.8, 3.1 Hz), 132.2 (d, J = 10.5 Hz), 125.7 (dq, J = 13.3, 3.7 Hz), 123.4 (d, J = 272 Hz), 52.0 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.4.

Methyl Bis(3-methoxyphenyl)phosphinate (3hb)[8].



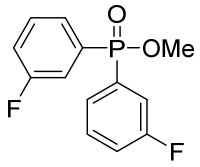
Colorless oil (58 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.31 (m, 6H), 7.08−7.02 (m, 2H), 3.82 (s, 6H), 3.77 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (d, J = 16.5 Hz), 132.3 (d, J = 135 Hz), 129.8 (d, J = 15.5 Hz), 123.8 (d, J = 9.8 Hz), 118.5 (d, J = 2.8 Hz), 116.4 (d, J = 11.3 Hz), 55.4, 51.6 (d, J = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.2.

Methyl Di-*m*-tolylphosphinate (3ib)[2].



Colorless oil (47 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 12.7 Hz, 2H), 7.55 (dd, J = 12.7, 5.6 Hz, 2H), 7.33−7.26 (m, 4H), 3.72 (d, J = 11.1 Hz, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3 (d, J = 13.1 Hz), 132.8 (d, J = 2.9 Hz), 132.0 (d, J = 10.1 Hz), 130.8 (d, J = 136 Hz), 128.5 (d, J = 10.0 Hz), 128.3 (d, J = 13.8 Hz), 51.4 (d, J = 6.1 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.9.

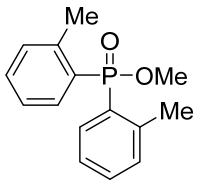
Methyl Bis(3-fluorophenyl)phosphinate (3jb).



Colorless oil (49 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.53 (m, 2H), 7.53−7.38 (m, 4H), 7.26−7.20 (m, 2H), 3.78 (d, J = 9.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (dd, J = 250, 18.7 Hz), 133.2 (dd, J = 138, 5.6 Hz), 130.8 (dd, J = 15.4, 7.4 Hz), 127.4 (dd, J = 9.5, 3.2 Hz), 119.7 (dd, J = 21.2, 2.3 Hz), 118.5 (dd, J =

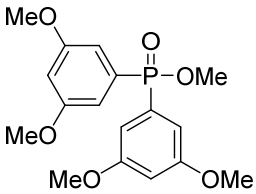
22.3, 10.8 Hz), 51.9 (d, J = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9 (d, J = 5.6 Hz); HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{11}F_2O_2PNa$ 291.0357, found 291.0353.

Methyl Di-*o*-tolylphosphinate (3kb)[2].



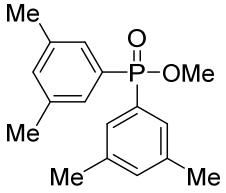
Colorless oil (51 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 13.3, 7.7 Hz, 2H), 7.41 (dd, J = 7.4, 7.4 Hz, 2H), 7.33−7.24 (m, 2H), 7.24−7.13 (m, 2H), 3.75 (d, J = 11.8 Hz, 3H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (d, J = 11.1 Hz), 133.6 (d, J = 10.0 Hz), 132.3 (d, J = 2.7 Hz), 131.4 (d, J = 12.6 Hz), 129.5 (d, J = 133 Hz), 125.5 (d, J = 12.7 Hz), 51.0 (d, J = 5.9 Hz), 21.1 (d, J = 4.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.2.

Methyl Bis(3,5-dimethoxyphenyl)phosphinate (3lb).



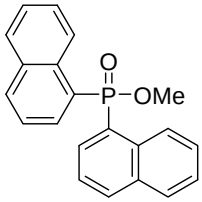
Colorless oil (67 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, J = 13.6, 2.3 Hz, 4H), 6.54 (dd, J = 2.3, 2.3 Hz, 2H), 3.75 (s, 12H), 3.73 (d, J = 11.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, J = 19.6 Hz), 132.5 (d, J = 137 Hz), 109.0 (d, J = 11.2 Hz), 104.5 (d, J = 2.5 Hz), 55.4, 51.6 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.5; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{21}O_6PNa$ 375.0968, found 375.0963.

Methyl Bis(3,5-dimethylphenyl)phosphinate (3mb)[2].



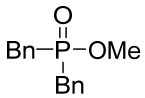
Colorless oil (55 mg, 95%): ^{1}H NHR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 12.5 Hz, 4H), 7.14 (s, 2H), 3.74 (d, J = 11.1 Hz, 3H), 2.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2 (d, J = 13.8 Hz), 133.9 (d, J = 2.9 Hz), 130.9 (d, J = 135 Hz), 129.2 (d, J = 10.1 Hz), 51.4 (d, J = 6.0 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.5.

Methyl Di(naphthalen-1-yl)phosphinate (3nb).



White amorphous solid (60 mg, 90%):^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, J = 6.2, 3.4 Hz, 2H), 8.13 (dd, J = 15.8, 7.1 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H), 7.89−7.86 (m, 2H), 7.54−7.48 (m, 6H), 3.85 (d, J = 11.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1 (d, J = 10.4 Hz), 133.7, 133.6 (d, J = 3.1 Hz), 133.0 (d, J = 10.3 Hz), 128.9 (d, J = 1.4 Hz), 127.5, 127.4 (d, J = 134 Hz), 126.5 (d, J = 4.8 Hz), 126.3, 124.6 (d, J = 15.0 Hz), 51.7 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.2; HRMS (ESI-Orbitrap) m/z: $[M + Na]^+$ calcd for $C_{21}H_{17}O_2PNa$ 355.0858, found 355.0855.

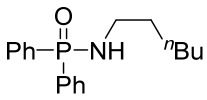
Methyl Dibenzylphosphinate (3ob)[2].



White amorphous solid (27 mg, 51%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.18 (m, 10H), 3.56 (d, J = 10.5 Hz, 3H), 3.08 (d, J = 16.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.3 (d, J = 7.6 Hz), 129.8 (d, J = 5.8 Hz), 128.6 (d, J = 2.6 Hz), 126.9 (d,

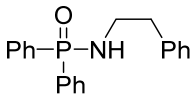
J = 3.1 Hz), 51.8 (d, J = 7.0 Hz), 35.6 (d, J = 87.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.2.

_N_-Hexyl-_P,P_-diphenylphosphinic Amide (5a)[9].



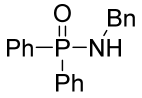
Colorless oil (59 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.82 (m, 4H), 7.53−7.37 (m, 6H), 2.94 (q, J = 7.7 Hz, 2H), 2.19 (br, 1H), 1.59−1.52 (m, 2H), 1.38−1.13 (m, 6H), 0.85 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5 (d, J = 130 Hz), 132.1 (d, J = 9.4 Hz), 131.8 (d, J = 2.6 Hz), 128.5 (d, J = 12.5 Hz), 40.8 (d, J = 1.7 Hz), 32.1 (d, J = 7.1 Hz), 31.4, 26.4, 22.5, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.6.

_N_-Phenethyl-_P,P_-diphenylphosphinic Amide (5b)[10].



White amorphous solid (63 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.76 (m, 4H), 7.50−7.43 (m, 2H), 7.42−7.35 (m, 4H), 7.32−7.14 (m, 5H), 3.28−3.15 (m, 2H), 3.11−3.06 (m, 1H), 2.86 (t, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 131.7 (d, J = 122 Hz), 132.0 (d, J = 9.5 Hz), 131.6 (d, J = 2.9 Hz), 128.8, 128.41, 128.40, 126.3, 42.1 (d, J = 1.3 Hz), 38.3 (d, J = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.8.

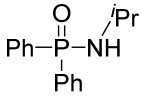
_N_-Benzyl-_P,P_-diphenylphosphinic Amide (5c)[11].



Colorless oil (60 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.90 (m, 4H), 7.57−7.41 (m, 6H), 7.41−7.23 (m, 5H), 4.13 (t, J = 7.5 Hz, 2H), 3.50−3.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7 (d, J = 8.2 Hz), 132.2 (d, J = 129 Hz), 132.2 (d,

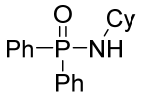
J = 9.5 Hz), 131.9 (d, J = 2.7 Hz), 128.6 (d, J = 4.0 Hz), 128.5, 127.7, 127.4, 44.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.8.

_N_-Isopropyl-_P,P_-diphenylphosphinic Amide (5d)[12].



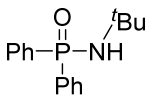
White amorphous solid (45 mg, 86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.87 (m, 4H), 7.50−7.33 (m, 6H), 3.44−3.27 (m, 1H), 2.72 (br, 1H), 1.22 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0 (d, J = 129 Hz), 132.1 (d, J = 9.4 Hz), 131.7 (d, J = 2.6 Hz), 128.5 (d, J = 12.5 Hz), 43.8, 26.2 (d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.9.

_N_-Cyclohexyl-_P,P_-diphenylphosphinic Amide (5e)[13].



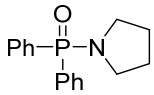
White amorphous solid (45 mg, 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.81 (m, 4H), 7.50−7.36 (m, 6H), 3.07−2.89 (m, 1H), 2.83−2.79 (m, 1H), 2.09−1.94 (m, 2H), 1.74−1.60 (m, 2H), 1.55−1.44 (m, 1H), 1.28−1.02 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2 (d, J = 130 Hz), 132.1 (d, J = 9.4 Hz), 131.7 (d, J = 2.7 Hz), 128.5 (d, J = 12.5 Hz), 50.6, 36.6 (d, J = 4.8 Hz), 25.3, 25.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.1.

_N_-(_tert_-Butyl)-_P,P_-diphenylphosphinic Amide (5f)[14].



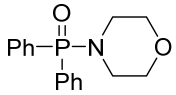
White amorphous solid (11 mg, 20%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.74 (m, 4H), 7.44−7.30 (m, 6H), 2.72 (br, 1H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9 (d, J = 128 Hz), 131.8 (d, J = 9.5 Hz), 131.4 (d, J = 2.7 Hz), 128.4 (d, J = 12.6 Hz), 53.2 (d, J = 3.2 Hz), 32.3 (d, J = 4.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7.

Diphenyl(pyrrolidin-1-yl)phosphine Oxide (5h)[15].



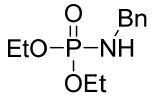
Yellow oil (53 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.75 (m, 4H), 7.49−7.32 (m, 6H), 3.15−2.99 (m, 4H), 1.90−1.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.7 (d, J = 130 Hz), 132.2 (d, J = 9.2 Hz), 131.6 (d, J = 2.7 Hz), 128.5 (d, J = 12.4 Hz), 46.9 (d, J = 2.1 Hz), 26.6 (d, J = 6.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.4.

Morpholinodiphenylphosphine Oxide (5i)[15].



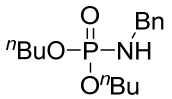
Yellow oil (42 mg, 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.81 (m, 4H), 7.54−7.42 (m, 6H), 3.77−3.63 (m, 4H), 3.17−2.99 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4 (d, J = 9.1 Hz), 132.0 (d, J = 2.6 Hz), 130.8 (d, J = 129 Hz), 128.7 (d, J = 12.4 Hz), 67.2 (d, J = 6.6 Hz), 45.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.2.

Diethyl Benzylphosphoramidate (5j)[16].



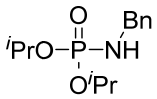
Yellow oil (24 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.54 (m, 4H), 7.53−7.48 (m, 1H), 4.45−4.15 (m, 6H), 3.04 (br, 1H), 1.54 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6 (d, J = 6.4 Hz), 128.5, 127.33, 127.28, 62.4 (d, J = 5.3 Hz), 45.3, 16.1 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.5.

Dibutyl Benzylphosphoramidate (5k).



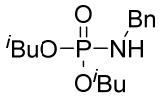
Yellow oil (18 mg, 30%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.16 (m, 5H), 4.03 (d, J = 9.7 Hz, 2H), 4.00−3.83 (m, 4H), 2.80 (br, 1H), 1.57 (dt, J = 14.6, 6.7 Hz, 4H), 1.39−1.27 (m, 4H), 0.86 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6 (d, J = 6.3 Hz), 128.5, 127.34, 127.28, 66.2 (d, J = 5.6 Hz), 45.4, 32.4 (d, J = 7.1 Hz), 18.8, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.6; HRMS (ESI-Orbitrap) m/z: $[M + Na]^+$ calcd for $C_{15}H_{26}NO_3PNa$ 322.1543, found 322.1539.

Diisopropyl Benzylphosphoramidate (5l)[16].



Yellow amorphous solid (19 mg, 35%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.19 (m, 5H), 4.69−4.49 (m, 2H), 4.05 (d, J = 9.1 Hz, 2H), 2.72 (br, 1H), 1.30 (d, J = 6.0 Hz, 6H), 1.25 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7 (d, J = 7.2 Hz), 128.5, 127.3(2C), 70.9 (d, J = 5.6 Hz), 45.4, 23.8 (d, J = 3.4 Hz), 23.7 (d, J = 4.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 6.6.

Diisobutyl Benzylphosphoramidate (5m).



Yellow amorphous solid (45 mg, 75%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.18 (m, 5H), 4.08 (d, J = 9.9 Hz, 2H), 3.83−3.63 (m, 4H), 2.97 (br, 1H), 1.97−1.84 (m, 2H), 0.92 (d, J = 3.2 Hz, 6H), 0.90 (d, J = 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6 (d, J = 6.2 Hz), 128.5, 127.3, 127.2, 72.3 (d, J = 5.9 Hz), 45.3, 29.1 (d, J = 7.4 Hz), 18.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.4; HRMS (ESI-Orbitrap) m/z: $[M + Na]^+$ calcd for $C_{15}H_{26}NO_3PNa$ 322.1543, found 322.1539.

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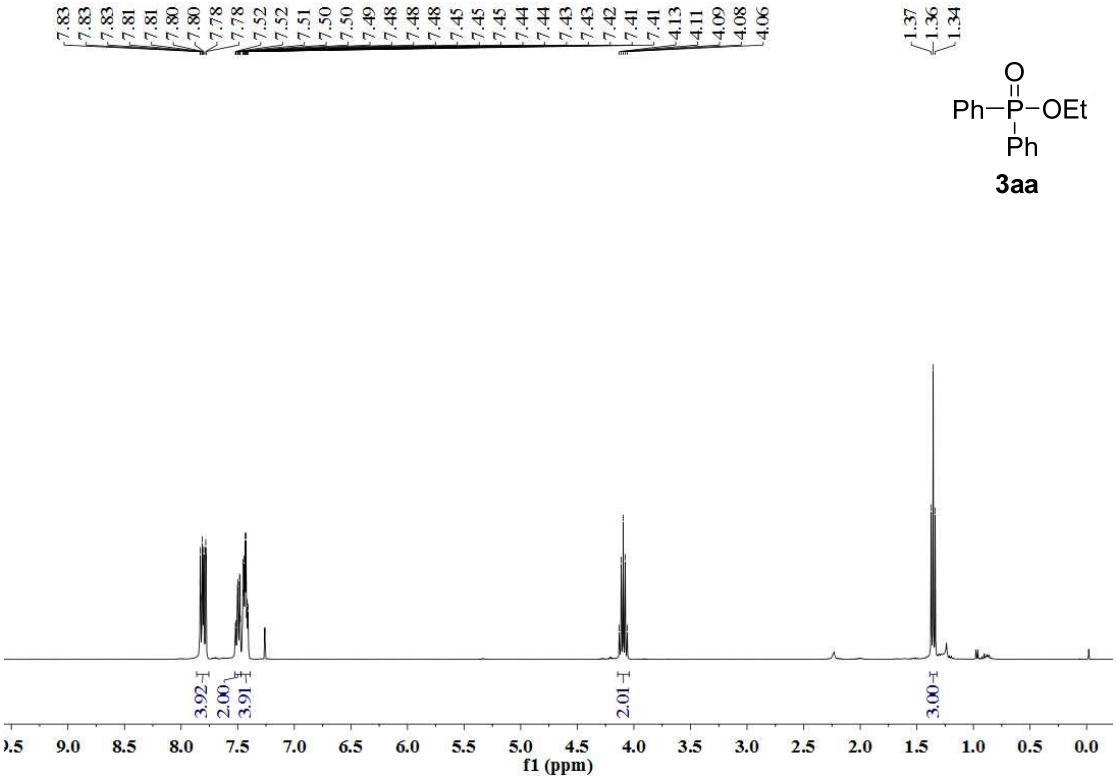
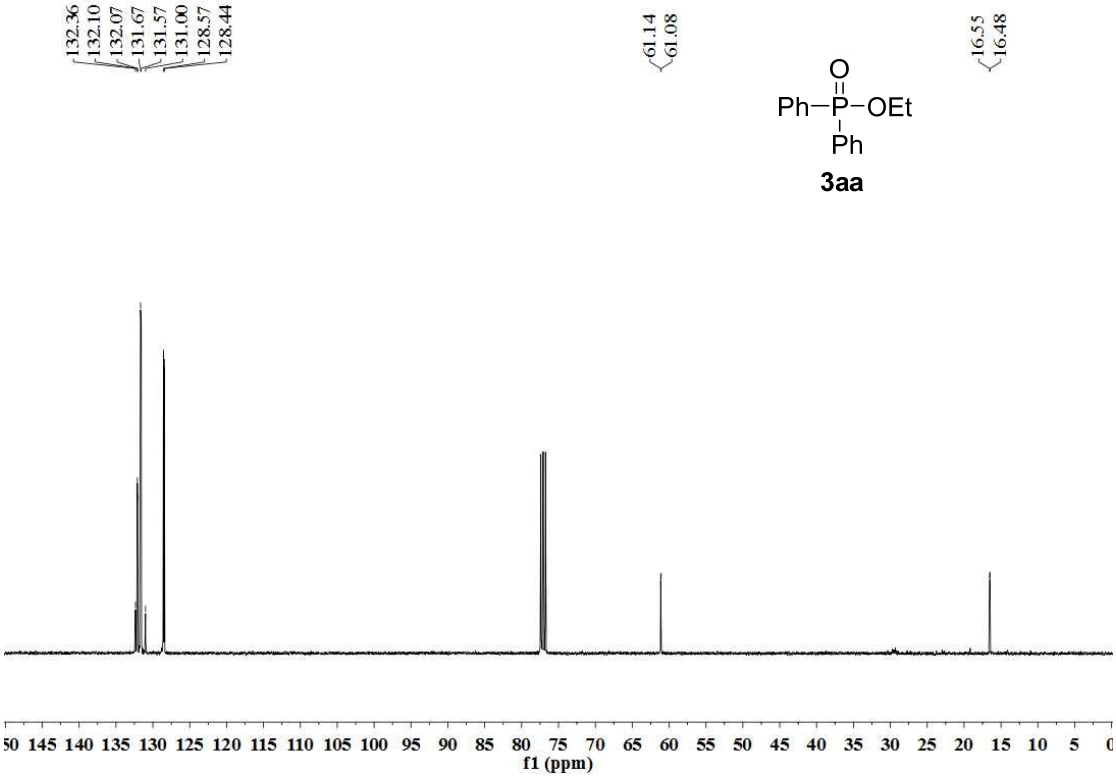
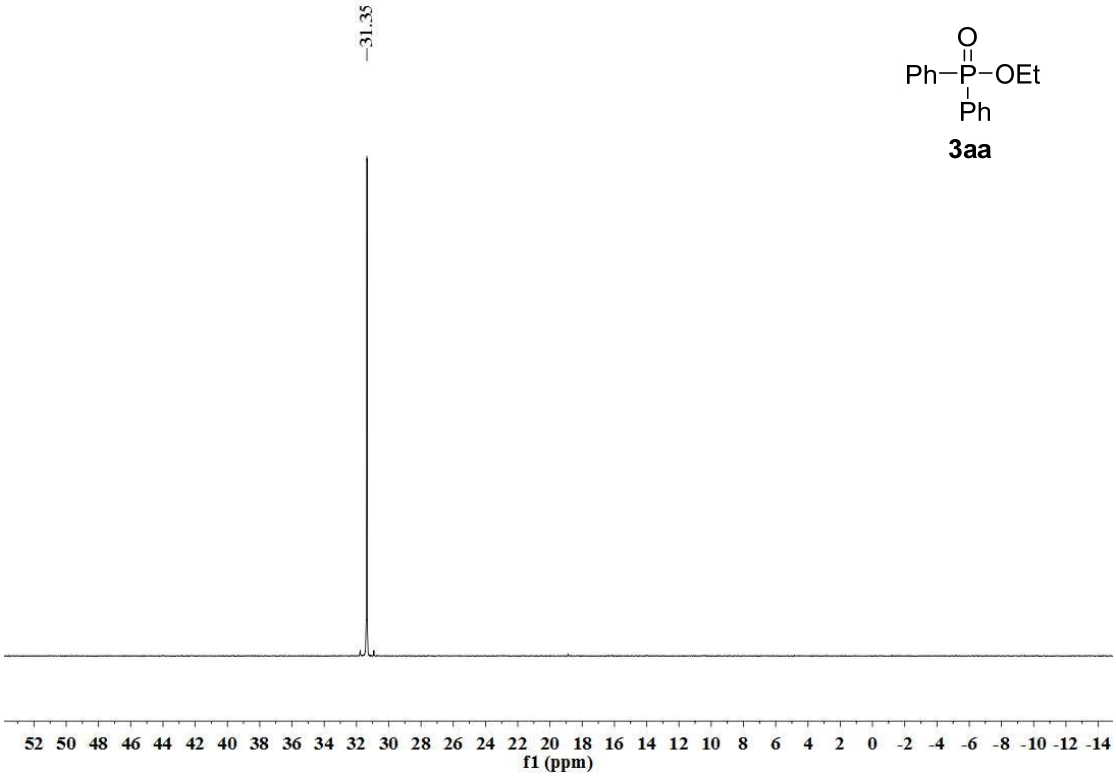
6. NMR Spectra for Products

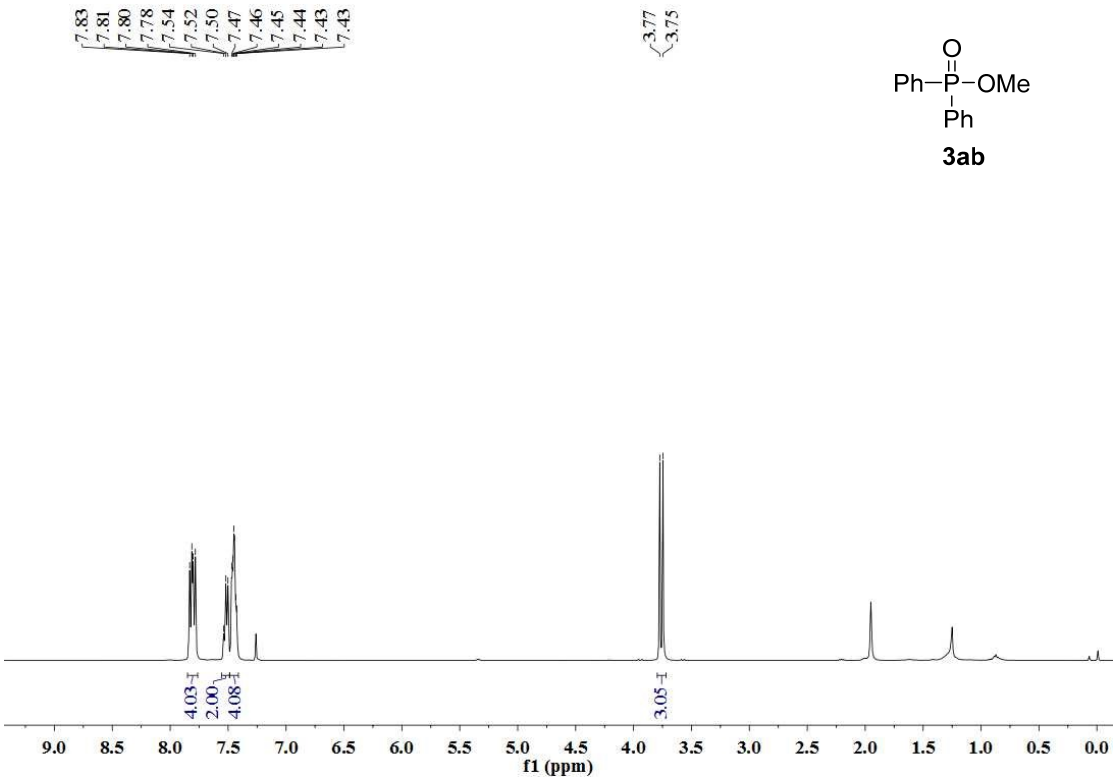





31.35
52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14
f1 (ppm)

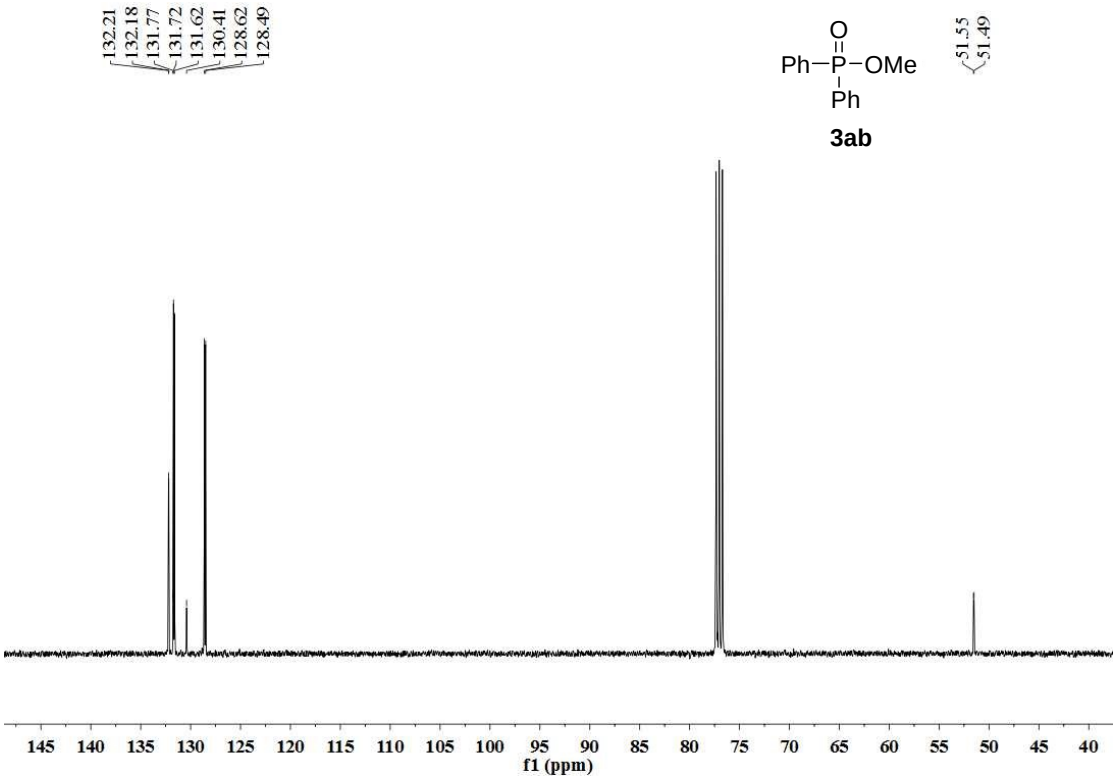
O
Ph
P
OEt
Ph

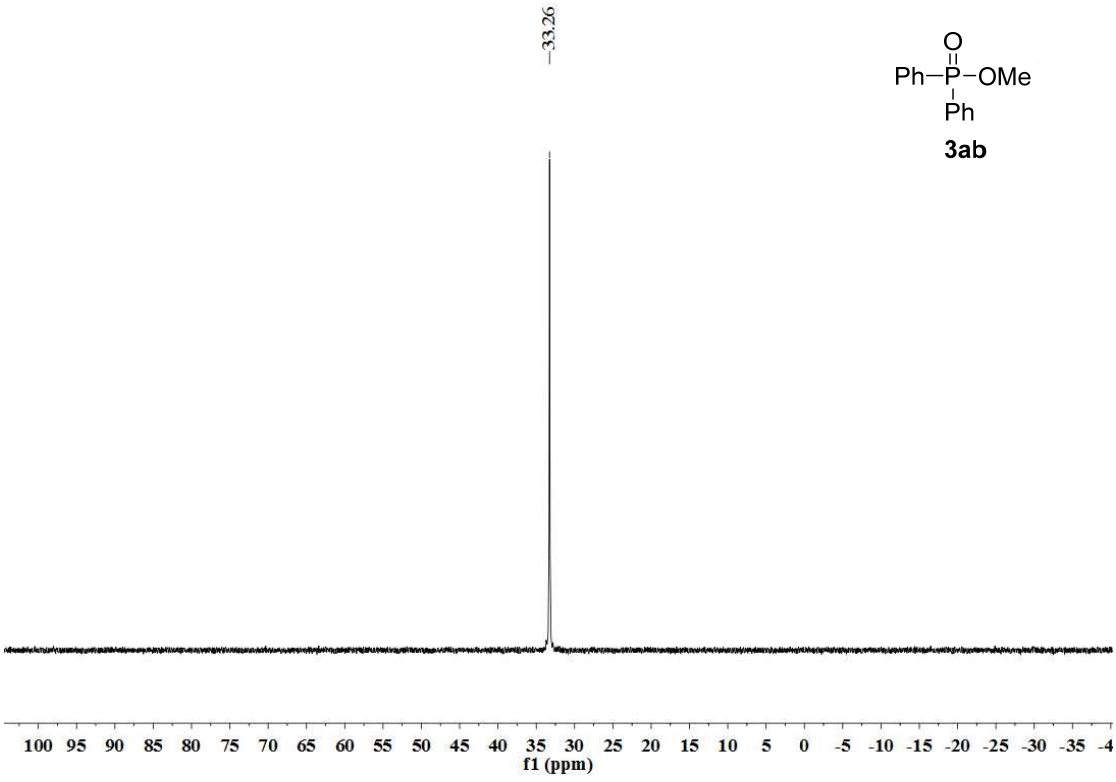
3aa

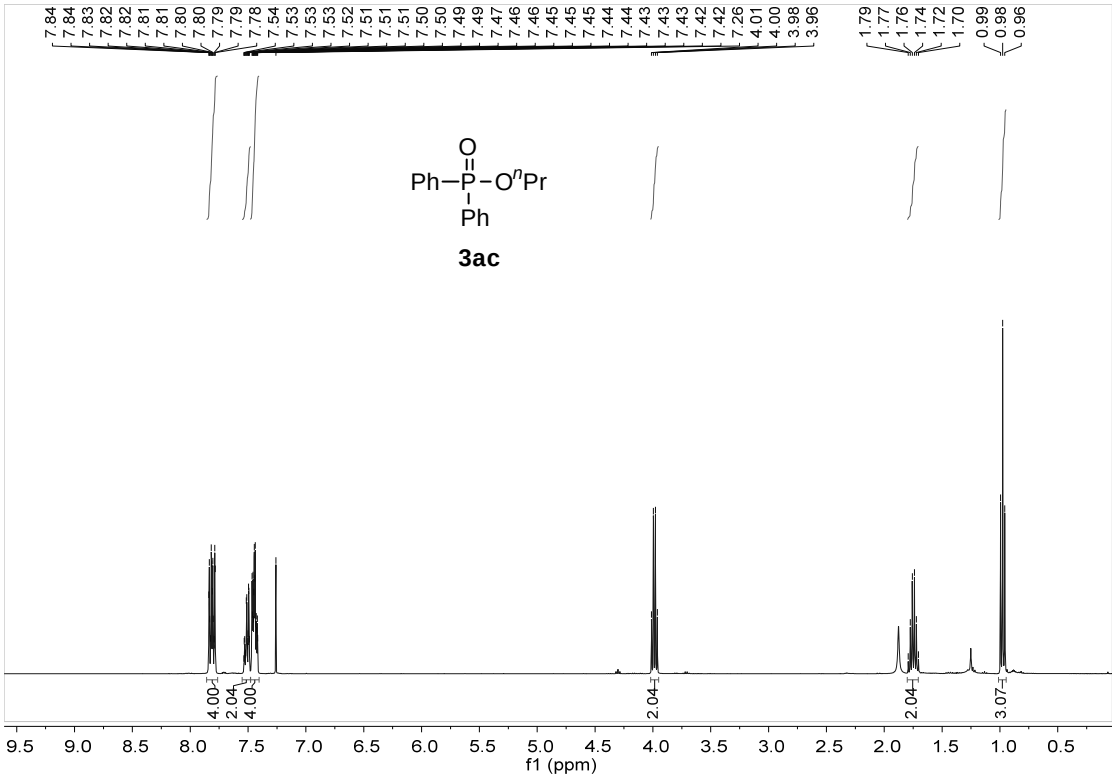

7.83
7.81
7.80
7.78
7.54
7.52
7.50
7.47
7.46
7.45
7.44
7.43
7.43
3.77
3.75
4.03
2.00
4.08
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

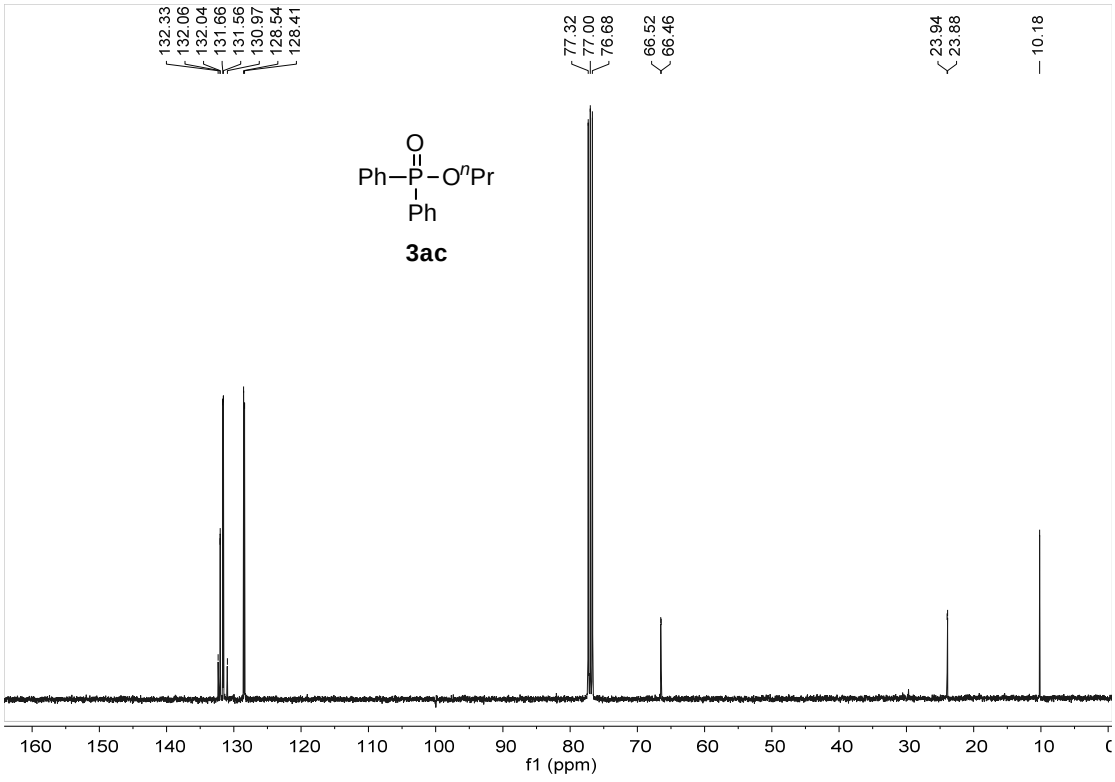
O
Ph
P
OMe
Ph

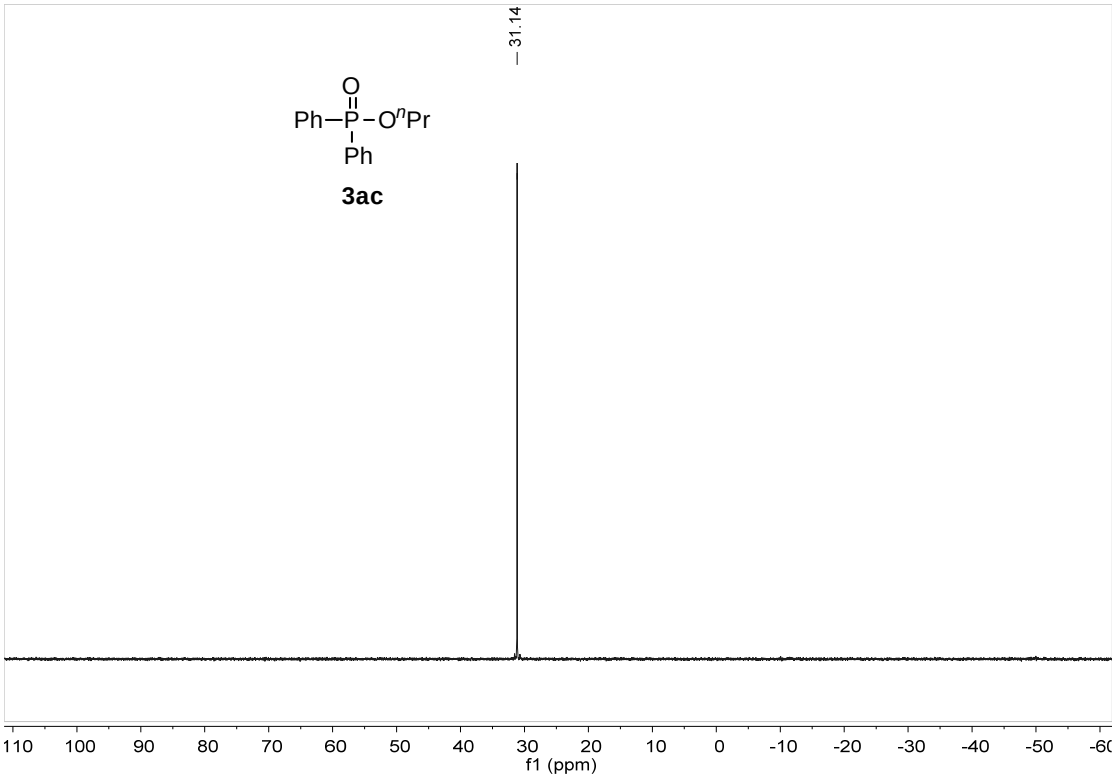
3ab

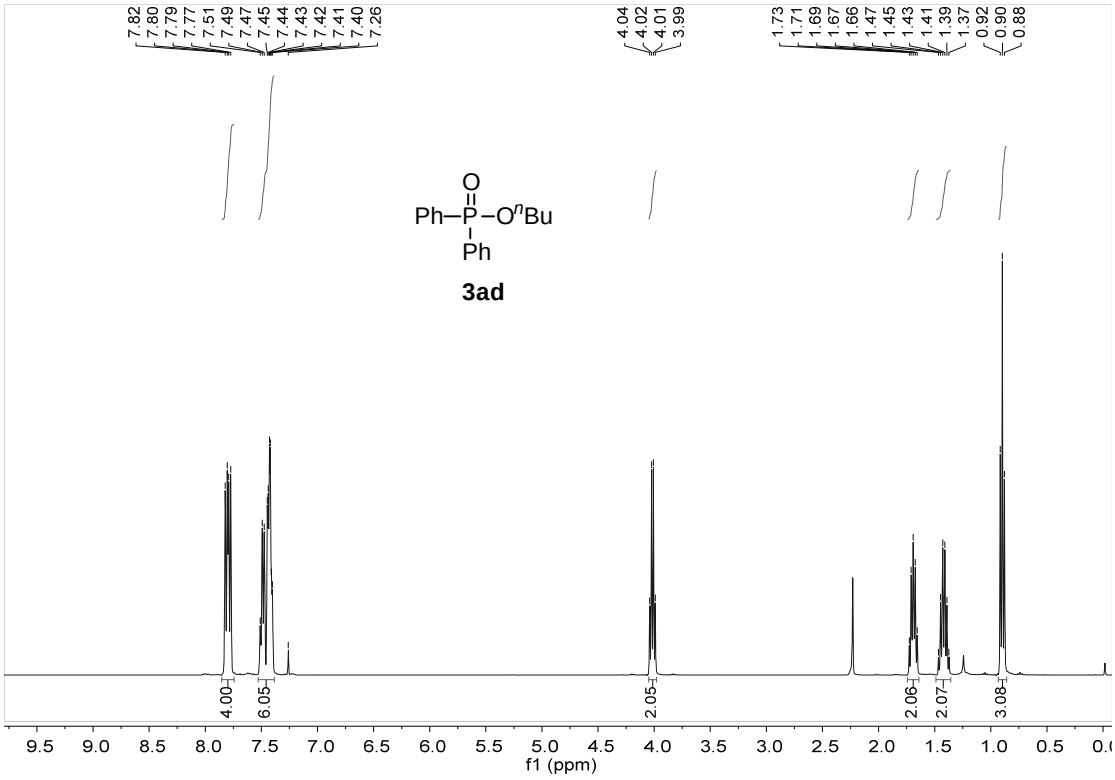

132.21
132.18
131.77
131.72
131.62
130.41
128.62
128.49
51.55
51.49
Ph—P(=O)—OMe
Ph
3ab
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

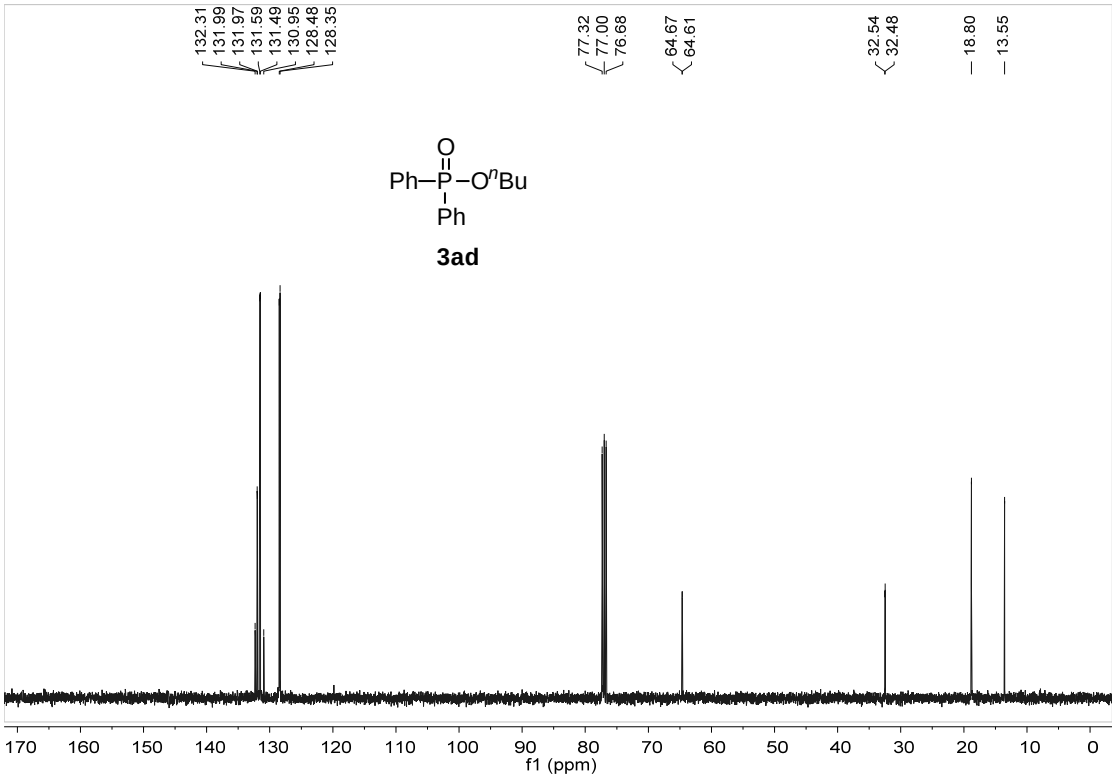

33.26
Ph—P(=O)—OMe
Ph
3ab
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -4
f1 (ppm)

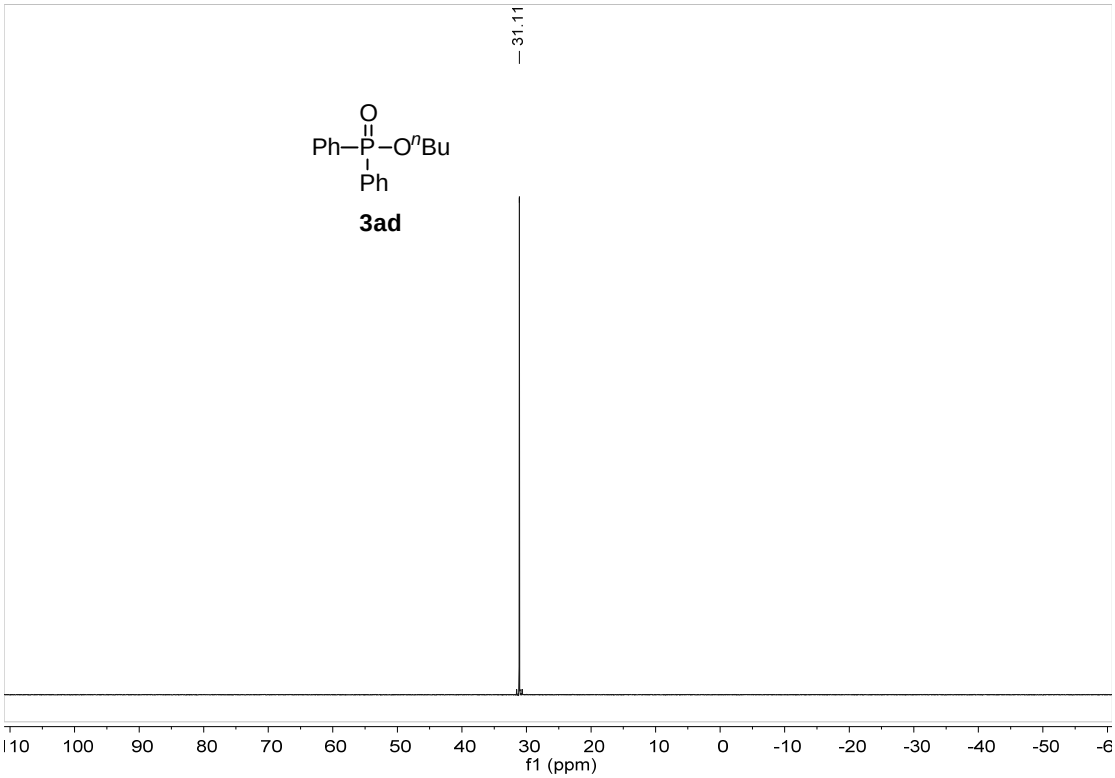

7.84 7.84 7.83 7.82 7.82 7.81 7.81 7.80 7.80 7.79 7.79 7.78 7.54 7.53 7.53 7.53 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.47 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.26 4.01 4.00 3.98 3.96
1.79 1.77 1.76 1.74 1.72 1.70
0.99 0.98 0.96
O
Ph—P—O^{n}Pr
Ph
3ac
4.00 2.04 4.00 2.04 2.04 3.07
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
f1 (ppm)

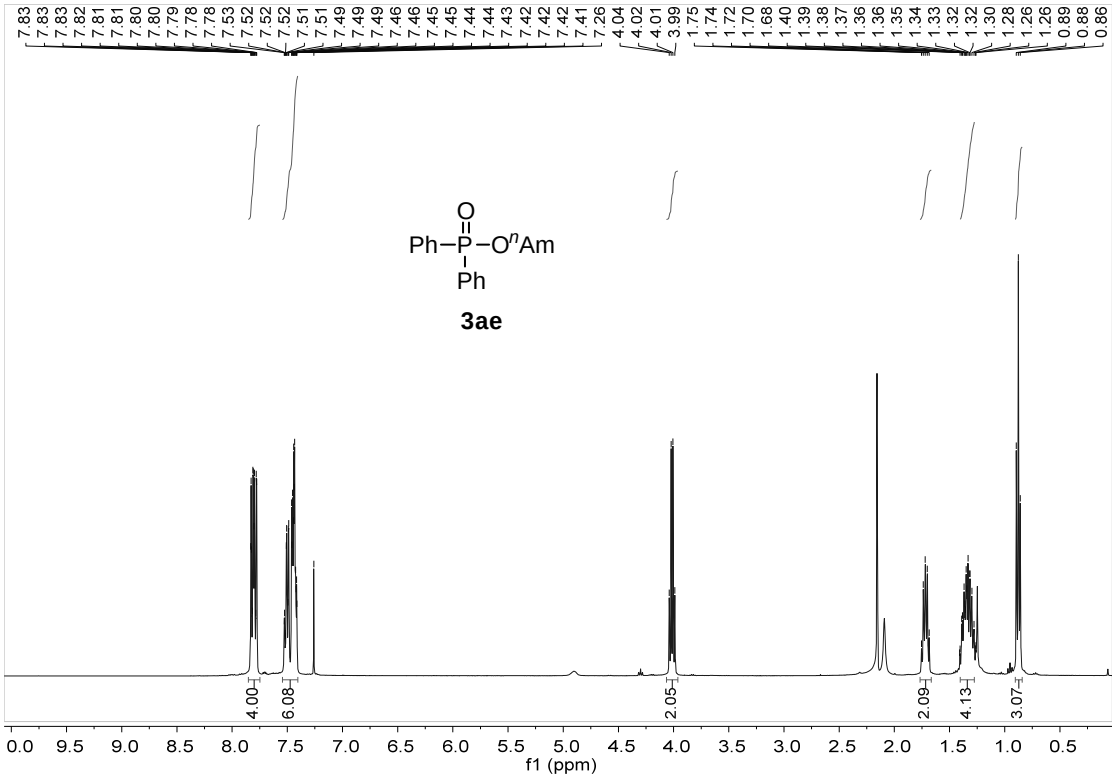

132.33 132.06 132.04 131.66 131.56 130.97 128.54 128.41
77.32 77.00 76.68
66.52 66.46
23.94 23.88
10.18
O
Ph—P—O^{n}Pr
Ph
3ac
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

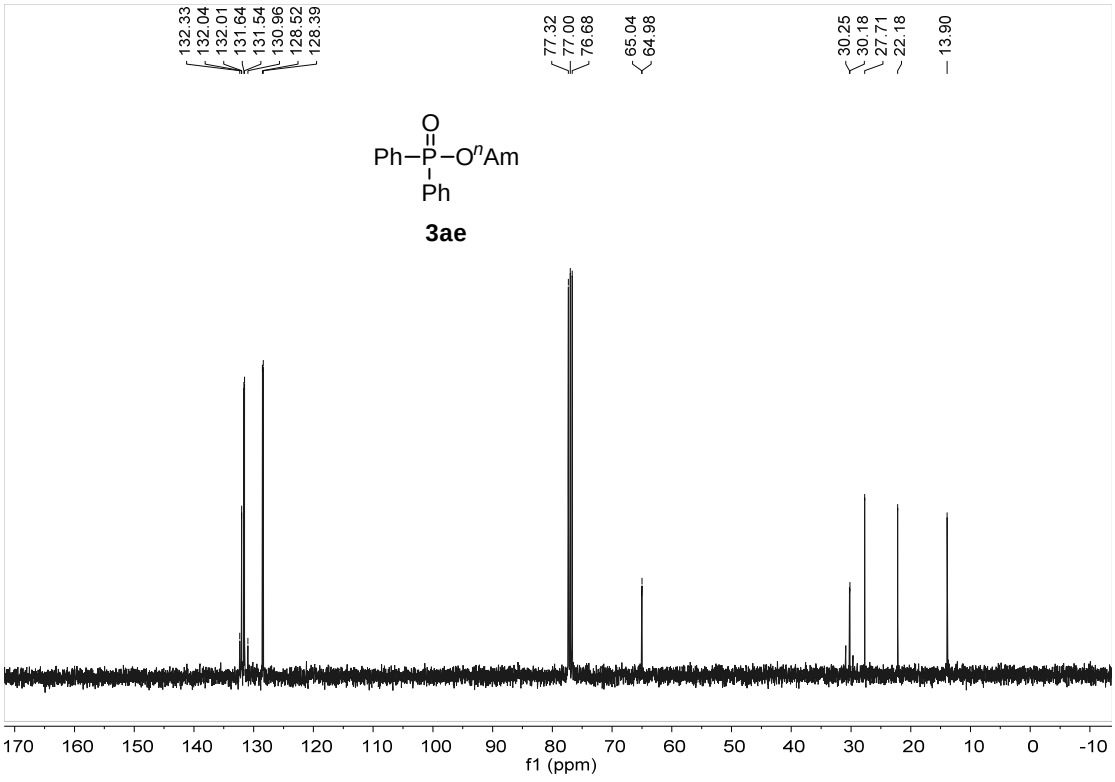

31.14
O
Ph—P—O^{n}Pr
Ph
3ac
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

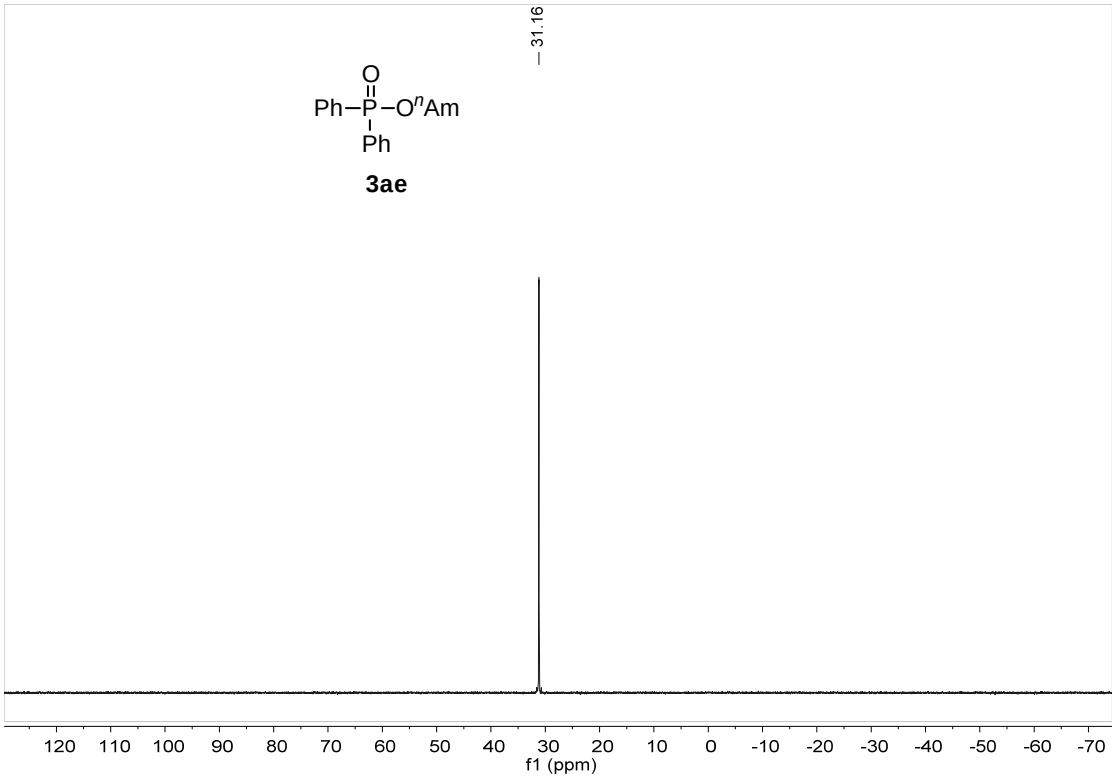

7.82 7.80 7.79 7.77 7.51 7.49 7.47 7.45 7.44 7.43 7.42 7.41 7.40 7.26
4.04 4.02 4.01 3.99
1.73 1.71 1.69 1.67 1.66 1.47 1.45 1.43 1.41 1.39 1.37 0.92 0.90 0.88
O
Ph—P—O^{n}Bu
Ph
3ad
4.00 6.05 2.05 2.06 2.07 3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

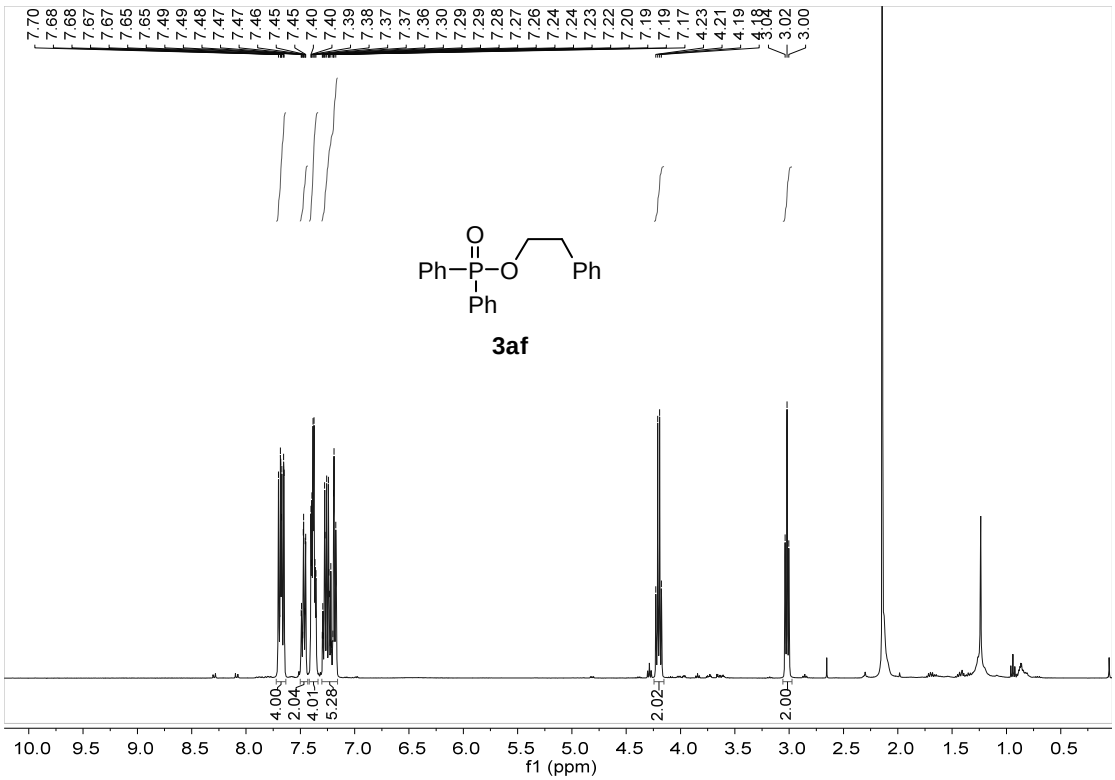

132.31
131.99
131.97
131.59
131.49
130.95
128.48
128.35
77.32
77.00
76.68
64.67
64.61
32.54
32.48
18.80
13.55
O
Ph—P—O^{n}Bu
Ph
3ad
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

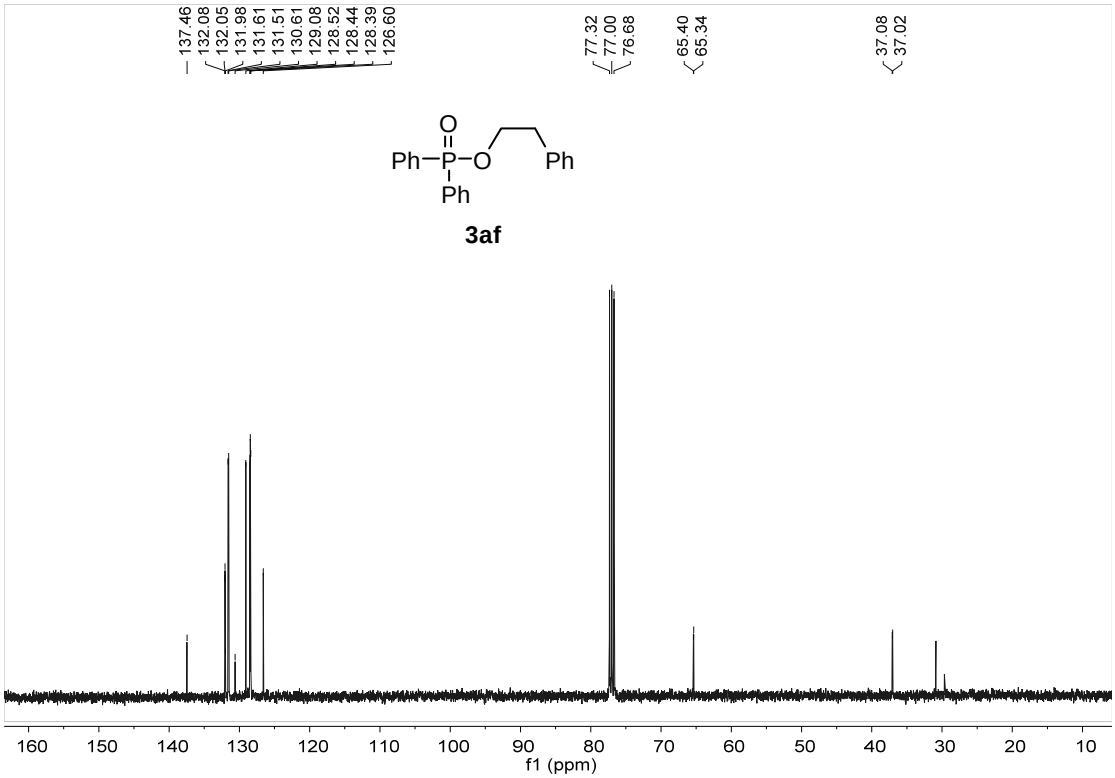

31.11
O
Ph—P—O^{n}Bu
Ph
3ad
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -6
f1 (ppm)

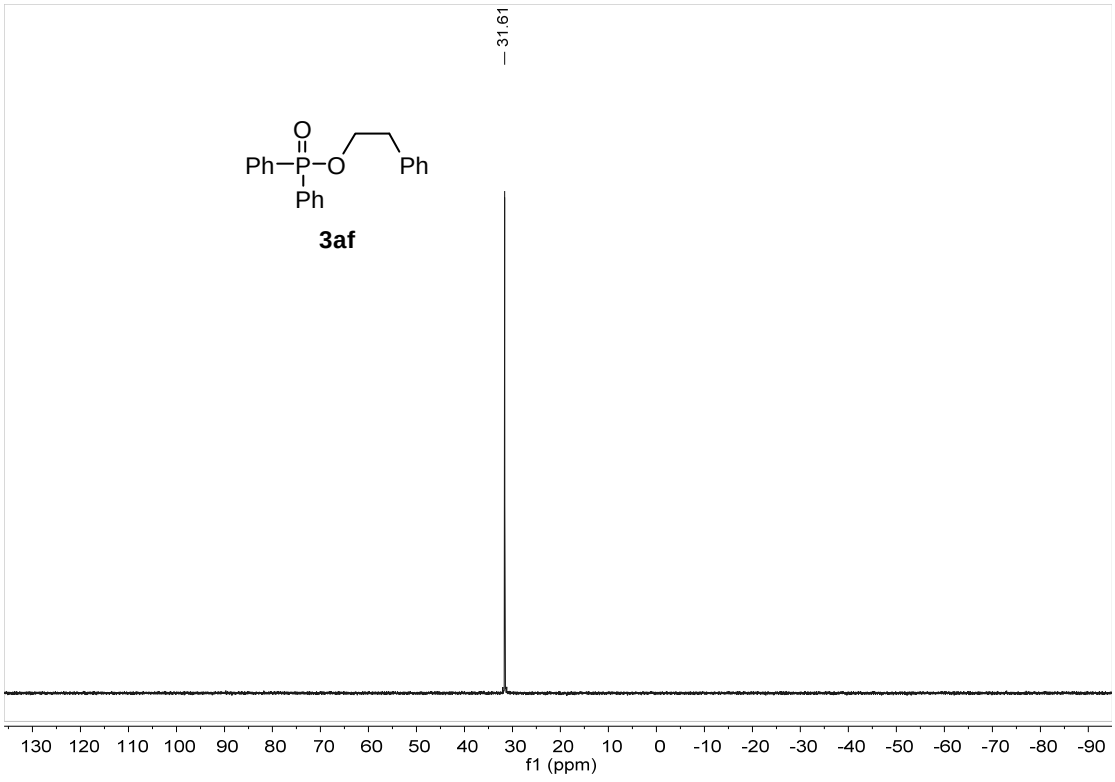

7.83 7.83 7.83 7.82 7.81 7.81 7.80 7.80 7.79 7.78 7.78 7.53 7.52 7.52 7.52 7.51 7.51 7.49 7.49 7.49 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.42 7.42 7.42 7.41 7.26 4.04 4.02 4.01 3.99 1.75 1.74 1.72 1.70 1.68 1.40 1.39 1.38 1.37 1.36 1.36 1.35 1.34 1.33 1.32 1.32 1.30 1.28 1.26 1.26 0.89 0.88 0.86
Ph–P(=O)(Ph)–O^{n}Am
3ae
4.00 6.08 2.05 2.09 4.13 3.07
0.0 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
f1 (ppm)

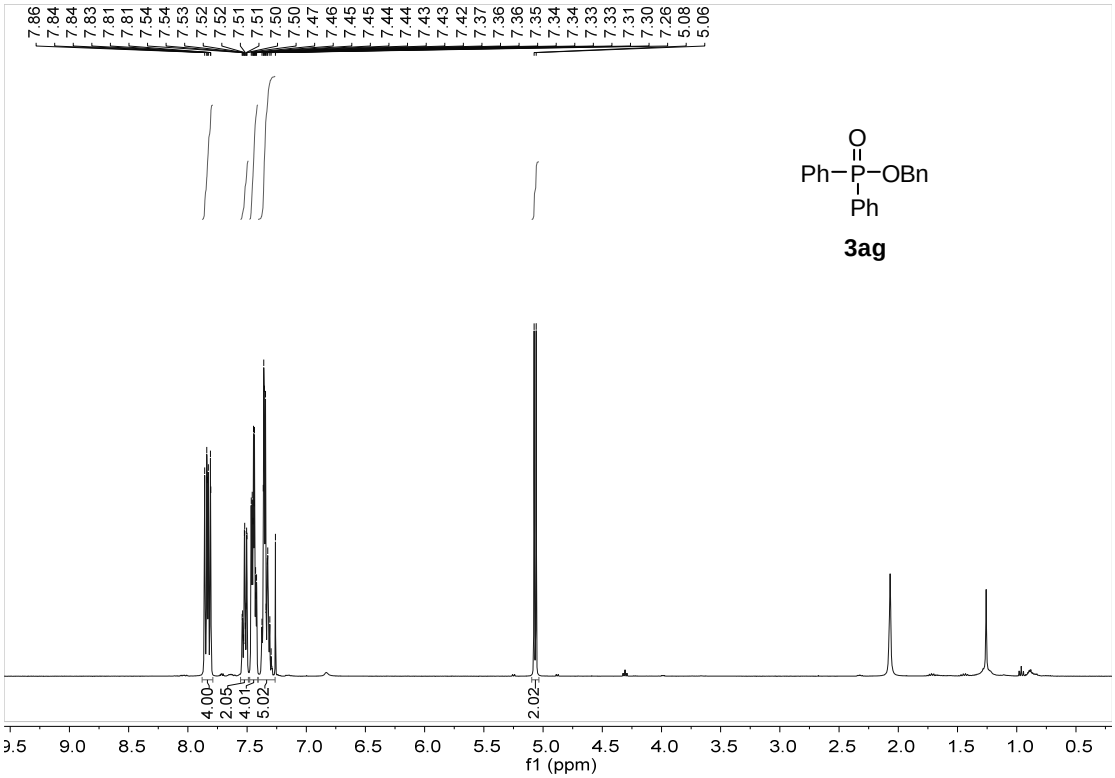

132.33 132.04 132.01 131.64 131.54 130.96 128.52 128.39
77.32 77.00 76.68
65.04 64.98
30.25 30.18 27.71 22.18
13.90
Ph–P(=O)(Ph)–O^{n}Am
3ae
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

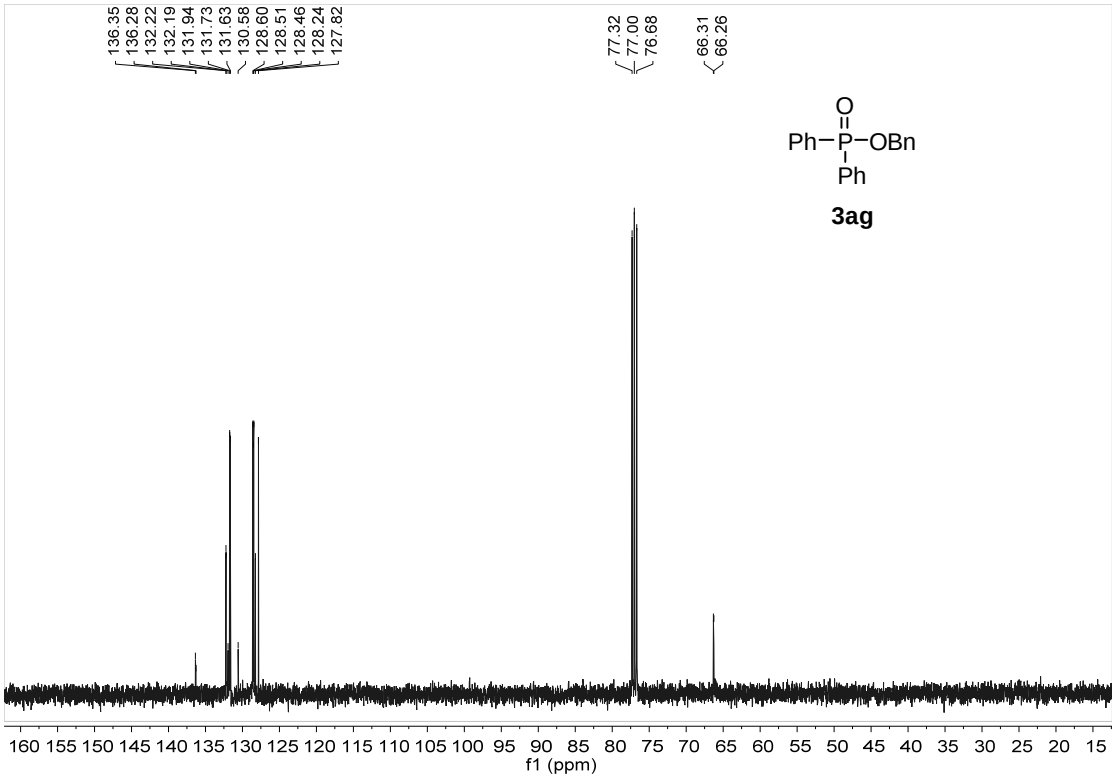

31.16
Ph–P(=O)(Ph)–O^{n}Am
3ae
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

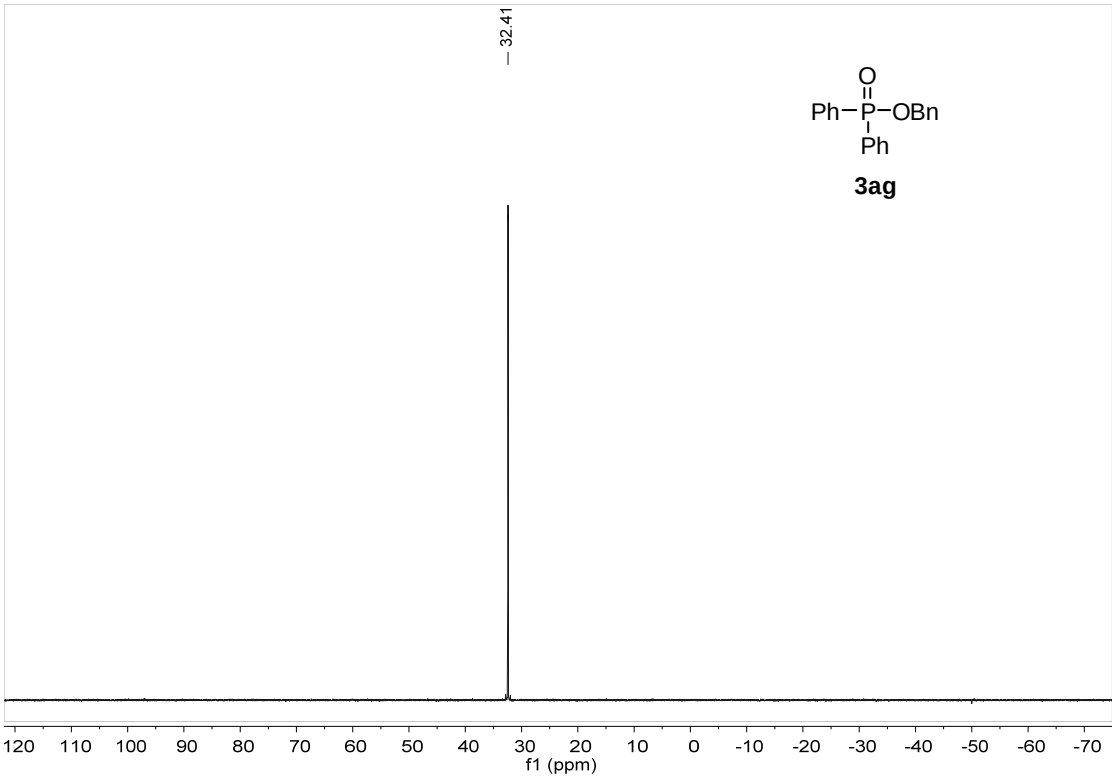

7.70 7.68 7.68 7.67 7.67 7.65 7.65 7.49 7.49 7.48 7.47 7.47 7.46 7.45 7.45 7.40 7.40 7.39 7.38 7.37 7.37 7.36 7.30 7.29 7.29 7.28 7.27 7.26 7.24 7.24 7.23 7.22 7.20 7.19 7.19 7.17 4.23 4.21 4.19 4.18 3.04 3.02 3.00
Ph–P(=O)(Ph)–O–Ph
3af
4.00 2.04 4.01 5.28 2.02 2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

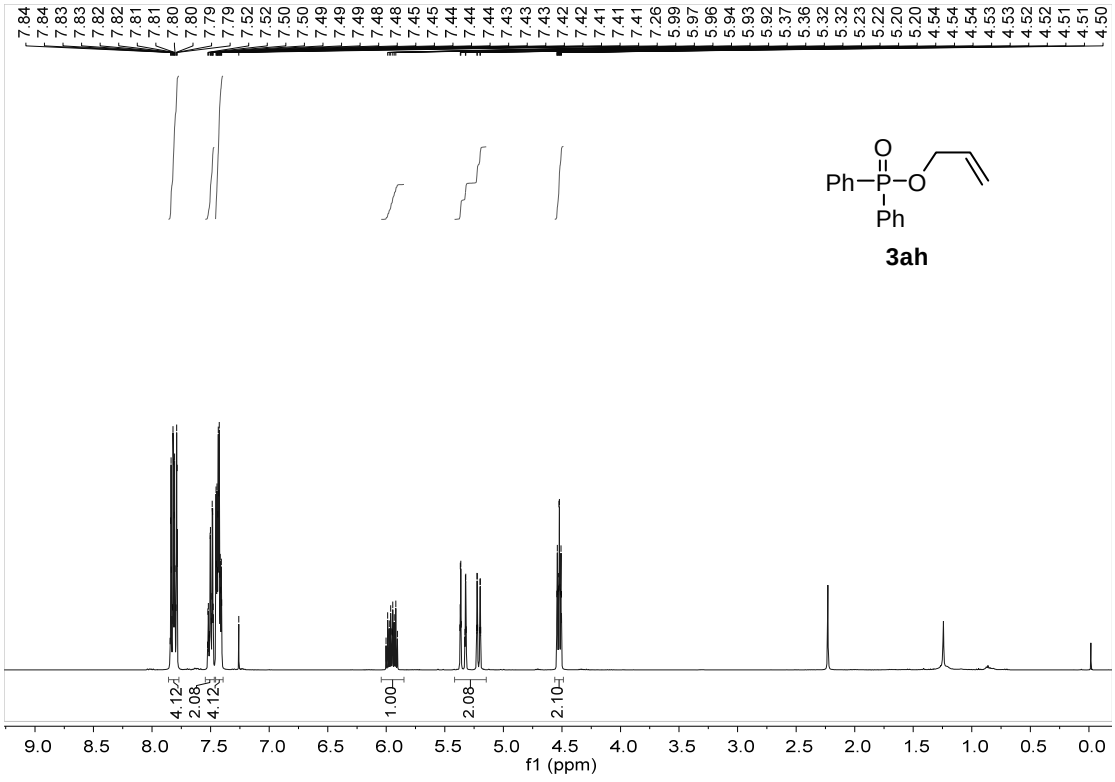

137.46
132.08
132.05
131.98
131.61
131.51
130.61
129.08
128.52
128.44
128.39
126.60
77.32
77.00
76.68
65.40
65.34
37.08
37.02
Ph
P
O
Ph
Ph
O
3af
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

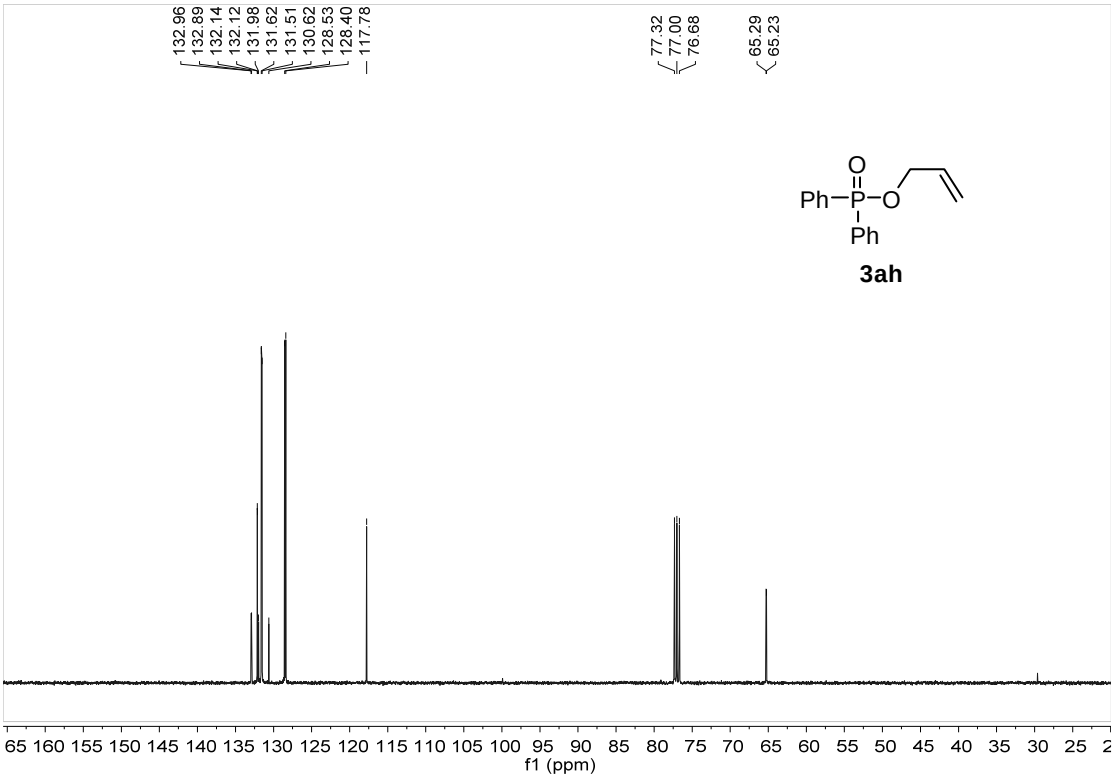

31.61
Ph
P
O
Ph
Ph
O
3af
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

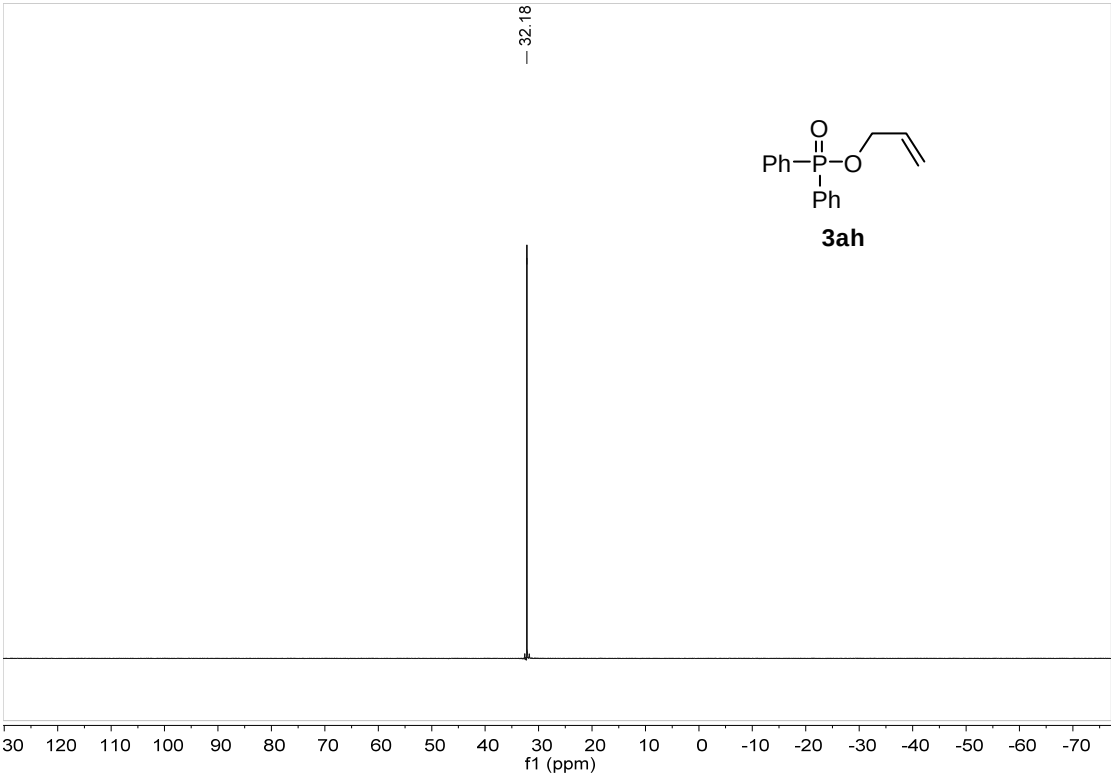

7.86
7.84
7.84
7.83
7.81
7.81
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.31
7.30
7.26
5.08
5.06
O
Ph–P–OBn
Ph
3ag
4.00
2.05
4.01
5.02
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

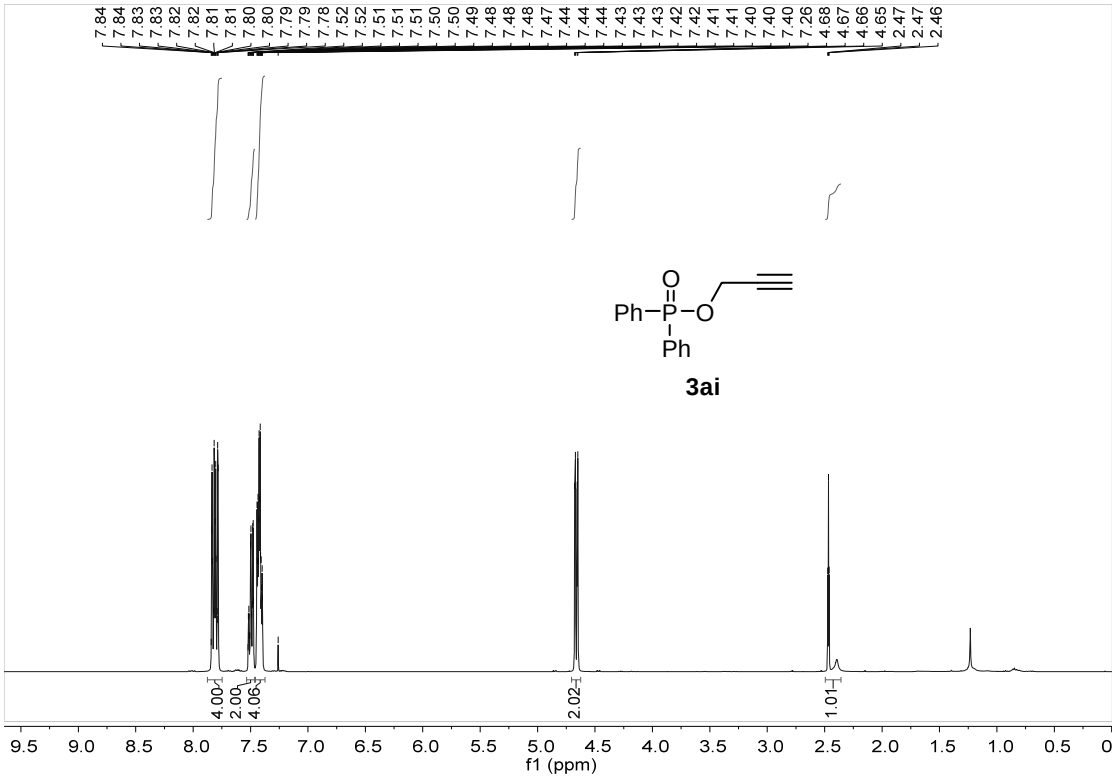

136.35
136.28
132.22
132.19
131.94
131.73
131.63
130.58
128.60
128.51
128.46
128.24
127.82
77.32
77.00
76.68
66.31
66.26
O
Ph–P–OBn
Ph
3ag
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

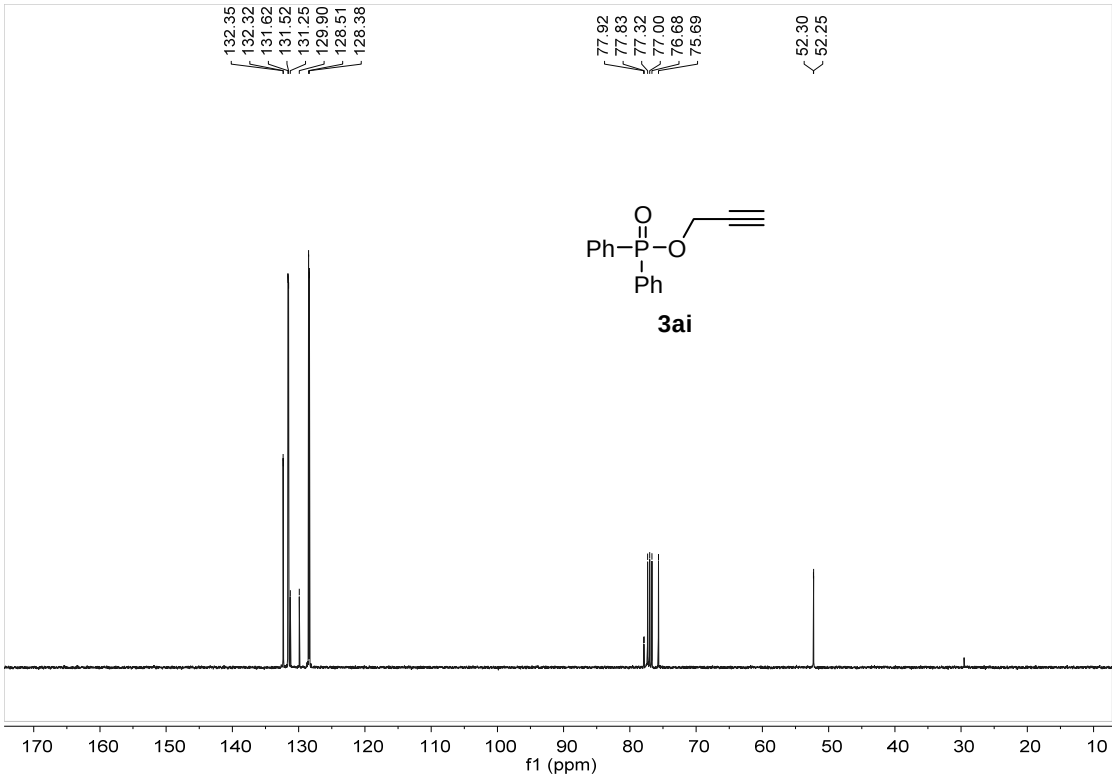

32.41
O
Ph–P–OBn
Ph
3ag
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

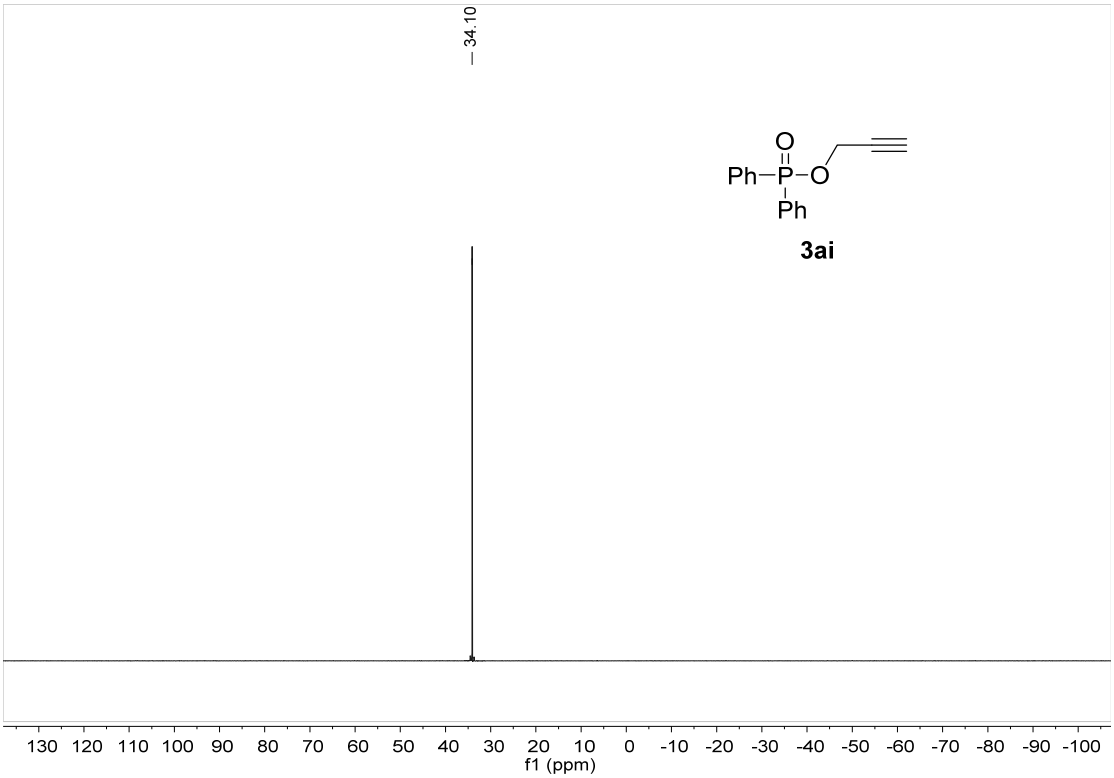

O
Ph–P–O
Ph
3ah
4.12
2.08
4.12
1.00
2.08
2.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


132.96
132.89
132.14
132.12
131.98
131.62
131.51
130.62
128.53
128.40
117.78
77.32
77.00
76.68
65.29
65.23
O
Ph—P—O
Ph
3ah
65 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 2
f1 (ppm)

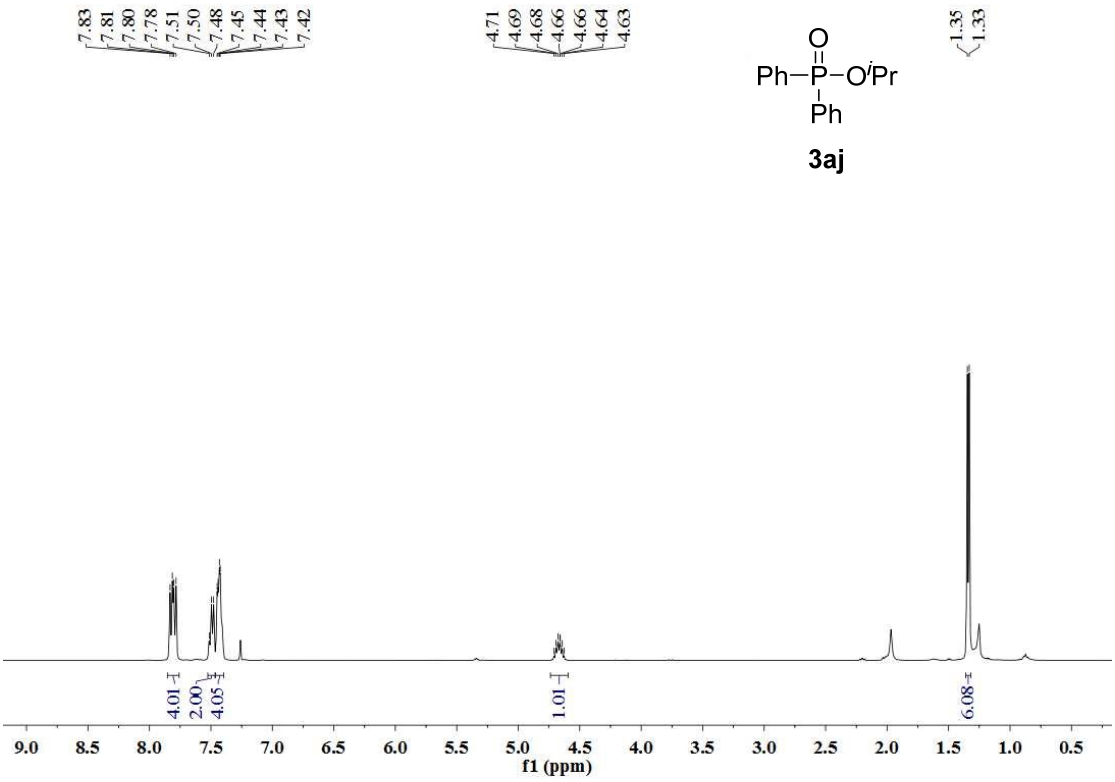

32.18
O
Ph—P—O
Ph
3ah
30 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)


7.84 7.84 7.83 7.83 7.82 7.82 7.81 7.81 7.80 7.80 7.79 7.79 7.78 7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.48 7.48 7.48 7.47 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.26 4.68 4.67 4.66 4.65 2.47 2.46
O
Ph–P–O
Ph
3ai
4.00
2.00
4.06
2.02
1.01
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
f1 (ppm)

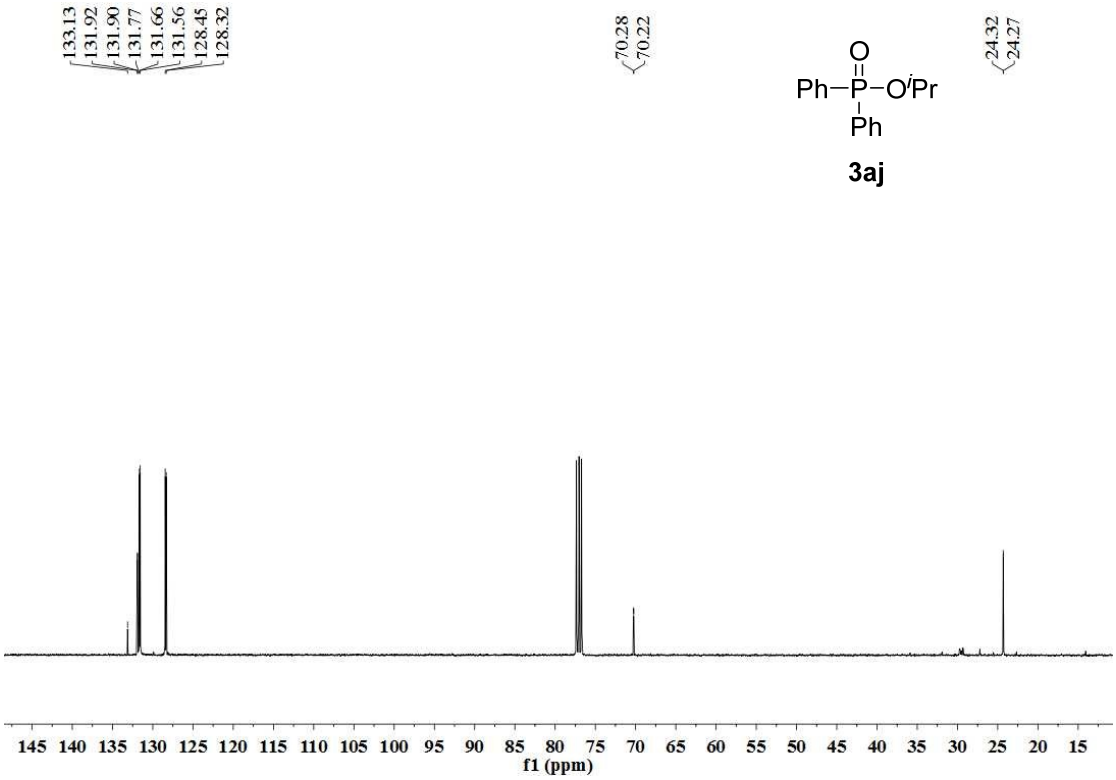

132.35 132.32 131.62 131.52 131.25 129.90 128.51 128.38
77.92 77.83 77.32 77.00 76.68 75.69
52.30 52.25
O
Ph–P–O
Ph
3ai
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

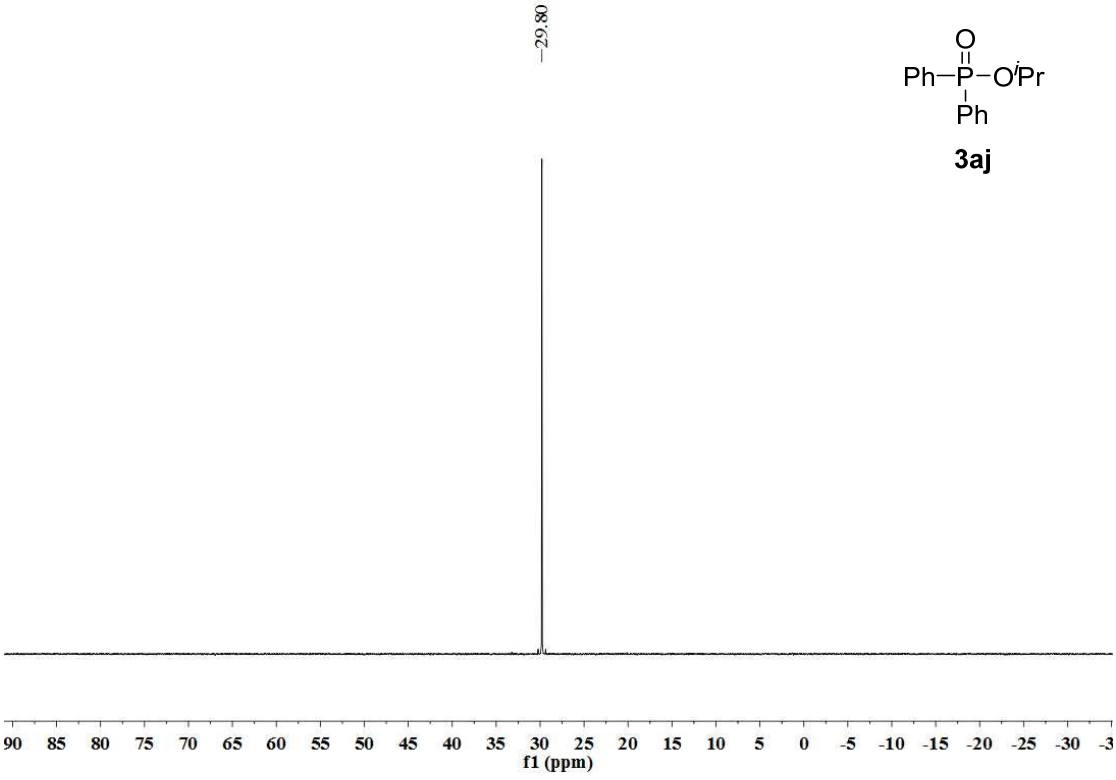

34.10
Ph–P(=O)(Ph)–O
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

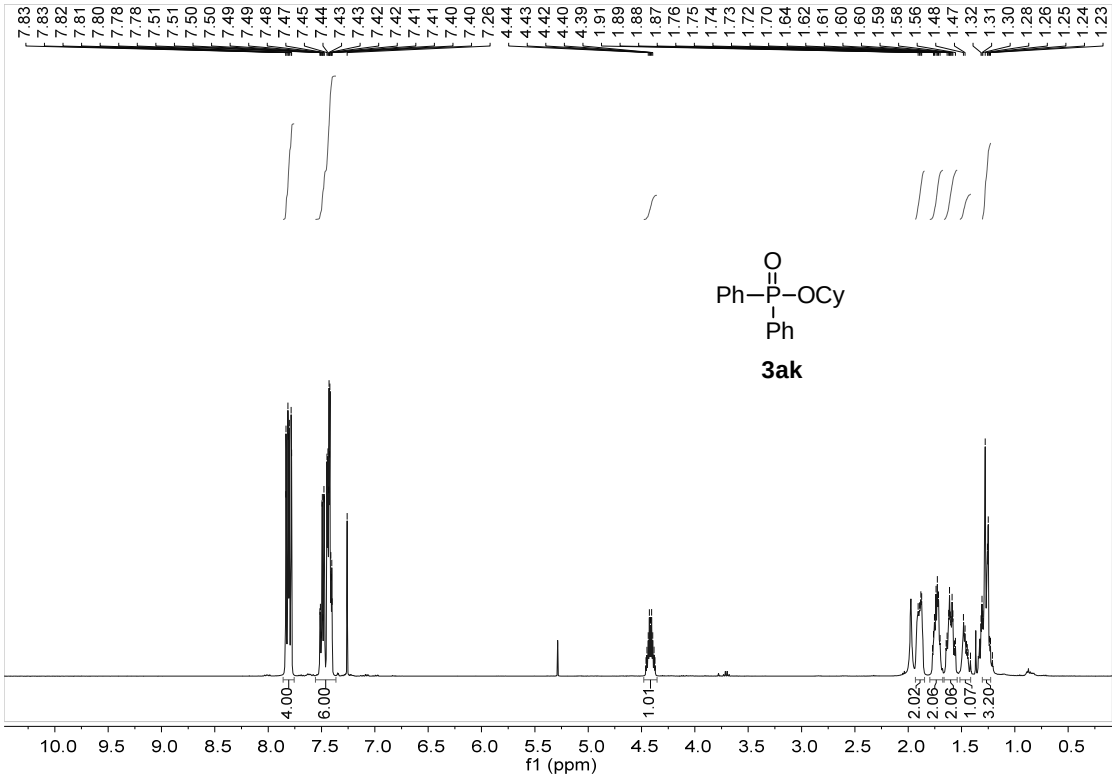
3ai

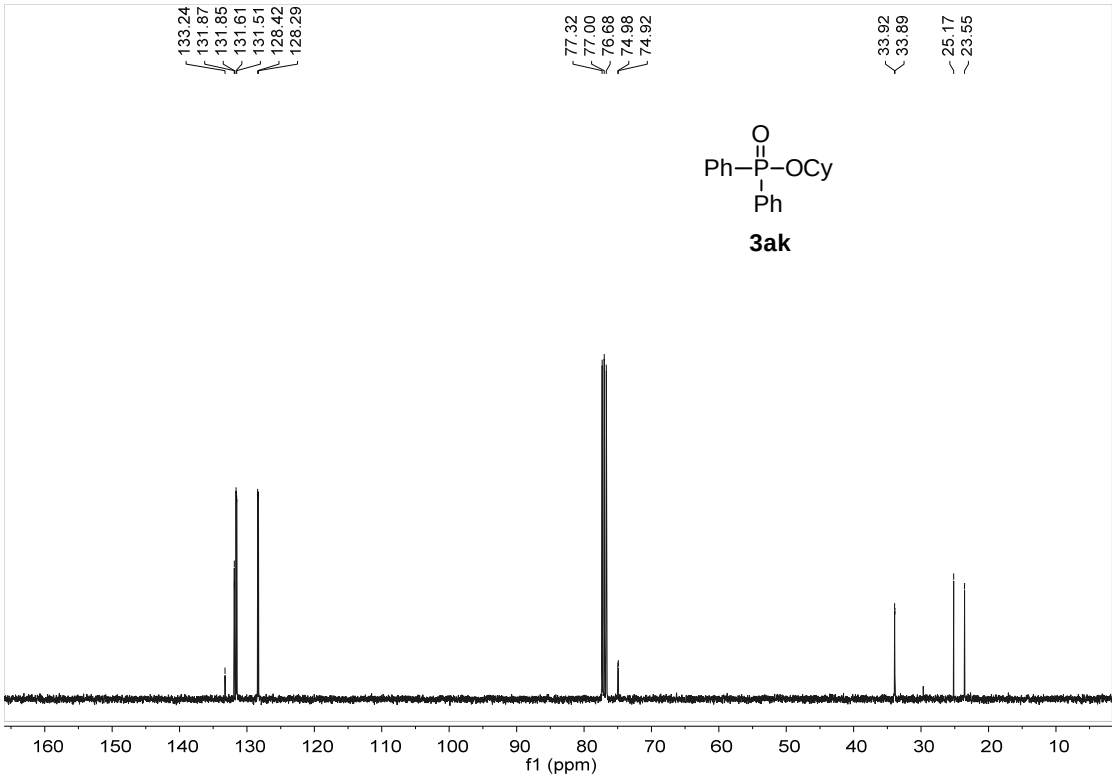

7.83
7.81
7.80
7.78
7.51
7.50
7.48
7.45
7.44
7.43
7.42
4.71
4.69
4.68
4.66
4.66
4.64
4.63
1.35
1.33
Ph–P(=O)(Ph)–OiPr
4.01
2.00
4.05
1.01
6.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

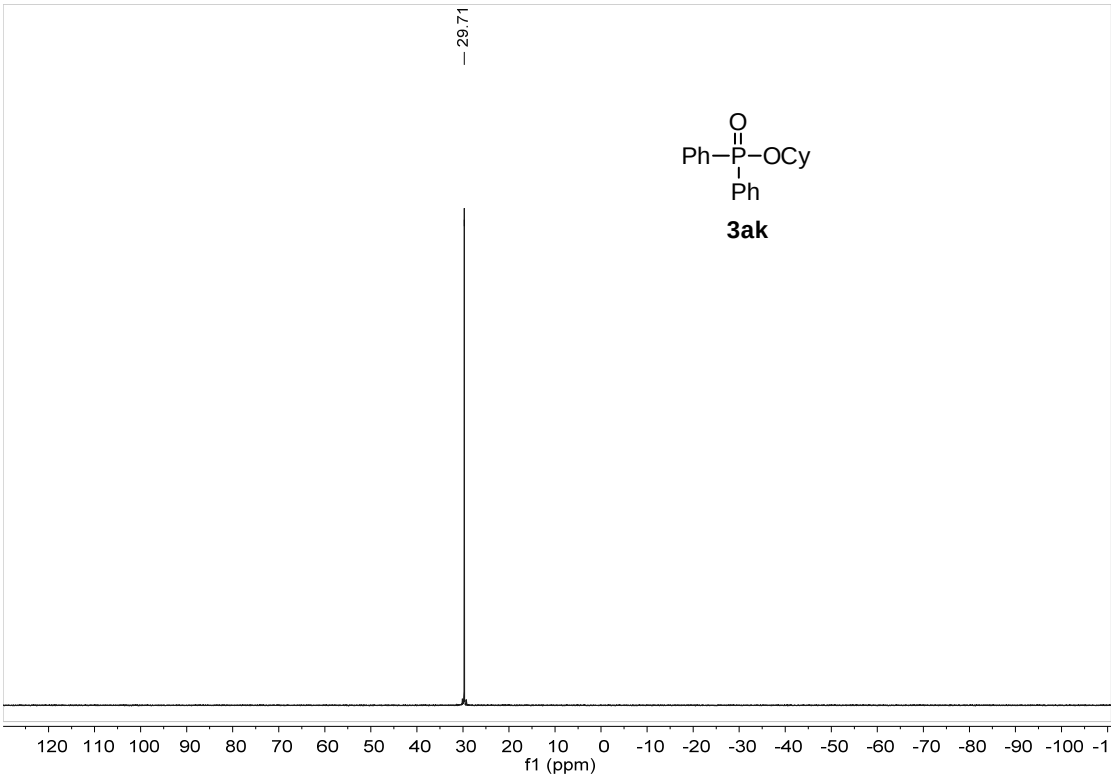
3aj

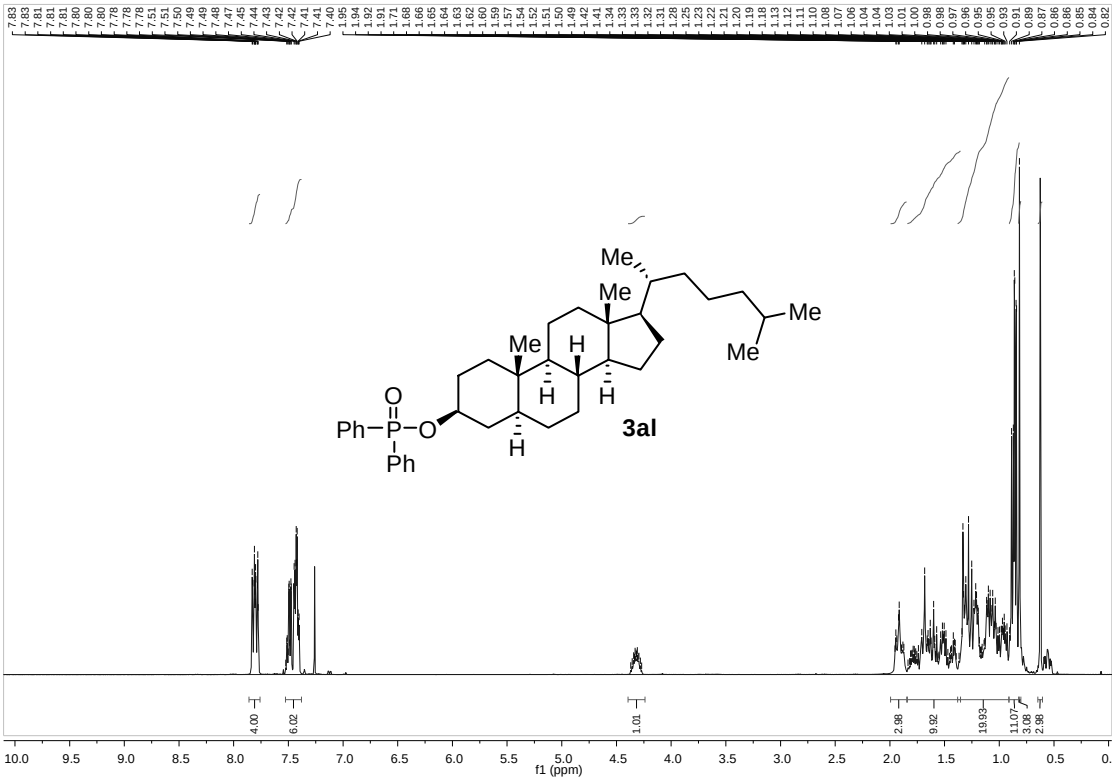

133.13
131.92
131.90
131.77
131.66
131.56
128.45
128.32
70.28
70.22
24.32
24.27
Ph—P(=O)(Ph)—OiPr
3aj
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

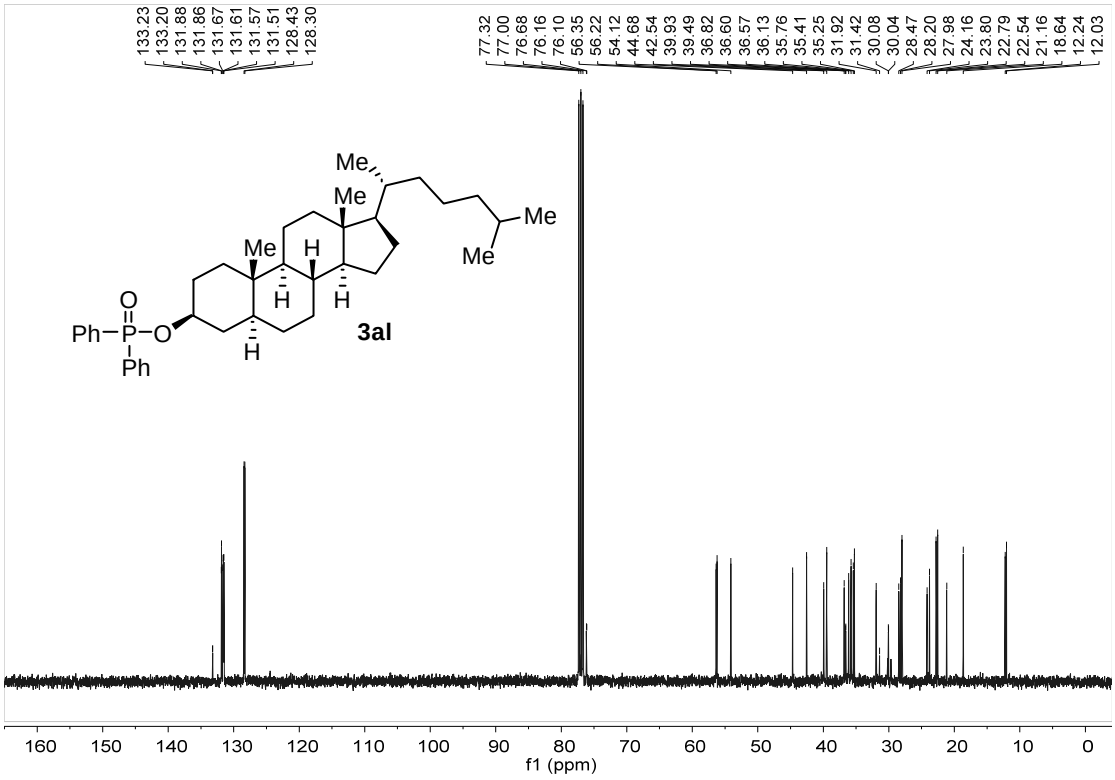

29.80
Ph—P(=O)(Ph)—OiPr
3aj
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -3
f1 (ppm)

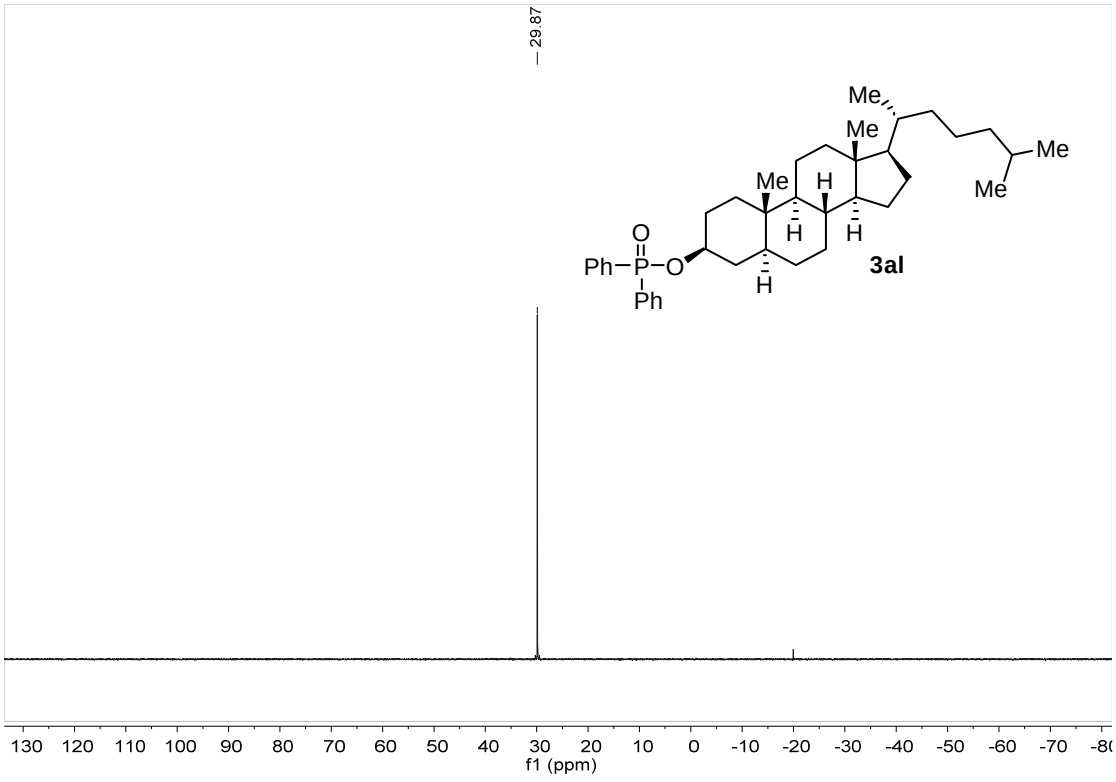

7.83 7.83 7.82 7.81 7.80 7.78 7.78 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.26
4.44 4.43 4.42 4.40 4.39 1.91 1.89 1.88 1.87 1.76 1.75 1.74 1.73 1.72 1.70 1.64 1.62 1.61 1.60 1.60 1.59 1.58 1.56 1.48 1.47 1.32 1.31 1.30 1.28 1.26 1.25 1.24 1.23
O
Ph—P—OCy
Ph
3ak
4.00
6.00
1.01
2.02
2.06
2.06
1.07
3.20
10.0 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
f1 (ppm)

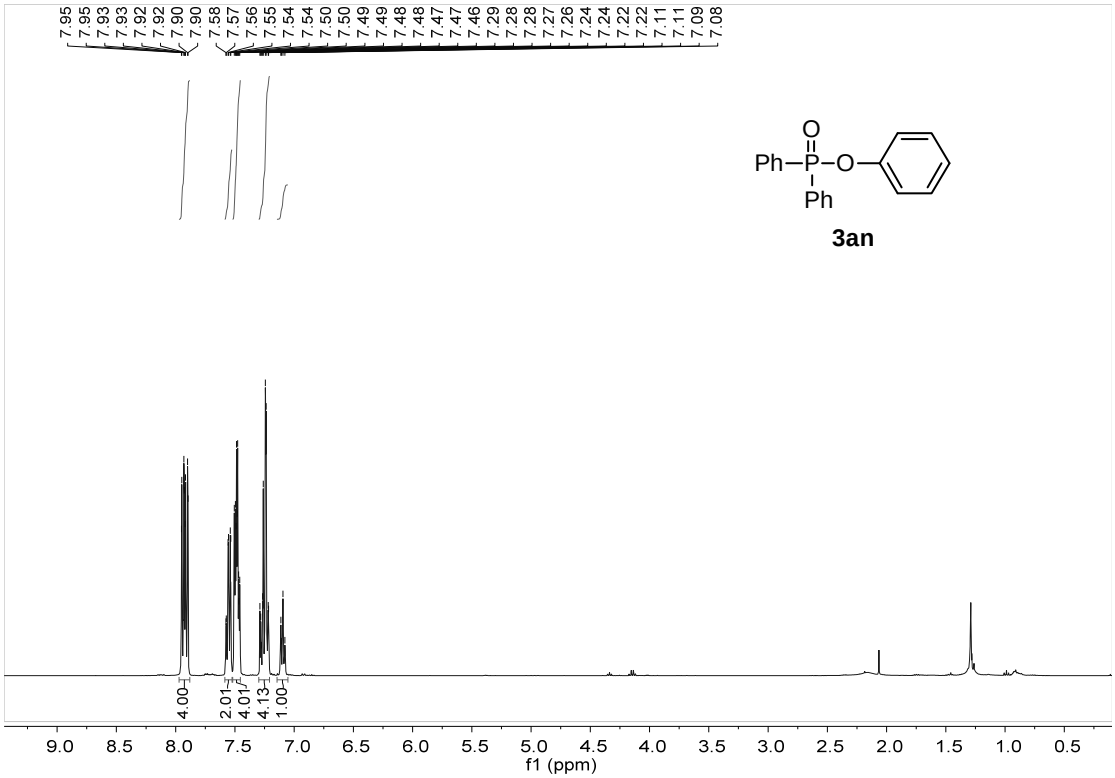

133.24 131.87 131.85 131.61 131.51 128.42 128.29
77.32 77.00 76.68 74.98 74.92
33.92 33.89
25.17 23.55
O
Ph—P—OCy
Ph
3ak
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

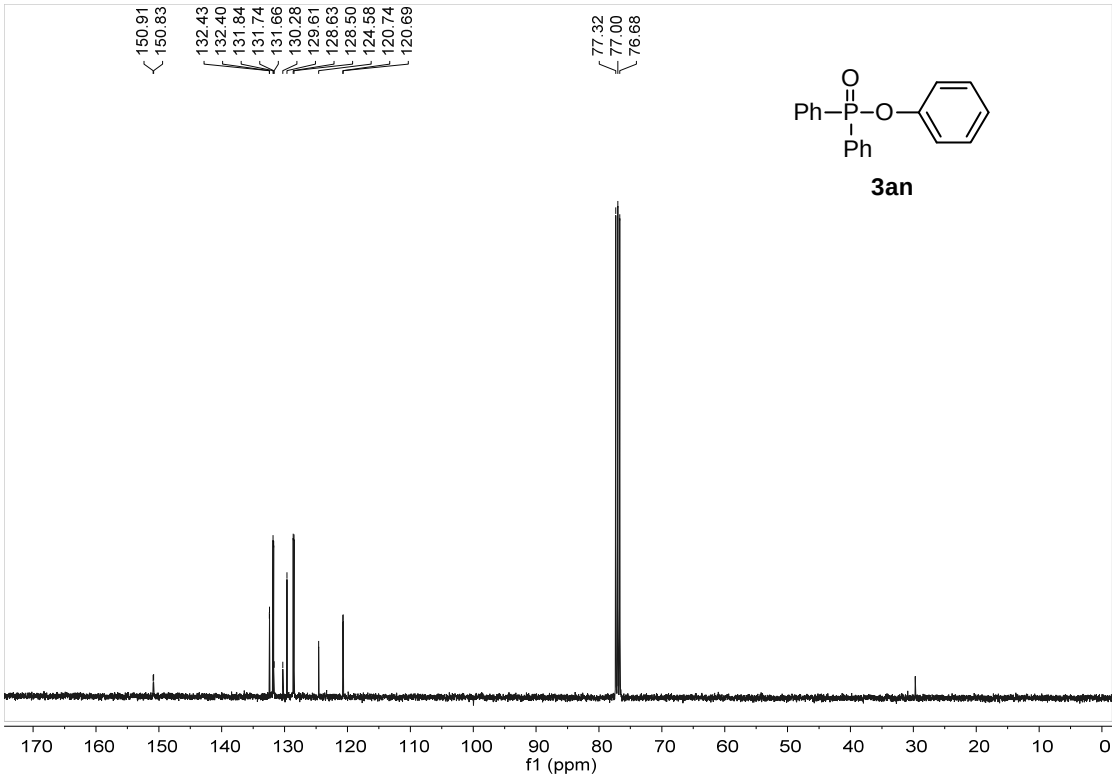

29.71
O
Ph—P—OCy
Ph
3ak
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -1
f1 (ppm)

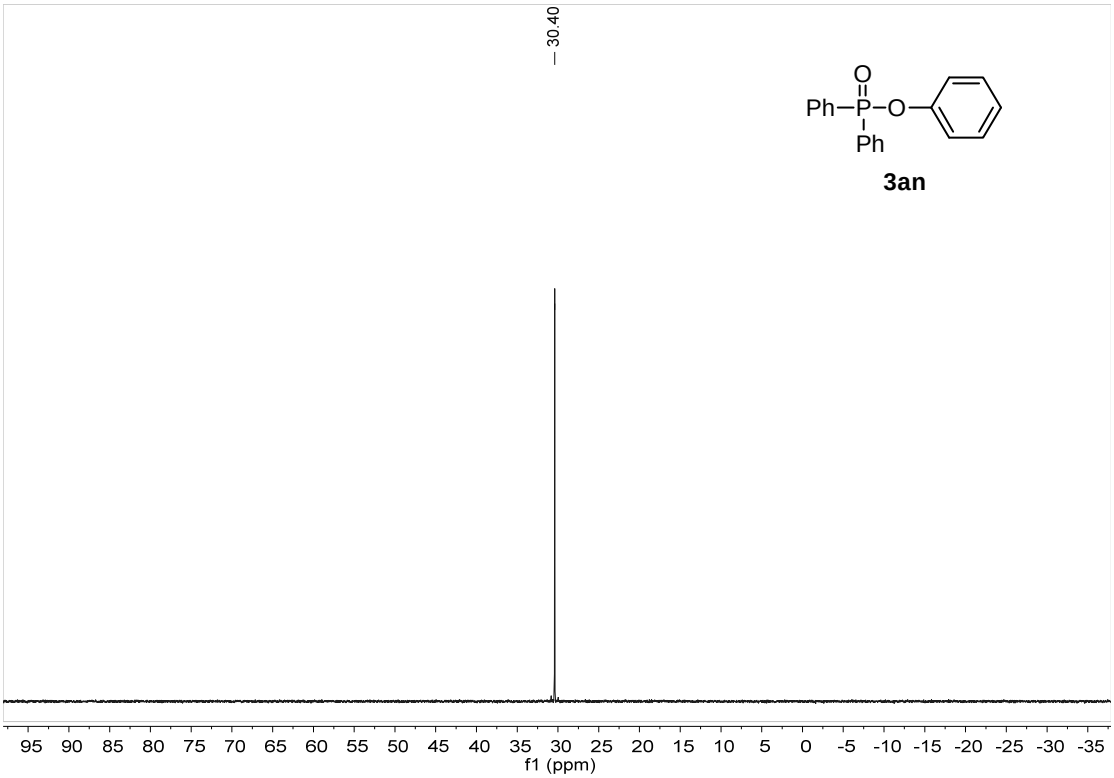

Me
Me
Me
Me
Me
H
H
H
H
O
Ph—P—O
Ph
3al
4.00
6.02
1.01
2.98
9.92
19.93
11.07
3.08
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

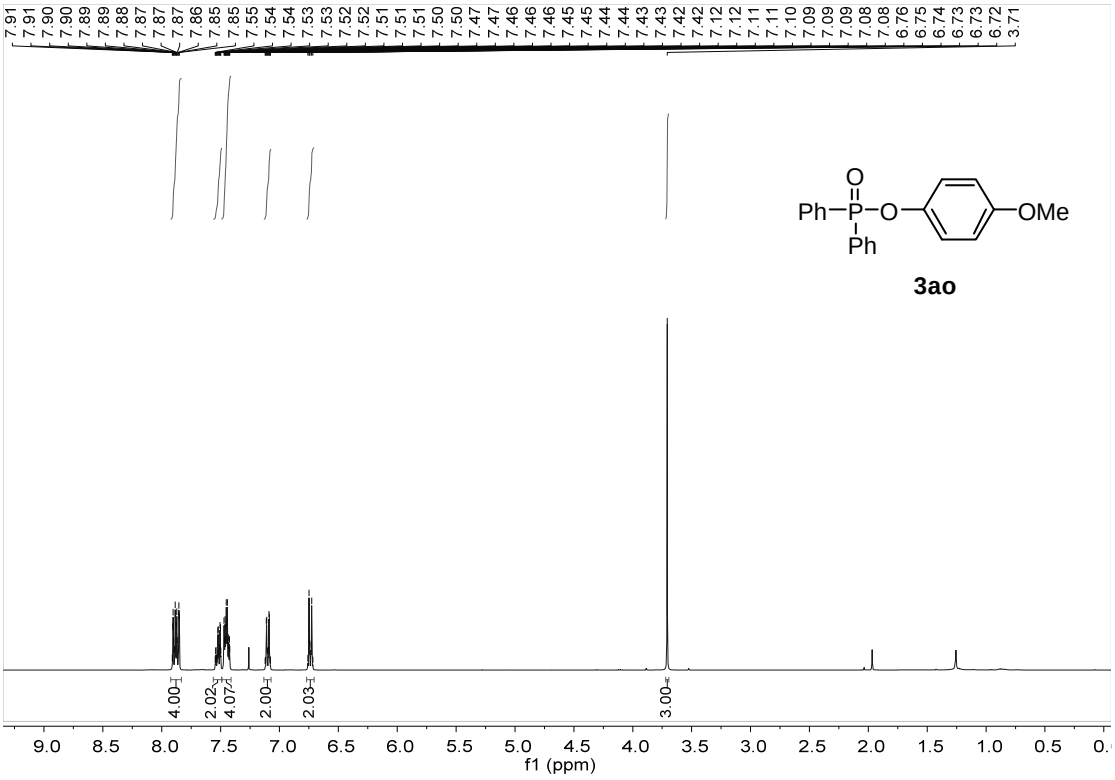

133.23
133.20
131.88
131.86
131.67
131.61
131.57
131.51
128.43
128.30
77.32
77.00
76.68
76.16
76.10
56.35
56.22
54.12
44.68
42.54
39.93
39.49
36.82
36.60
36.57
36.13
35.76
35.41
35.25
31.92
31.42
30.08
30.04
28.47
28.20
27.98
24.16
23.80
22.79
22.54
21.16
18.64
12.24
12.03
Me
Me
Me
Me
Me
H
H
H
H
O
Ph–P–O
Ph
3al
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

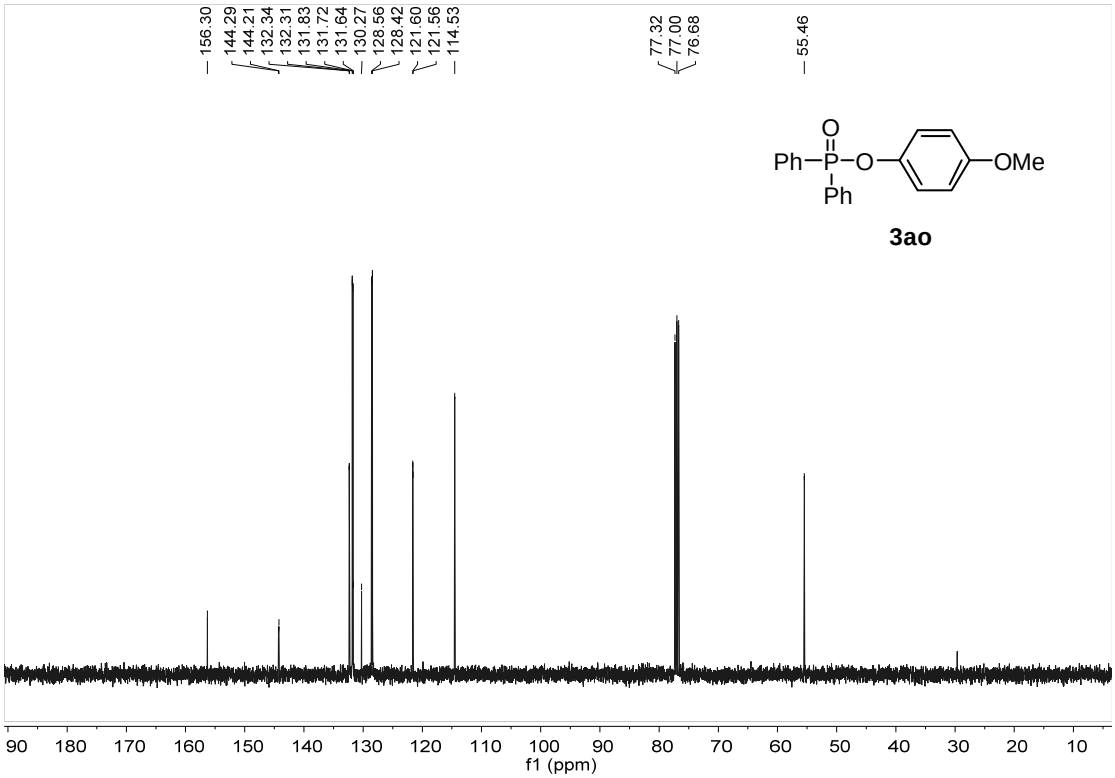

29.87
Me
Me
Me
Me
Me
H
H
H
H
O
Ph–P–O
Ph
3al
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

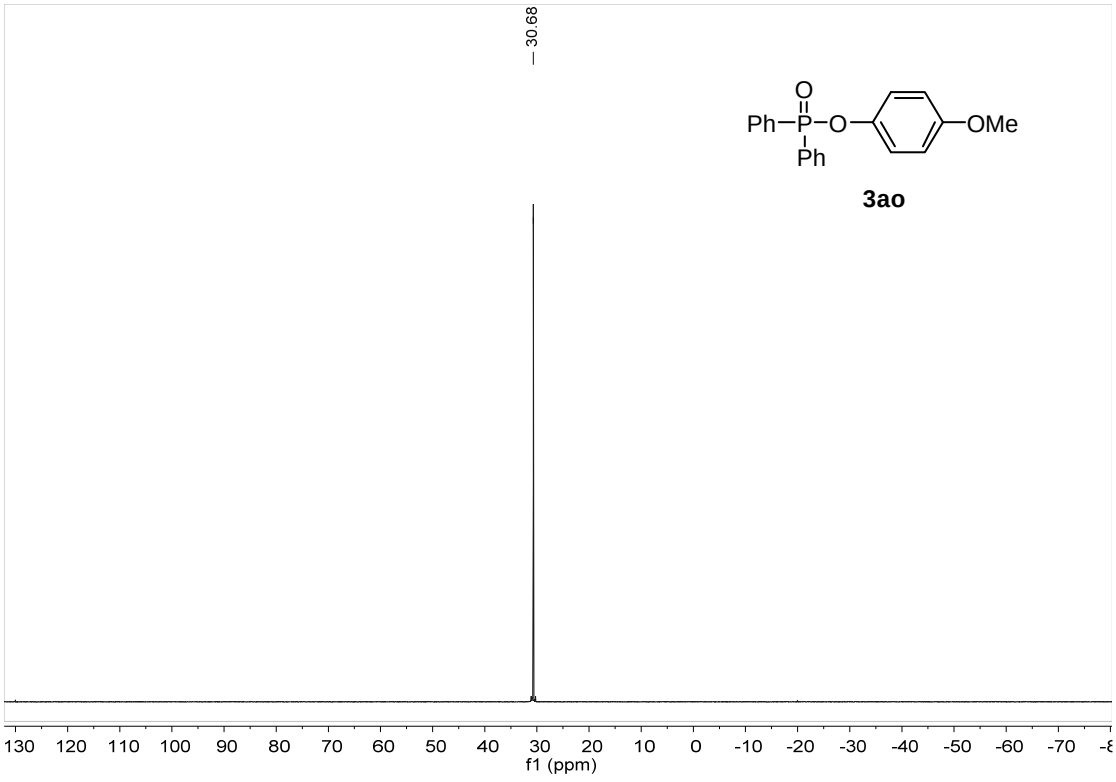

7.95
7.95
7.93
7.93
7.92
7.92
7.90
7.90
7.58
7.57
7.56
7.55
7.54
7.54
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.29
7.28
7.28
7.27
7.26
7.24
7.24
7.22
7.22
7.11
7.11
7.09
7.08
Ph
P
O
Ph
3an
4.00
2.01
4.01
4.13
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

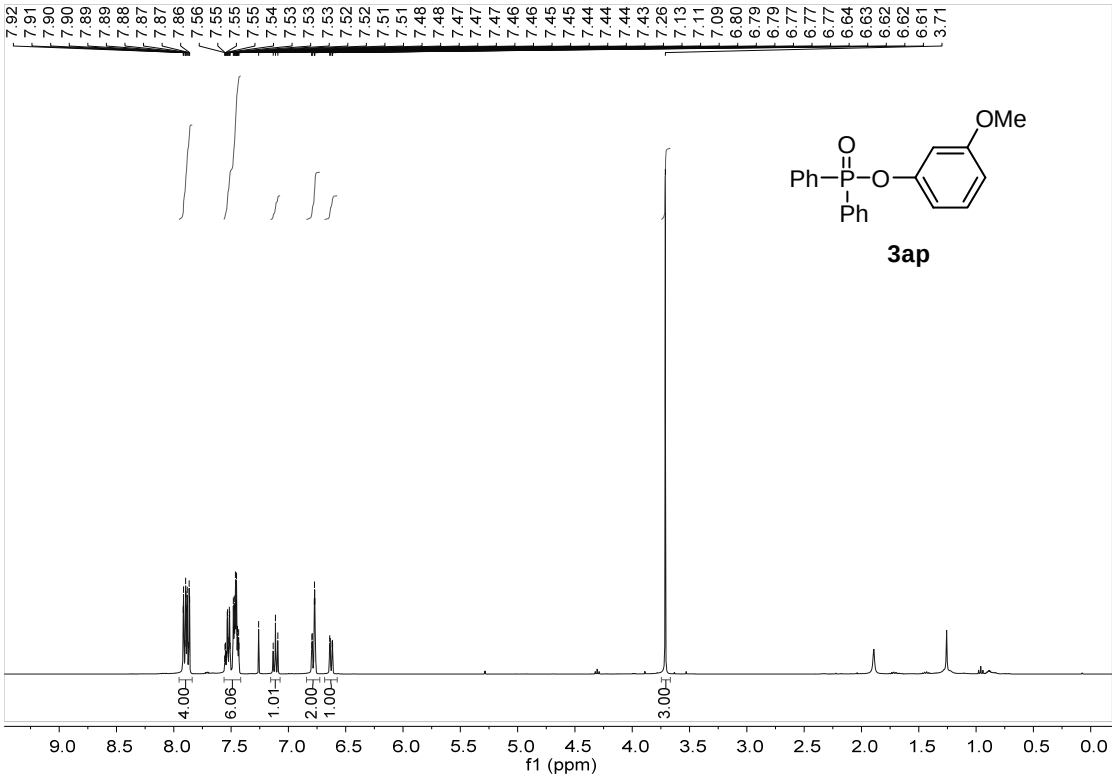

150.91
150.83
132.43
132.40
131.84
131.74
131.66
130.28
129.61
128.63
128.50
124.58
120.74
120.69
77.32
77.00
76.68
Ph
P
O
Ph
3an
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

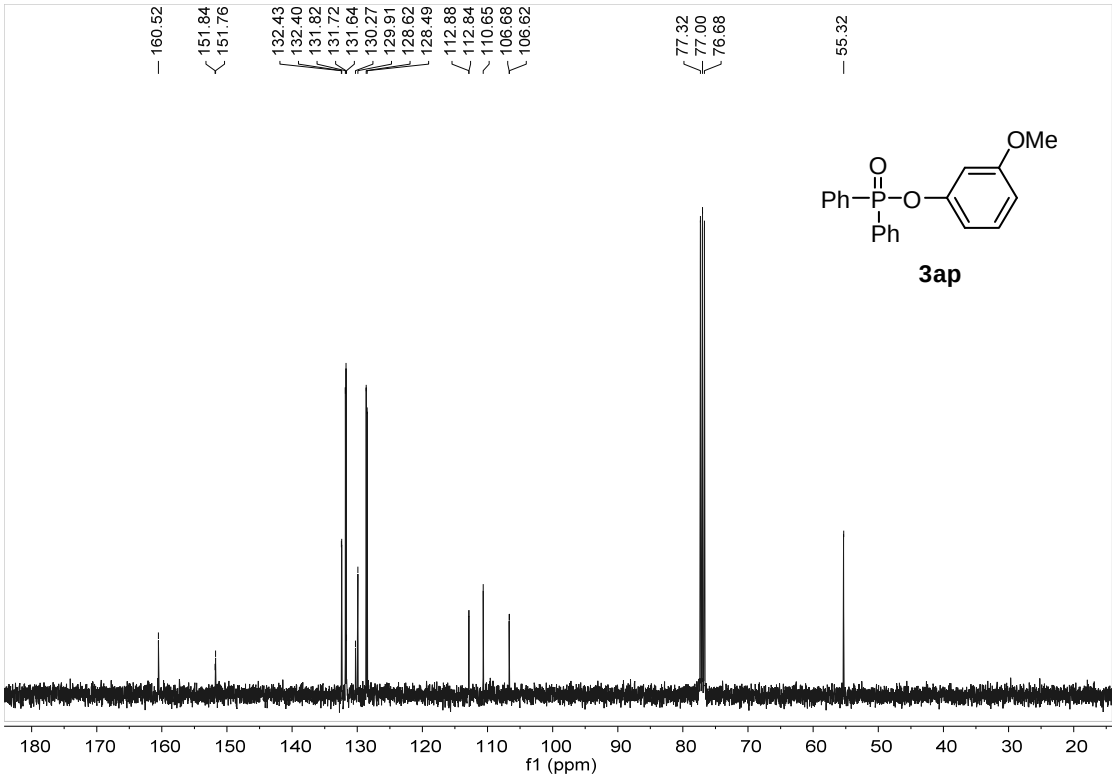

30.40
Ph
P
O
Ph
3an
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)

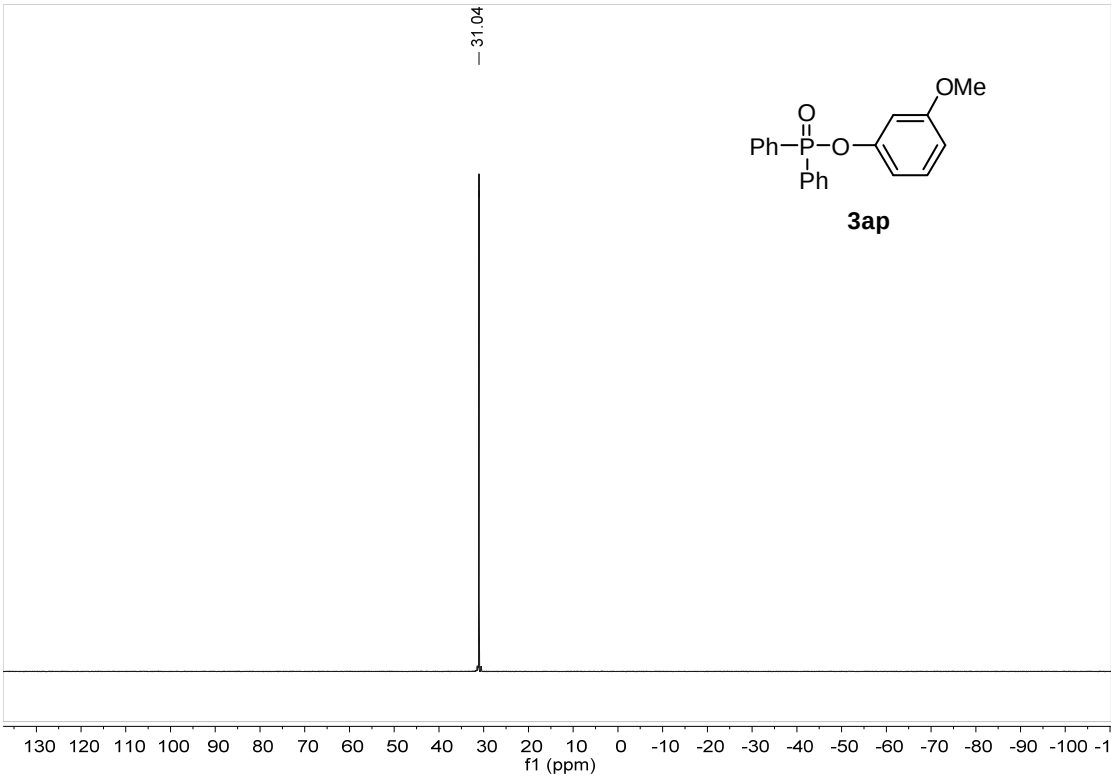

7.91 7.91 7.90 7.90 7.89 7.89 7.88 7.87 7.87 7.87 7.86 7.85 7.85 7.55 7.54 7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.12 7.12 7.11 7.11 7.10 7.09 7.09 7.09 7.08 7.08 6.76 6.75 6.74 6.73 6.73 6.72 3.71
Ph
P
O
OMe
Ph
3ao
4.00
2.02
4.07
2.00
2.03
3.00
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
f1 (ppm)


156.30
144.29
144.21
132.34
132.31
131.83
131.72
131.64
130.27
128.56
128.42
121.60
121.56
114.53
77.32
77.00
76.68
55.46
O
Ph–P–O
Ph
OMe
3ao
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

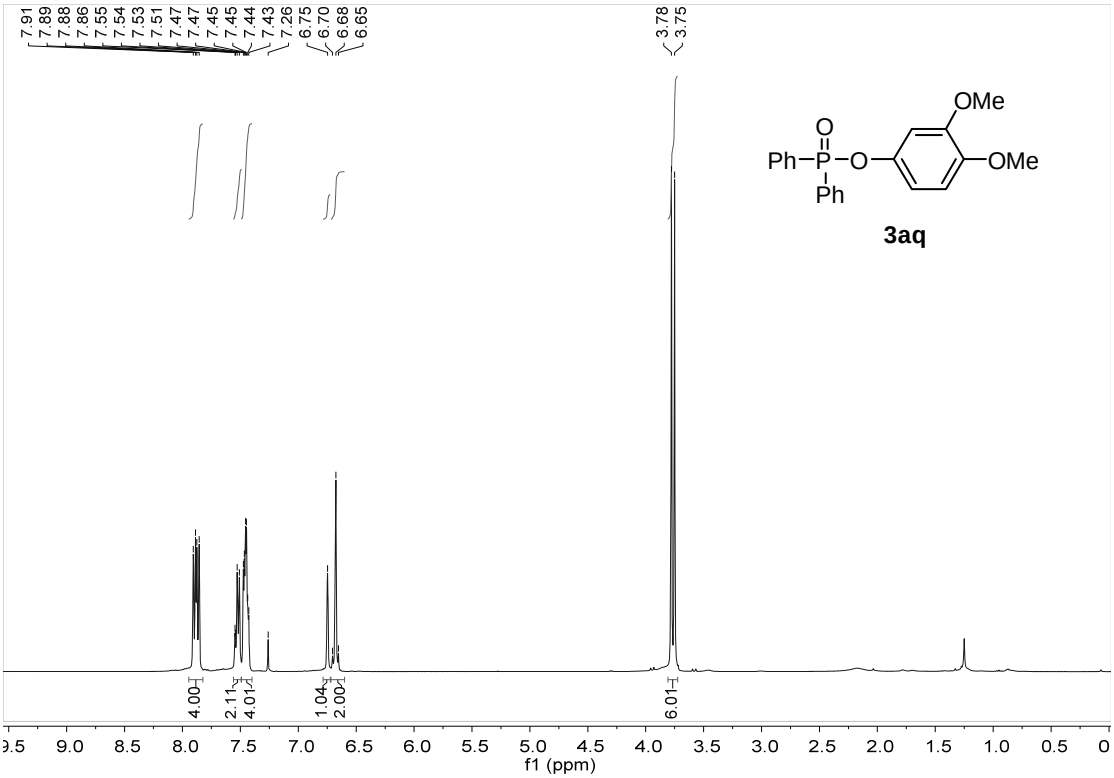

30.68
O
Ph–P–O
Ph
OMe
3ao
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)


7.92 7.91 7.90 7.90 7.89 7.89 7.88 7.87 7.87 7.86 7.56 7.55 7.55 7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.48 7.48 7.47 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.26 7.13 7.11 7.09 6.80 6.79 6.79 6.77 6.77 6.77 6.64 6.63 6.62 6.62 6.61 3.71
OMe
O
Ph–P–O
Ph
3ap
4.00 6.06 1.01 2.00 1.00 3.00
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)

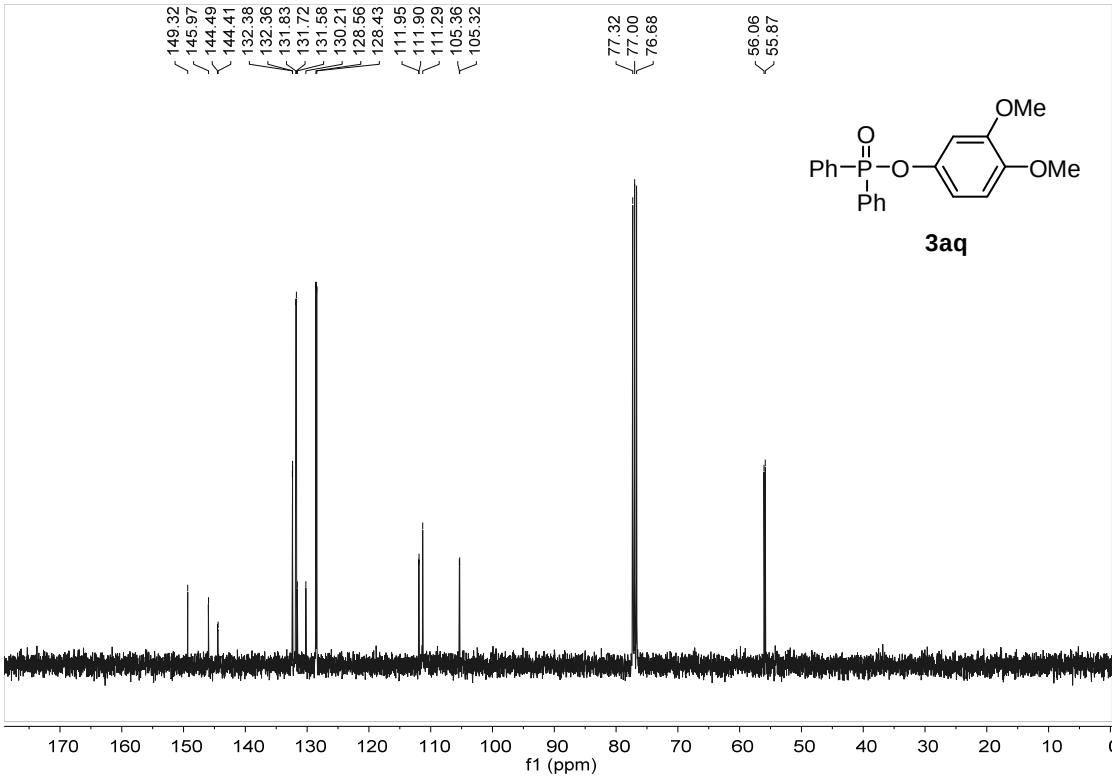

160.52
151.84 151.76
132.43 132.40 131.82 131.72 131.64 130.27 129.91 128.62 128.49
112.88 112.84 110.65 106.68 106.62
77.32 77.00 76.68
55.32
OMe
O
Ph–P–O
Ph
3ap
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

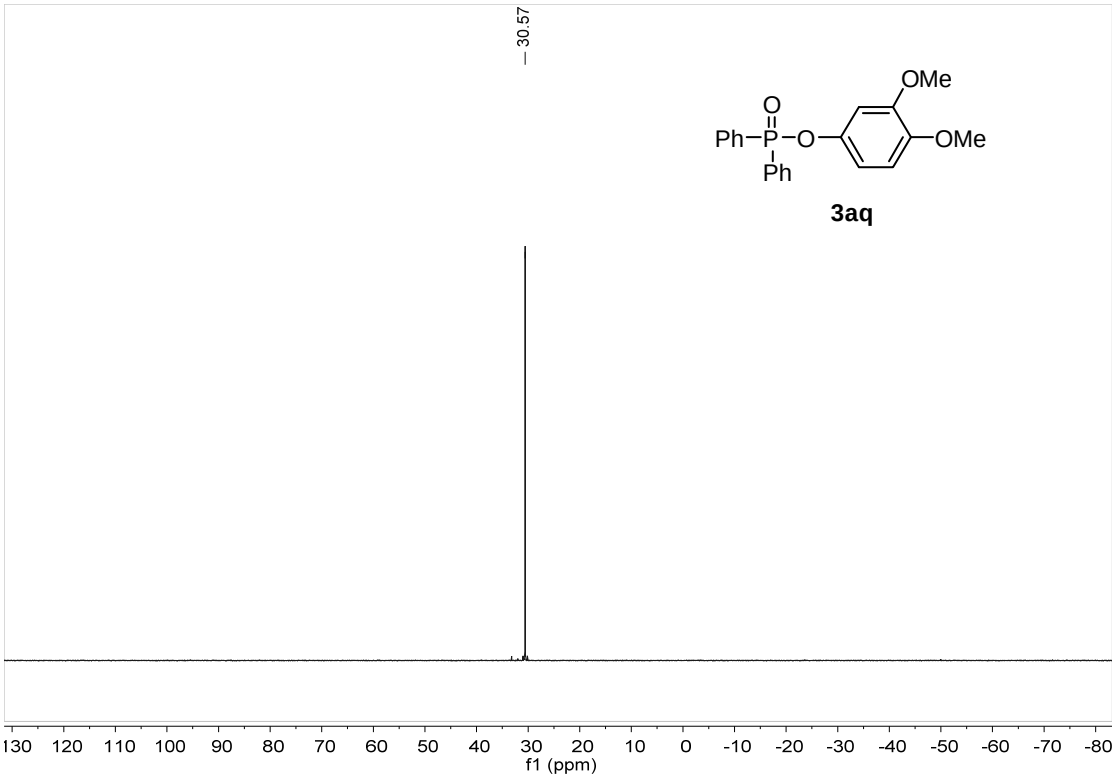

31.04
OMe
O
Ph–P–O
Ph
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -1
f1 (ppm)

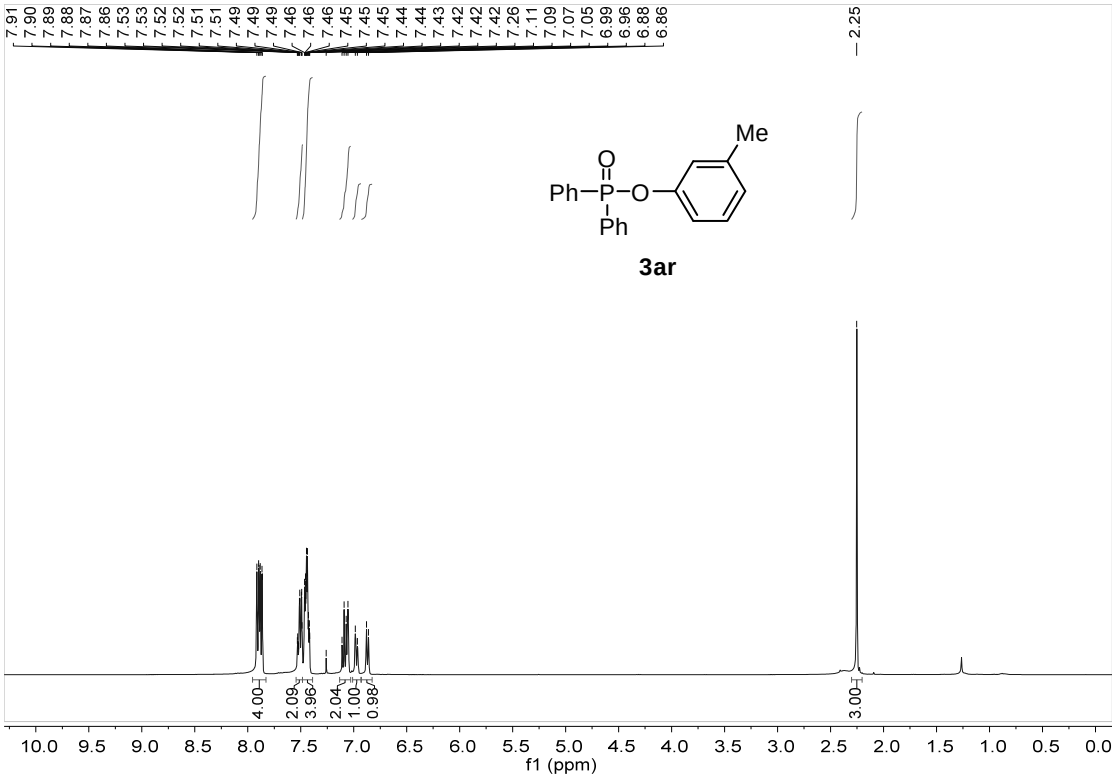
3ap

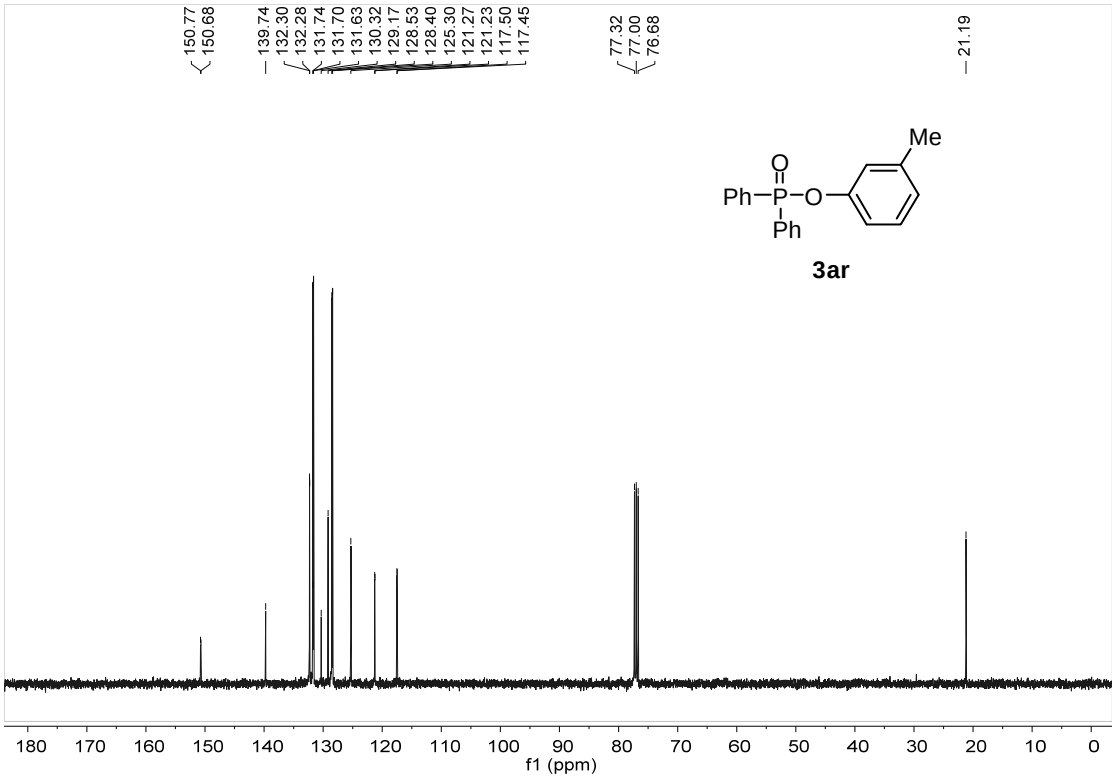

7.91
7.89
7.88
7.86
7.55
7.54
7.53
7.51
7.47
7.47
7.45
7.45
7.44
7.43
7.26
6.75
6.70
6.68
6.65
3.78
3.75
OMe
O
Ph–P–O
OMe
Ph
4.00
2.11
4.01
1.04
2.00
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

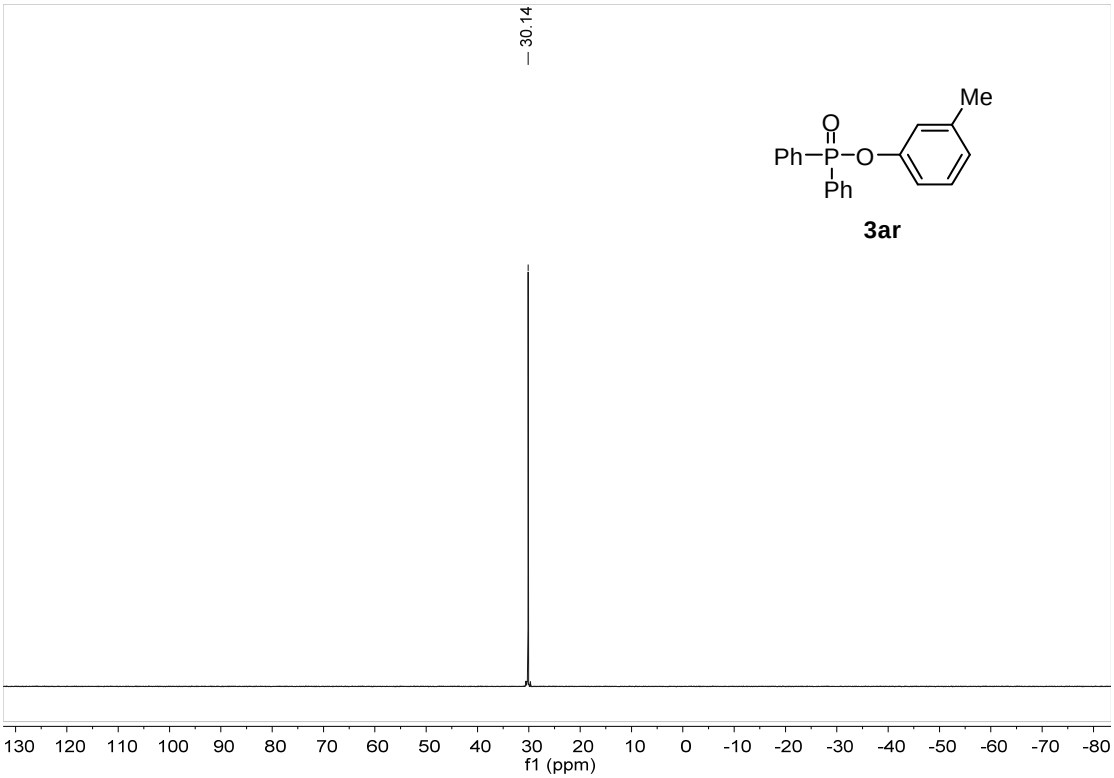
3aq

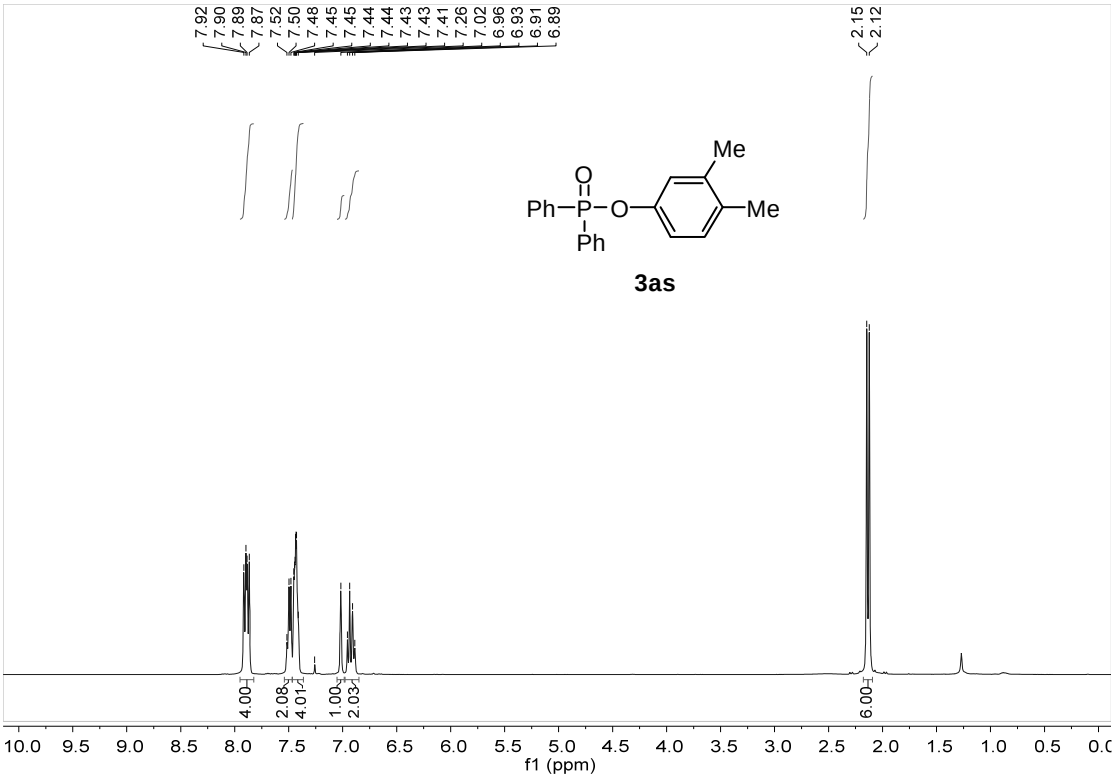

149.32
145.97
144.49
144.41
132.38
132.36
131.83
131.72
131.58
130.21
128.56
128.43
111.95
111.90
111.29
105.36
105.32
77.32
77.00
76.68
56.06
55.87
OMe
O
Ph
P
O
OMe
Ph
3aq
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

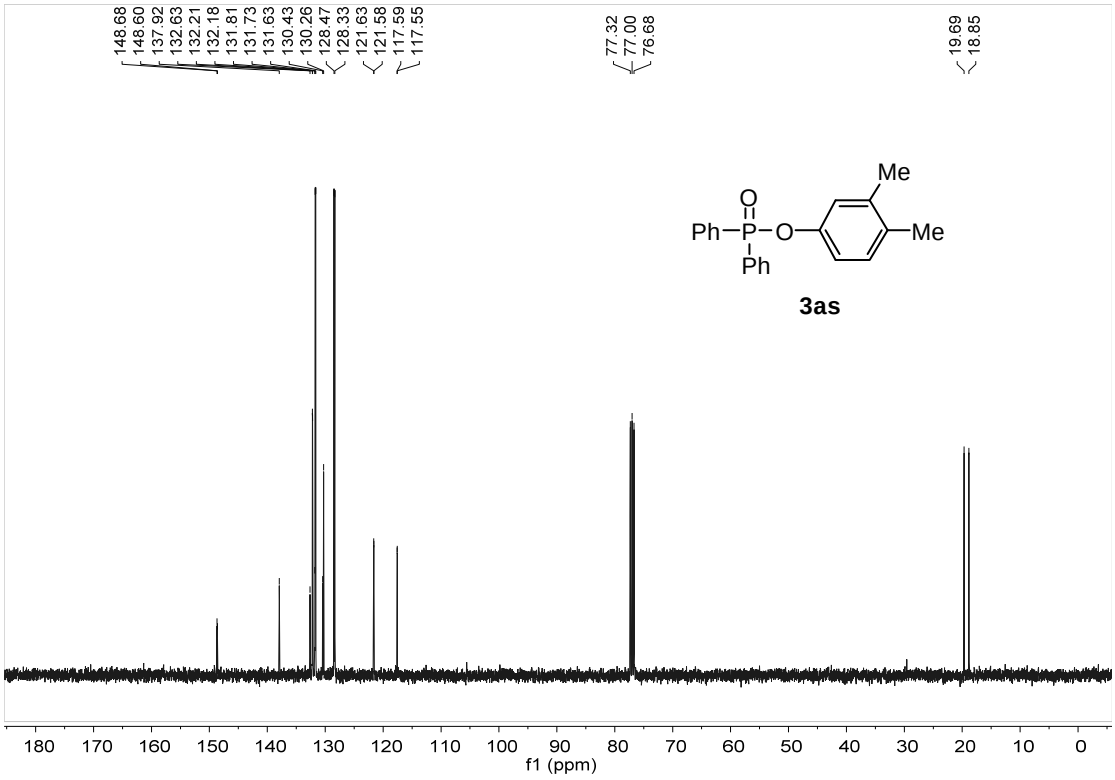

30.57
OMe
O
Ph
P
O
OMe
Ph
3aq
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

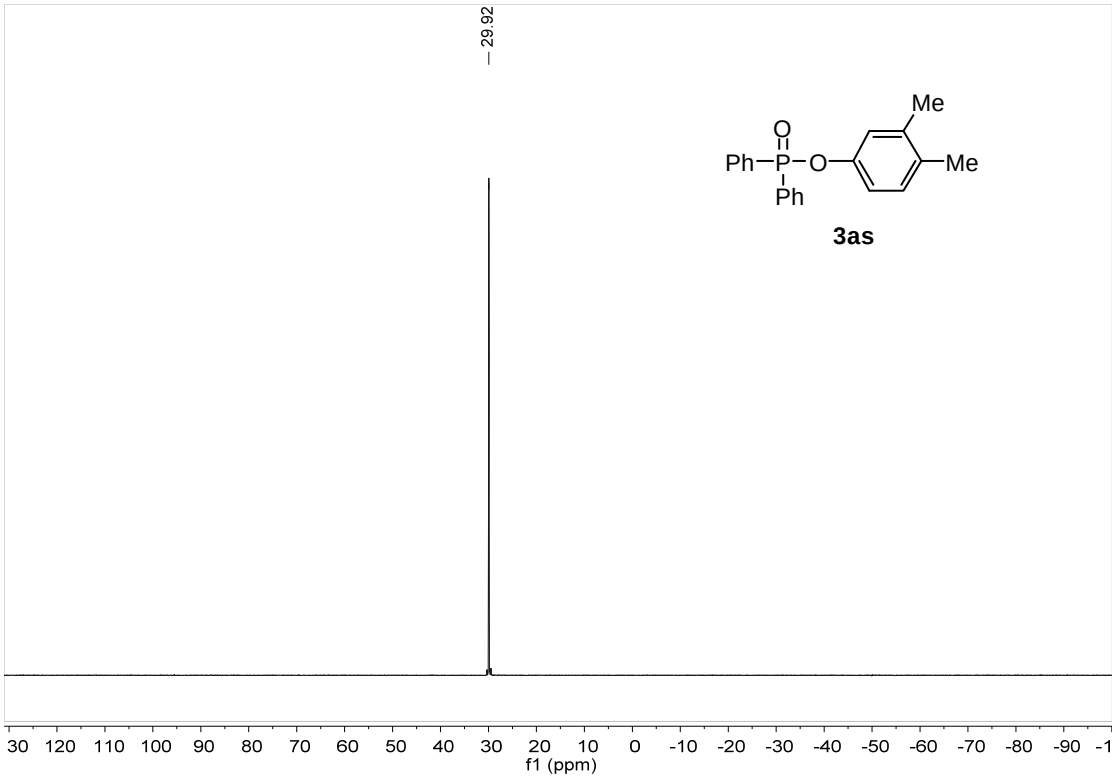

7.91
7.90
7.89
7.88
7.87
7.86
7.53
7.53
7.52
7.52
7.51
7.51
7.49
7.49
7.49
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.42
7.42
7.42
7.26
7.11
7.09
7.07
7.05
6.99
6.96
6.88
6.86
2.25
Me
O
Ph–P–O
Ph
3ar
4.00
2.09
3.96
2.04
1.00
0.98
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

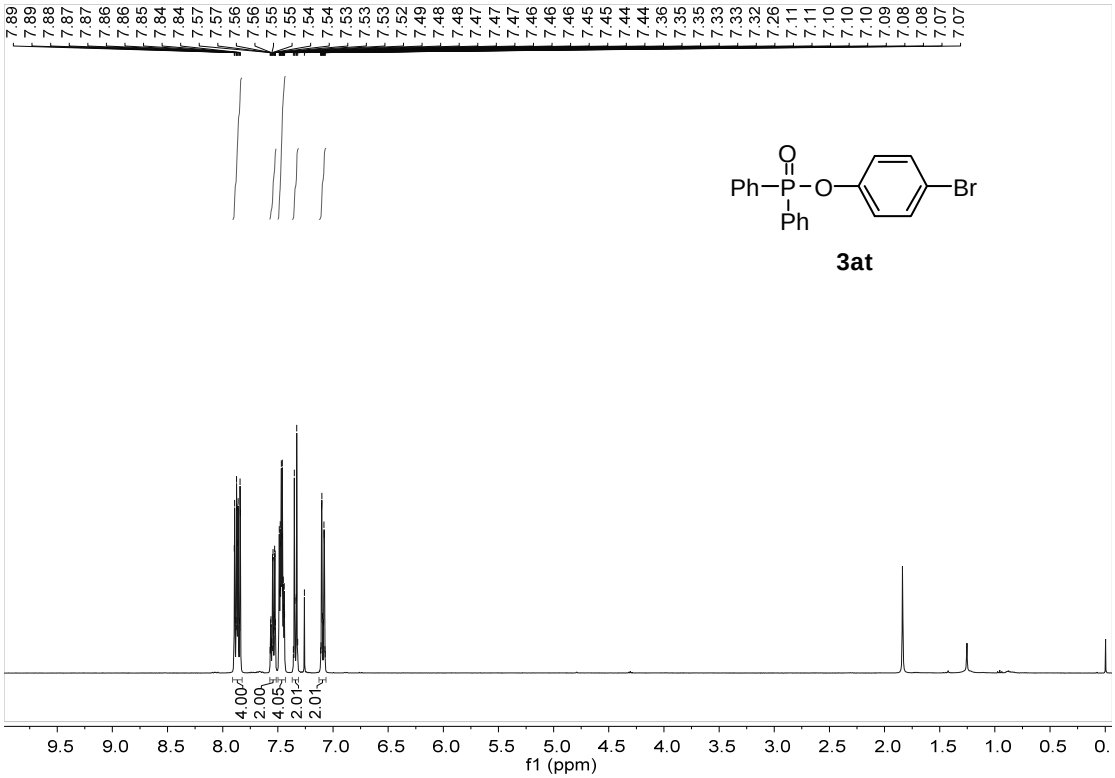

150.77
150.68
139.74
132.30
132.28
131.74
131.70
131.63
130.32
129.17
128.53
128.40
125.30
121.27
121.23
117.50
117.45
77.32
77.00
76.68
21.19
Me
O
Ph–P–O
Ph
3ar
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

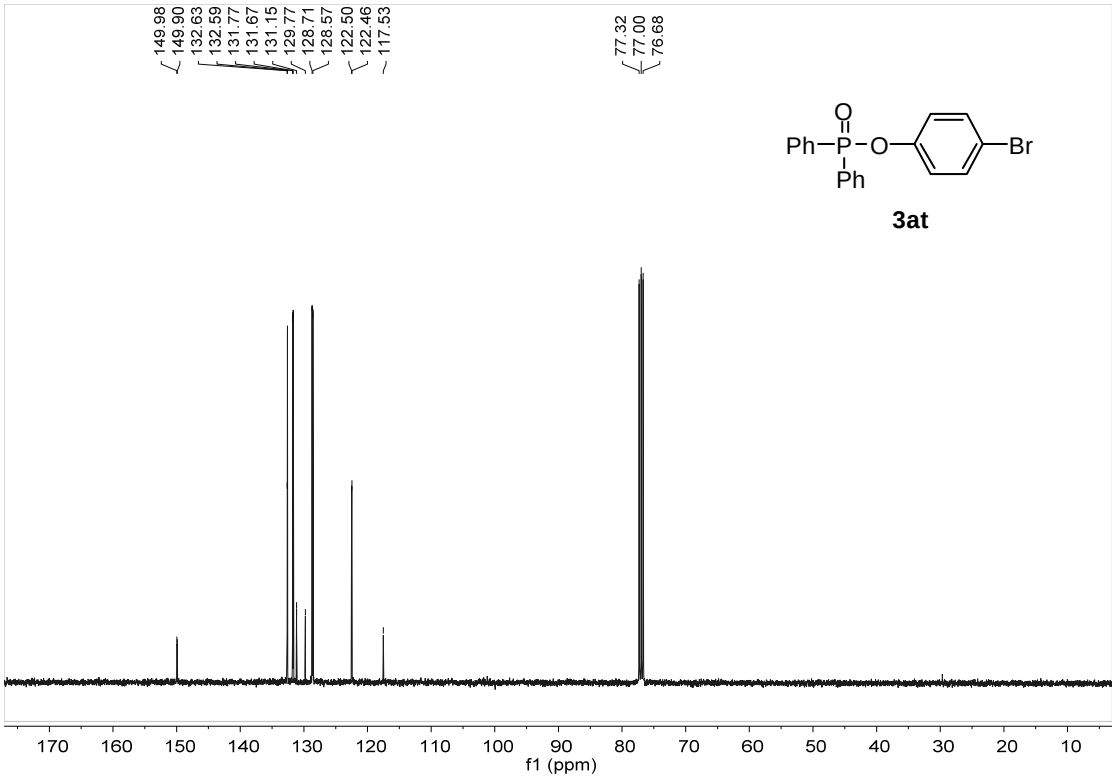

30.14
Me
O
Ph—P—O
Ph
3ar
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

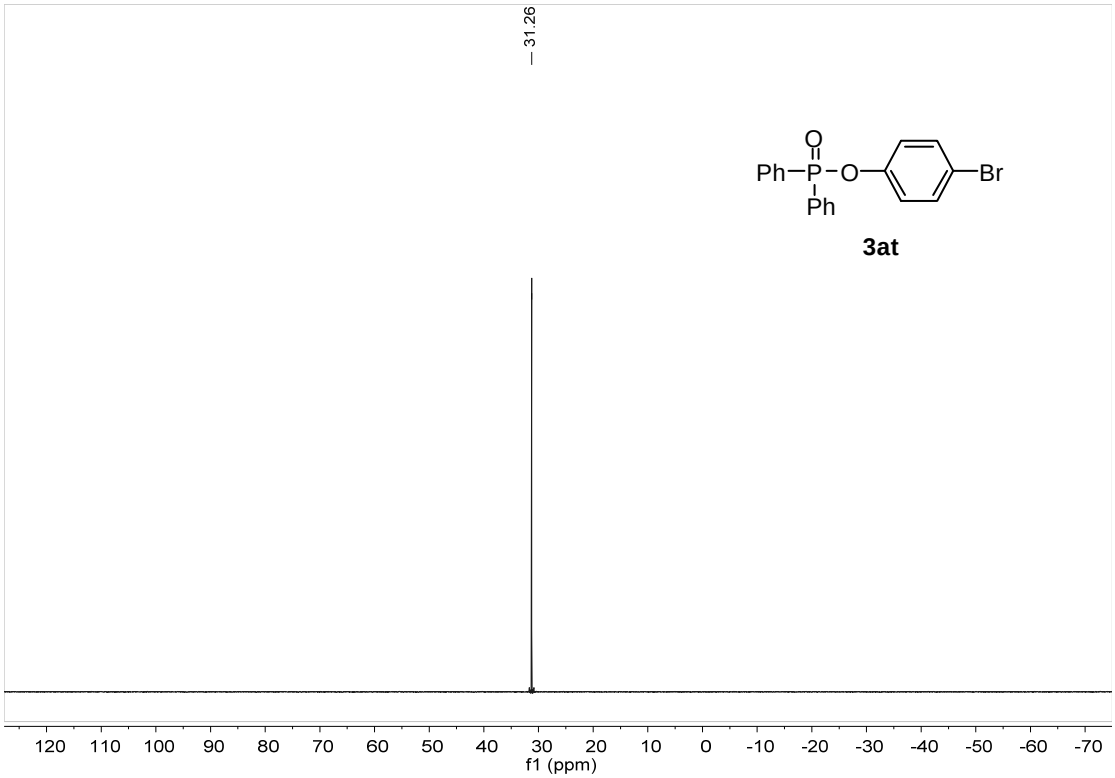

7.92
7.90
7.89
7.87
7.52
7.50
7.48
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.41
7.26
7.02
6.96
6.93
6.91
6.89
2.15
2.12
Me
O
Ph—P—O
Me
Ph
3as
4.00
2.08
4.01
1.00
2.03
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

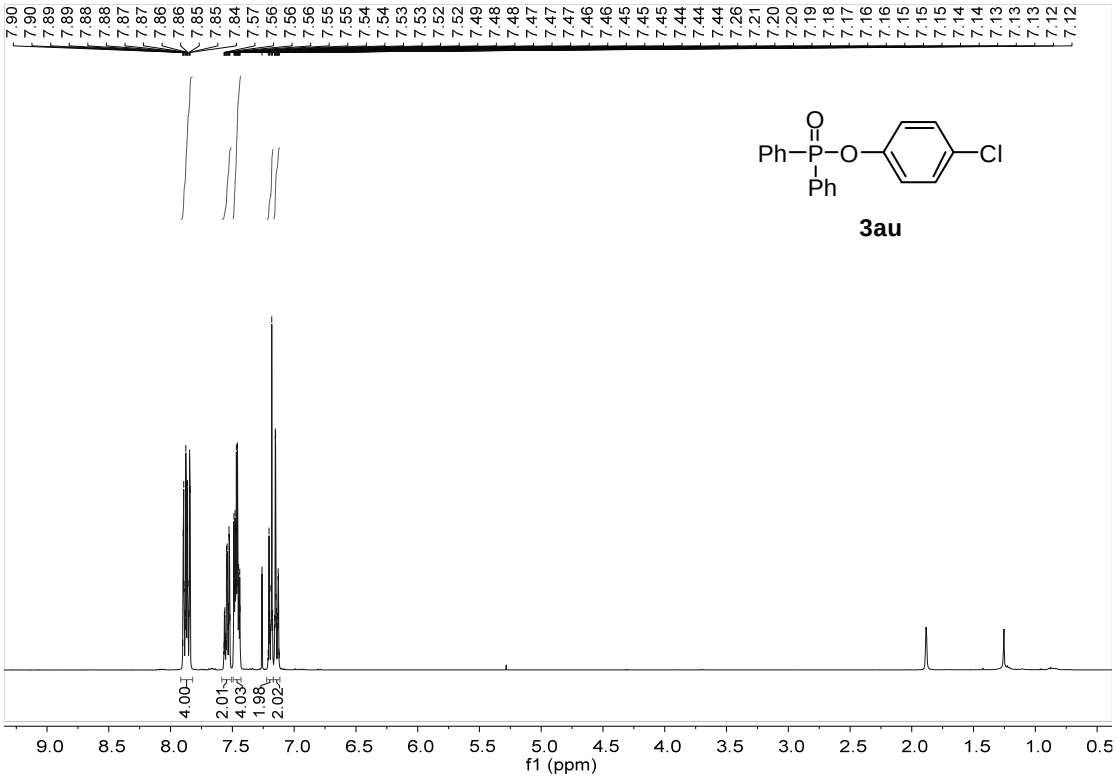

148.68
148.60
137.92
132.63
132.21
132.18
131.81
131.73
131.63
130.43
130.26
128.47
128.33
121.63
121.58
117.59
117.55
77.32
77.00
76.68
19.69
18.85
Me
O
Ph
P
O
Me
Ph
3as
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

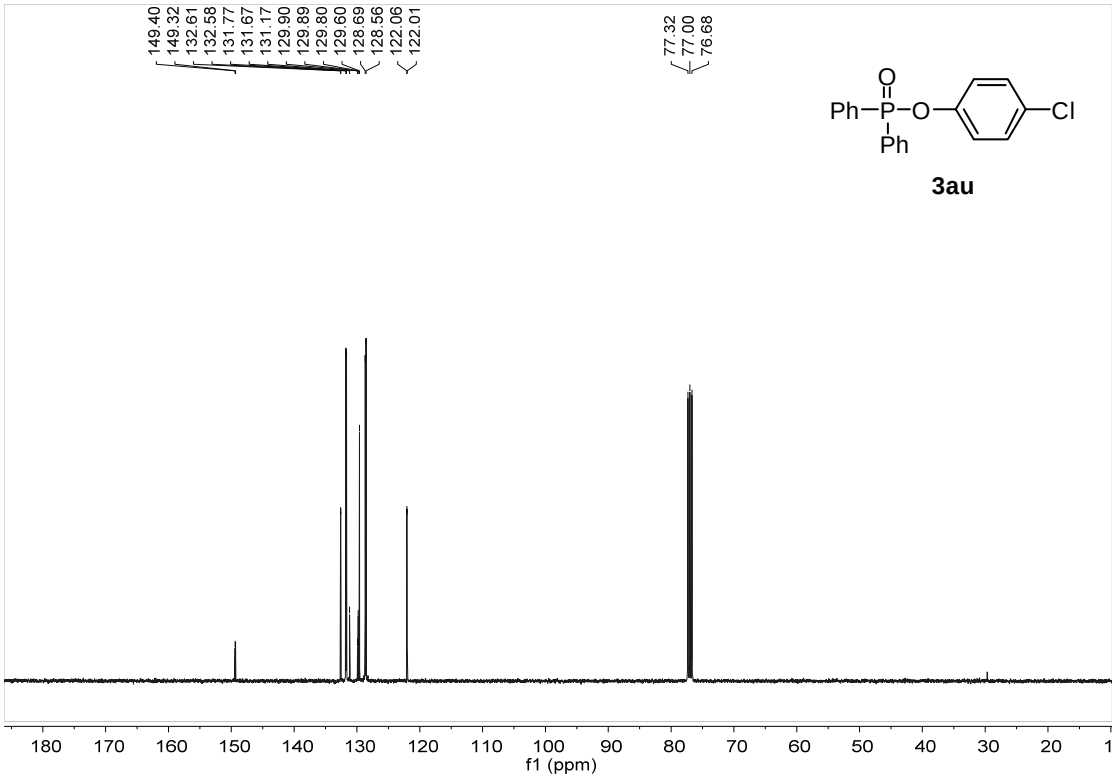

29.92
Me
O
Ph
P
O
Me
Ph
3as
30 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1
f1 (ppm)

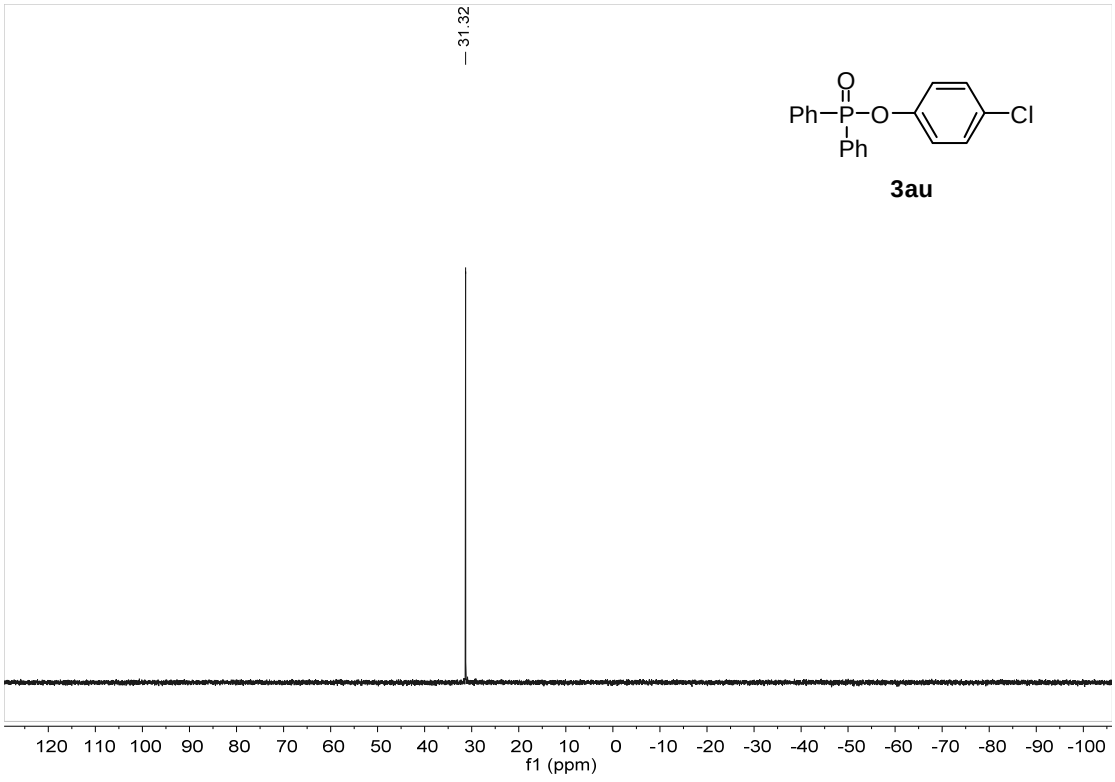

7.89 7.89 7.88 7.87 7.87 7.86 7.86 7.85 7.84 7.84 7.57 7.57 7.56 7.56 7.55 7.55 7.54 7.54 7.53 7.53 7.53 7.52 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.44 7.44 7.36 7.35 7.35 7.33 7.33 7.32 7.26 7.11 7.11 7.10 7.10 7.09 7.08 7.08 7.07 7.07
Ph P O Br Ph
3at
4.00 2.00 4.05 2.01 2.01
9.5 9.0 8.5 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.
f1 (ppm)

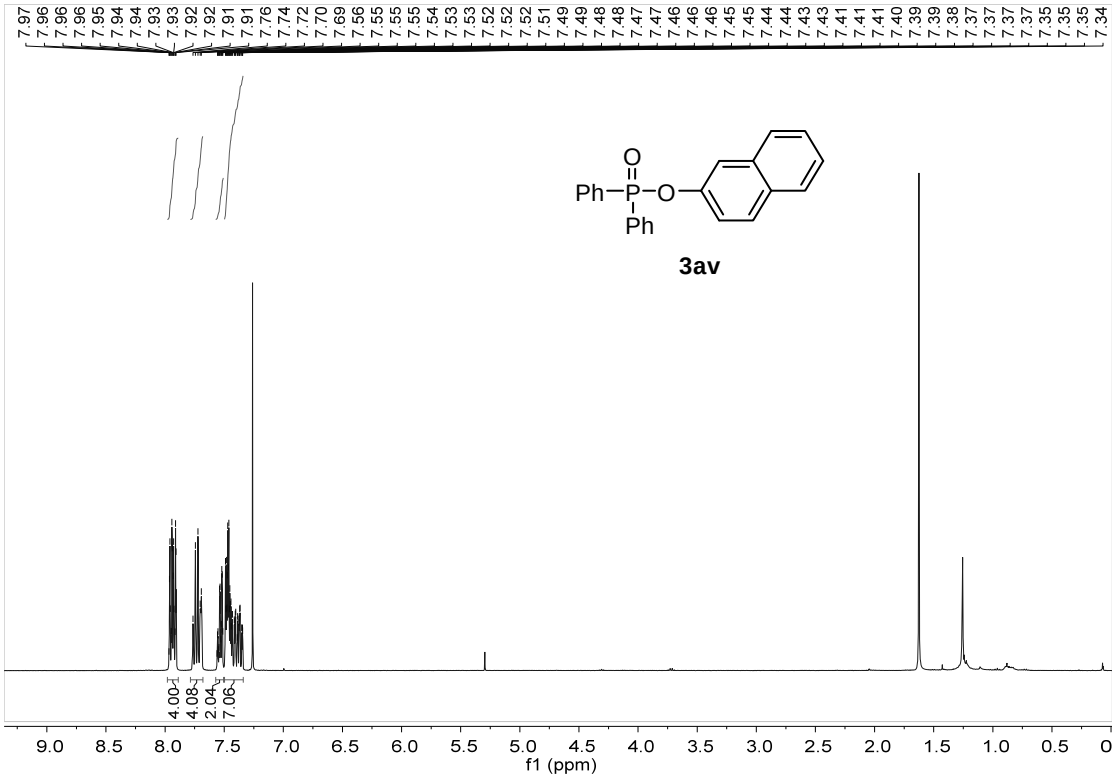

149.98 149.90 132.63 132.59 131.77 131.67 131.15 129.77 128.71 128.57 122.50 122.46 117.53
77.32 77.00 76.68
Ph P O Br Ph
3at
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

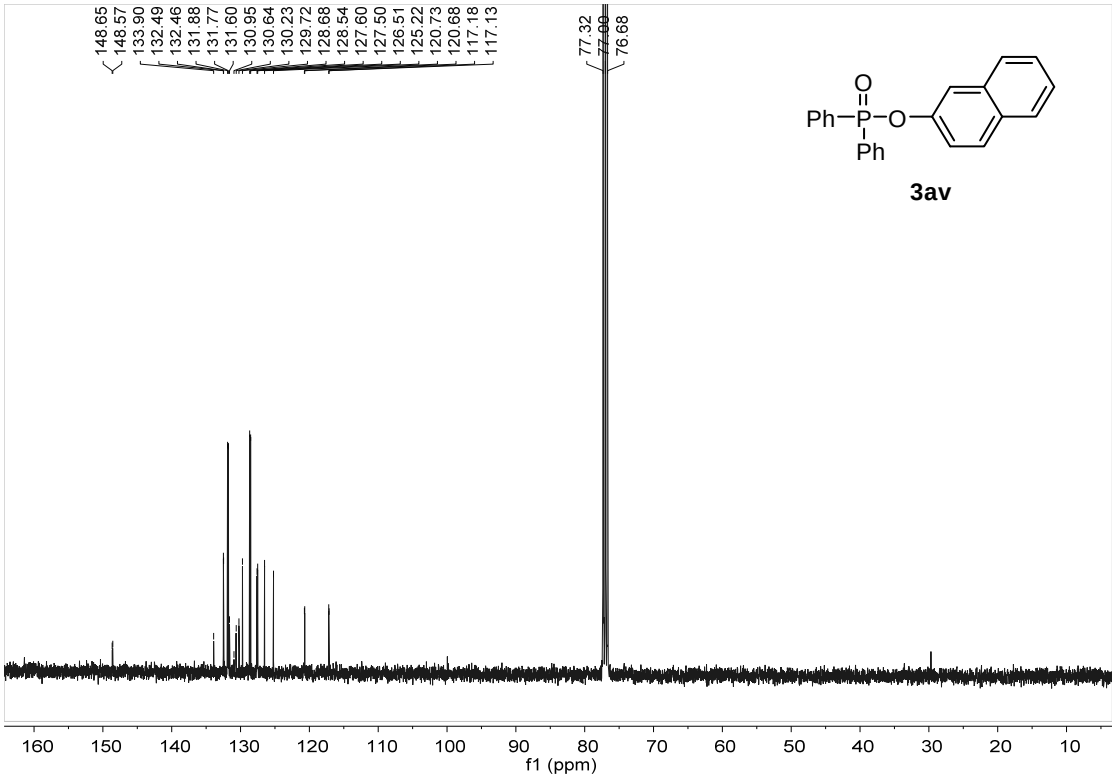

31.26
Ph
P
O
Br
Ph
3at
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

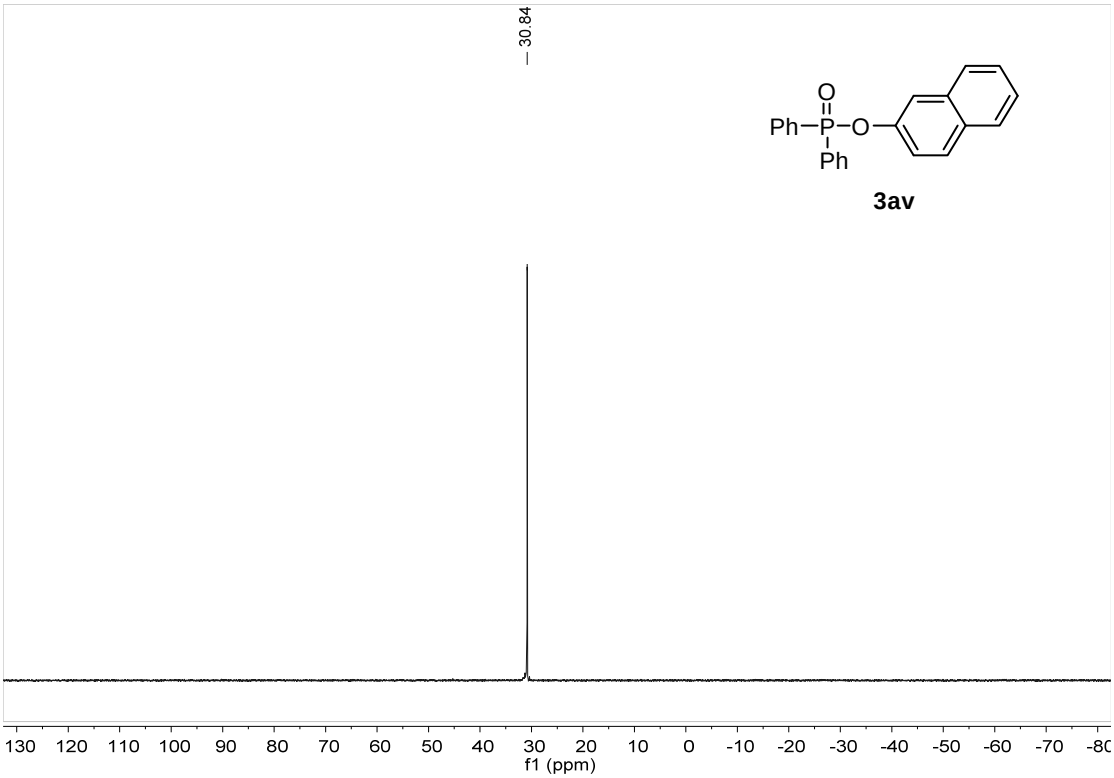

7.90 7.90 7.89 7.89 7.88 7.88 7.87 7.87 7.86 7.86 7.85 7.85 7.84 7.57 7.56 7.56 7.56 7.55 7.55 7.54 7.54 7.53 7.53 7.52 7.52 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.26 7.21 7.20 7.20 7.19 7.18 7.17 7.16 7.16 7.15 7.15 7.15 7.14 7.14 7.13 7.13 7.12 7.12
Ph
P
O
Cl
Ph
3au
4.00
2.01
4.03
1.98
2.02
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
f1 (ppm)

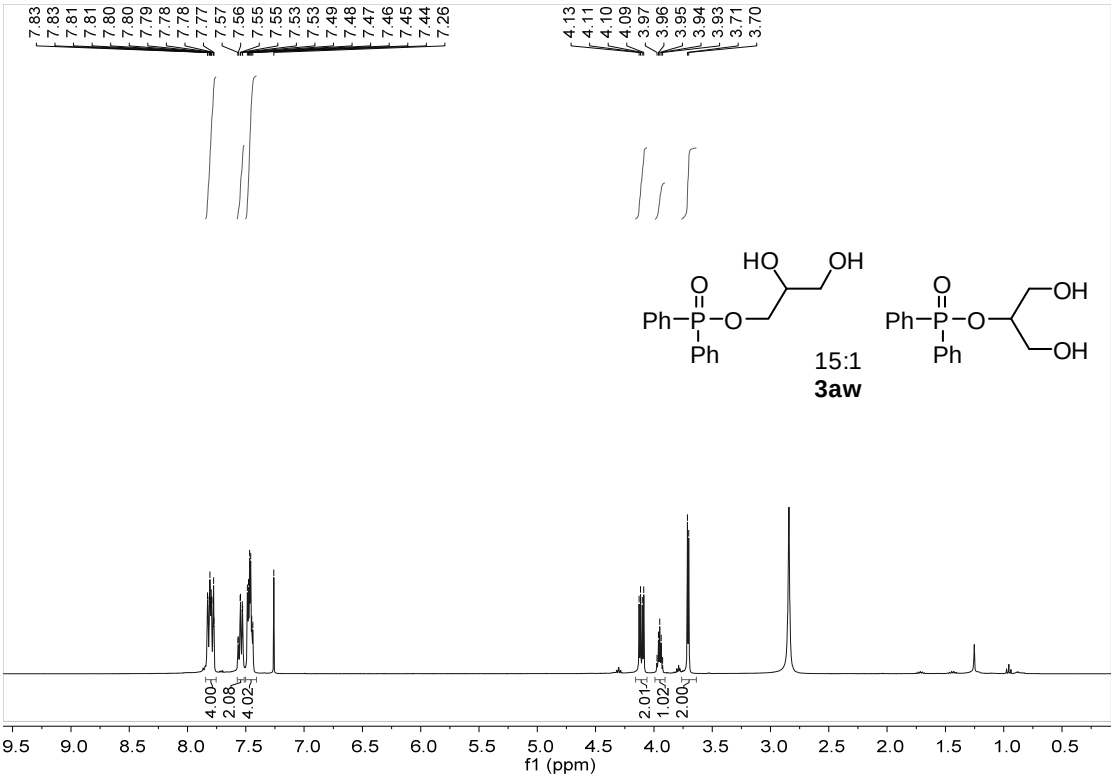

149.40
149.32
132.61
132.58
131.77
131.67
131.17
129.90
129.89
129.80
129.60
128.69
128.56
122.06
122.01
77.32
77.00
76.68
Ph
P
O
Cl
Ph
3au
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
f1 (ppm)

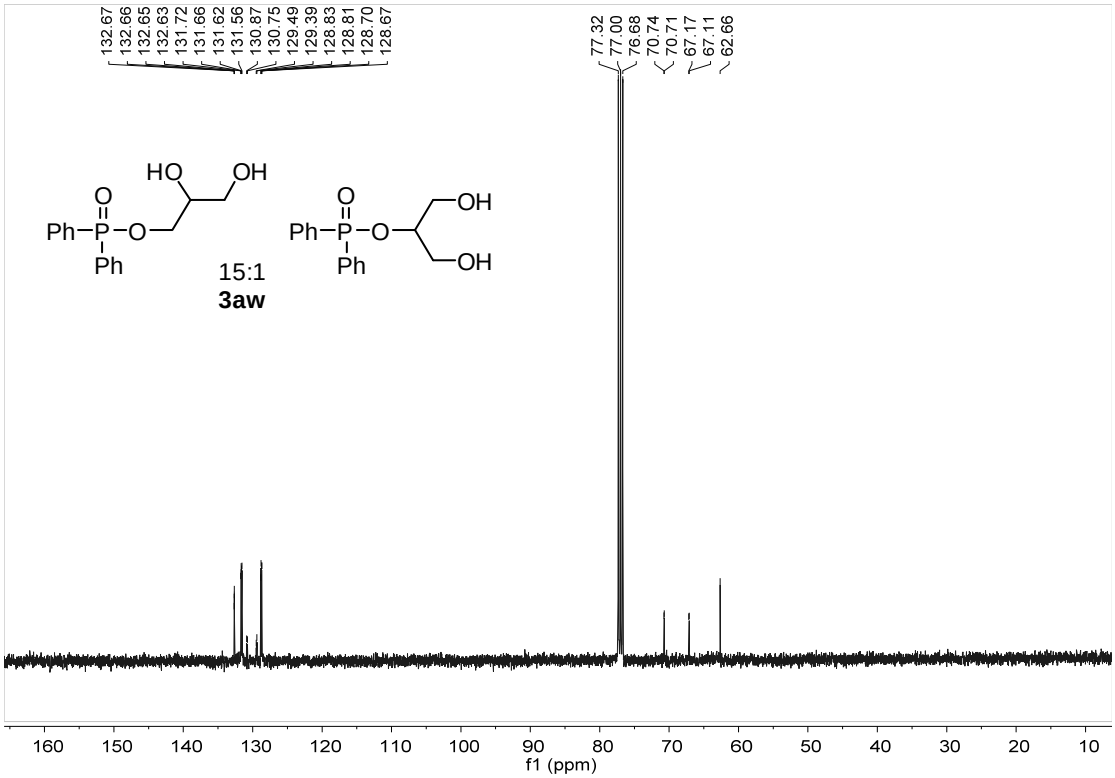

31.32
Ph
P
O
Cl
Ph
3au
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

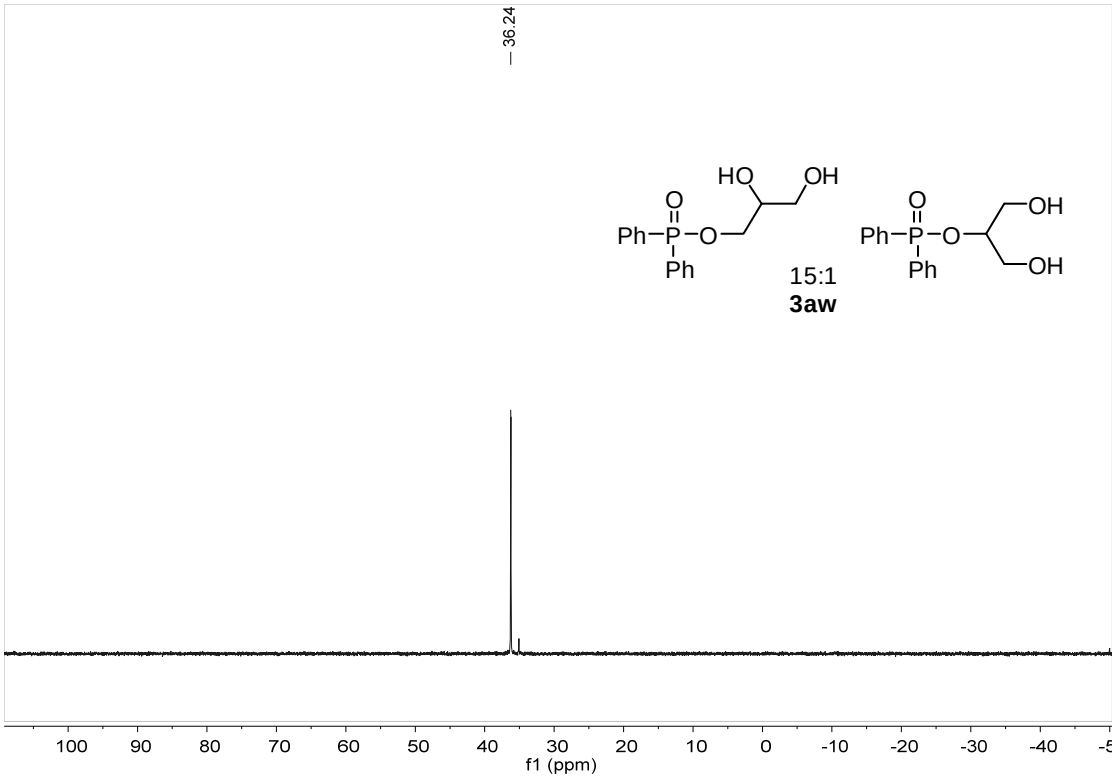

7.97 7.96 7.96 7.96 7.95 7.94 7.94 7.93 7.93 7.92 7.92 7.91 7.91 7.76 7.74 7.72 7.70 7.69 7.56 7.55 7.55 7.54 7.53 7.53 7.52 7.52 7.51 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.41 7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.37 7.37 7.35 7.35 7.34
O
Ph–P–O
Ph
3av
4.00
4.08
2.04
7.06
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
f1 (ppm)

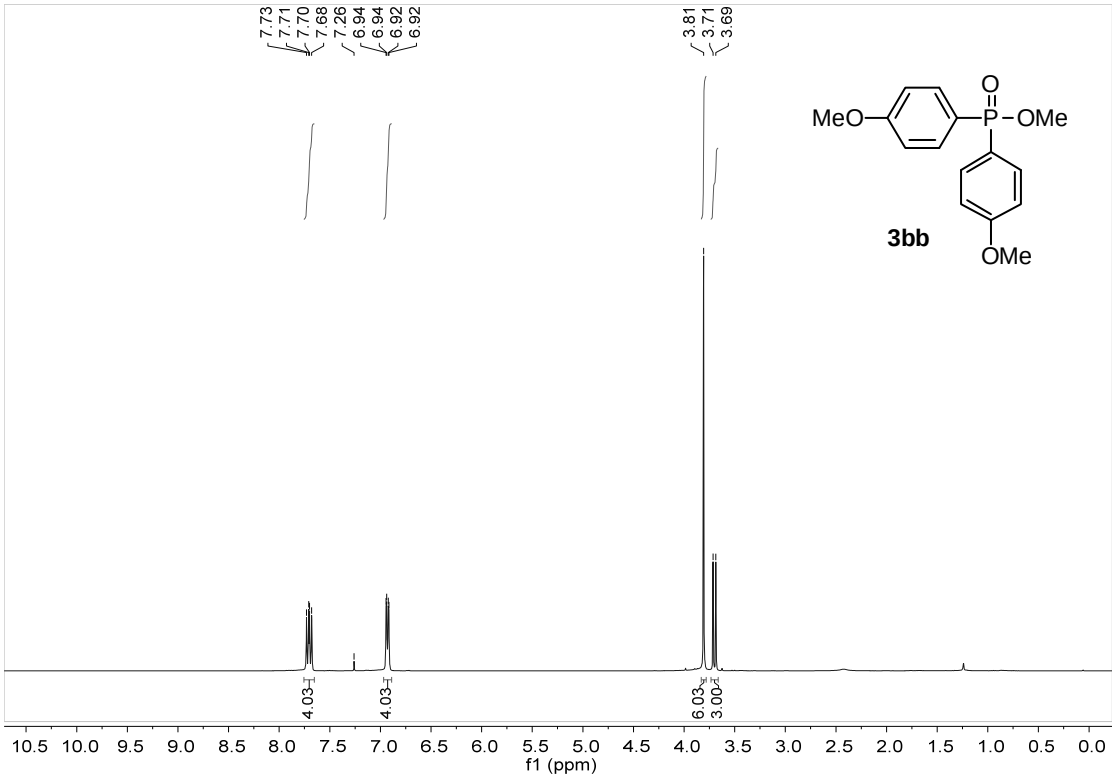

148.65 148.57 133.90 132.49 132.46 131.88 131.77 131.60 130.95 130.64 130.23 129.72 128.68 128.54 127.60 127.50 126.51 125.22 120.73 120.68 117.18 117.13
77.32 77.00 76.68
O
Ph–P–O
Ph
3av
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

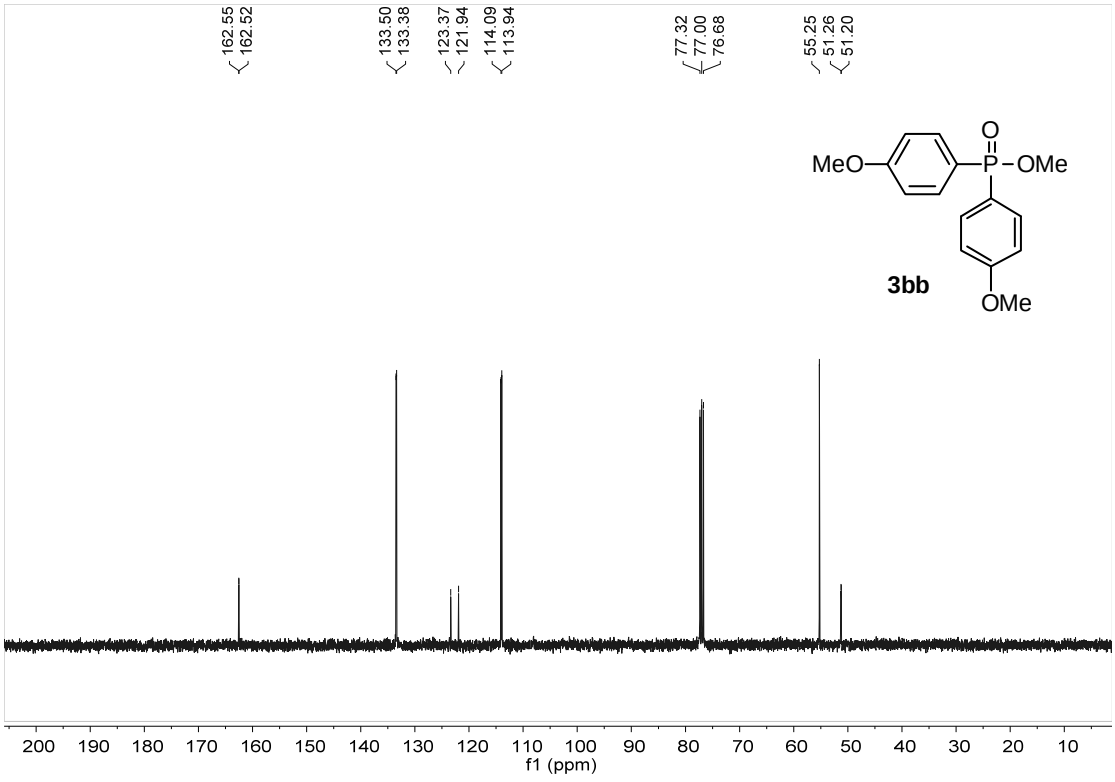

30.84
Ph–P(=O)(Ph)–O
3av
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

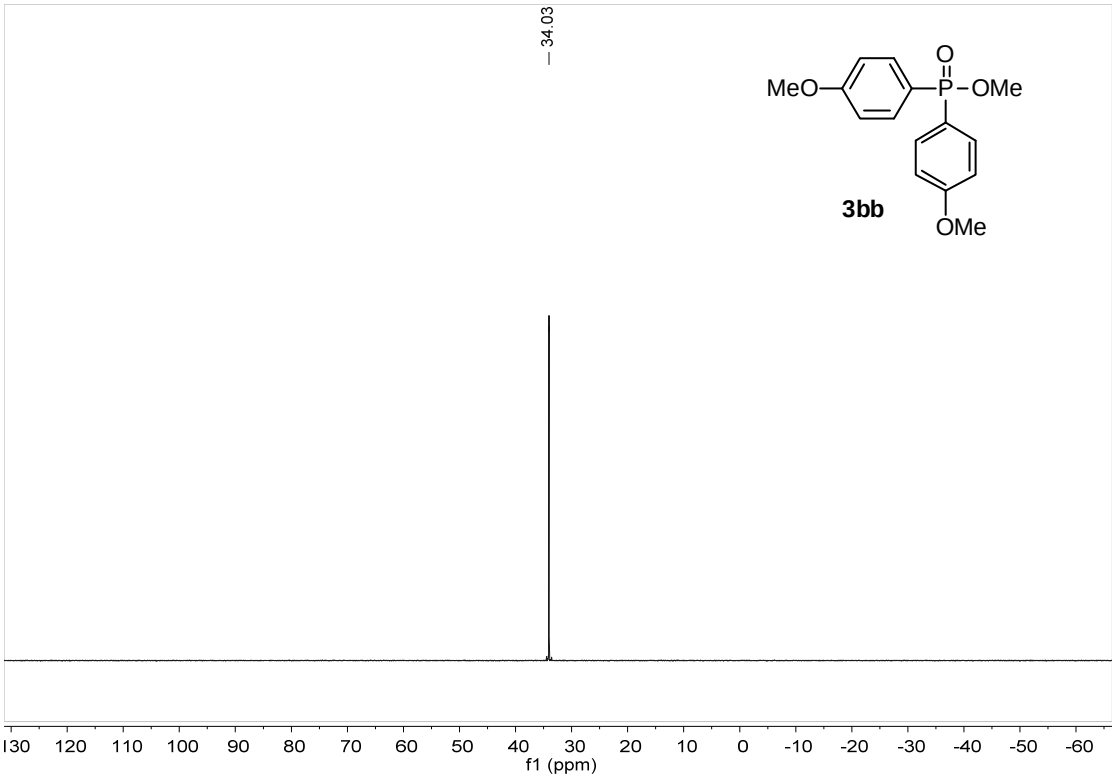

7.83 7.83 7.81 7.81 7.80 7.80 7.79 7.78 7.78 7.77 7.57 7.56 7.55 7.55 7.53 7.53 7.49 7.48 7.47 7.46 7.45 7.44 7.26
4.13 4.11 4.10 4.09 3.97 3.96 3.95 3.94 3.93 3.71 3.70
HO OH
Ph–P(=O)(Ph)–O
15:1
3aw
OH OH
4.00 2.08 4.02 2.01 1.02 2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

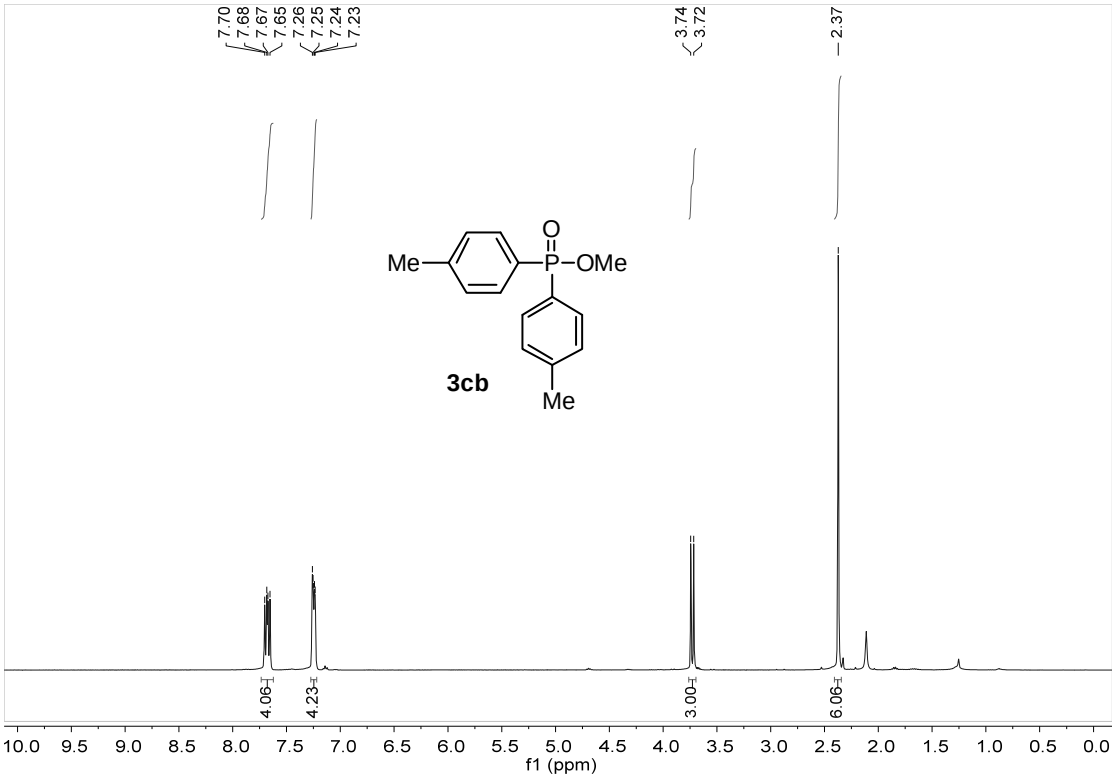

132.67
132.66
132.65
132.63
131.72
131.66
131.62
131.56
130.87
130.75
129.49
129.39
128.83
128.81
128.70
128.67
77.32
77.00
76.68
70.74
70.71
67.17
67.11
62.66
HO
OH
O
Ph–P–O
Ph
15:1
3aw
OH
OH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

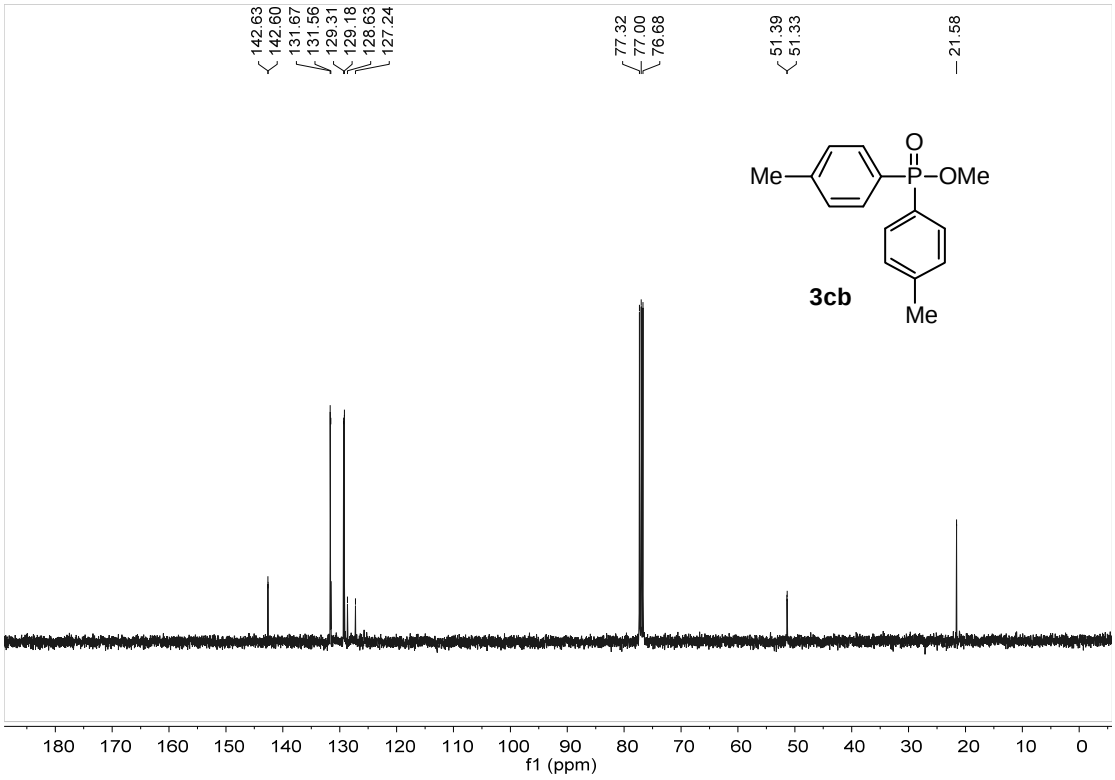

36.24
HO
OH
O
Ph–P–O
Ph
15:1
3aw
OH
OH
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

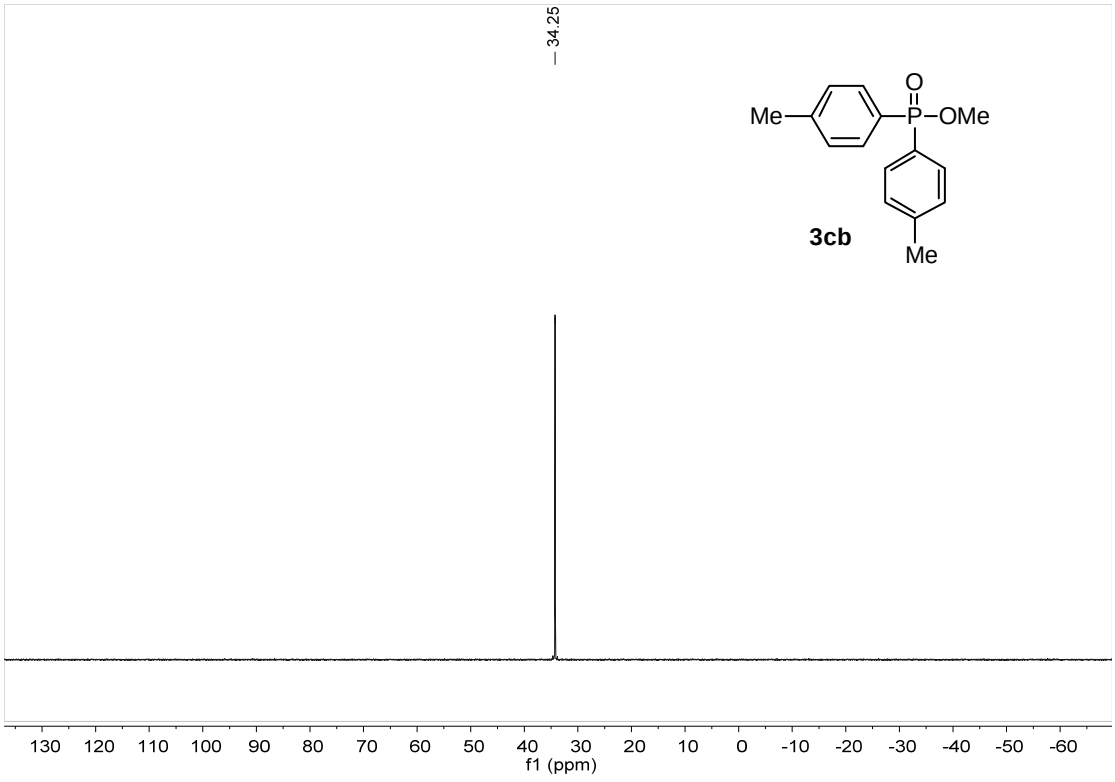

7.73
7.71
7.70
7.68
7.26
6.94
6.94
6.92
6.92
3.81
3.71
3.69
MeO
O
P
OMe
3bb
OMe
4.03
4.03
6.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

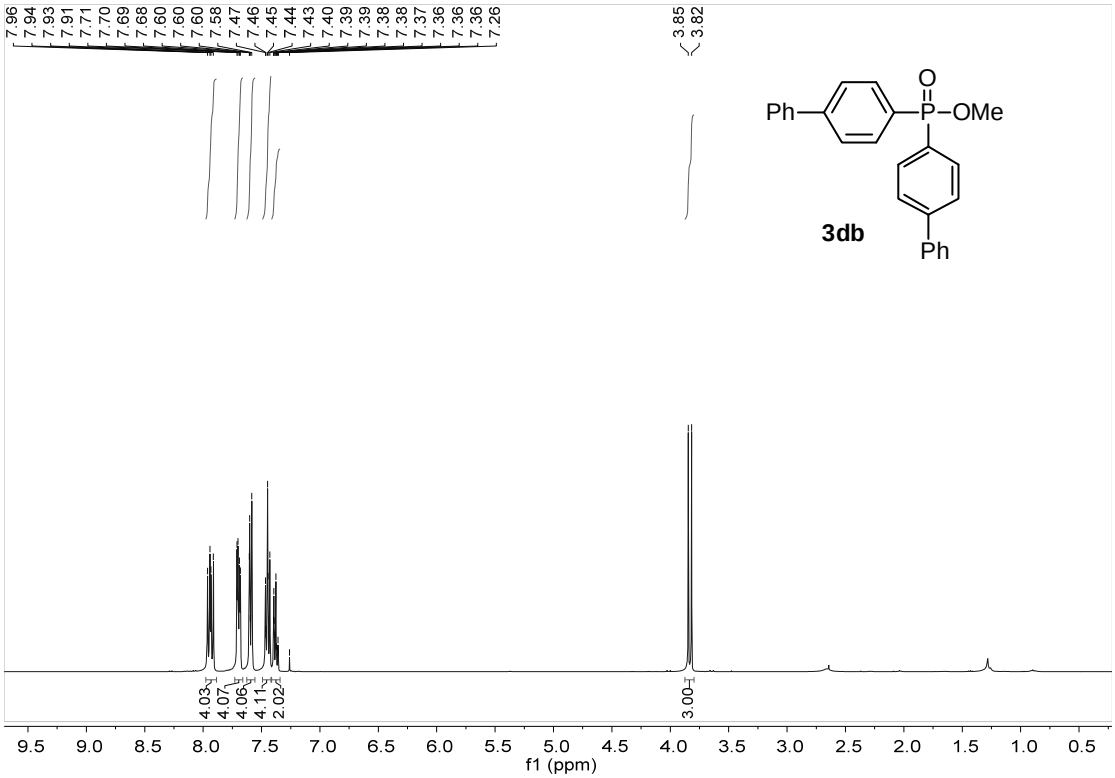

162.55
162.52
133.50
133.38
123.37
121.94
114.09
113.94
77.32
77.00
76.68
55.25
51.26
51.20
MeO
O
P
OMe
3bb
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

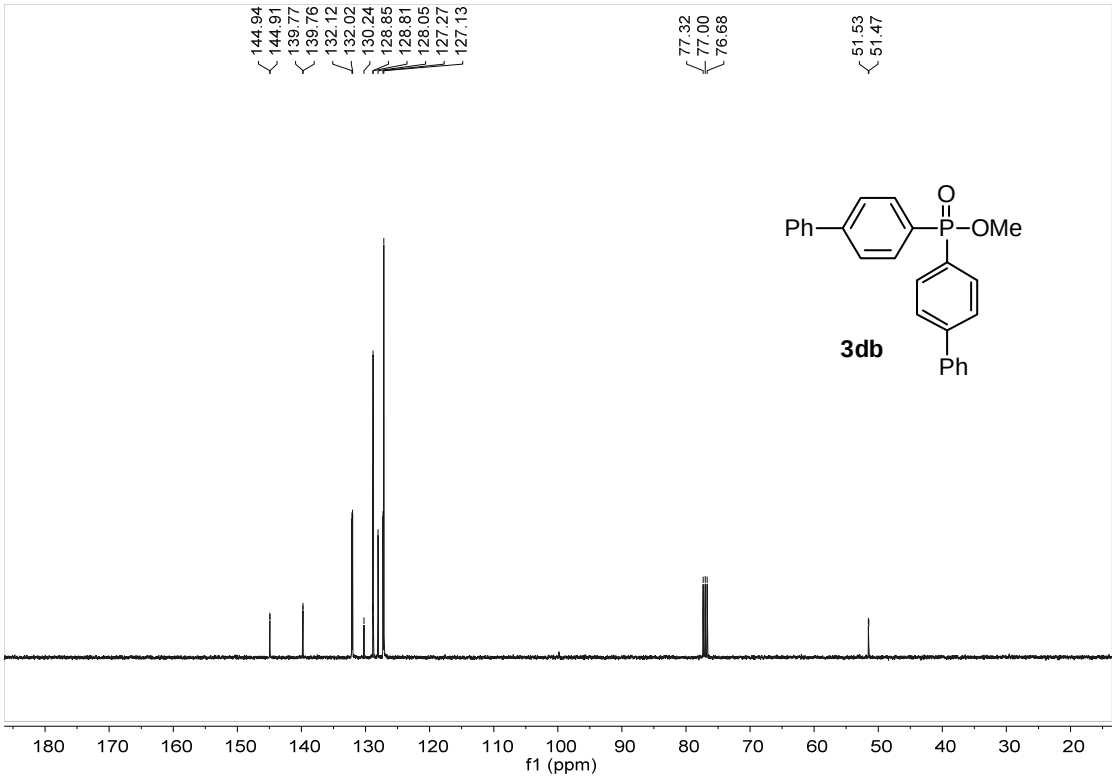

34.03
MeO
O
P
OMe
3bb
OMe
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

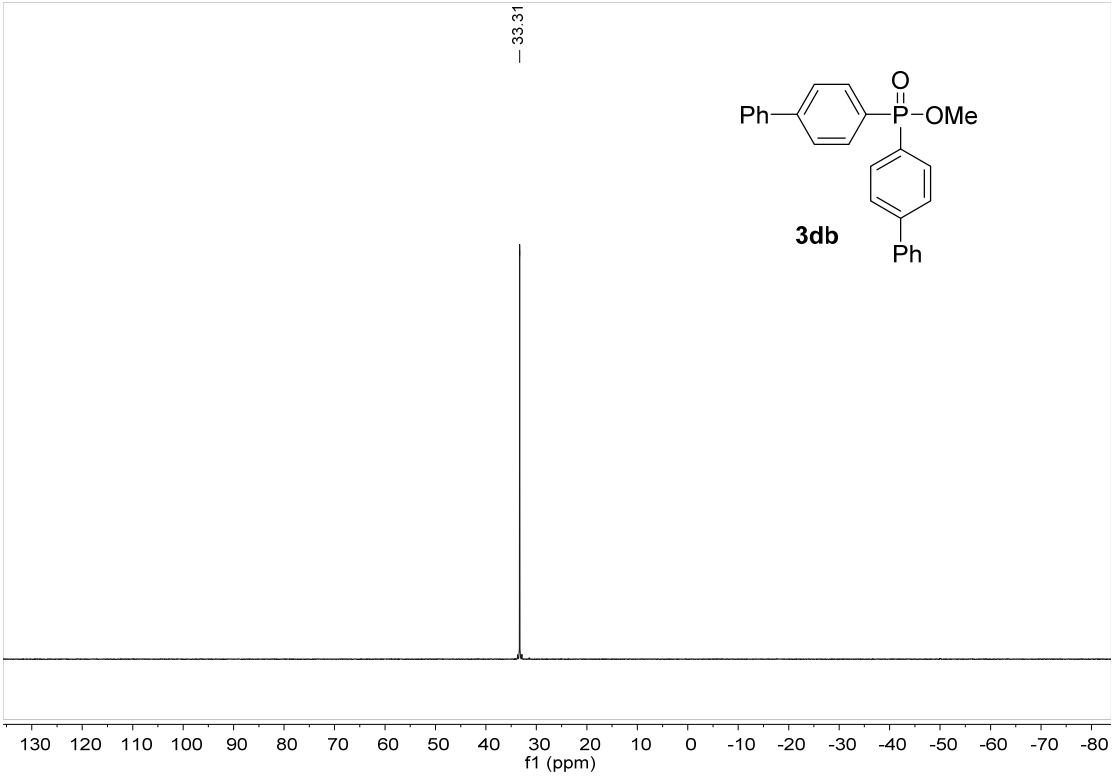

7.70
7.68
7.67
7.65
7.26
7.25
7.24
7.23
3.74
3.72
2.37
Me
O
P
OMe
3cb
Me
4.06
4.23
3.00
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

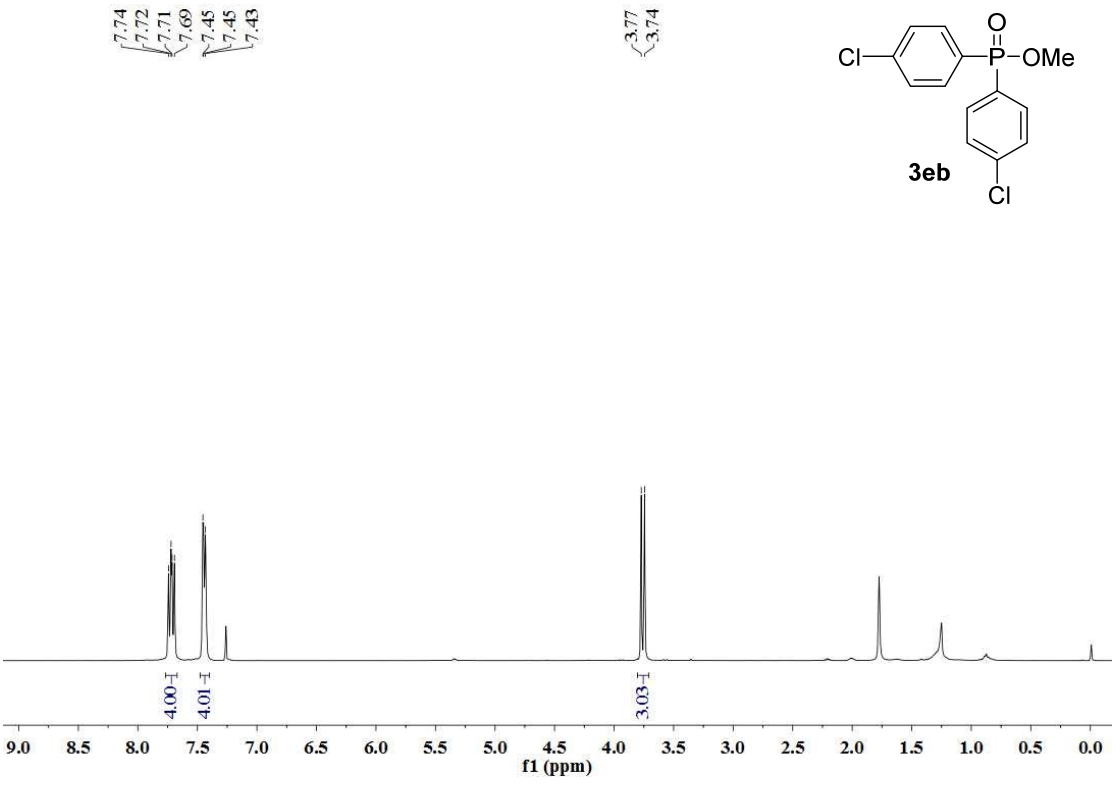

142.63
142.60
131.67
131.56
129.31
129.18
128.63
127.24
77.32
77.00
76.68
51.39
51.33
21.58
Me
O
P–OMe
Me
3cb
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

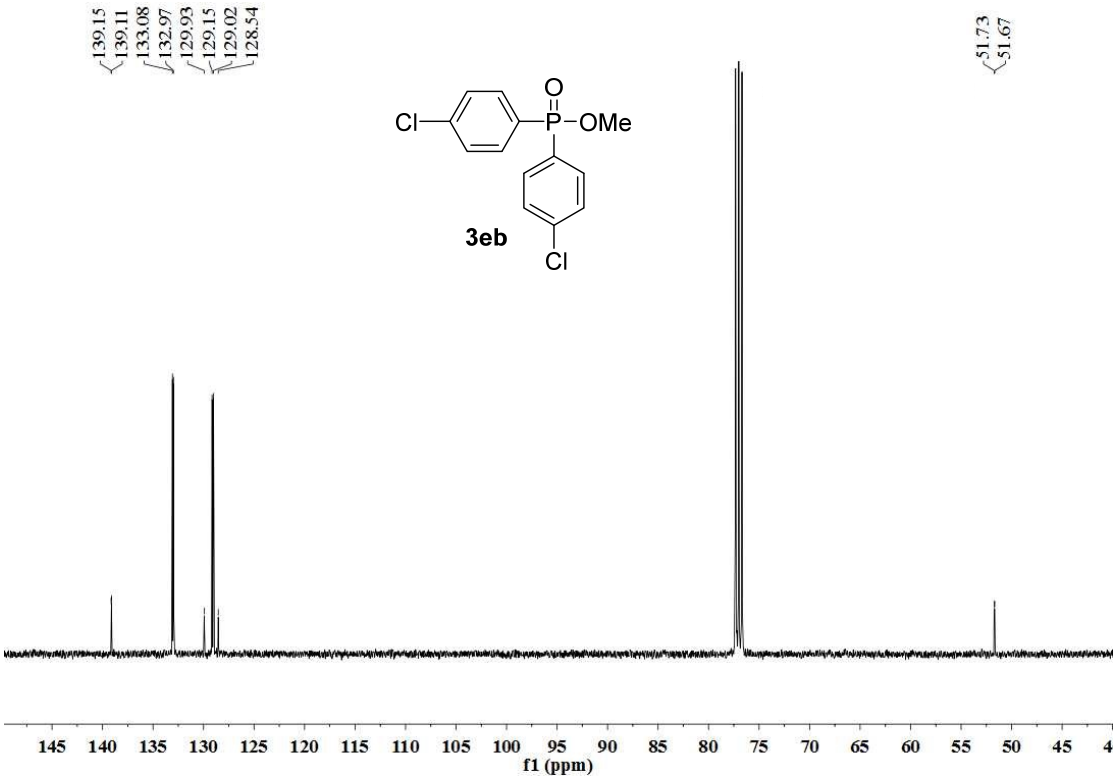

34.25
Me
O
P–OMe
Me
3cb
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

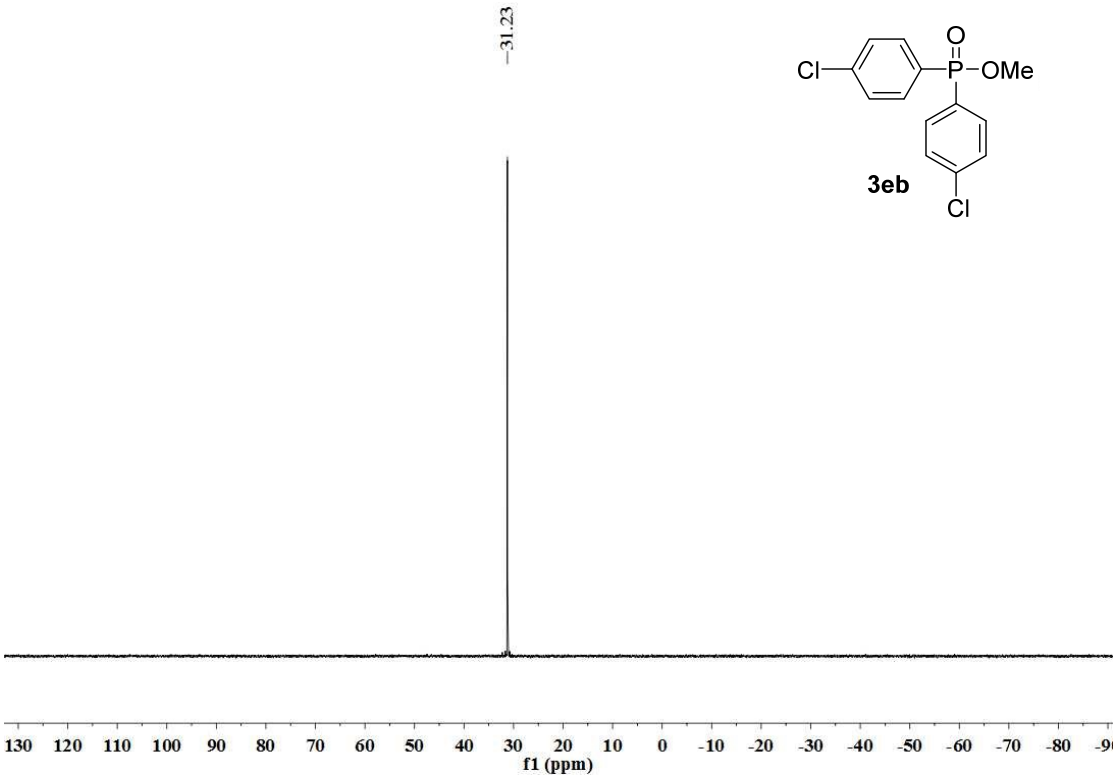

7.96
7.94
7.93
7.91
7.71
7.70
7.69
7.68
7.60
7.60
7.60
7.58
7.47
7.46
7.45
7.44
7.43
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.26
3.85
3.82
Ph
P
O
OMe
Ph
3db
4.03
4.07
4.06
4.11
2.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

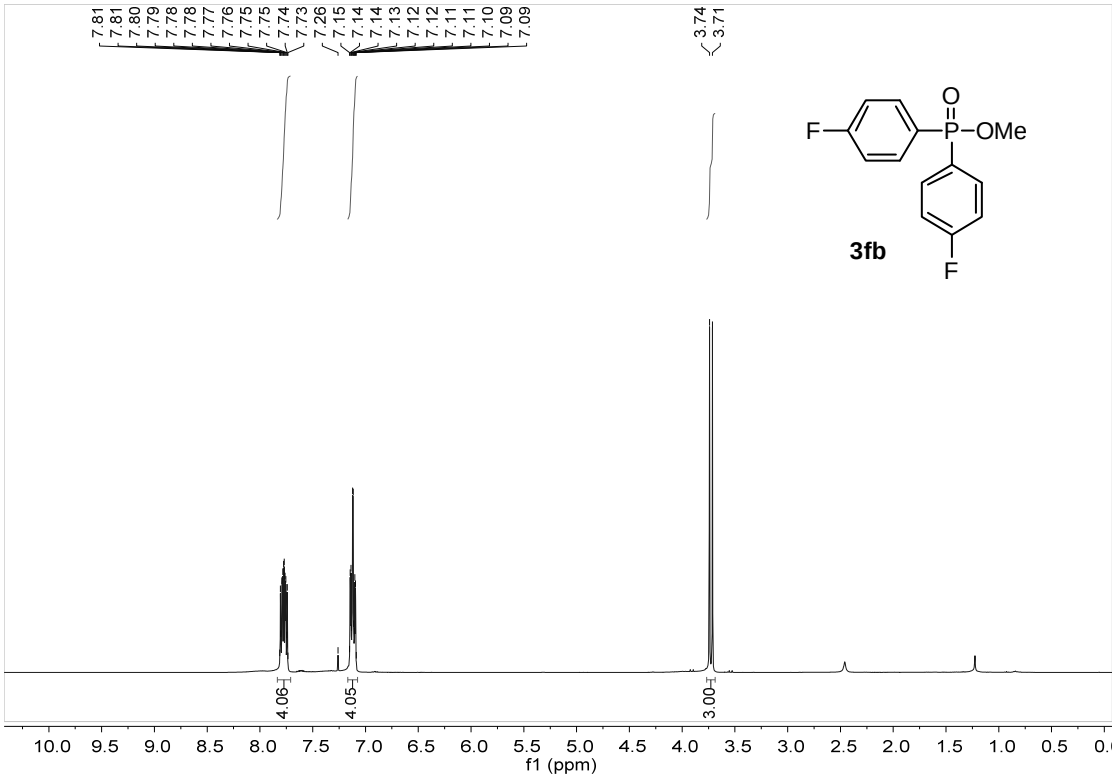

144.94
144.91
139.77
139.76
132.12
132.02
130.24
128.85
128.81
128.05
127.27
127.13
77.32
77.00
76.68
51.53
51.47
Ph
P
O
OMe
Ph
3db
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

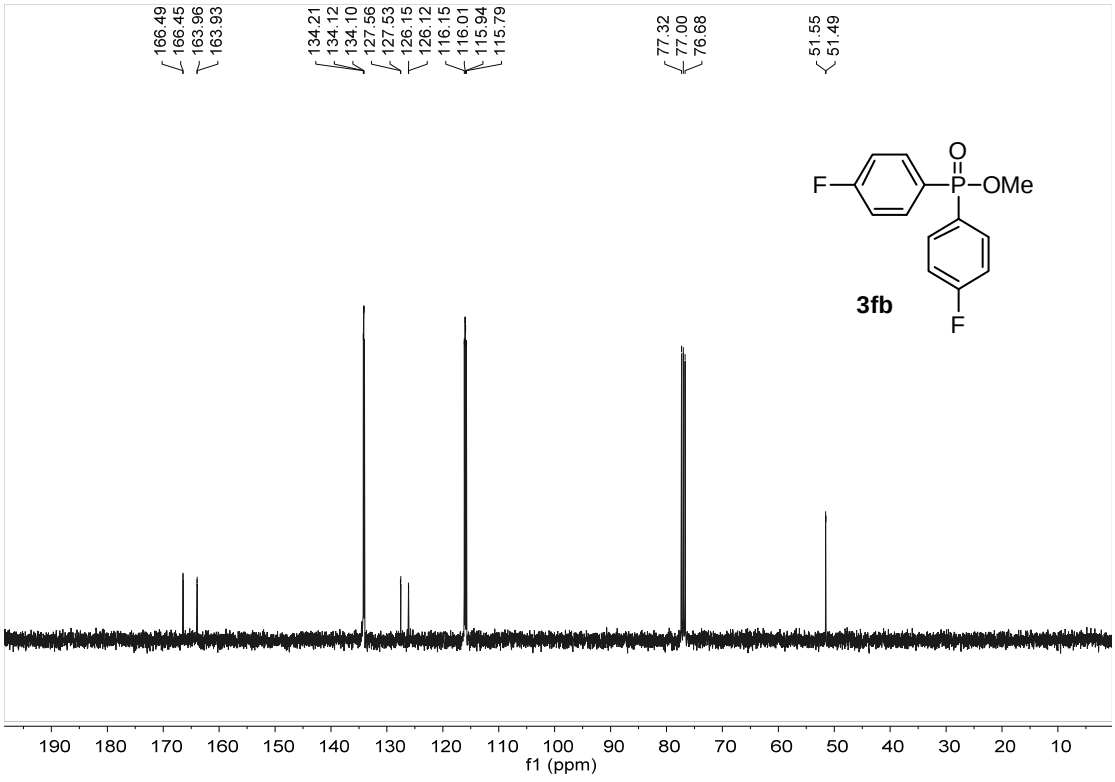

33.31
Ph
O
P
OMe
Ph
3db
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

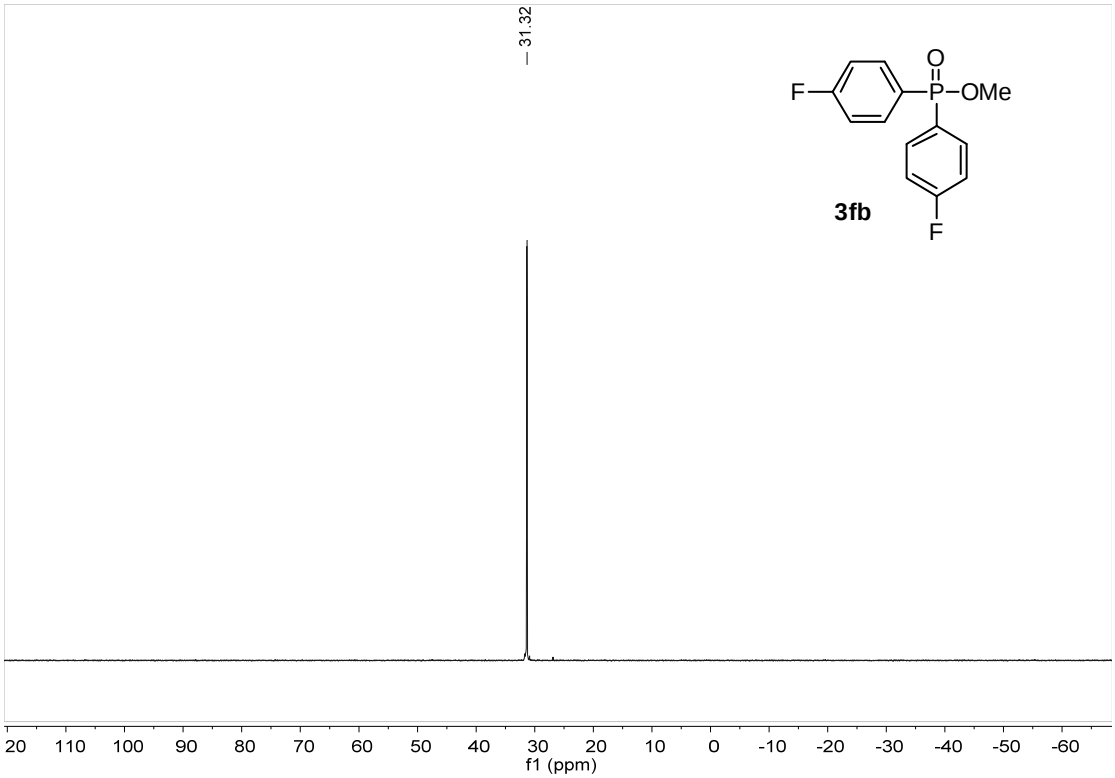

7.74
7.72
7.71
7.69
7.45
7.45
7.43
3.77
3.74
Cl
O
P
OMe
3eb
Cl
4.00
4.01
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

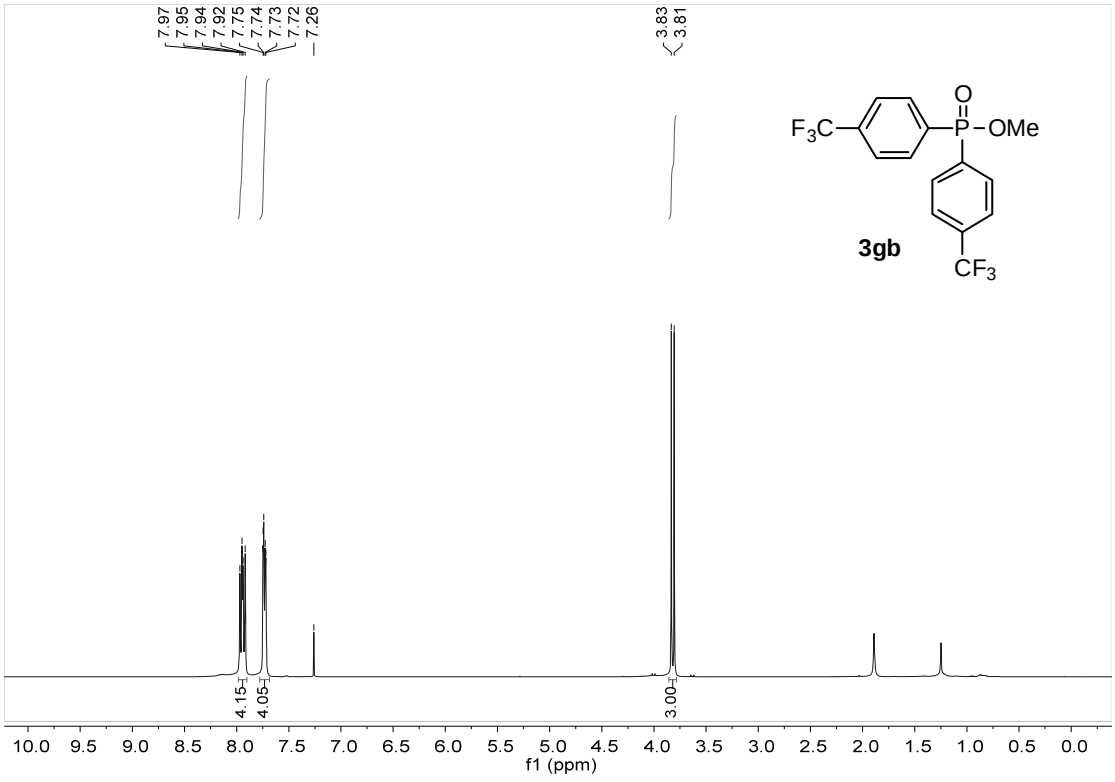

139.15
139.11
133.08
132.97
129.93
129.15
129.02
128.54
51.73
51.67
Cl
O
P
OMe
Cl
3eb
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 4
f1 (ppm)

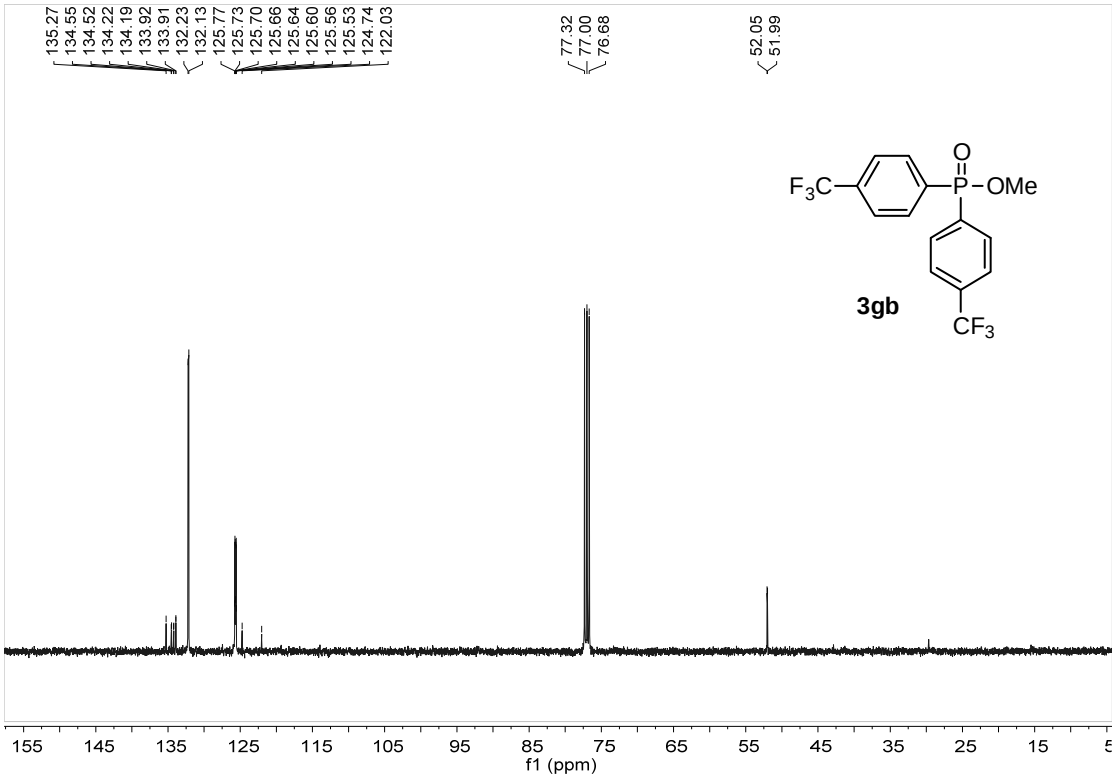

31.23
Cl
O
P
OMe
3eb
Cl
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -9
f1 (ppm)

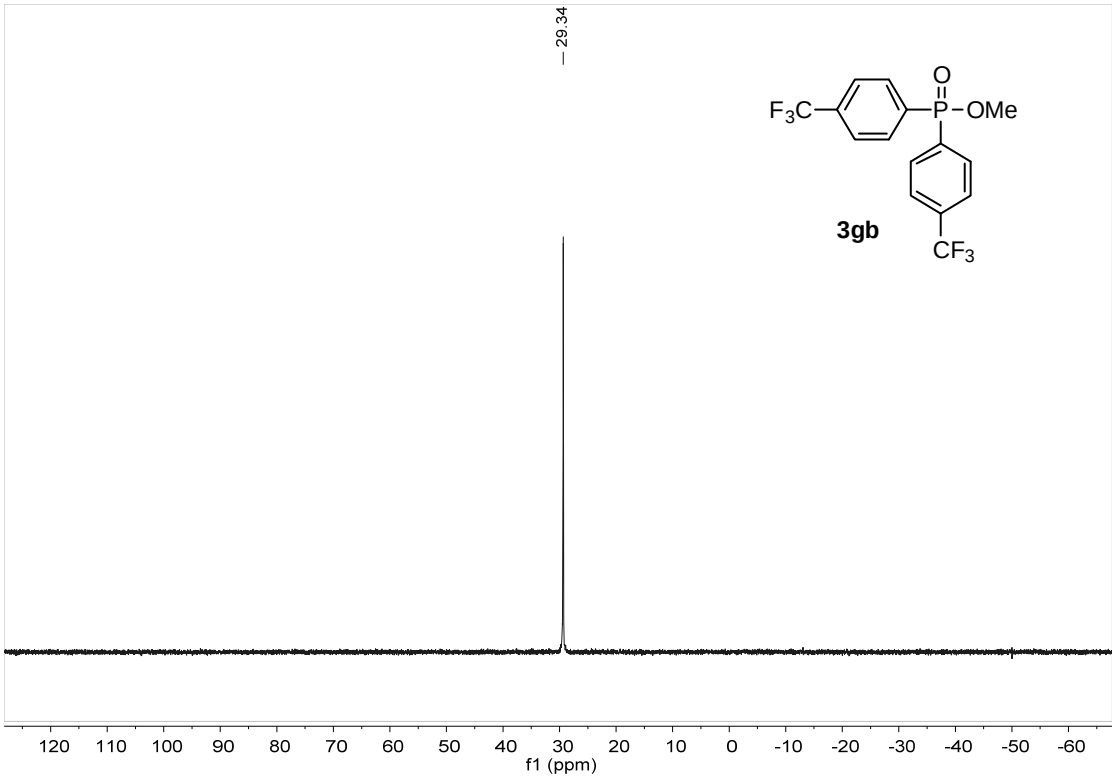

7.81
7.81
7.80
7.79
7.78
7.78
7.77
7.76
7.75
7.75
7.74
7.73
7.26
7.15
7.14
7.14
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.09
3.74
3.71
F
O
P
OMe
3fb
F
4.06
4.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

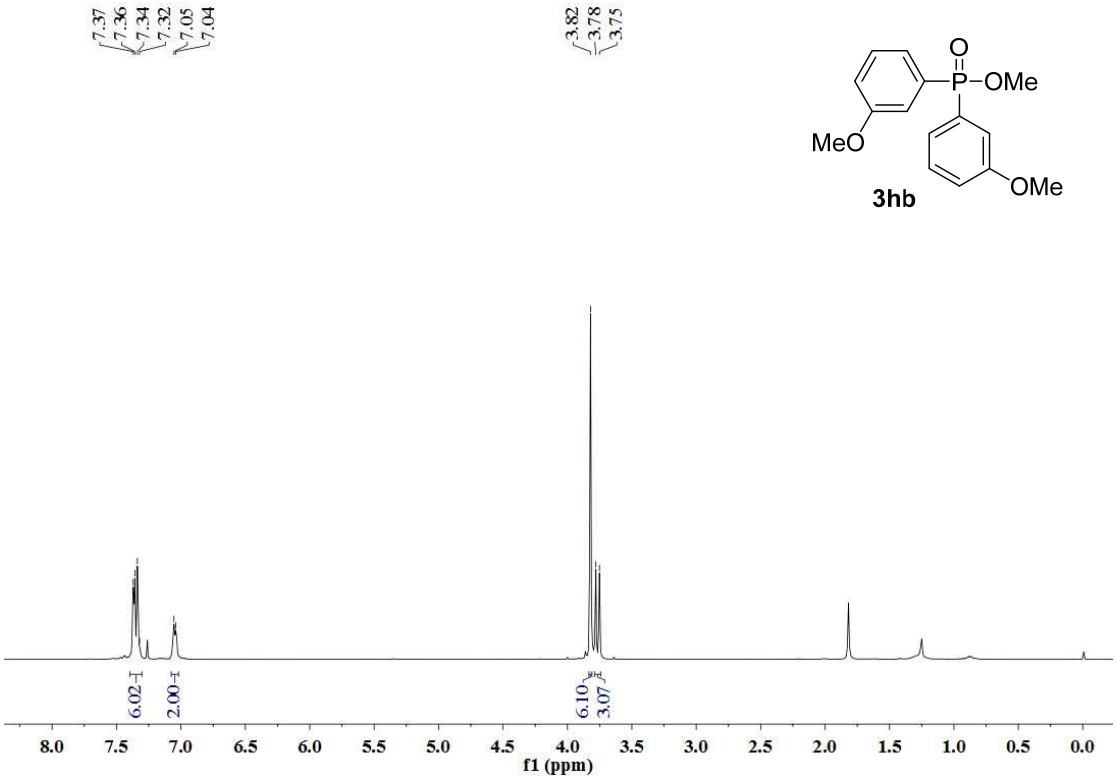

166.49
166.45
163.96
163.93
134.21
134.12
134.10
127.56
127.53
126.15
126.12
116.15
116.01
115.94
115.79
77.32
77.00
76.68
51.55
51.49
F
O
P
OMe
3fb
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

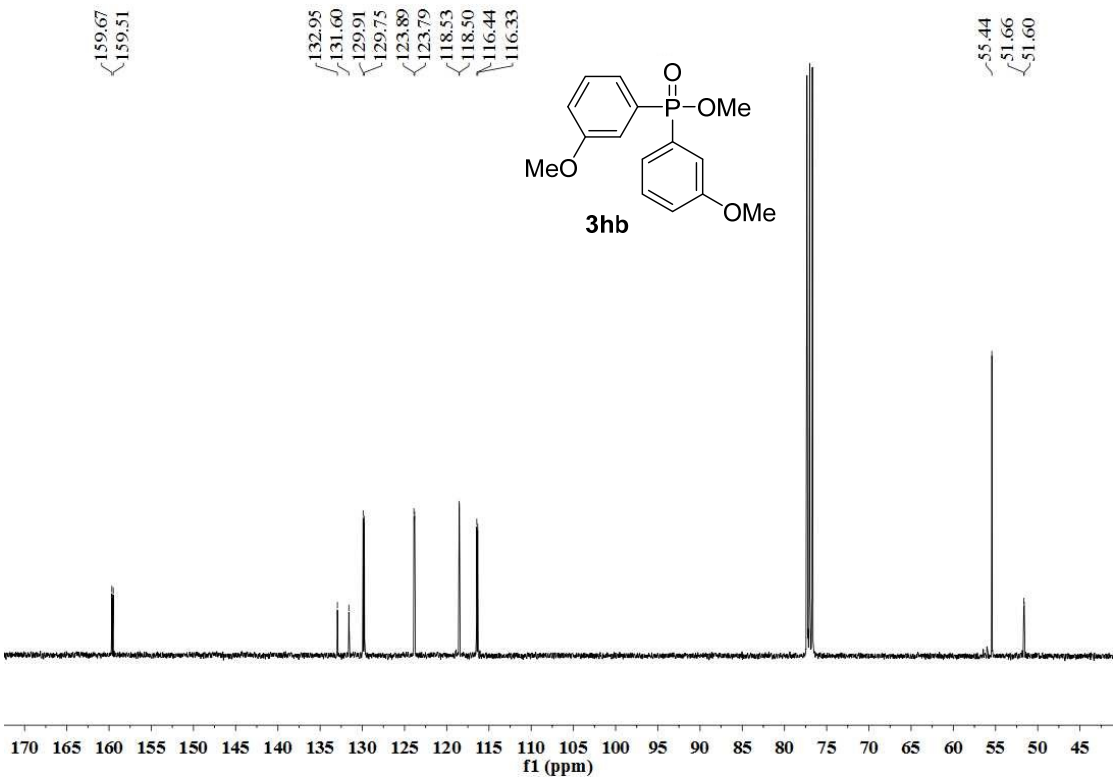

31.32
F
O
P
OMe
F
3fb
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

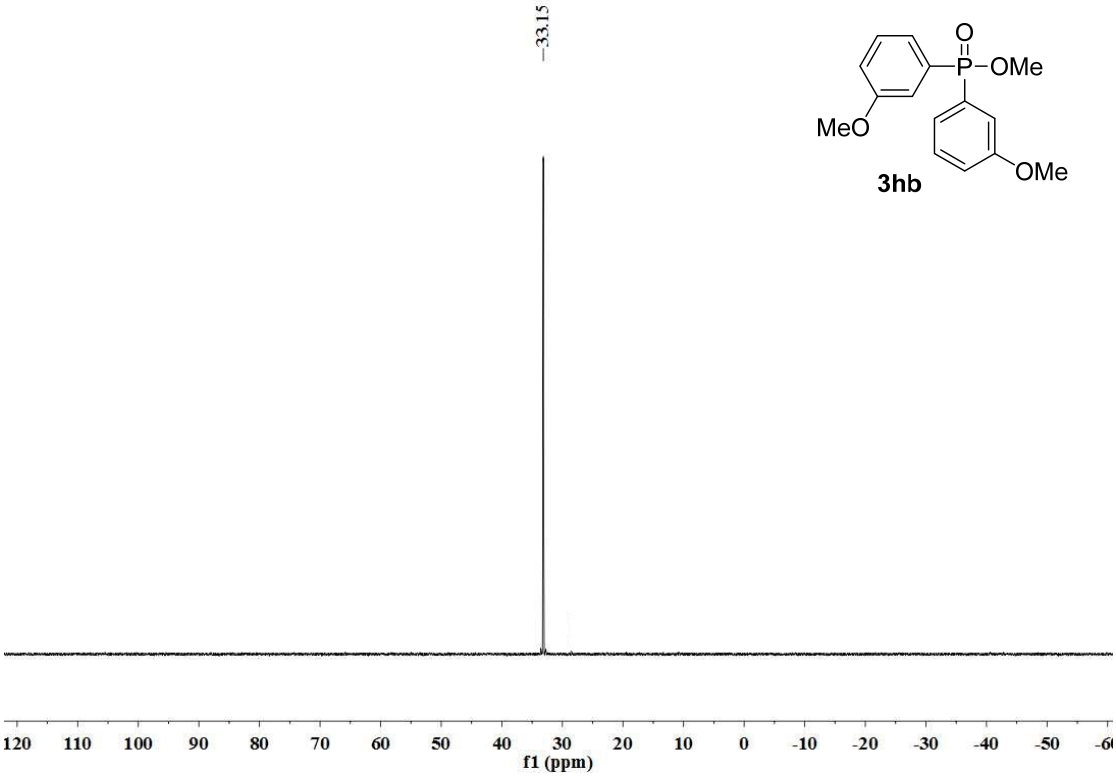

7.97
7.95
7.94
7.92
7.75
7.74
7.73
7.72
7.26
3.83
3.81
F3C
O
P
OMe
3gb
CF3
4.15
4.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

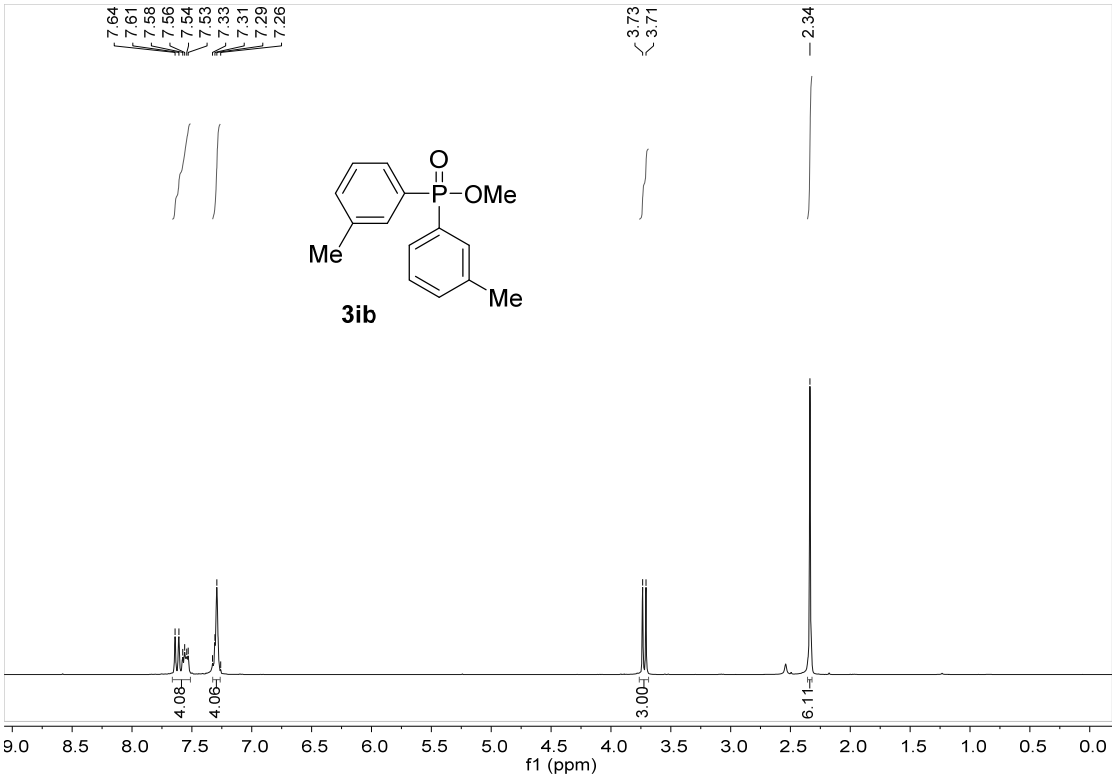

135.27
134.55
134.52
134.22
134.19
133.92
133.91
132.23
132.13
125.77
125.73
125.70
125.66
125.64
125.60
125.56
125.53
124.74
122.03
77.32
77.00
76.68
52.05
51.99
F3C
O
P
OMe
3gb
CF3
155 145 135 125 115 105 95 85 75 65 55 45 35 25 15
f1 (ppm)

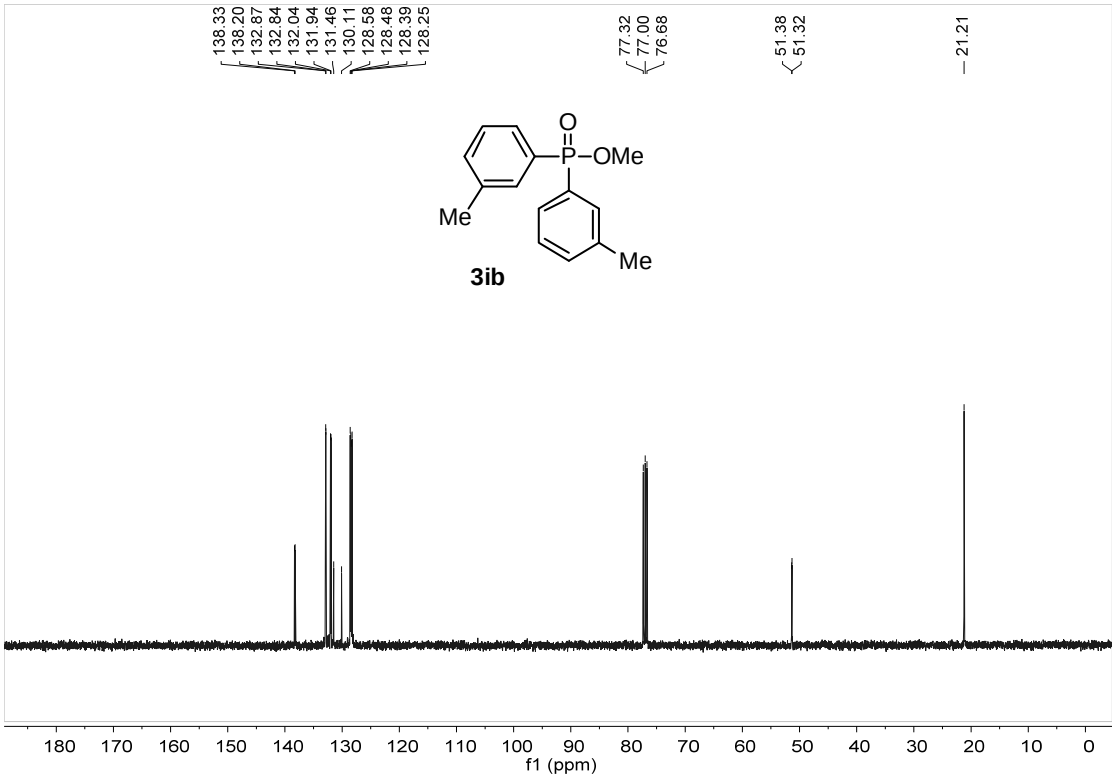

29.34
F3C
O
P
OMe
3gb
CF3
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

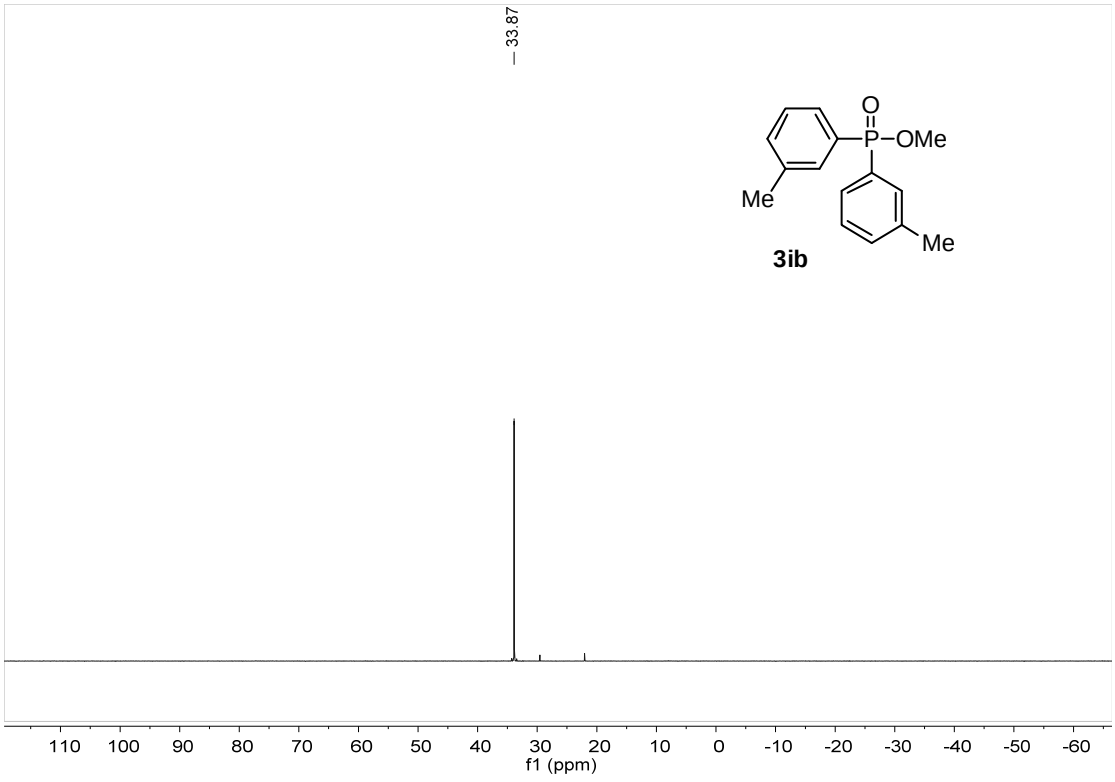

7.37
7.36
7.34
7.32
7.05
7.04
3.82
3.78
3.75
O
P–OMe
MeO
OMe
3hb
6.02
2.00
6.10
3.07
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

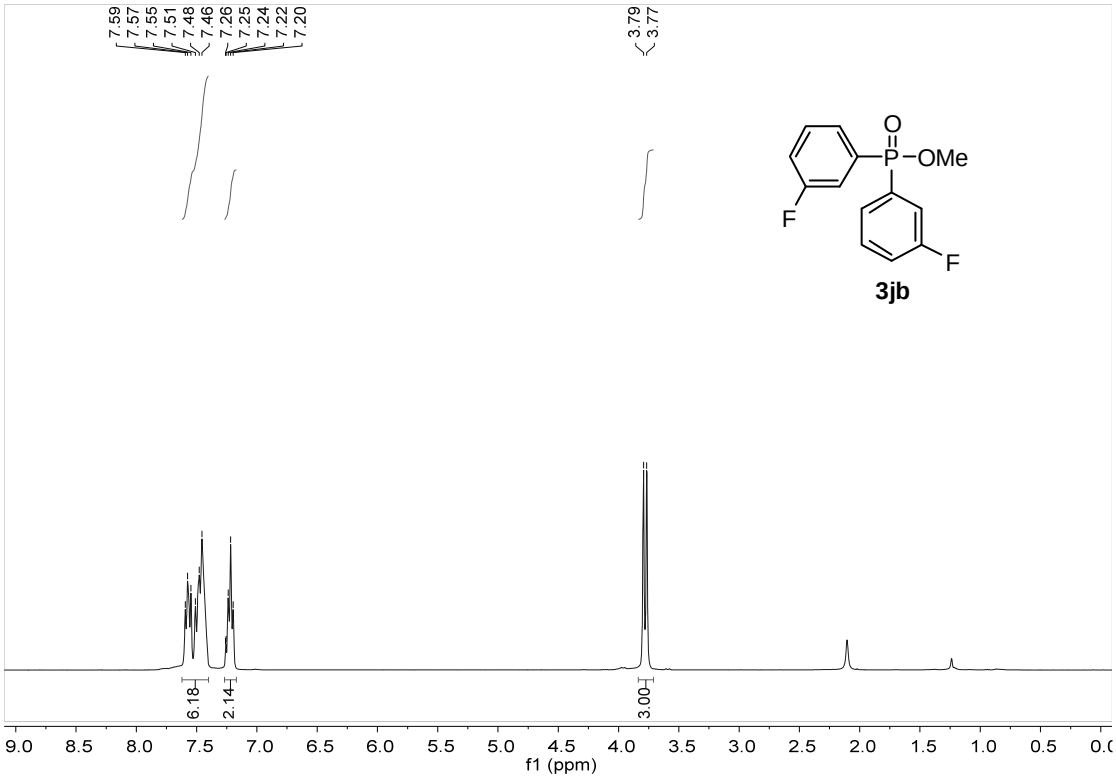

159.67
159.51
132.95
131.60
129.91
129.75
123.89
123.79
118.53
118.50
116.44
116.33
55.44
51.66
51.60
O
P–OMe
MeO
OMe
3hb
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
f1 (ppm)

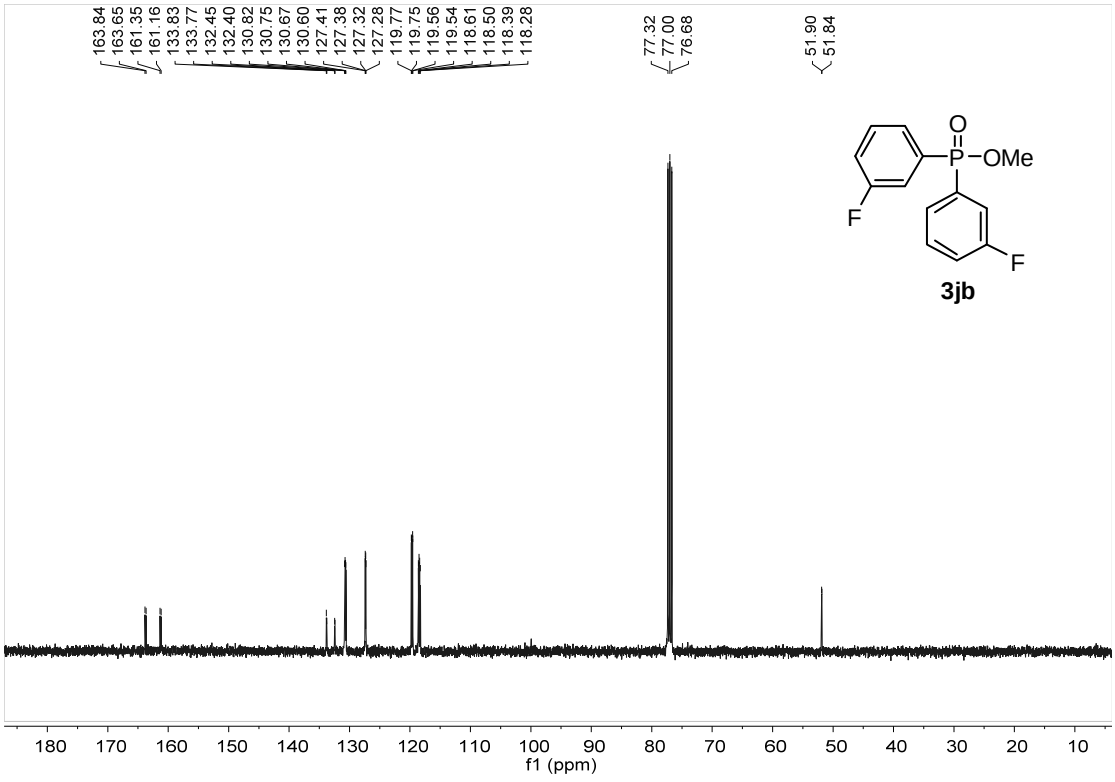

33.15
O
P–OMe
MeO
OMe
3hb
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

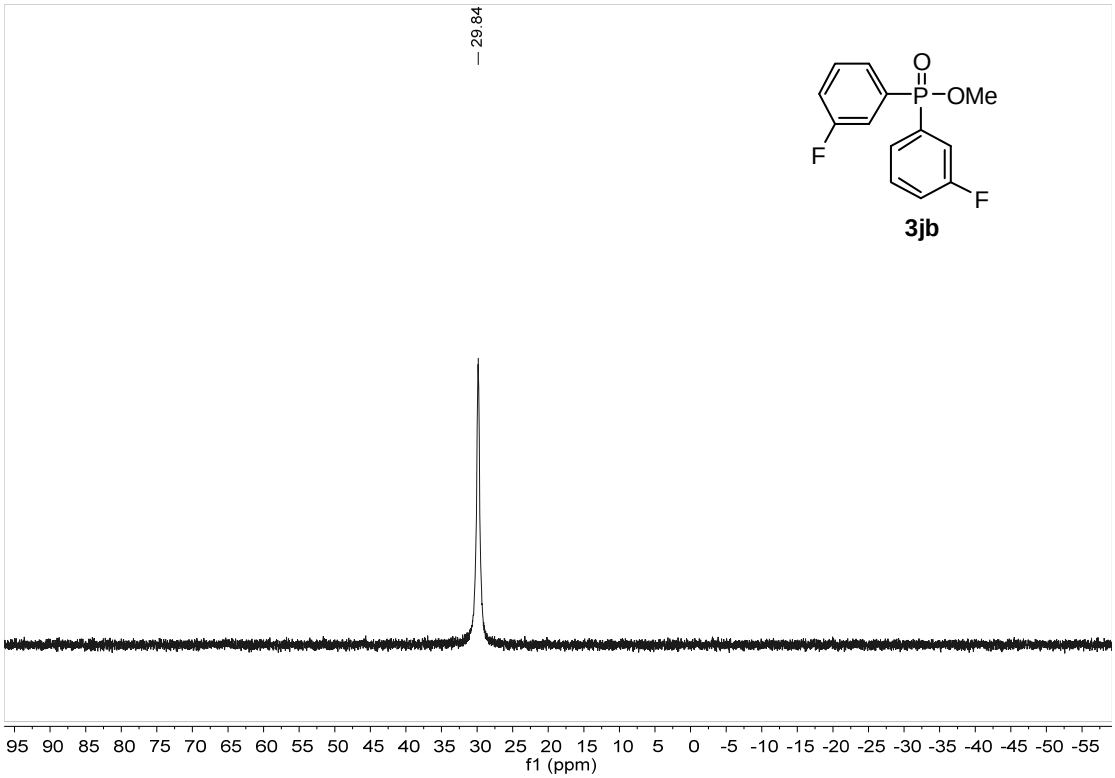

7.64
7.61
7.58
7.56
7.54
7.53
7.33
7.31
7.29
7.26
3.73
3.71
2.34
O
P–OMe
Me
Me
3ib
4.08
4.06
3.00
6.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

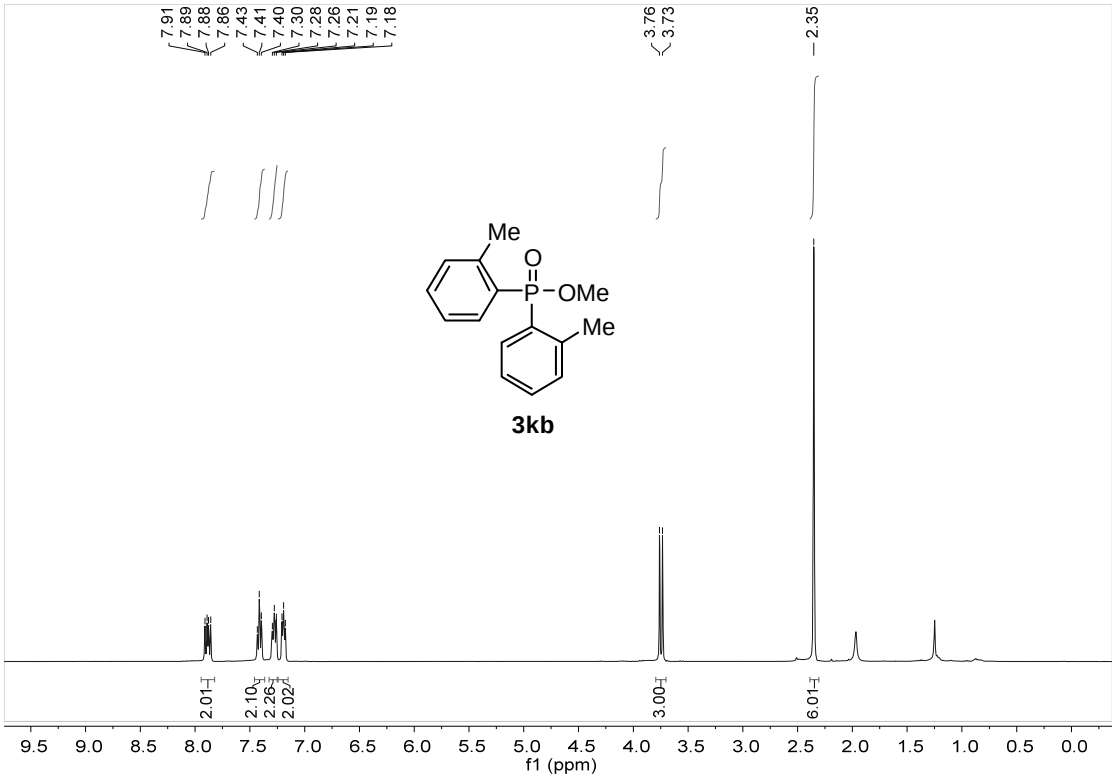

138.33
138.20
132.87
132.84
132.04
131.94
131.46
130.11
128.58
128.48
128.39
128.25
77.32
77.00
76.68
51.38
51.32
21.21
O
P–OMe
Me
Me
3ib
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

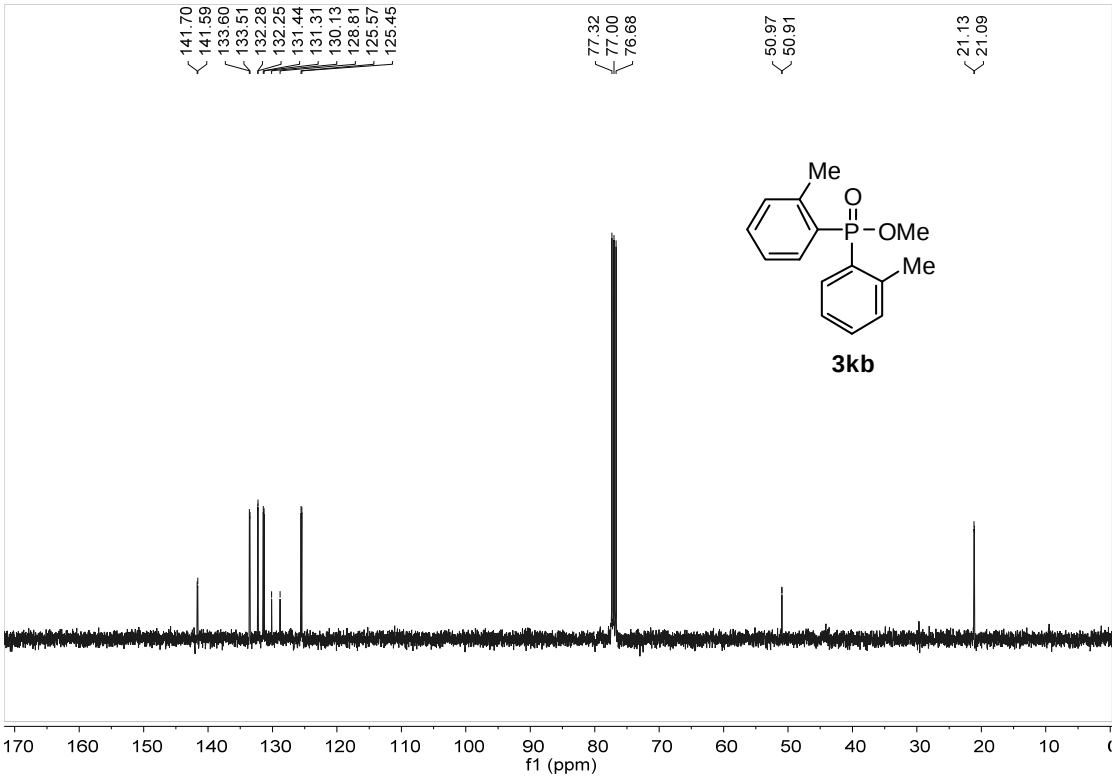

33.87
O
P–OMe
Me
Me
3ib
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

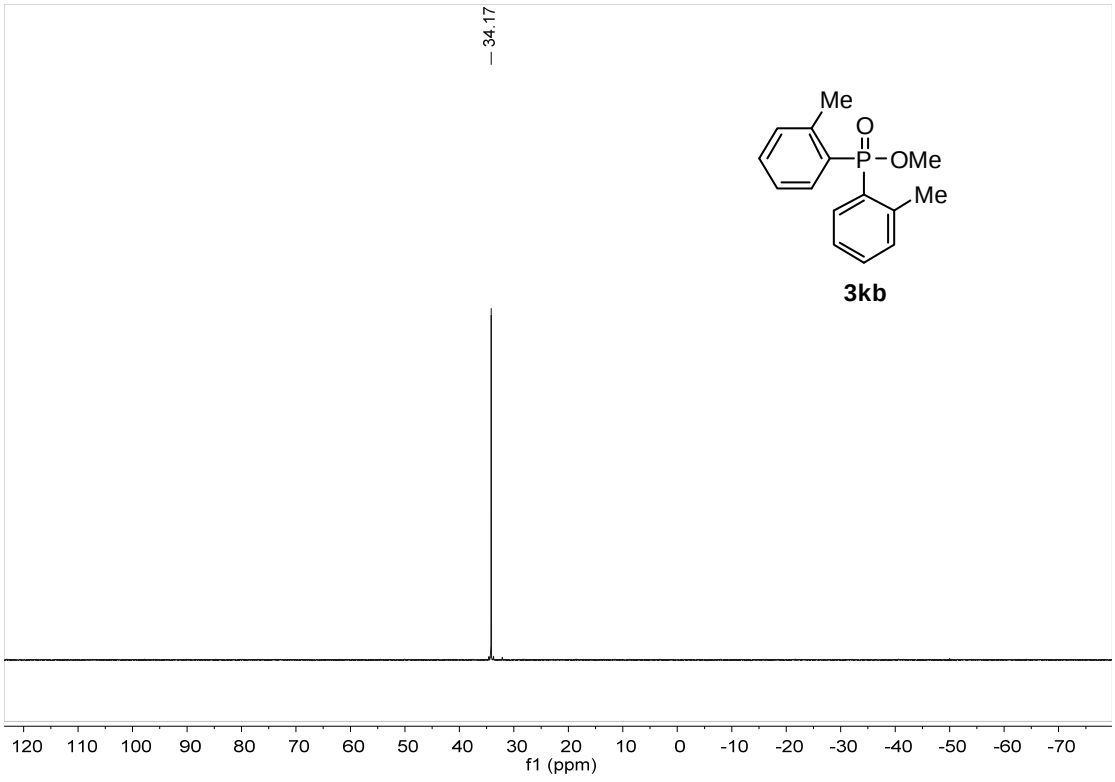

7.59
7.57
7.55
7.51
7.48
7.46
7.26
7.25
7.24
7.22
7.20
3.79
3.77
O
P
OMe
F
F
3jb
6.18
2.14
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

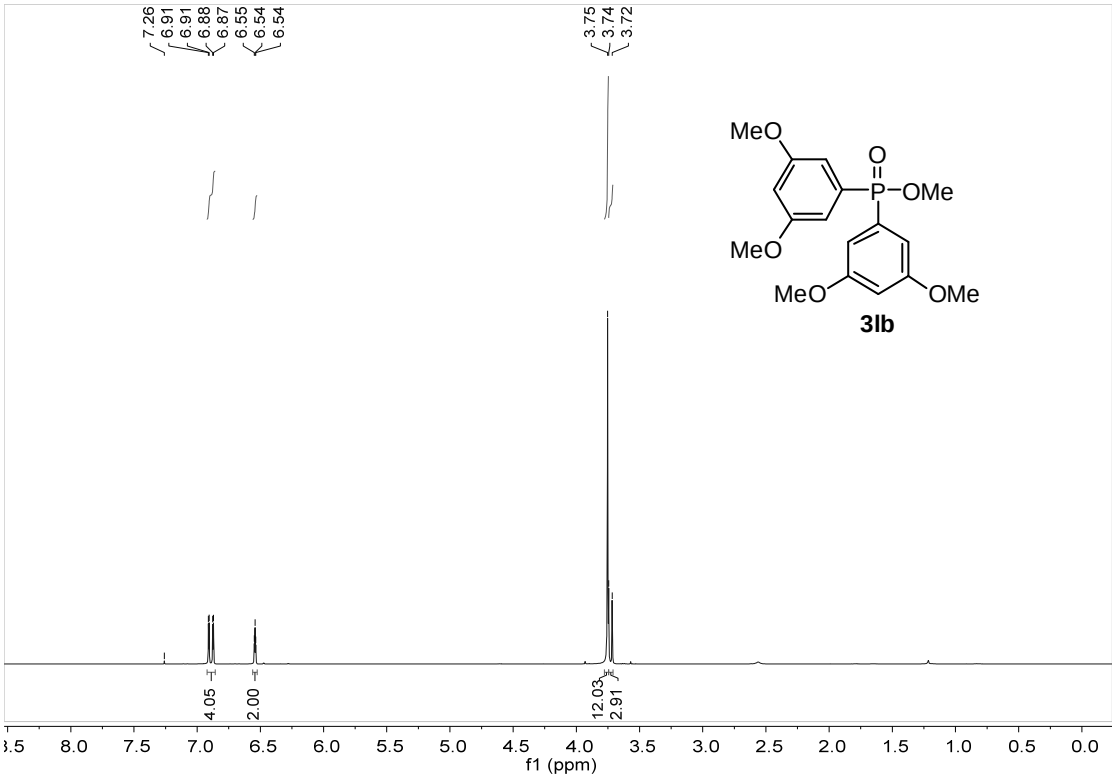

163.84
163.65
161.35
161.16
133.83
133.77
132.45
132.40
130.82
130.75
130.67
130.60
127.41
127.38
127.32
127.28
119.77
119.75
119.56
119.54
118.61
118.50
118.39
118.28
77.32
77.00
76.68
51.90
51.84
O
P
OMe
F
F
3jb
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


29.84
O
P
OMe
F
F
3jb
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
f1 (ppm)

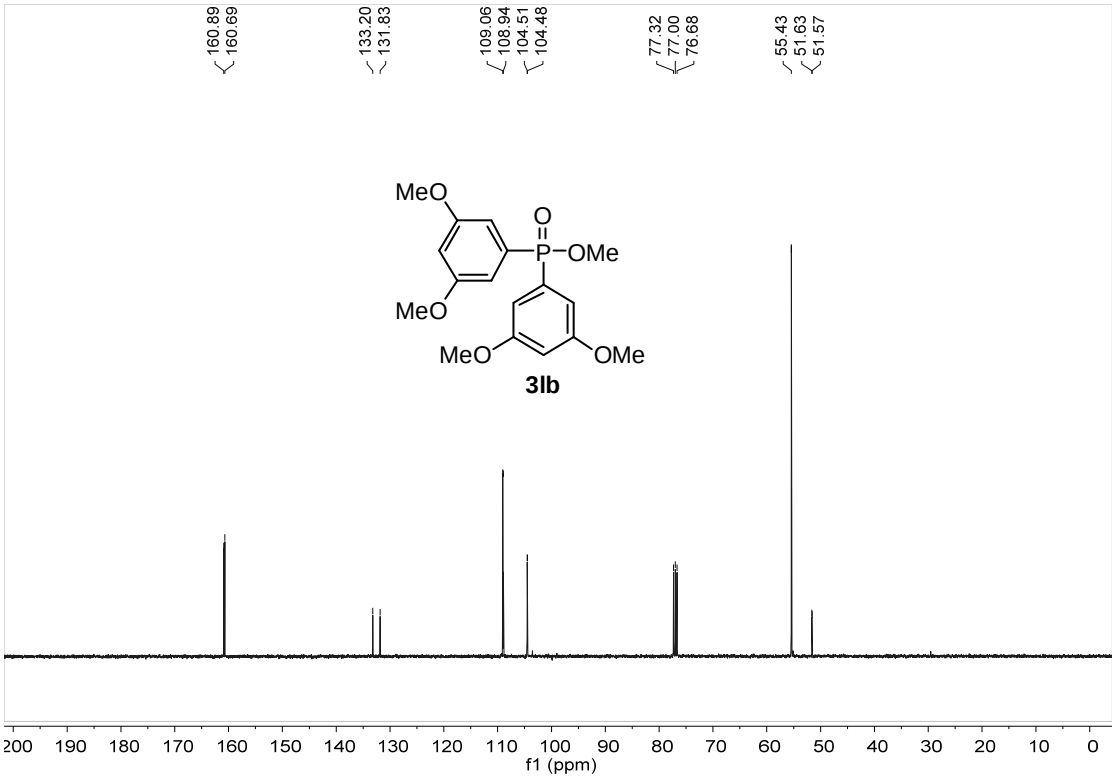

7.91
7.89
7.88
7.86
7.43
7.41
7.40
7.30
7.28
7.26
7.21
7.19
7.18
3.76
3.73
2.35
Me
O
P
OMe
Me
3kb
2.01
2.10
2.26
2.02
3.00
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.70
141.59
133.60
133.51
132.28
132.25
131.44
131.31
130.13
128.81
125.57
125.45
77.32
77.00
76.68
50.97
50.91
21.13
21.09
Me
O
P
OMe
Me
3kb
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

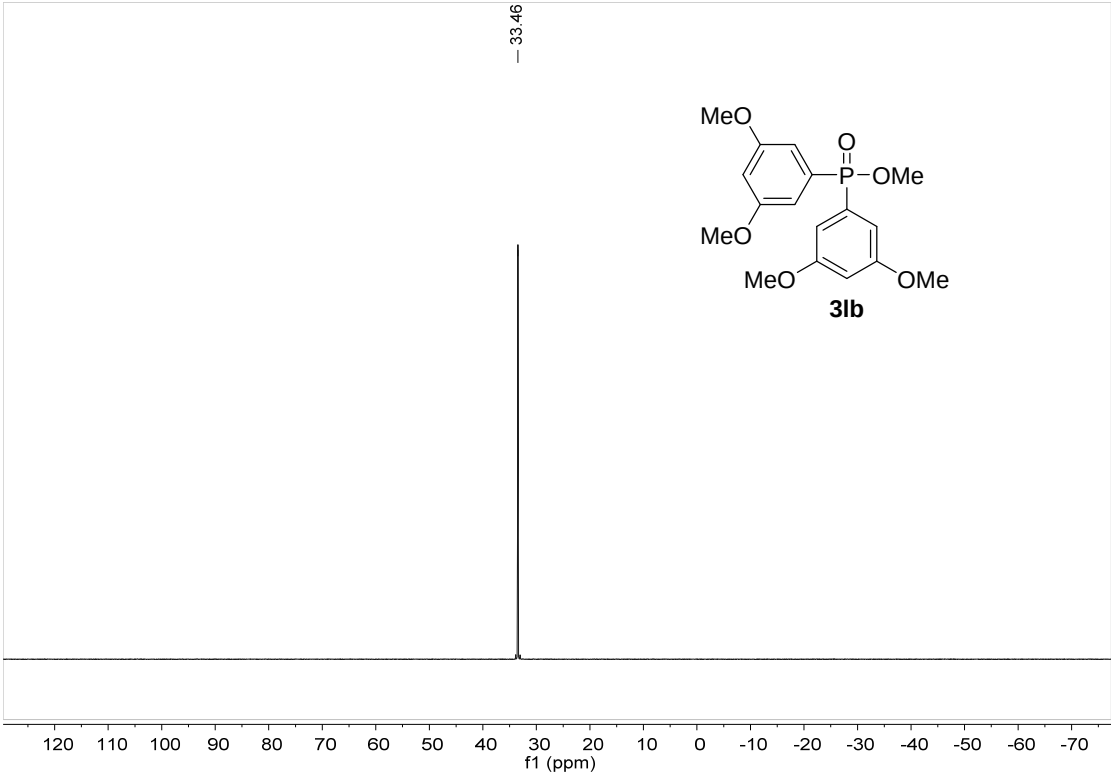

34.17
Me
O
P
OMe
Me
3kb
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)


7.26
6.91
6.91
6.88
6.87
6.55
6.54
6.54
3.75
3.74
3.72
MeO
O
P–OMe
MeO
MeO
OMe
4.05
2.00
12.03
2.91
f1 (ppm)

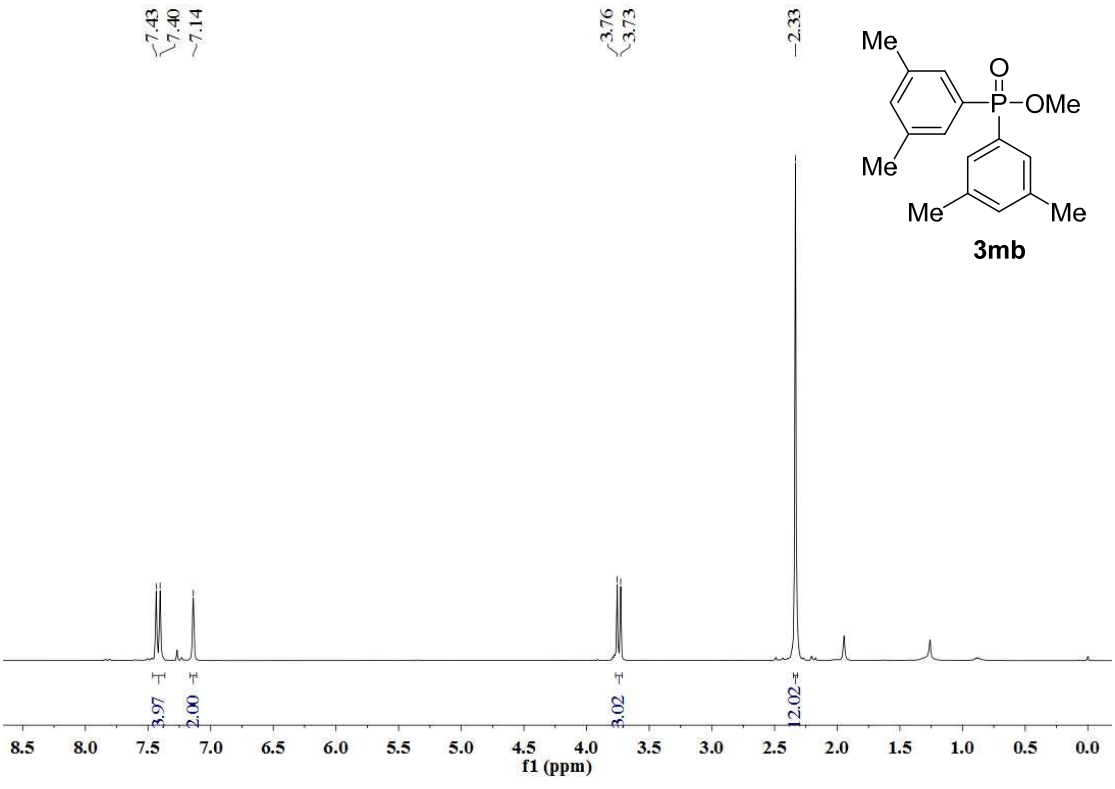
3lb


160.89
160.69
133.20
131.83
109.06
108.94
104.51
104.48
77.32
77.00
76.68
55.43
51.63
51.57
MeO
O
P–OMe
MeO
MeO
OMe
f1 (ppm)

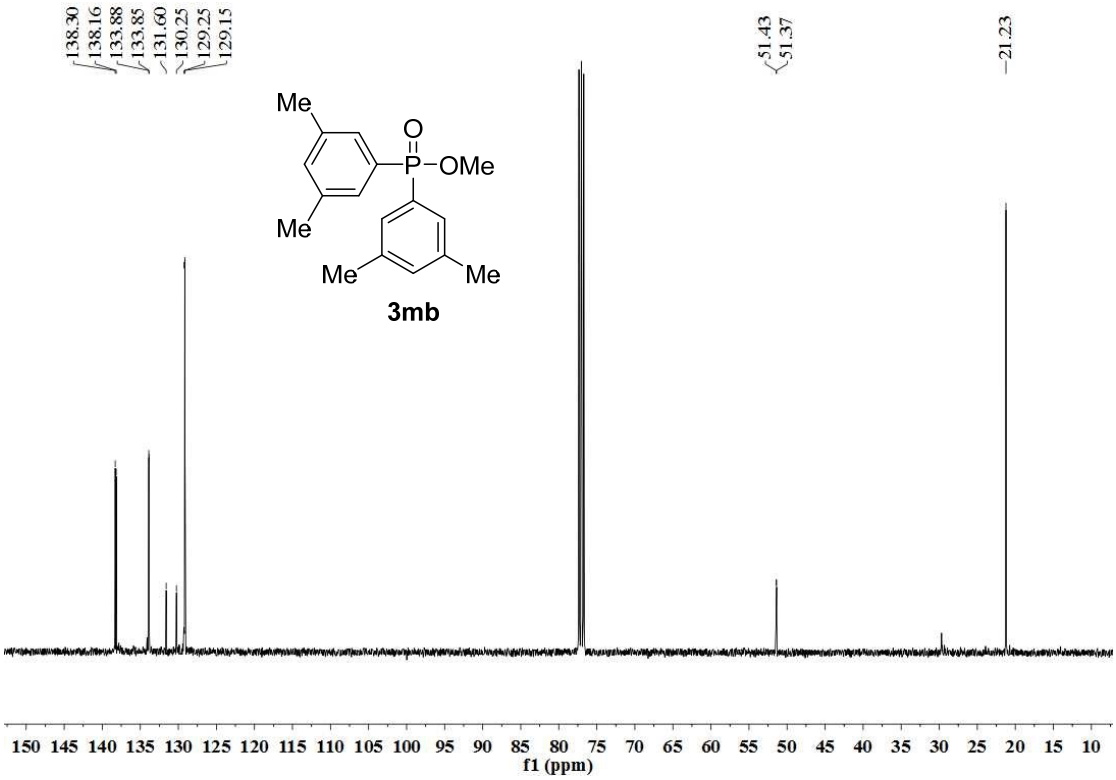
3lb

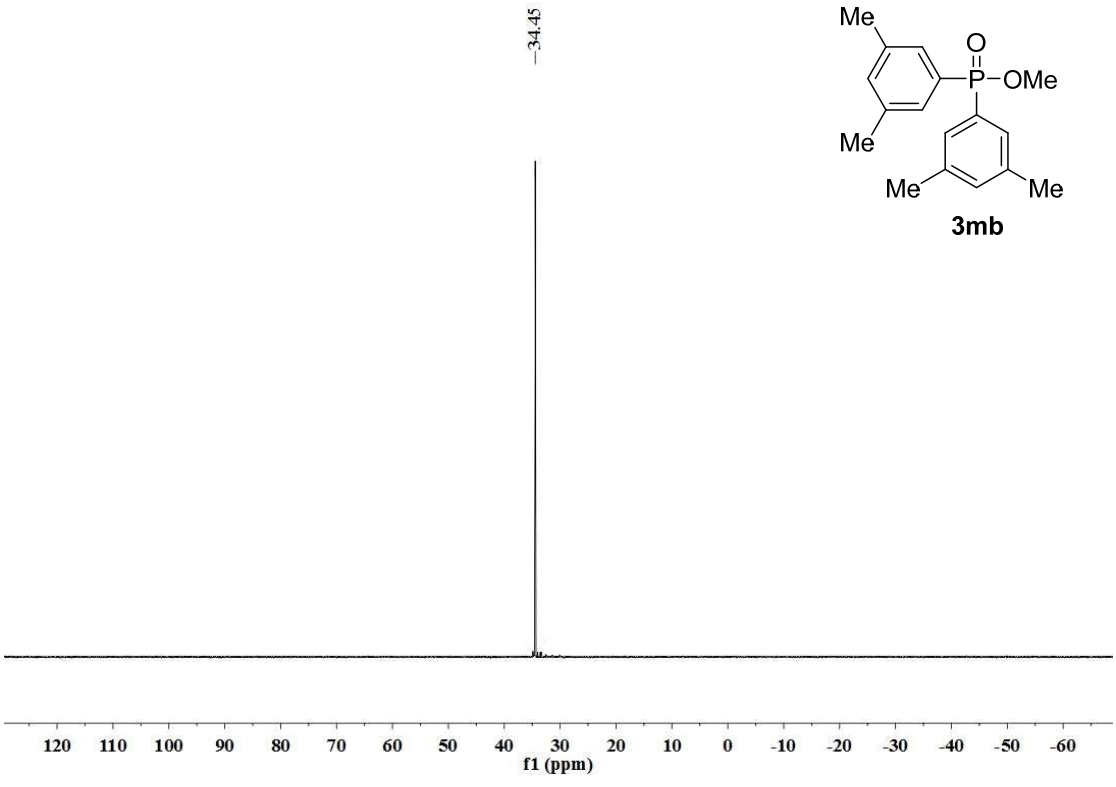

33.46
MeO
O
P
OMe
MeO
MeO
OMe
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

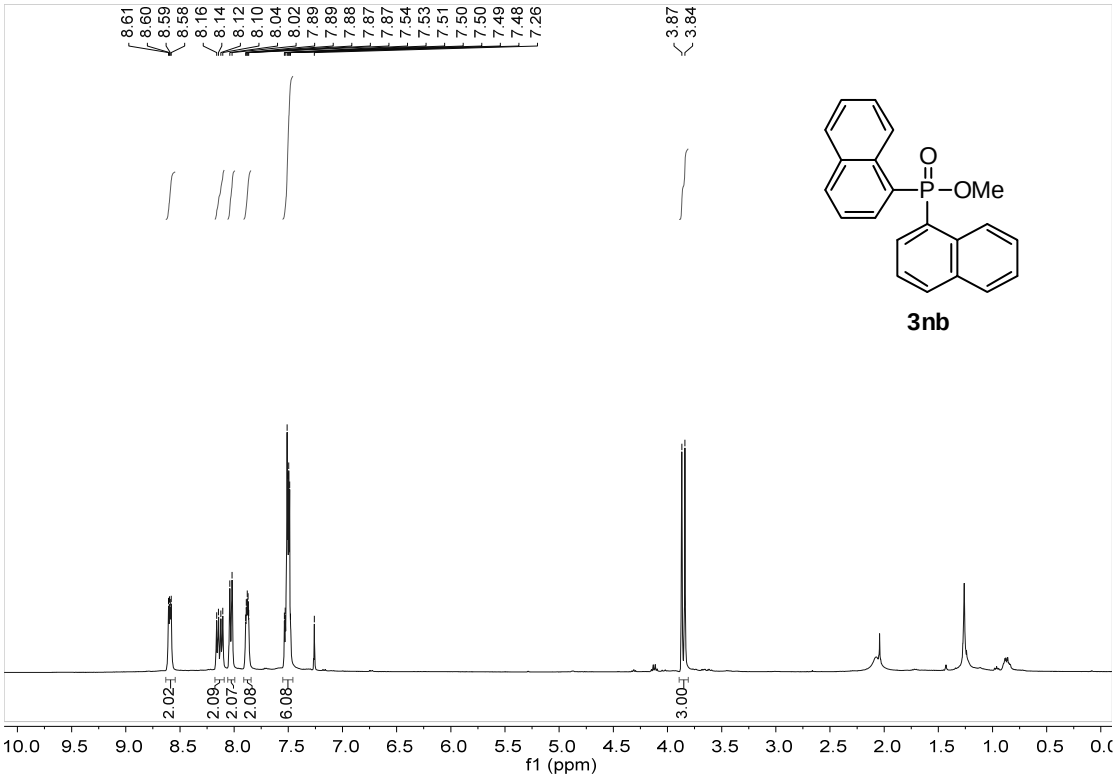
3lb


7.43
7.40
7.14
3.76
3.73
2.33
Me
O
P
OMe
Me
Me
Me
3.97
2.00
3.02
12.02
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)

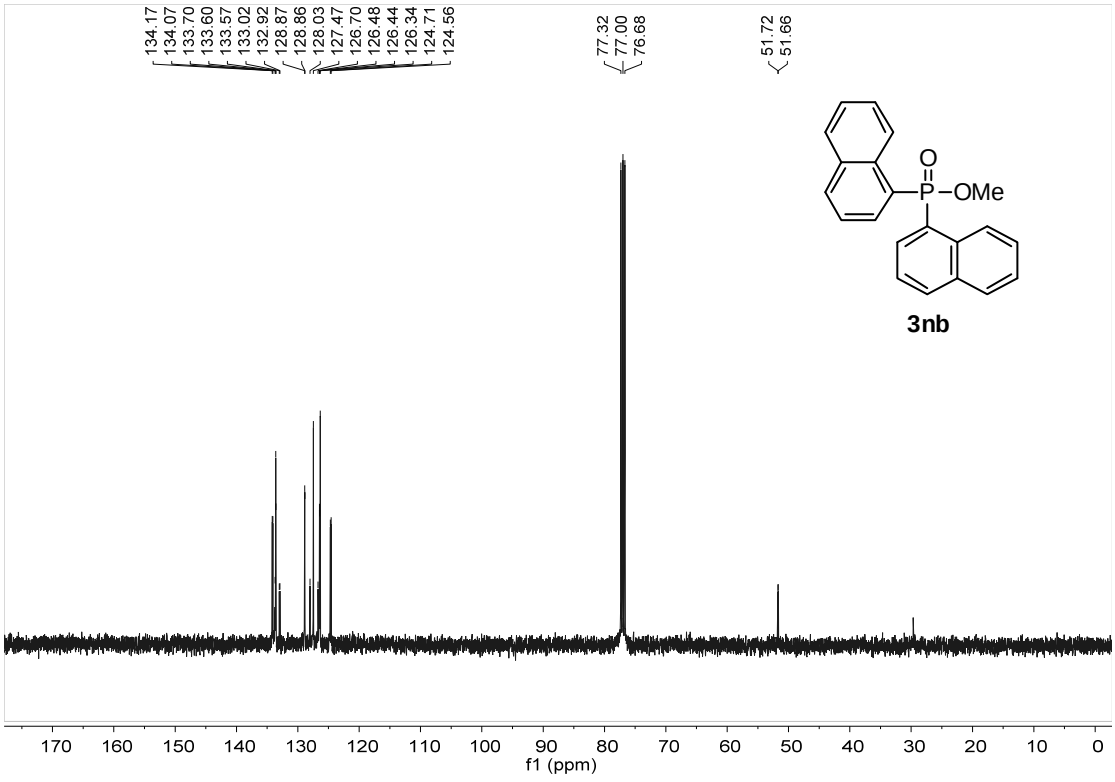
3mb


138.30
138.16
133.88
133.85
131.60
130.25
129.25
129.15
51.43
51.37
21.23
Me
O
P–OMe
Me
Me
Me
3mb
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
f1 (ppm)

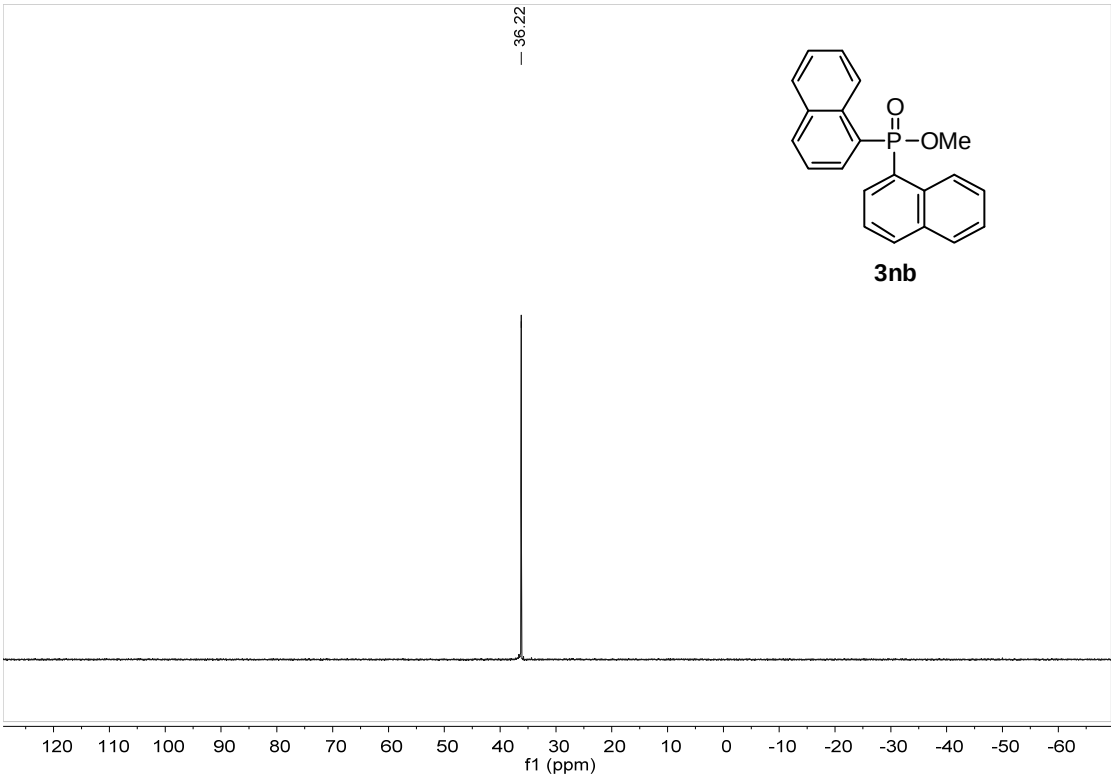

34.45
Me
O
P–OMe
Me
Me
Me
3mb
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

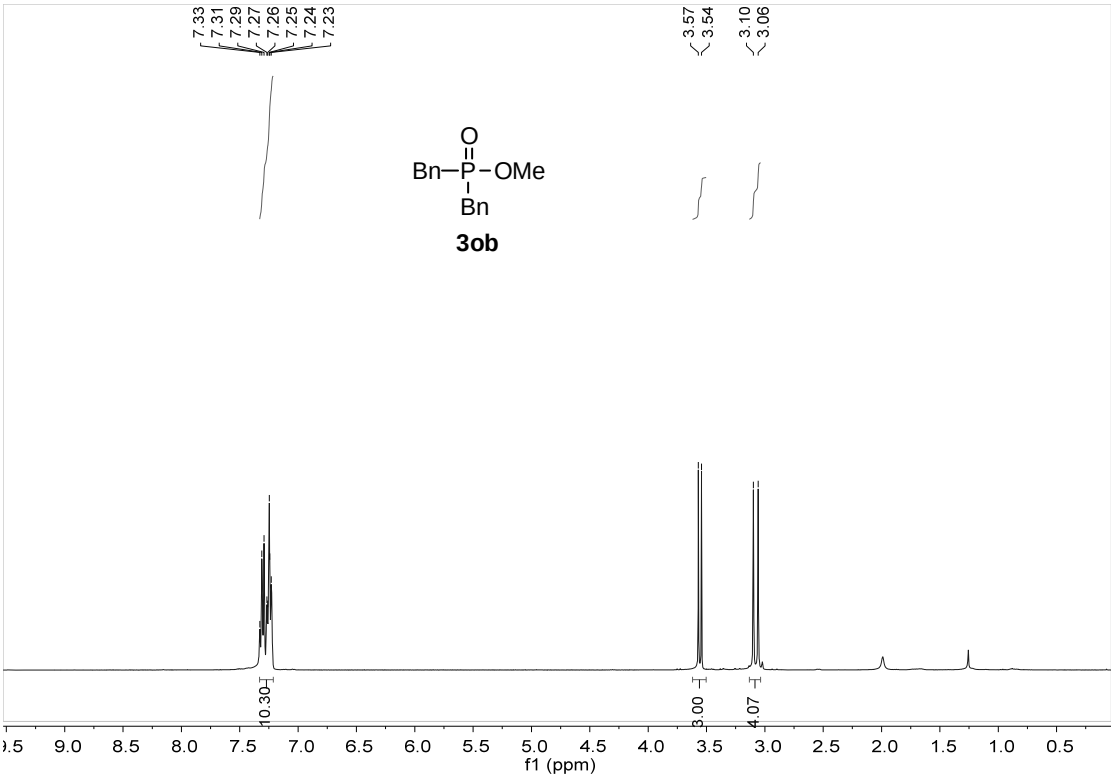

8.61
8.60
8.59
8.58
8.16
8.14
8.12
8.10
8.04
8.02
7.89
7.89
7.88
7.87
7.87
7.54
7.53
7.51
7.50
7.50
7.49
7.48
7.26
3.87
3.84
O
P–OMe
2.02
2.09
2.07
2.08
6.08
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

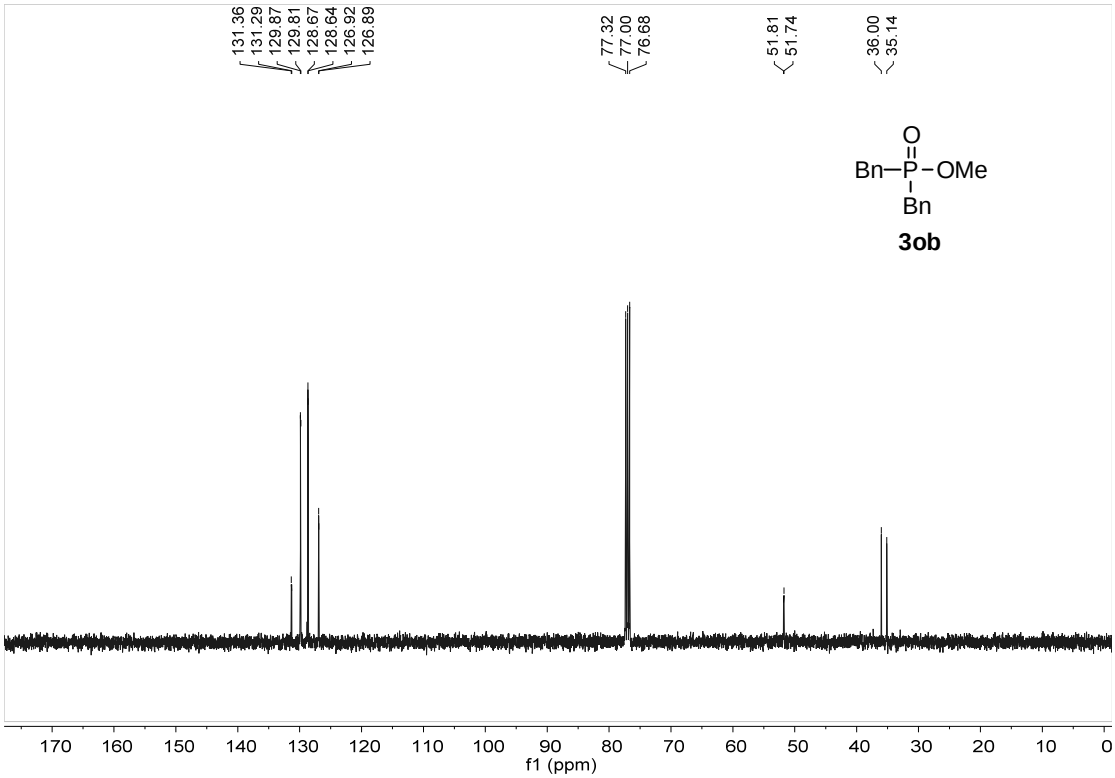
3nb

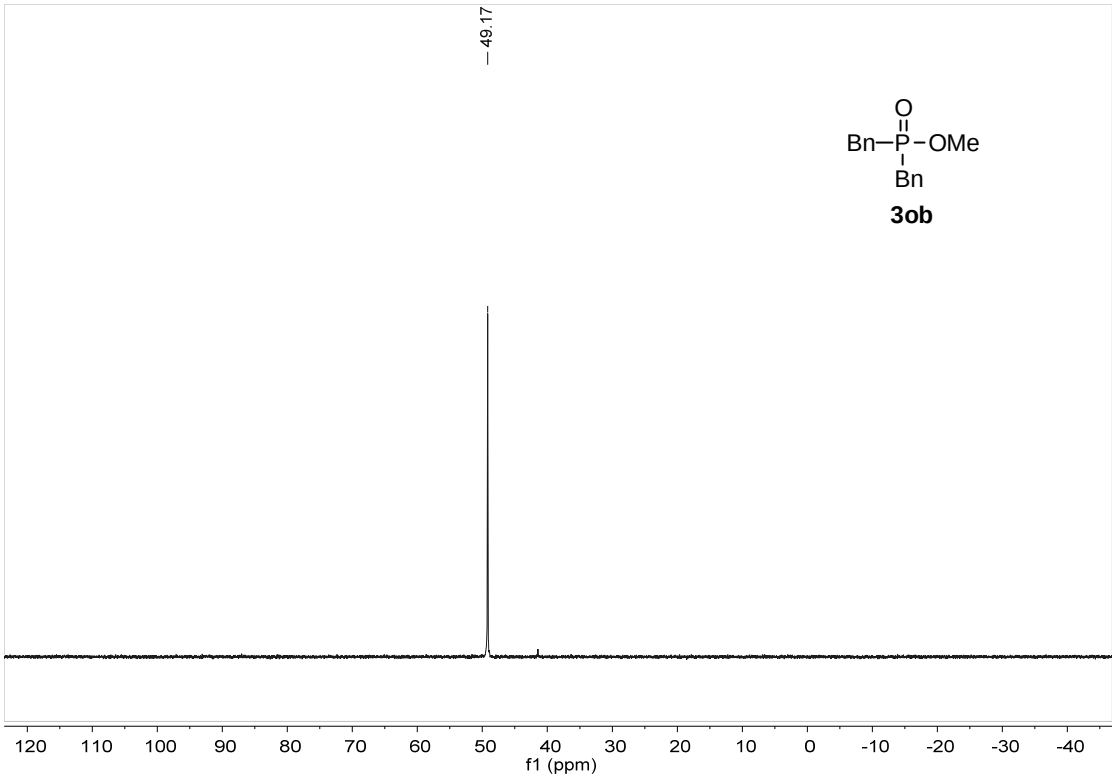

134.17
134.07
133.70
133.60
133.57
133.02
132.92
128.87
128.86
128.03
127.47
126.70
126.48
126.44
126.34
124.71
124.56
77.32
77.00
76.68
51.72
51.66
O
P–OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

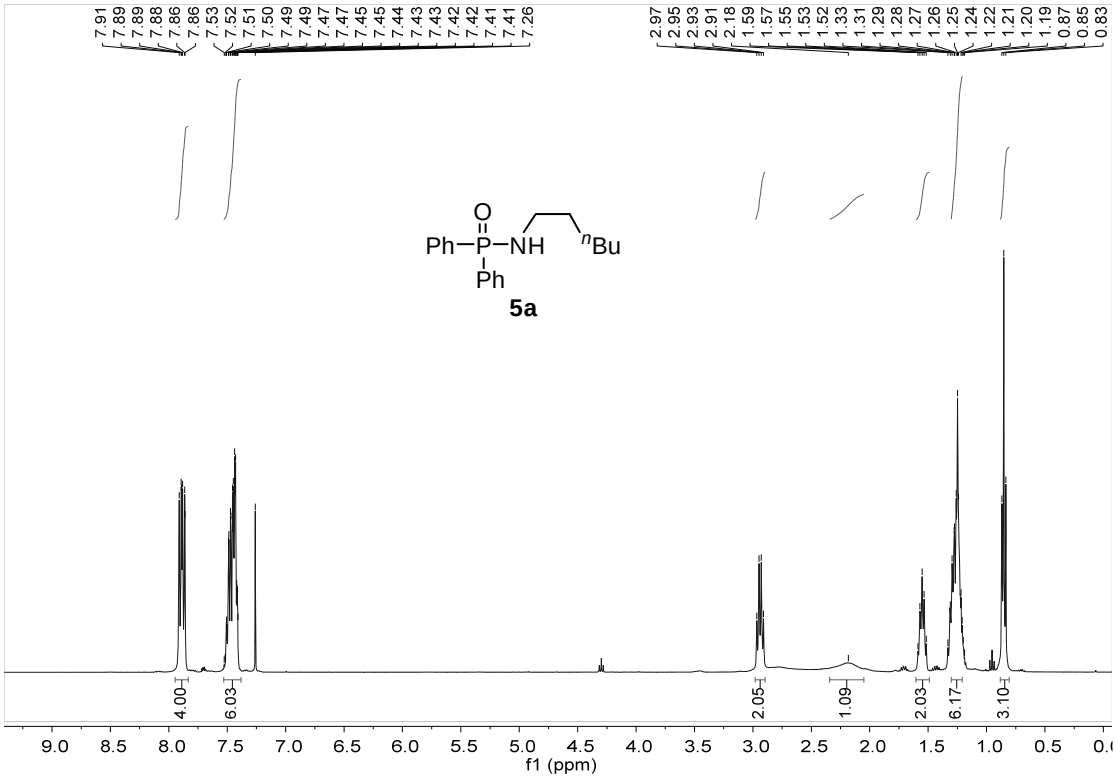
3nb

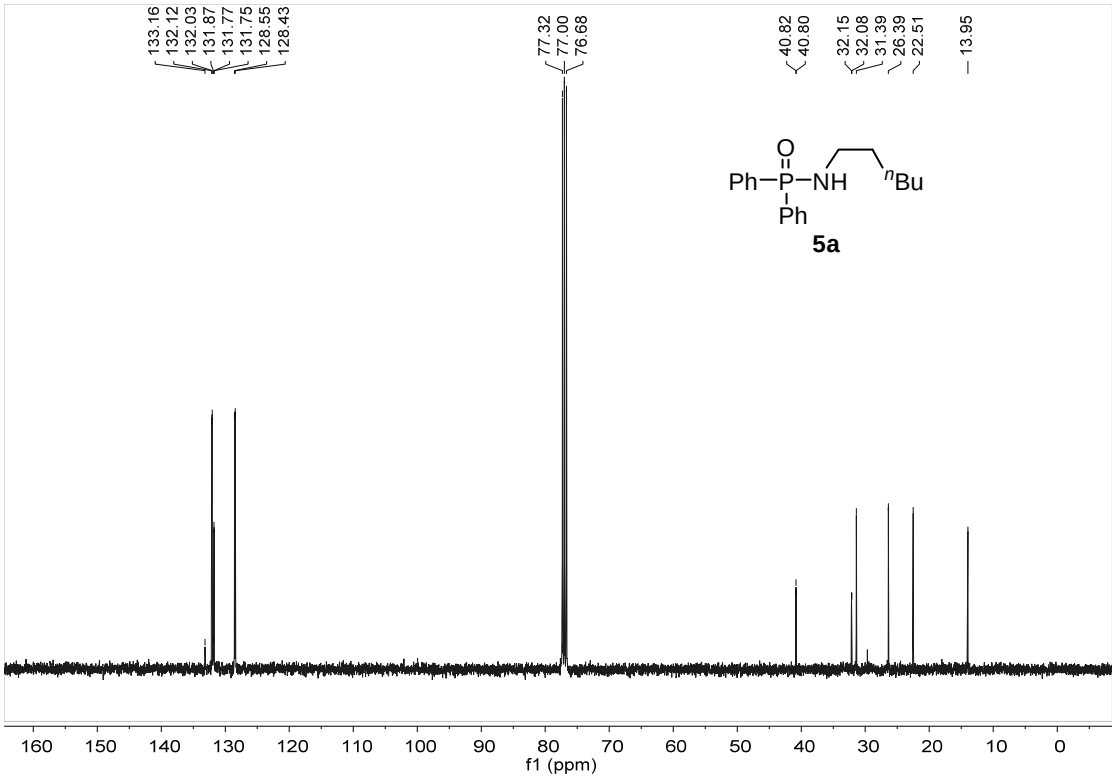

36.22
O
P–OMe
3nb
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

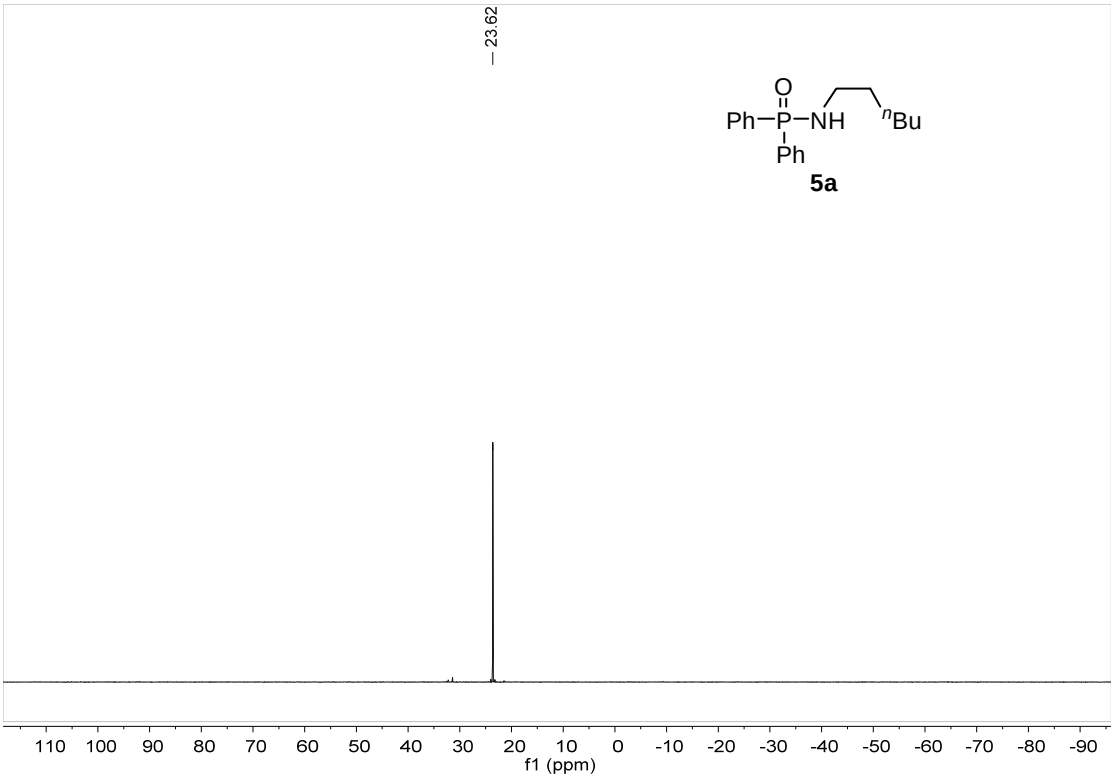

7.33
7.31
7.29
7.27
7.26
7.25
7.24
7.23
3.57
3.54
3.10
3.06
O
Bn–P–OMe
Bn
3ob
10.30
3.00
4.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

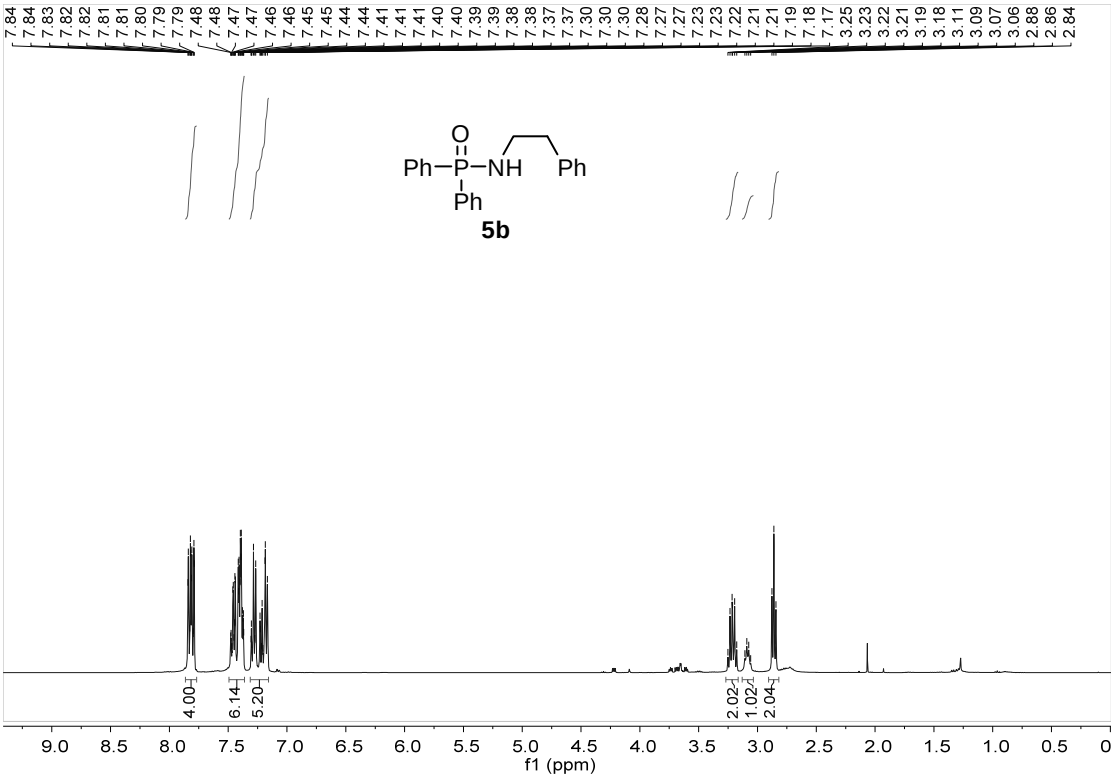

131.36
131.29
129.87
129.81
128.67
128.64
126.92
126.89
77.32
77.00
76.68
51.81
51.74
36.00
35.14
O
Bn—P—OMe
Bn
3ob
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

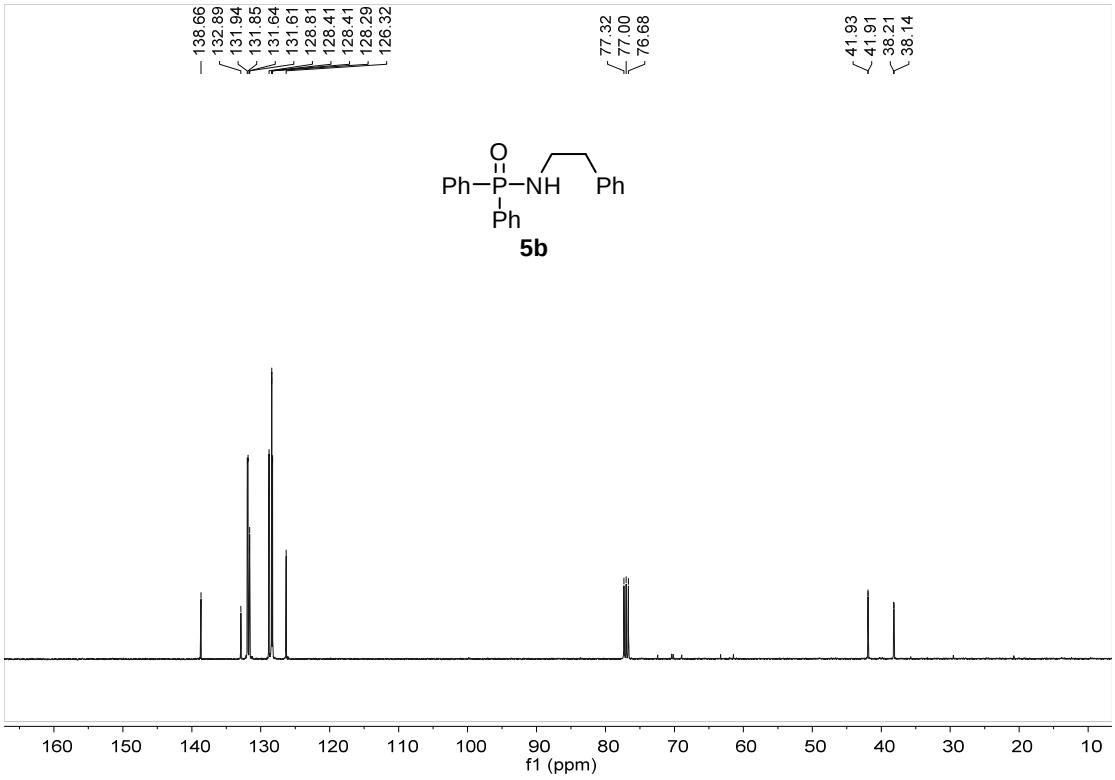

49.17
O
Bn—P—OMe
Bn
3ob
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

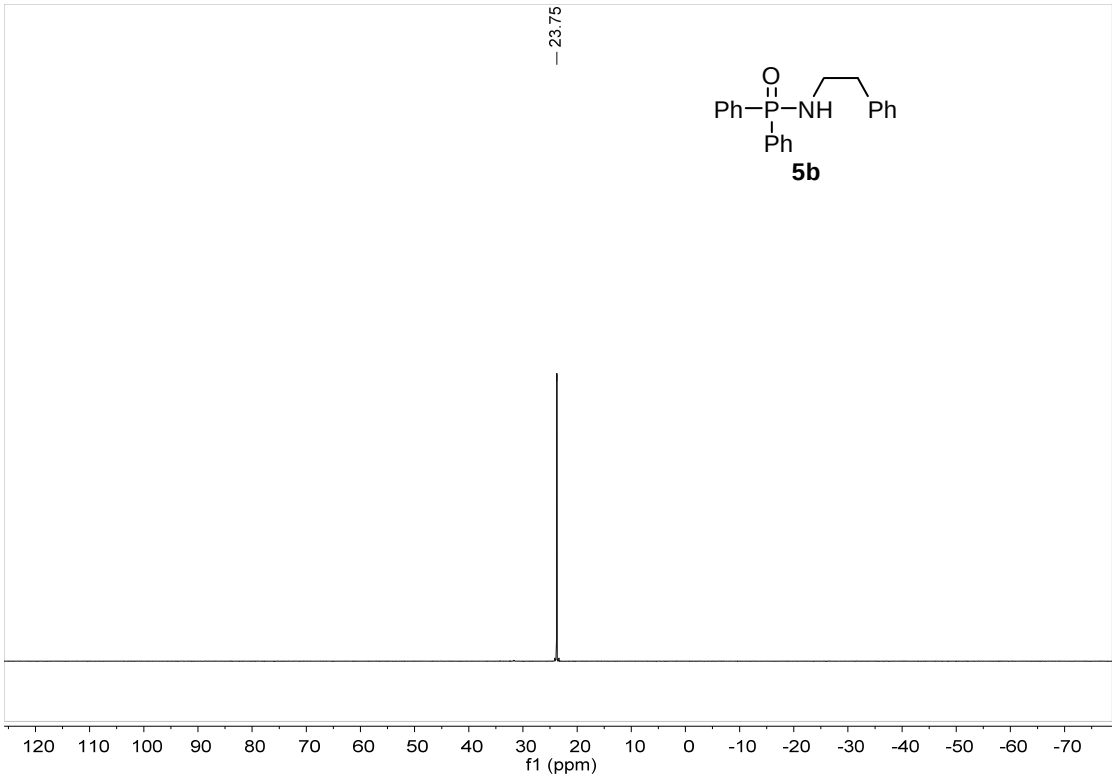

7.91 7.89 7.89 7.88 7.86 7.86 7.53 7.52 7.51 7.50 7.49 7.49 7.47 7.47 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.26
2.97 2.95 2.93 2.91 2.18 1.59 1.57 1.55 1.53 1.52 1.33 1.31 1.29 1.28 1.27 1.26 1.25 1.24 1.22 1.21 1.20 1.19 0.87 0.85 0.83
Ph–P(=O)(Ph)–NH–nBu
5a
4.00 6.03 2.05 1.09 2.03 6.17 3.10
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
f1 (ppm)

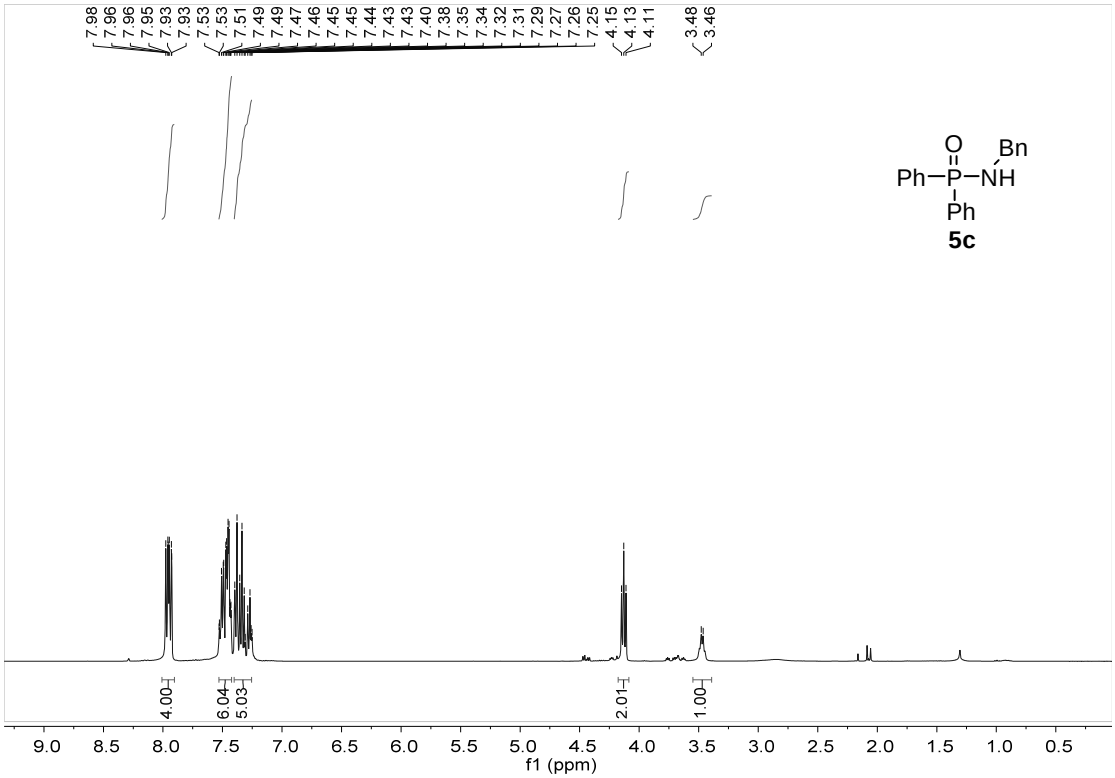

133.16 132.12 132.03 131.87 131.77 131.75 128.55 128.43
77.32 77.00 76.68
40.82 40.80 32.15 32.08 31.39 26.39 22.51 13.95
Ph–P(=O)(Ph)–NH–nBu
5a
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

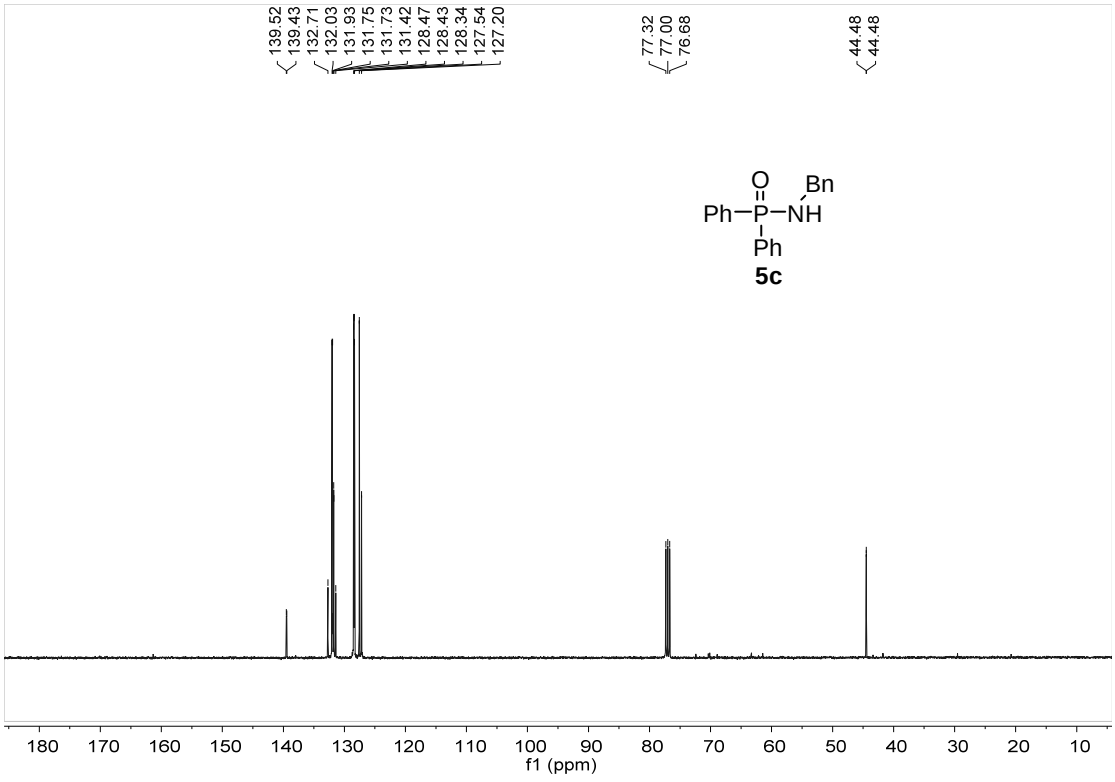

23.62
Ph
P
O
NH
nBu
Ph
5a
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

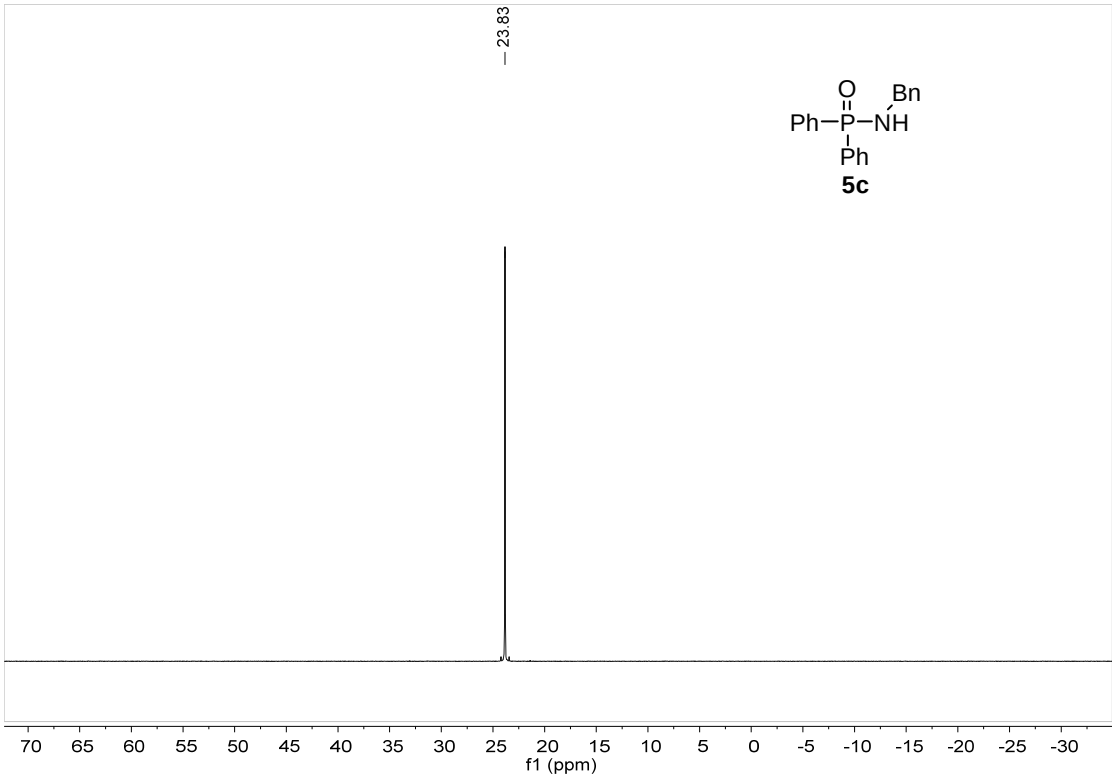

7.84 7.84 7.83 7.82 7.82 7.81 7.81 7.80 7.79 7.79 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.30 7.30 7.28 7.27 7.27 7.23 7.23 7.22 7.21 7.21 7.19 7.18 7.17 3.25 3.23 3.22 3.21 3.19 3.18 3.11 3.09 3.07 3.06 2.88 2.86 2.84
Ph
P
O
NH
Ph
Ph
5b
4.00
6.14
5.20
2.02
1.02
2.04
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
f1 (ppm)

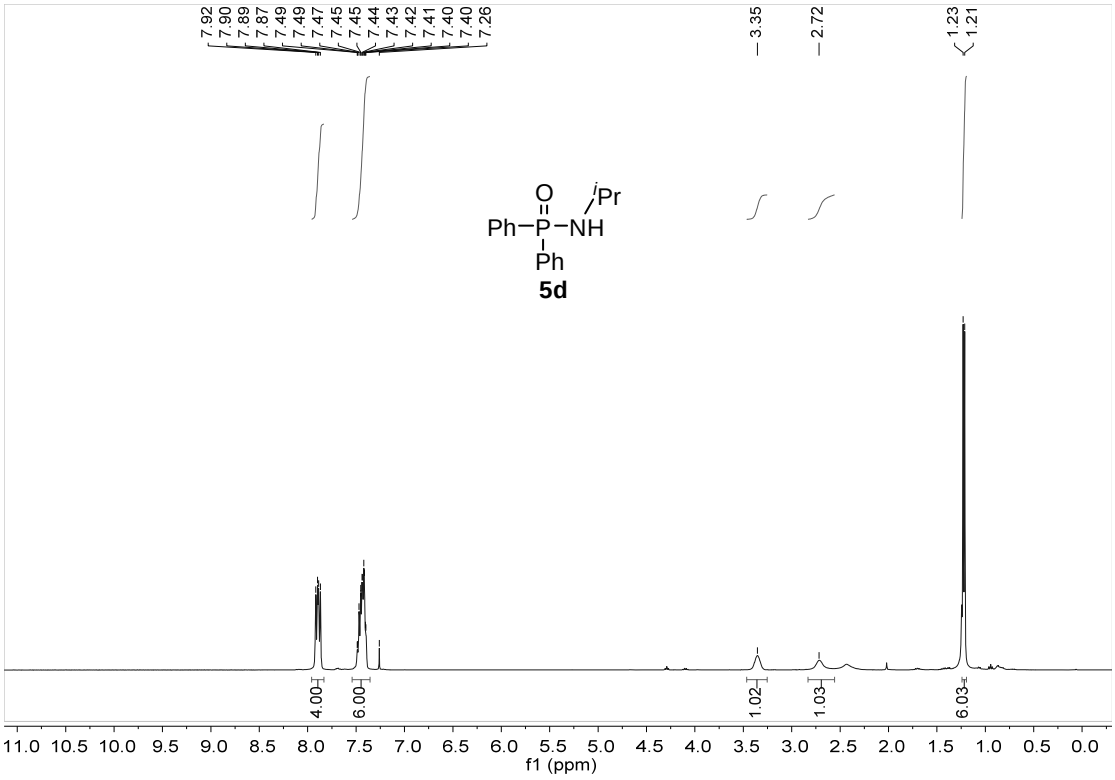

138.66
132.89
131.94
131.85
131.64
131.61
128.81
128.41
128.41
128.29
126.32
77.32
77.00
76.68
41.93
41.91
38.21
38.14
O
Ph—P—NH
Ph
Ph
5b
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

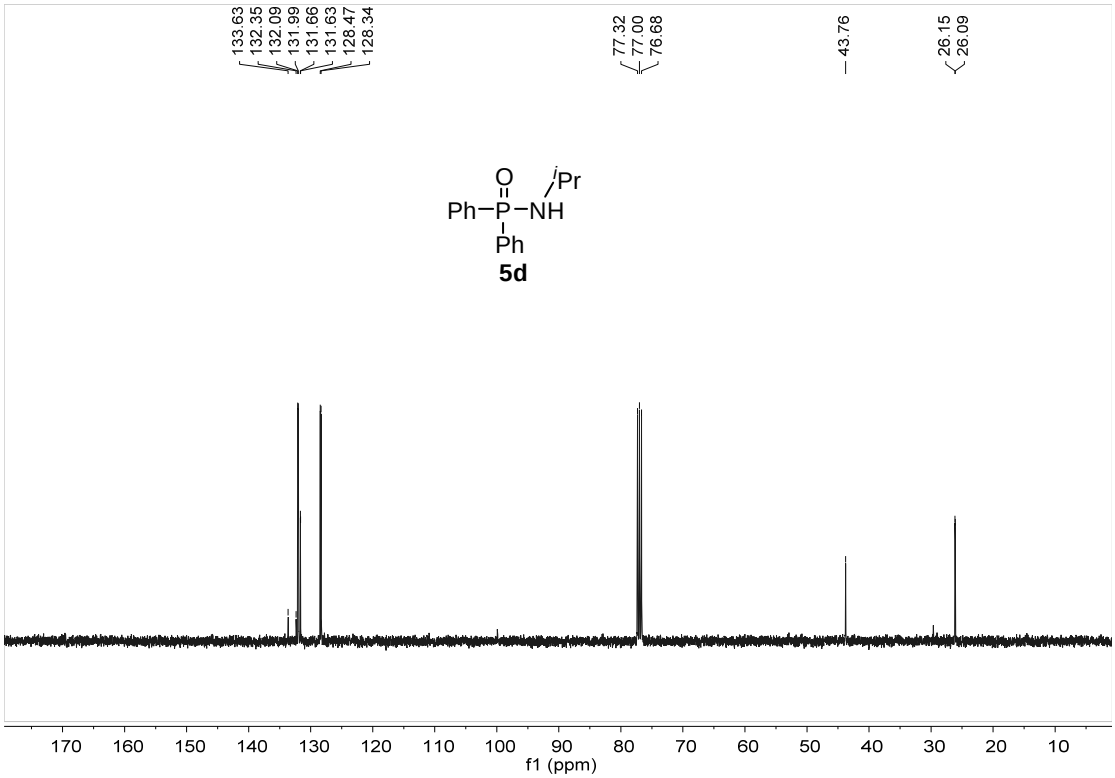

23.75
O
Ph—P—NH
Ph
Ph
Ph
5b
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

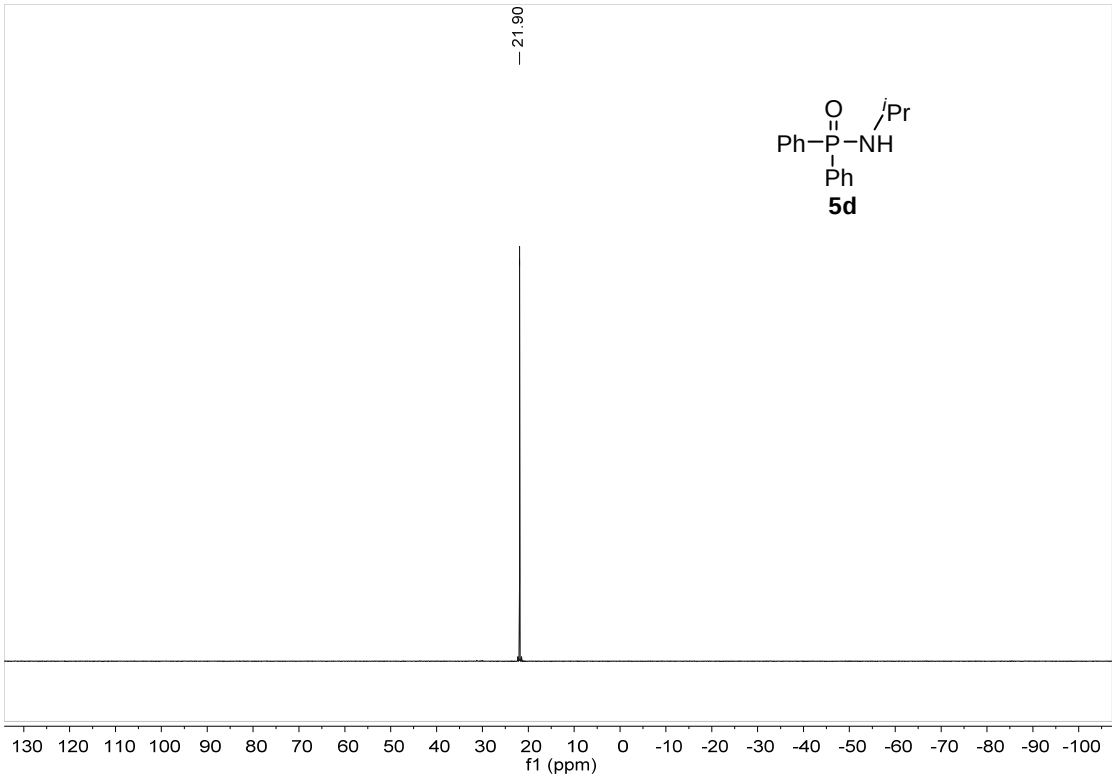

7.98
7.96
7.96
7.95
7.93
7.93
7.53
7.53
7.51
7.49
7.49
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.40
7.38
7.35
7.34
7.32
7.31
7.29
7.27
7.26
7.25
4.15
4.13
4.11
3.48
3.46
O
Bn
Ph—P—NH
Ph
5c
4.00
6.04
5.03
2.01
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

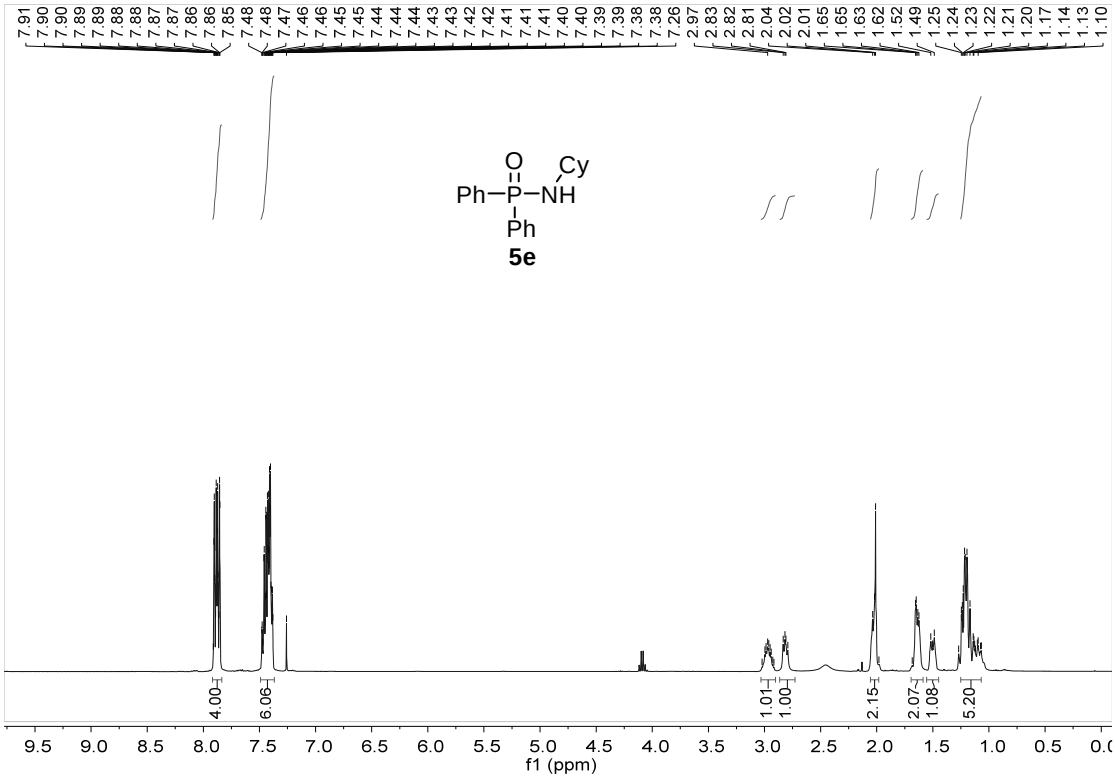

139.52
139.43
132.71
132.03
131.93
131.75
131.73
131.42
128.47
128.43
128.34
127.54
127.20
77.32
77.00
76.68
44.48
44.48
O
Bn
Ph—P—NH
Ph
5c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

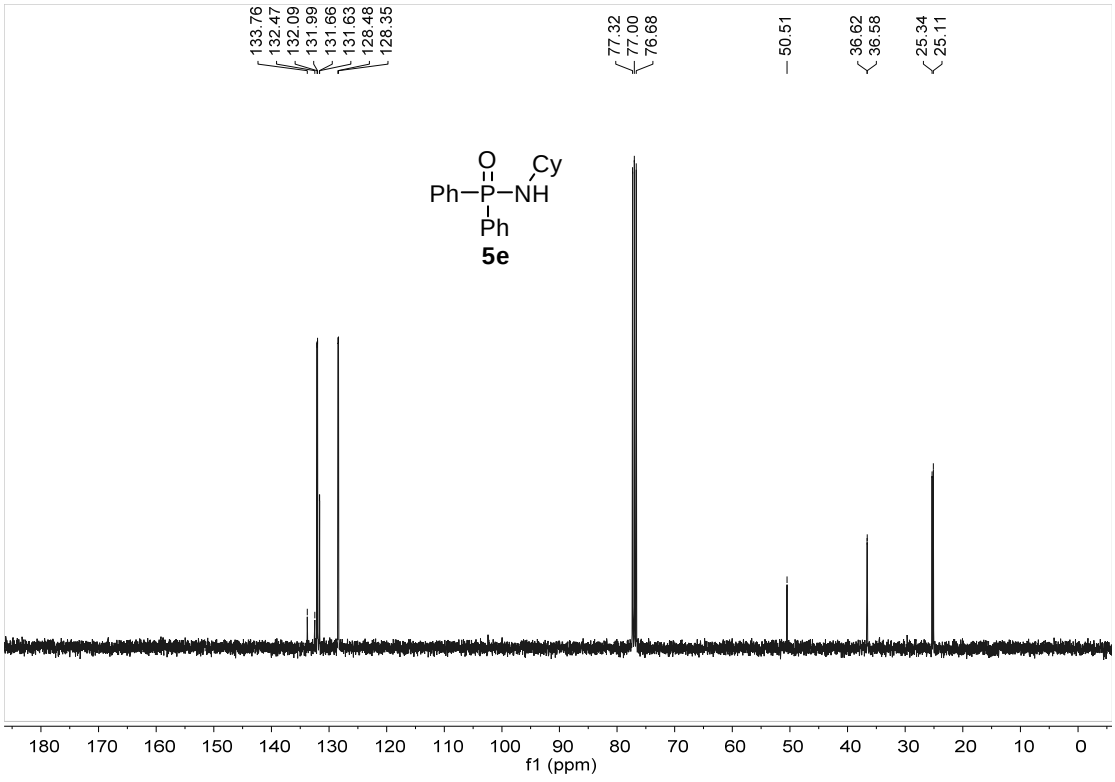

23.83
Ph–P(=O)(Ph)–NH–Bn
5c
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
f1 (ppm)

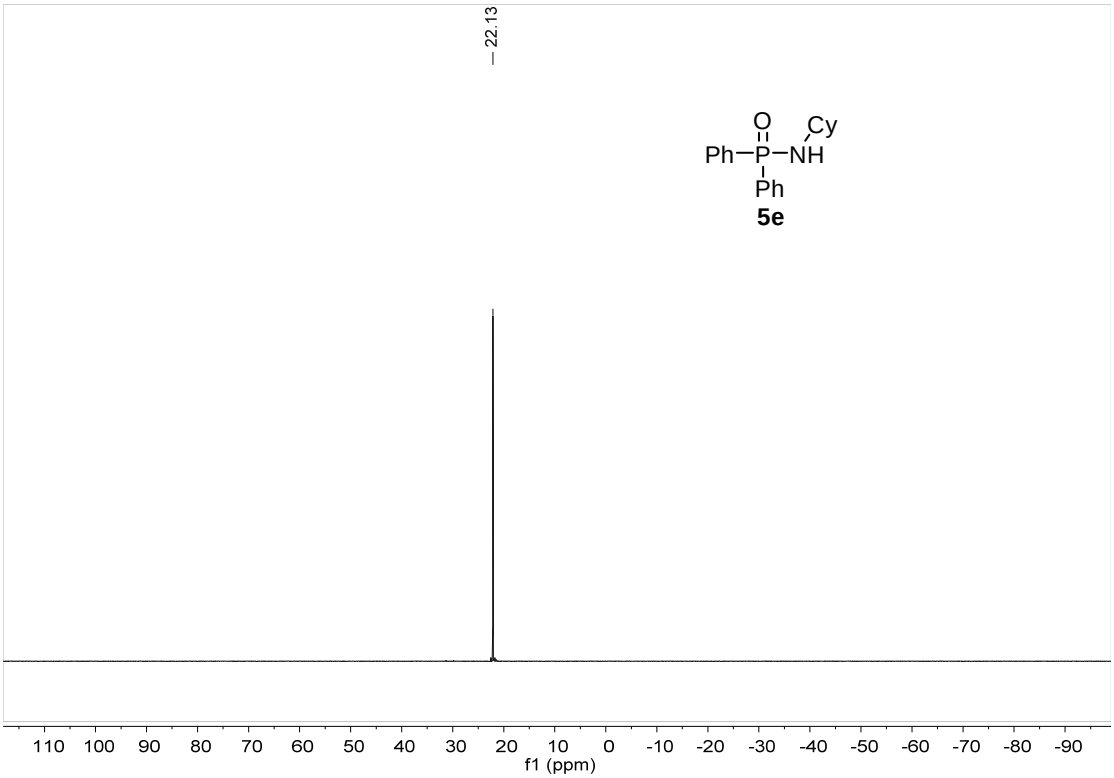

7.92 7.90 7.89 7.87 7.49 7.49 7.47 7.45 7.45 7.44 7.43 7.42 7.41 7.40 7.40 7.26
3.35
2.72
1.23 1.21
Ph–P(=O)(Ph)–NH–iPr
5d
4.00
6.00
1.02
1.03
6.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

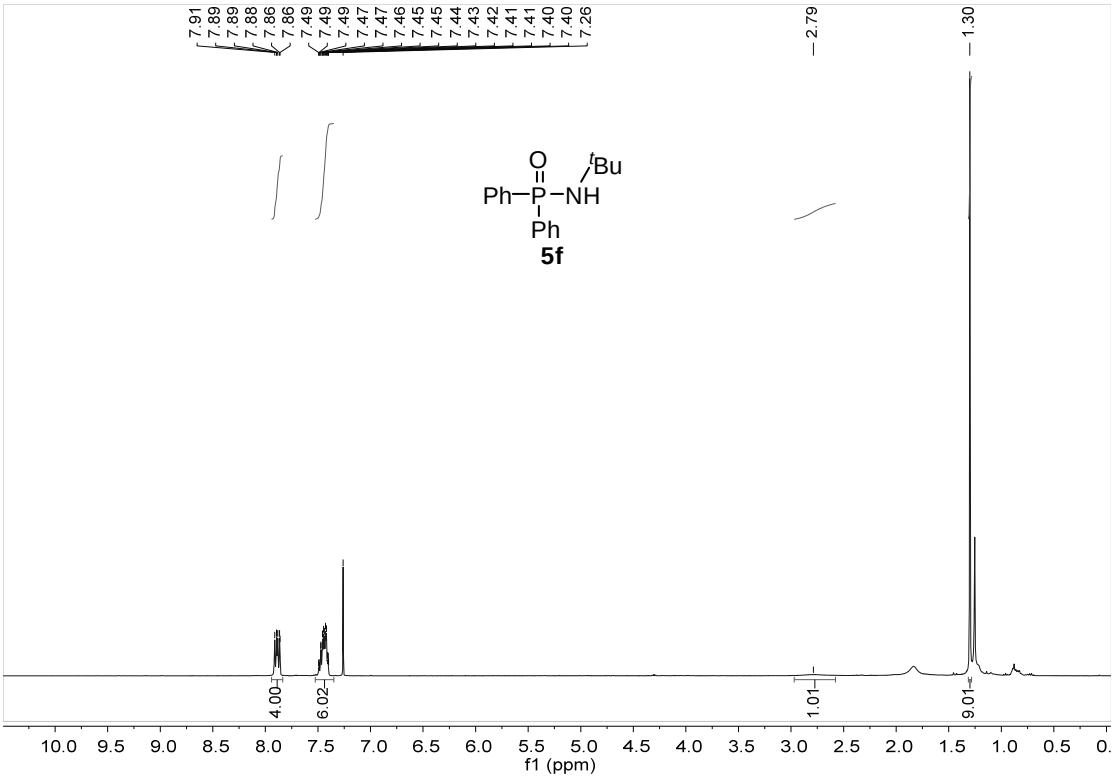

133.63
132.35
132.09
131.99
131.66
131.63
128.47
128.34
77.32
77.00
76.68
43.76
26.15
26.09
O
iPr
Ph–P–NH
Ph
5d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

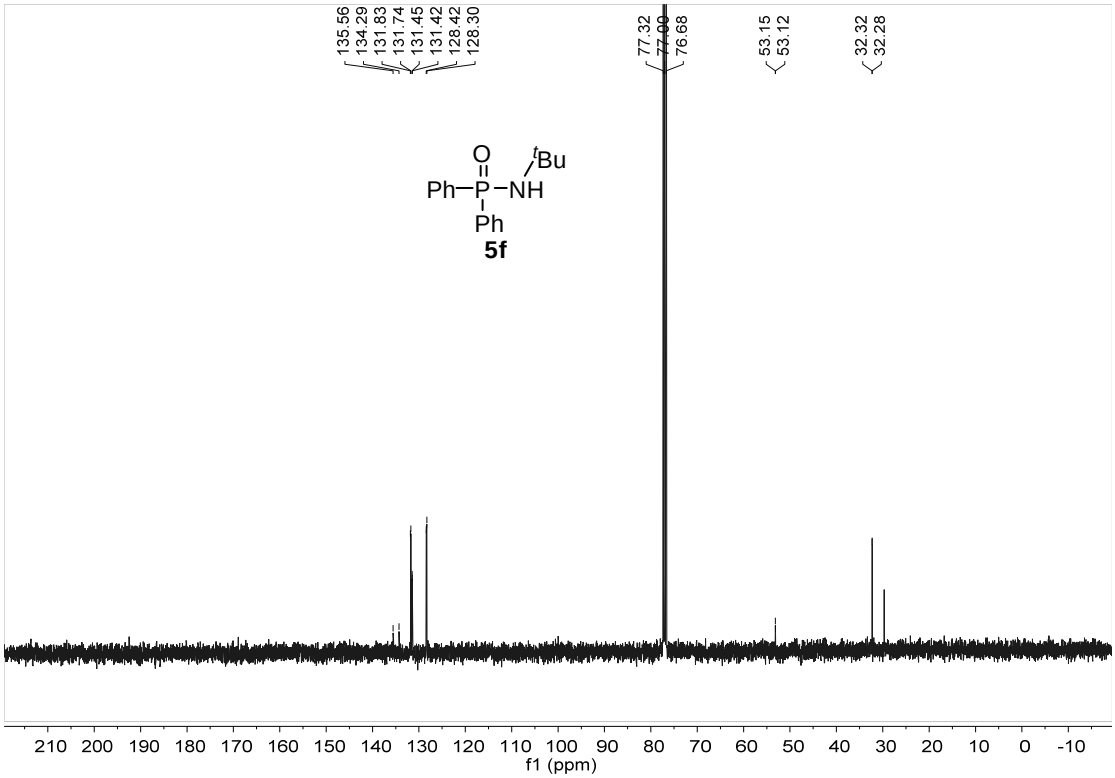

21.90
O
iPr
Ph–P–NH
Ph
5d
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

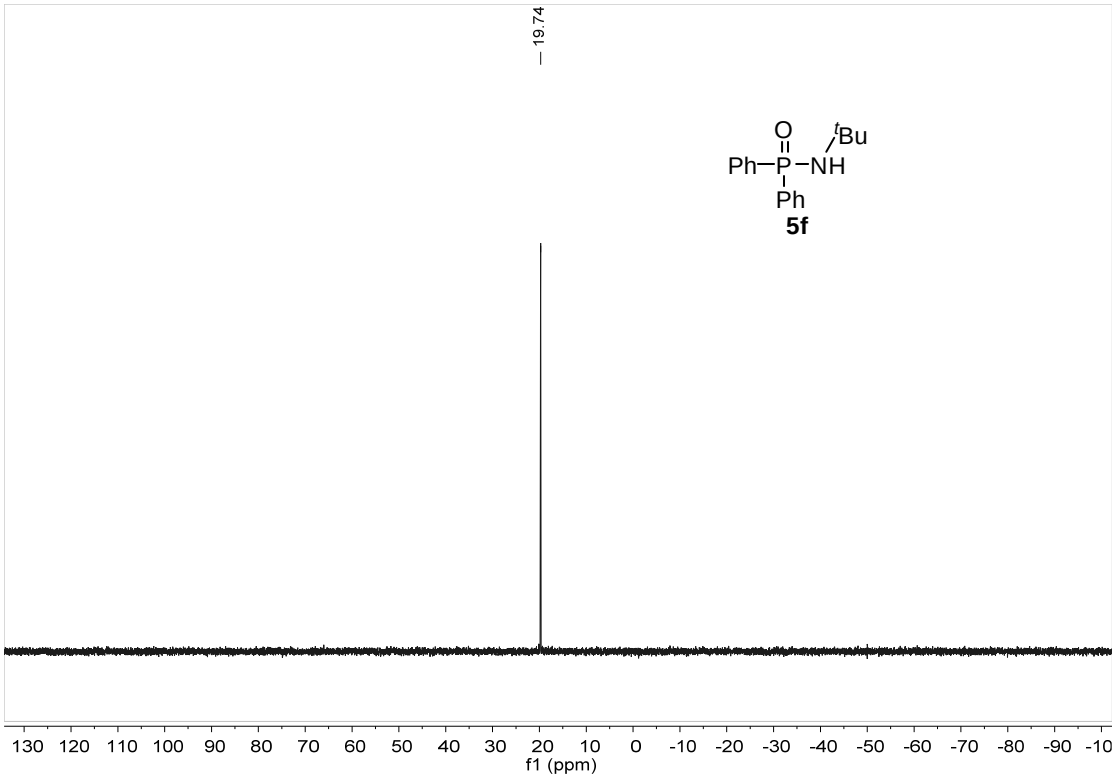

7.91 7.90 7.90 7.89 7.89 7.88 7.88 7.87 7.87 7.86 7.86 7.85 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.26 2.97 2.83 2.82 2.81 2.04 2.02 2.01 1.65 1.65 1.63 1.62 1.52 1.49 1.25 1.24 1.23 1.22 1.21 1.20 1.17 1.14 1.13 1.10
O
Cy
Ph—P—NH
Ph
5e
4.00 6.06 1.01 1.00 2.15 2.07 1.08 5.20
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
f1 (ppm)

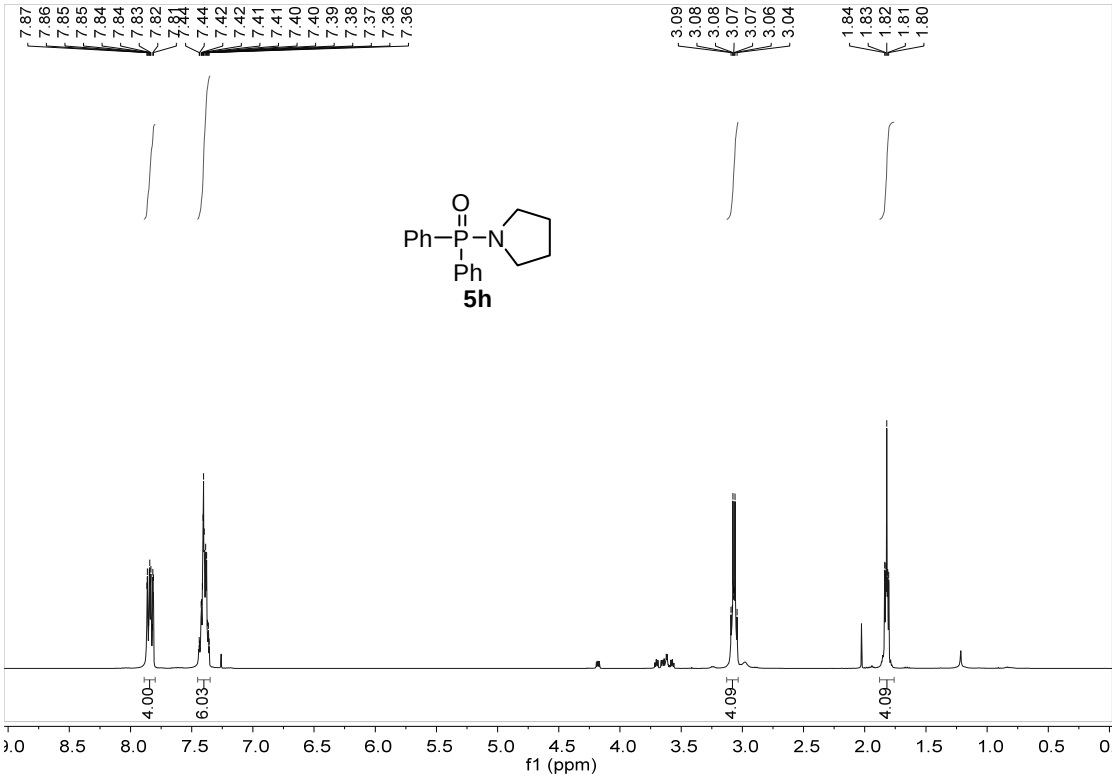

133.76 132.47 132.09 131.99 131.66 131.63 128.48 128.35
77.32 77.00 76.68
50.51
36.62 36.58
25.34 25.11
O
Cy
Ph—P—NH
Ph
5e
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

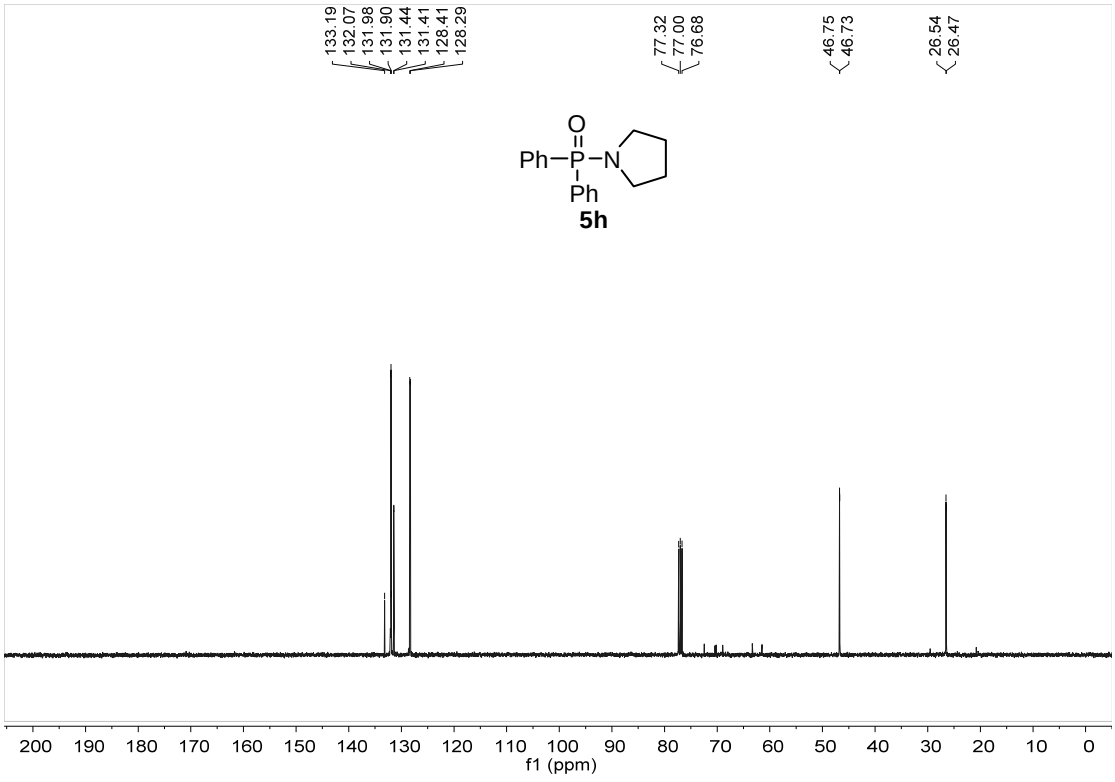

22.13
O
Cy
Ph—P—NH
Ph
5e
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

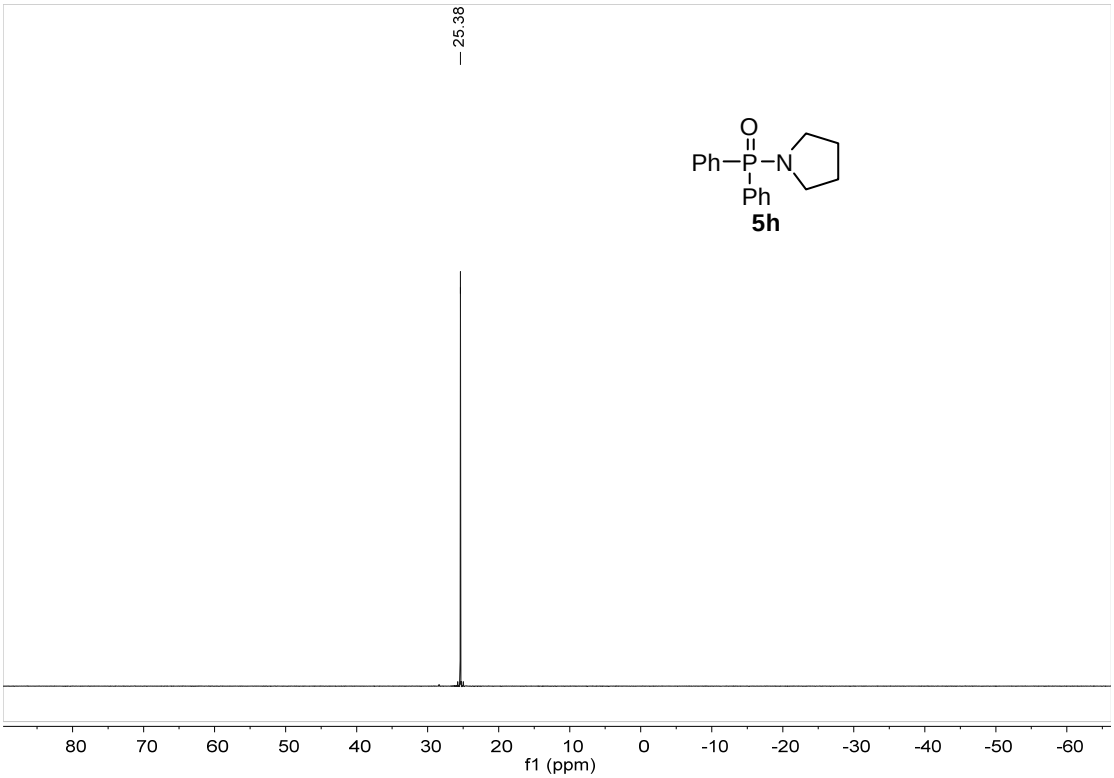

7.91
7.89
7.89
7.88
7.86
7.86
7.49
7.49
7.49
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.26
2.79
1.30
O
tBu
Ph—P—NH
Ph
5f
4.00
6.02
1.01
9.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

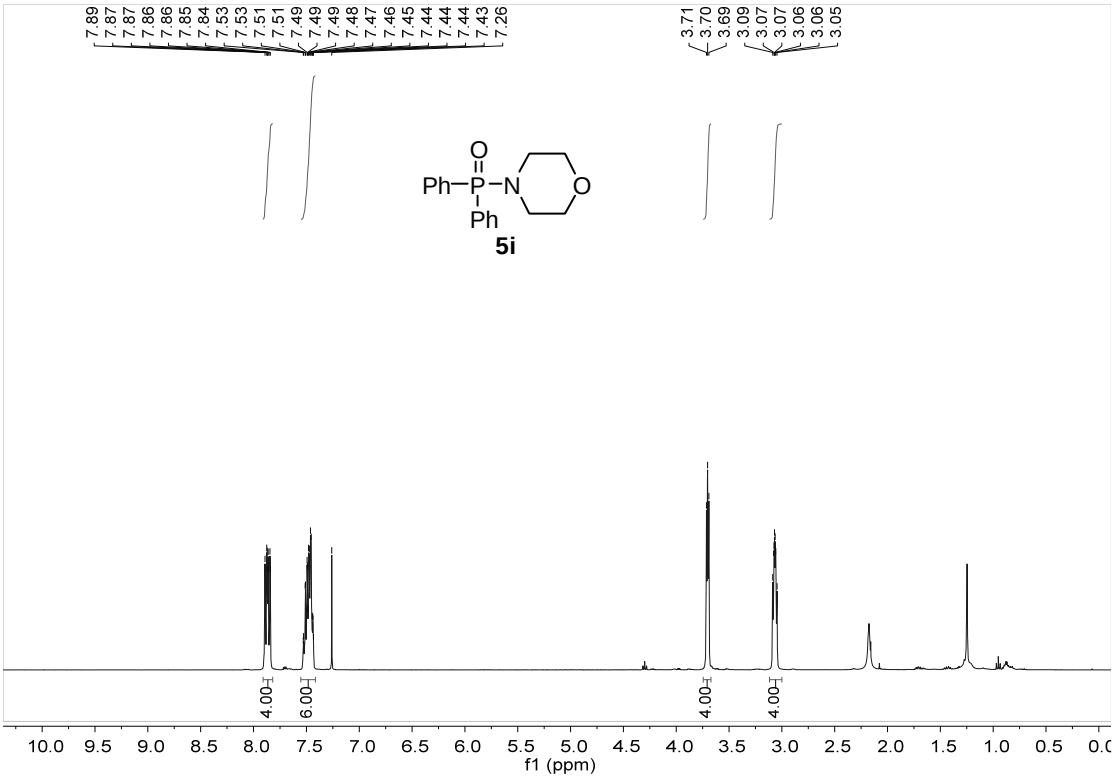

135.56
134.29
131.83
131.74
131.45
131.42
128.42
128.30
77.32
77.00
76.68
53.15
53.12
32.32
32.28
O
tBu
Ph—P—NH
Ph
5f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

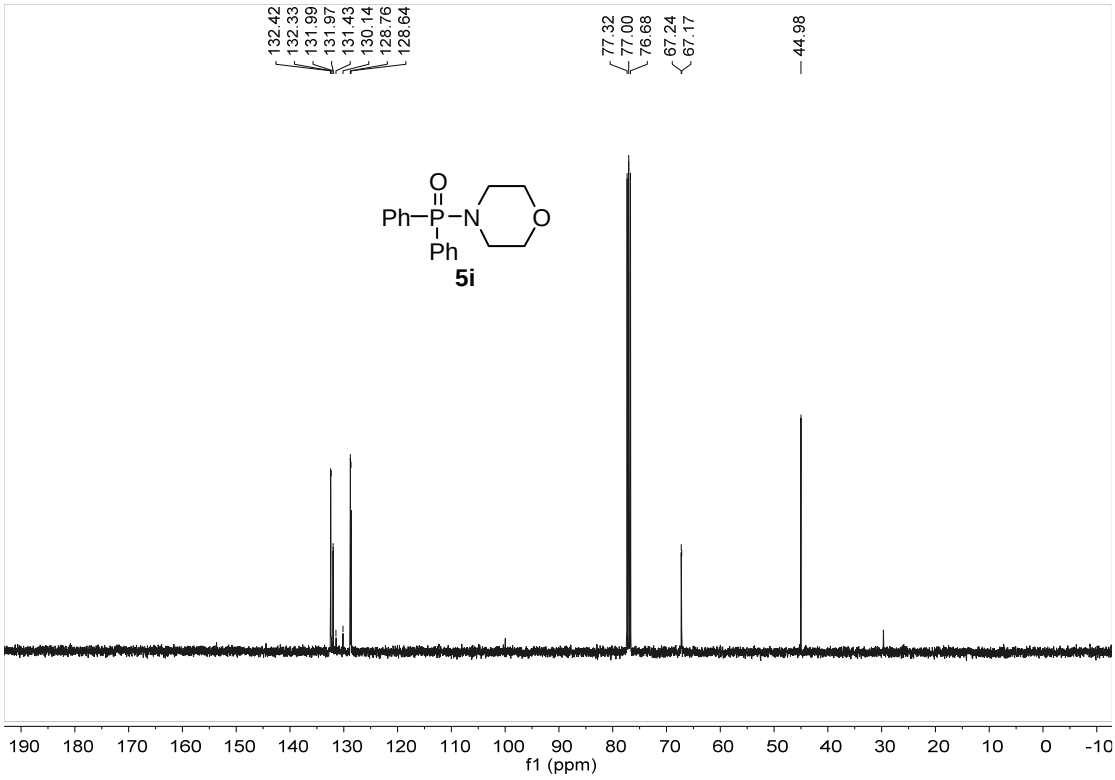

19.74
O
tBu
Ph—P—NH
Ph
5f
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)

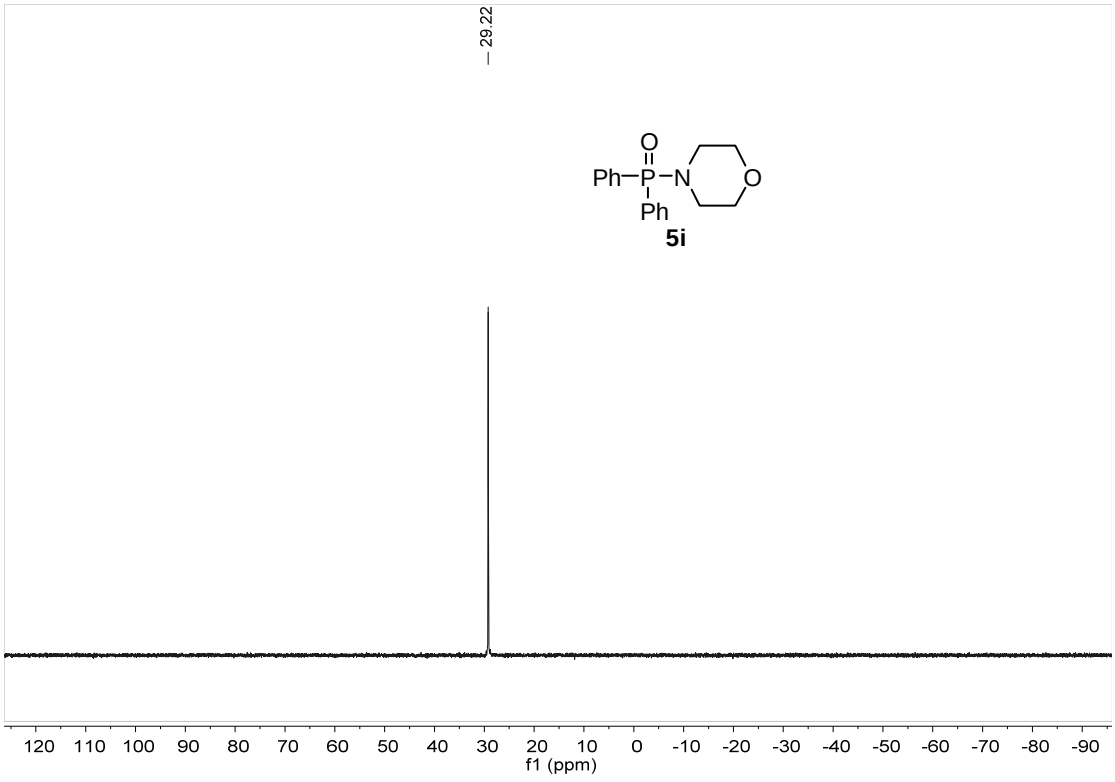

7.87
7.86
7.85
7.85
7.84
7.84
7.83
7.82
7.81
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.36
3.09
3.08
3.08
3.07
3.07
3.06
3.04
1.84
1.83
1.82
1.81
1.80
O
Ph–P–N
Ph
5h
4.00
6.03
4.09
4.09
f1 (ppm)

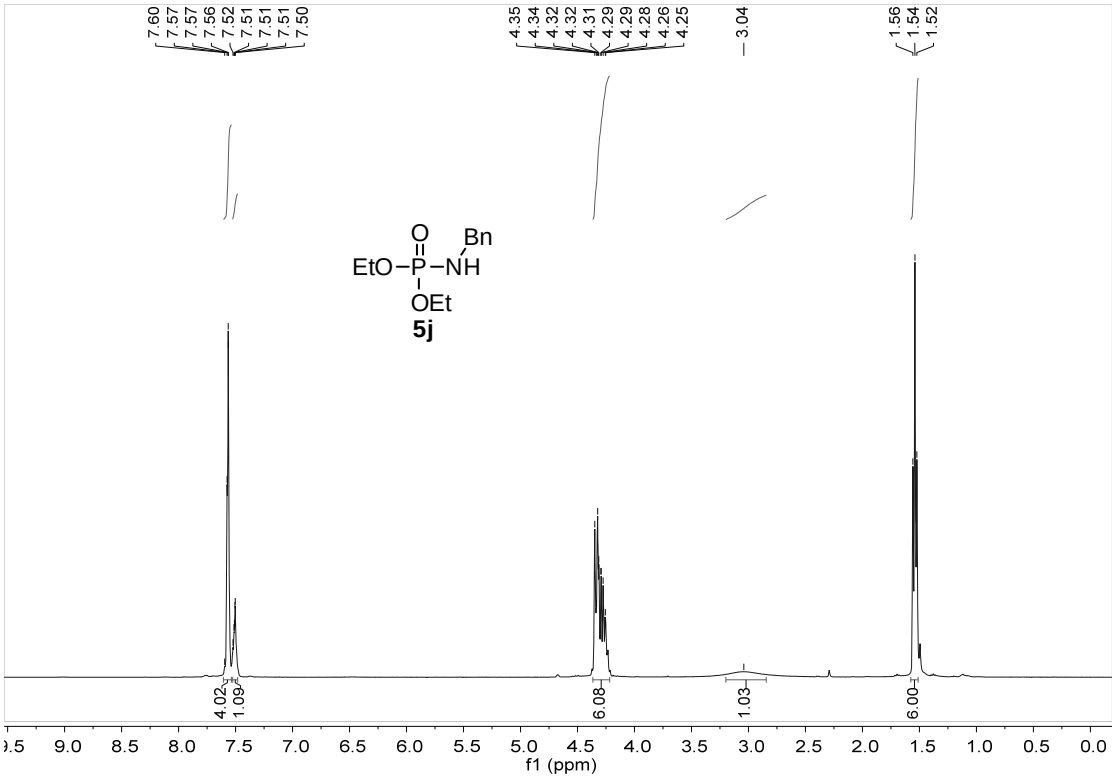

133.19
132.07
131.98
131.90
131.44
131.41
128.41
128.29
77.32
77.00
76.68
46.75
46.73
26.54
26.47
O
Ph–P–N
Ph
5h
f1 (ppm)

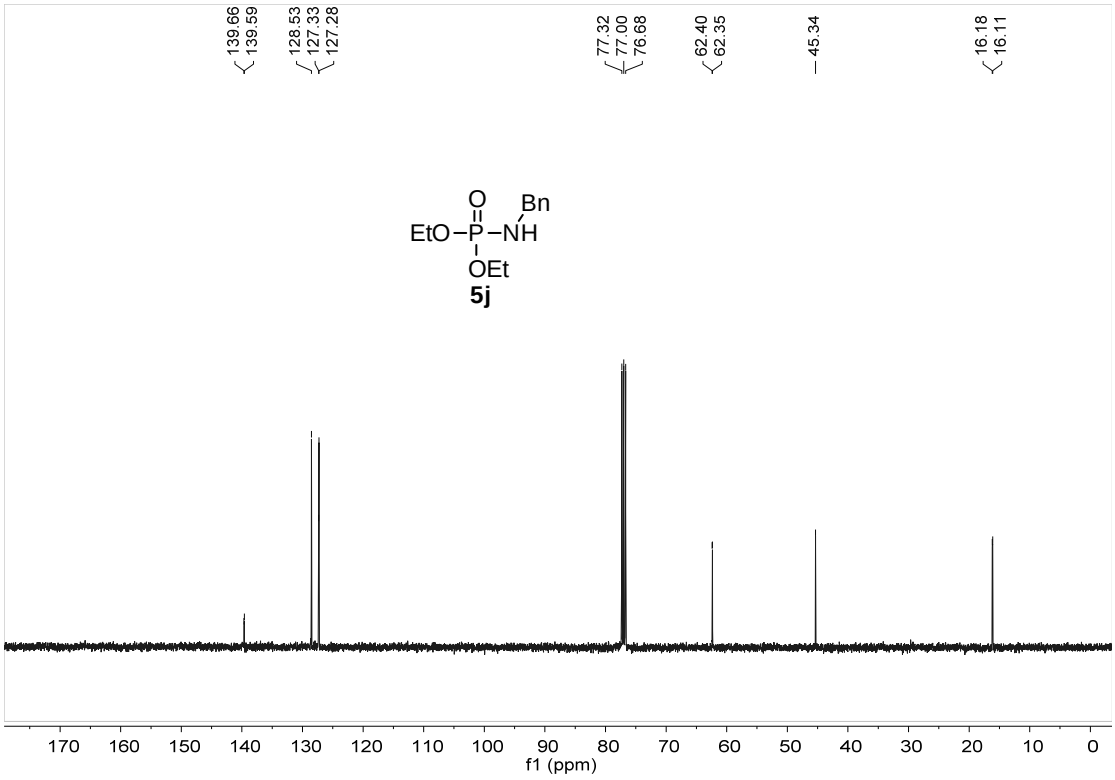

25.38
Ph
P
N
O
Ph
5h
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

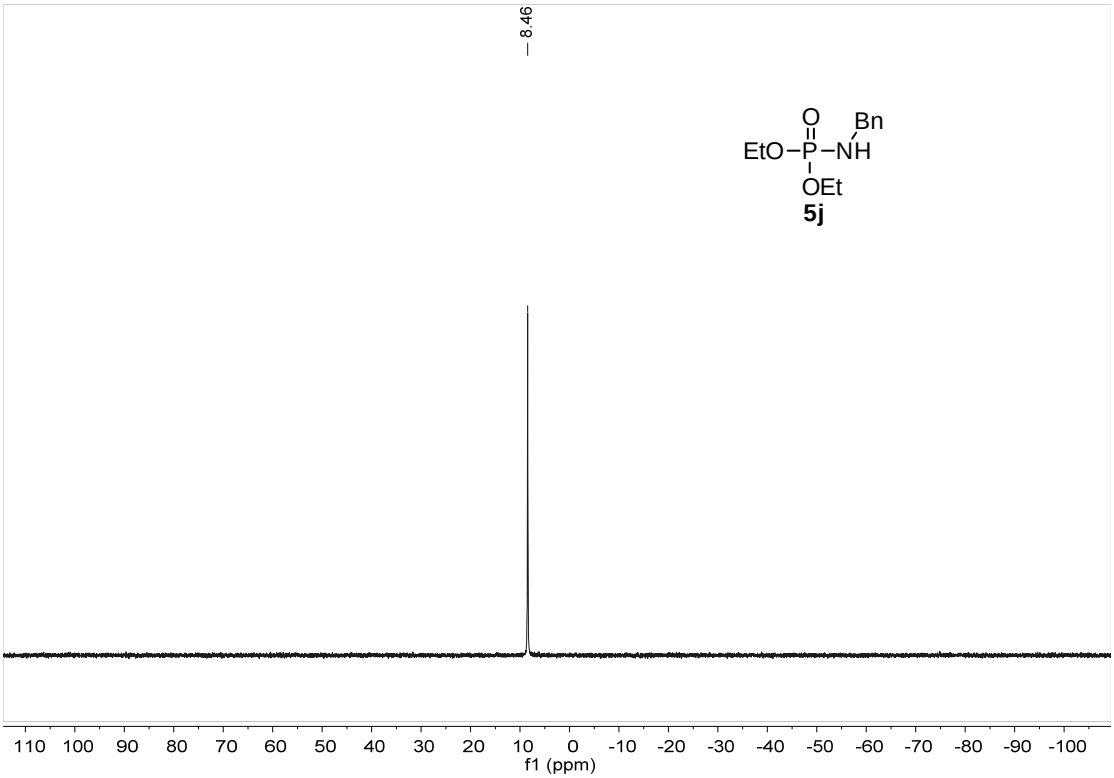

7.89 7.87 7.87 7.86 7.86 7.85 7.84 7.53 7.51 7.51 7.49 7.49 7.49 7.48 7.47 7.46 7.45 7.44 7.44 7.44 7.43 7.26
3.71 3.70 3.69 3.09 3.07 3.07 3.06 3.06 3.05
Ph
P
N
O
O
Ph
5i
4.00
6.00
4.00
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

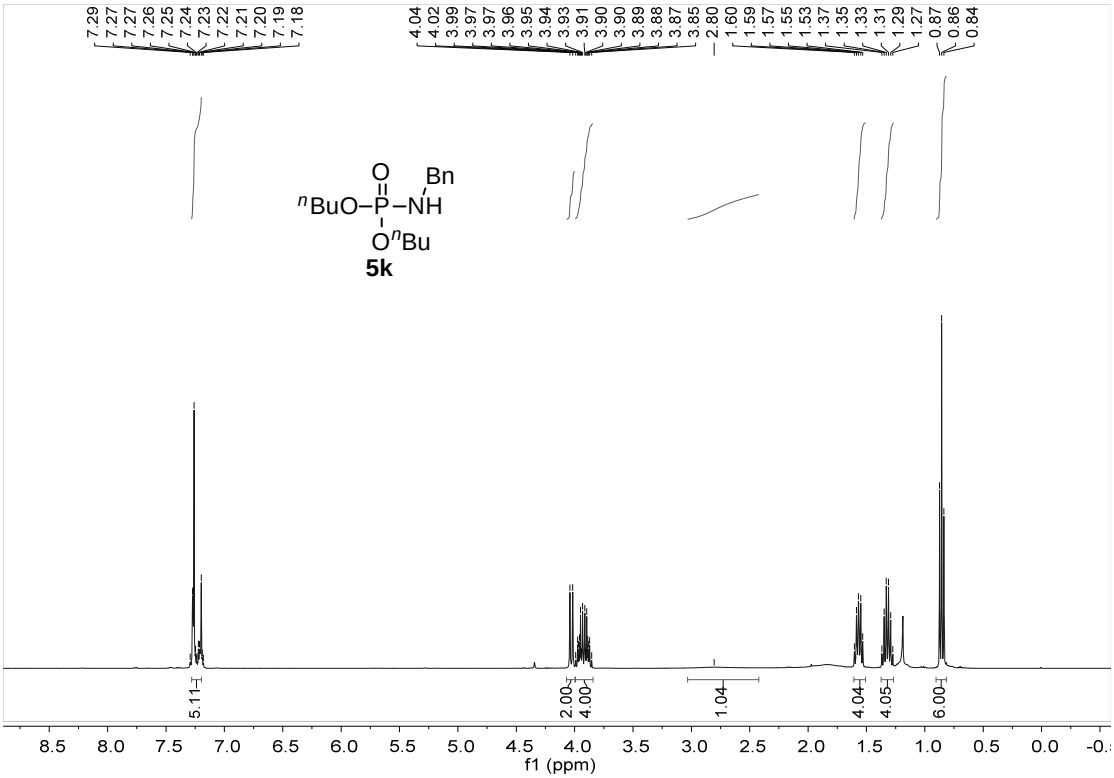

132.42
132.33
131.99
131.97
131.43
130.14
128.76
128.64
77.32
77.00
76.68
67.24
67.17
44.98
O
Ph—P—N
O
Ph
5i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

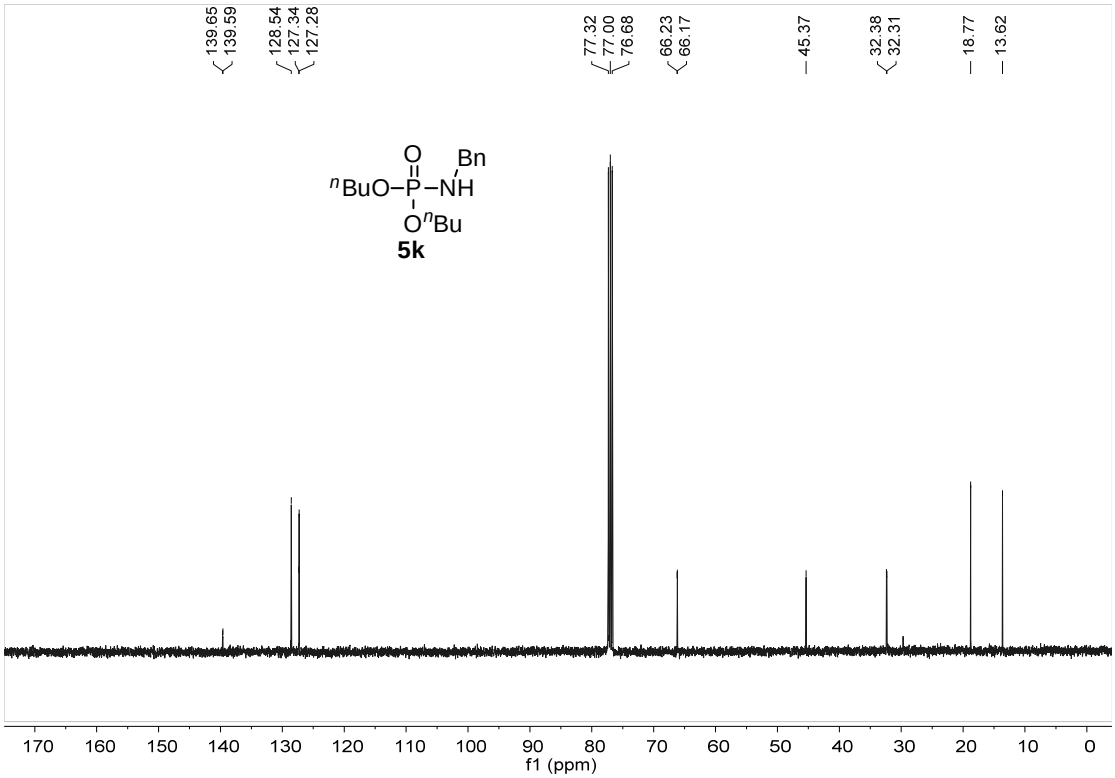

29.22
O
Ph—P—N
O
Ph
5i
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

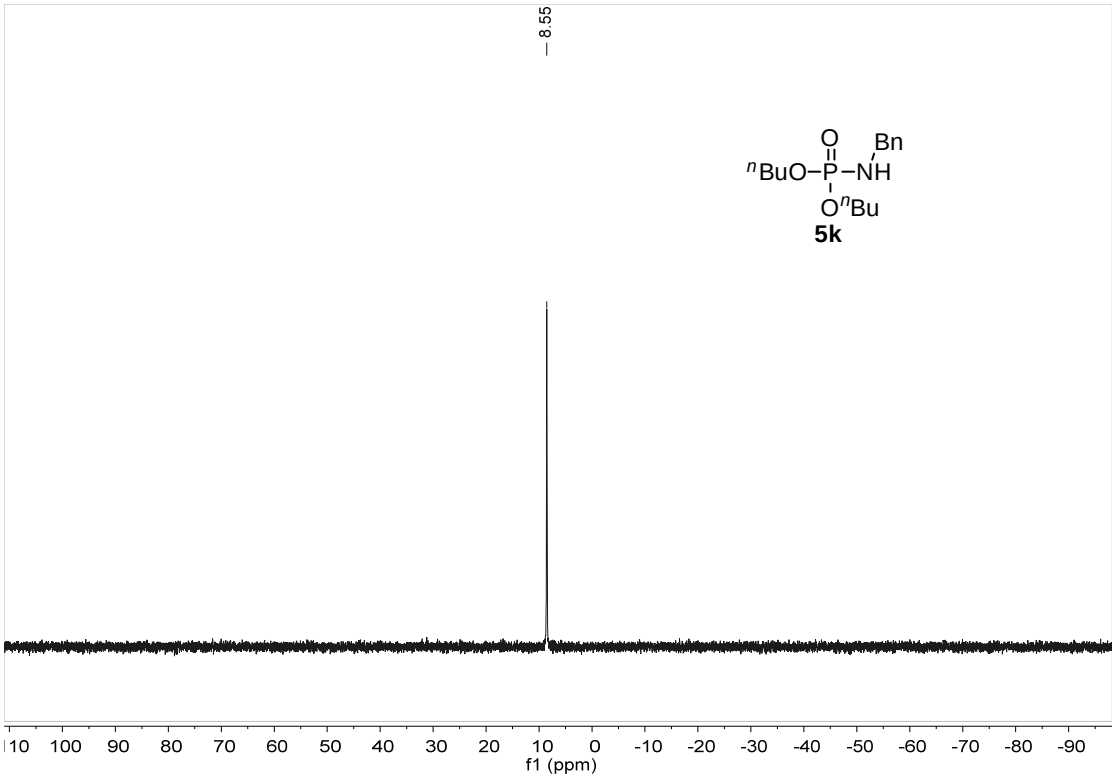

7.60
7.57
7.57
7.56
7.52
7.51
7.51
7.51
7.50
4.35
4.34
4.32
4.32
4.31
4.29
4.29
4.28
4.26
4.25
3.04
1.56
1.54
1.52
O
Bn
EtO−P−NH
OEt
5j
4.02
1.09
6.08
1.03
6.00
f1 (ppm)

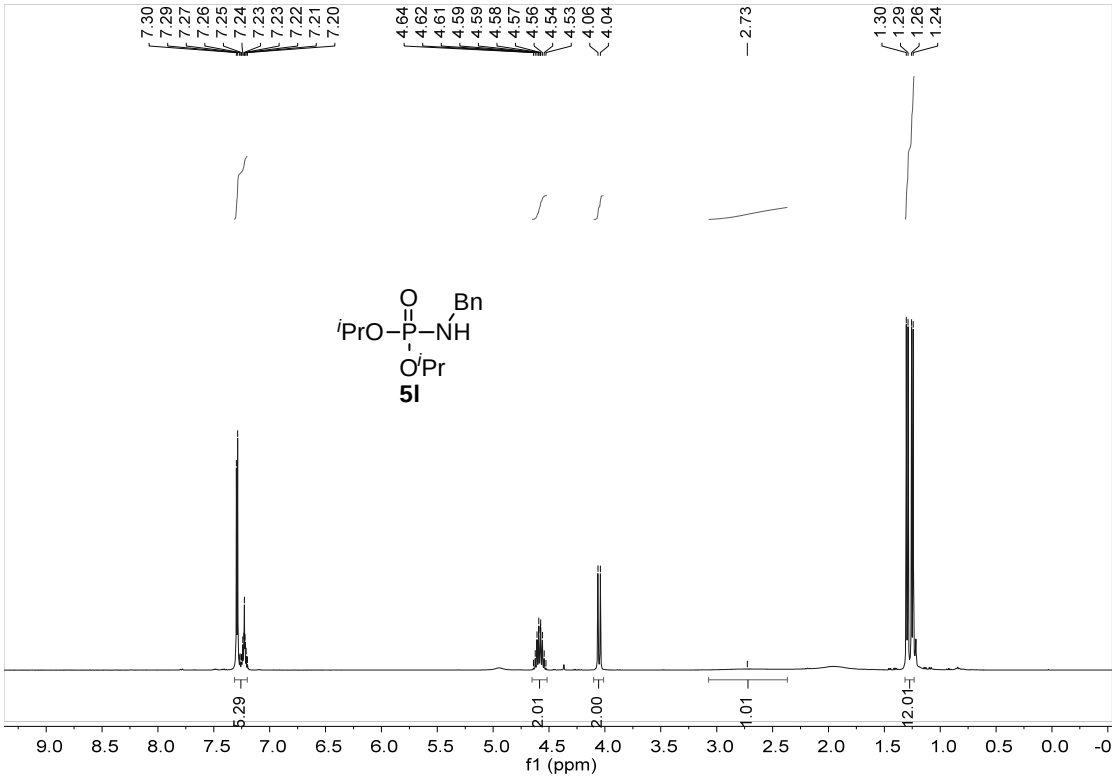

139.66
139.59
128.53
127.33
127.28
77.32
77.00
76.68
62.40
62.35
45.34
16.18
16.11
O
Bn
EtO−P−NH
OEt
5j
f1 (ppm)

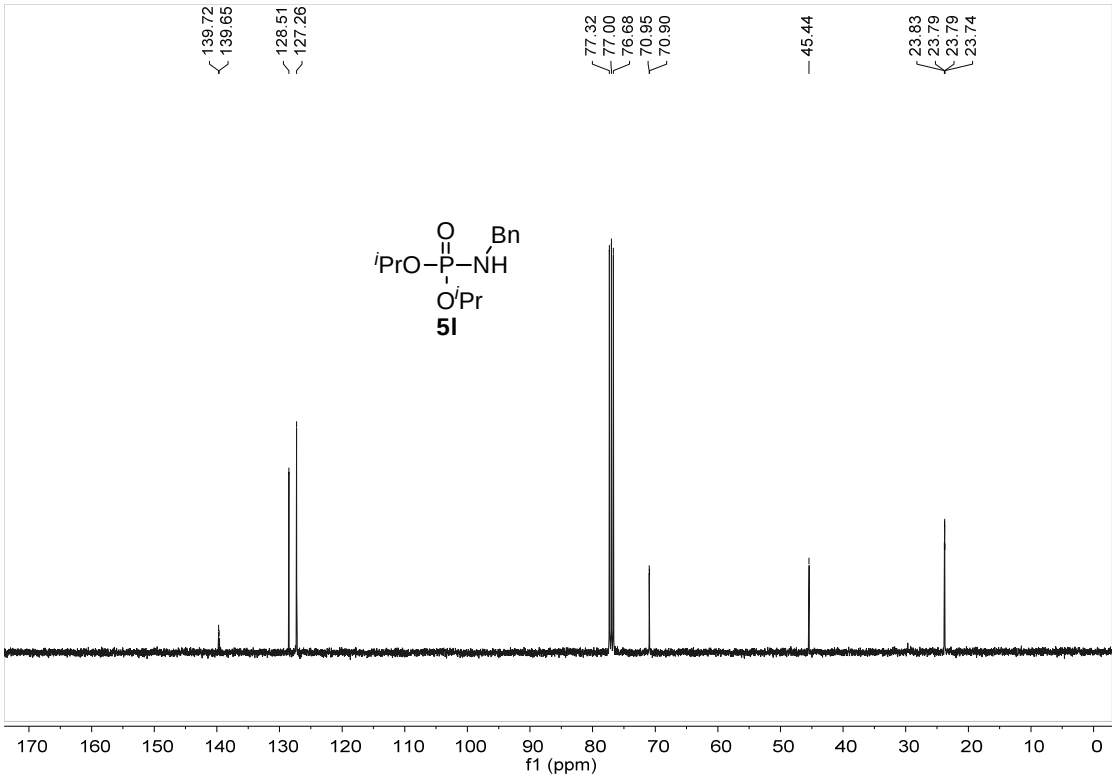

8.46
O
Bn
EtO–P–NH
OEt
5j
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

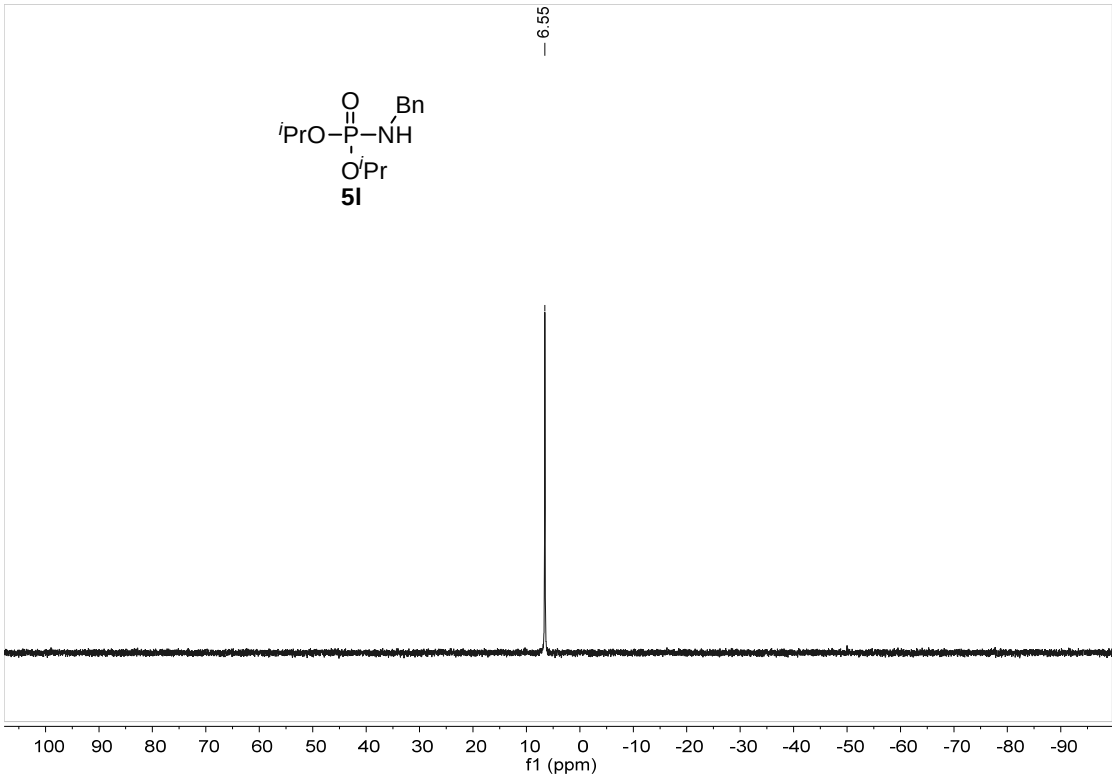

7.29 7.27 7.27 7.26 7.25 7.24 7.23 7.22 7.21 7.20 7.19 7.18
4.04 4.02 3.99 3.97 3.97 3.96 3.95 3.94 3.93 3.91 3.90 3.90 3.89 3.88 3.87 3.85
2.80
1.60 1.59 1.57 1.55 1.53 1.37 1.35 1.33 1.31 1.29 1.27
0.87 0.86 0.84
O
Bn
nBuO–P–NH
OnBu
5k
5.11
2.00
4.00
1.04
4.04
4.05
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

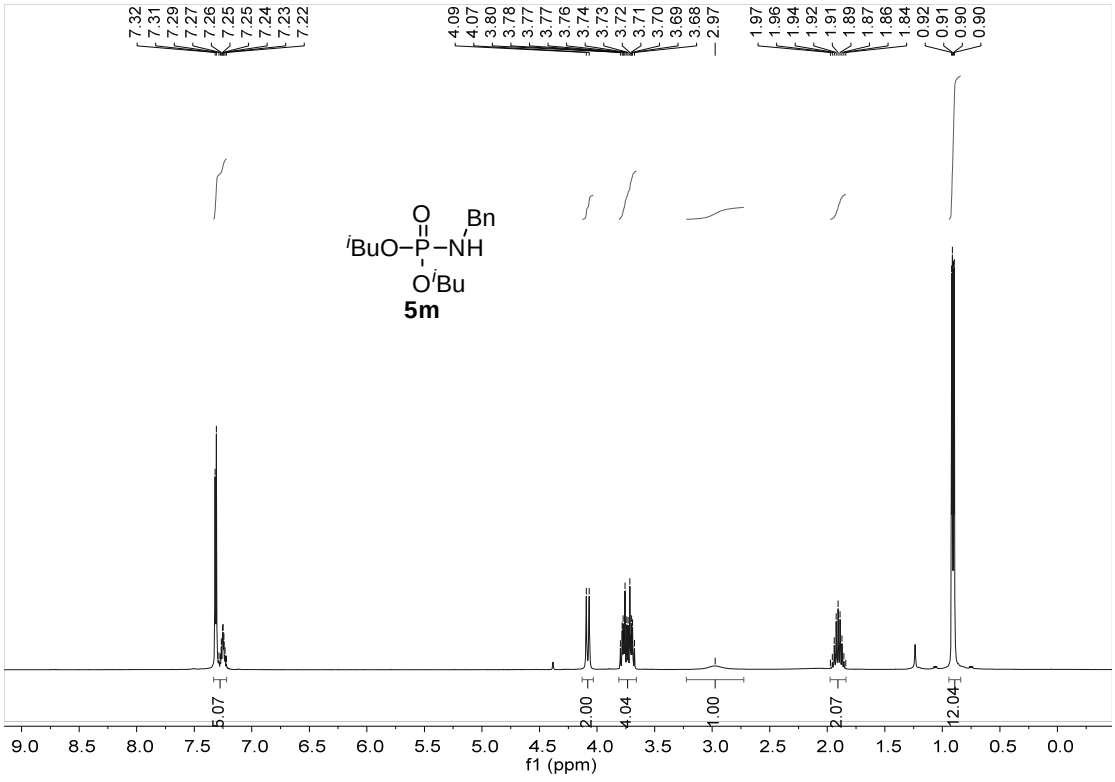

139.65
139.59
128.54
127.34
127.28
77.32
77.00
76.68
66.23
66.17
45.37
32.38
32.31
18.77
13.62
O
Bn
nBuO–P–NH
OnBu
5k
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

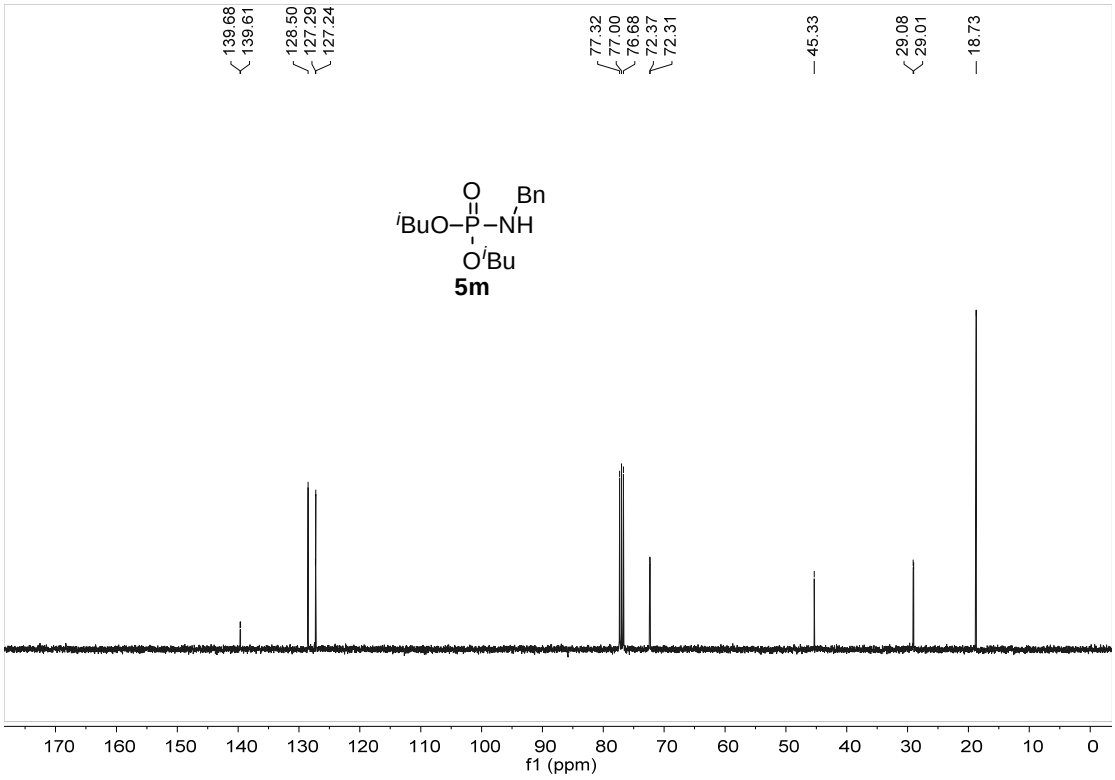

8.55
O
Bn
nBuO–P–NH
OnBu
5k
10 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

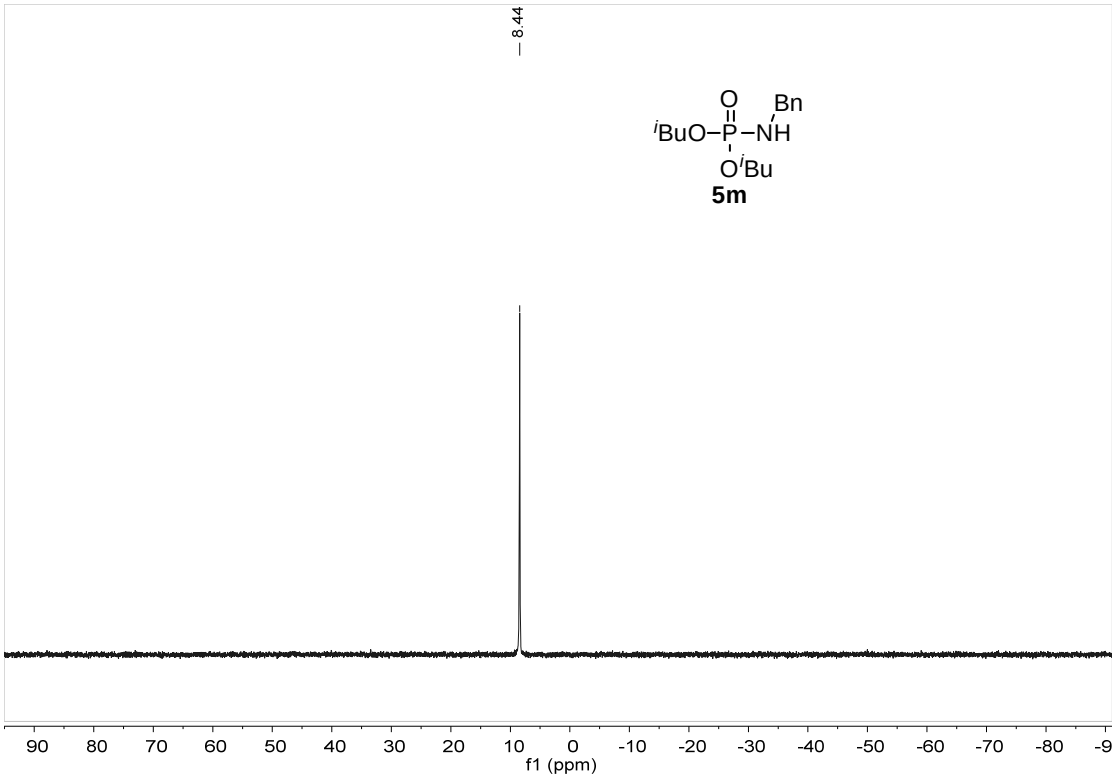

7.30
7.29
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.20
4.64
4.62
4.61
4.59
4.59
4.58
4.57
4.56
4.54
4.53
4.06
4.04
2.73
1.30
1.29
1.26
1.24
O
Bn
iPrO–P–NH
OiPr
5l
5.29
2.01
2.00
1.01
12.01
f1 (ppm)


139.72
139.65
128.51
127.26
77.32
77.00
76.68
70.95
70.90
45.44
23.83
23.79
23.79
23.74
O
Bn
iPrO–P–NH
OiPr
5l
f1 (ppm)


6.55
O
Bn
iPrO–P–NH
OiPr
5l
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


7.32 7.31 7.29 7.27 7.26 7.25 7.25 7.24 7.23 7.22
4.09 4.07 3.80 3.78 3.77 3.77 3.76 3.74 3.73 3.72 3.71 3.70 3.69 3.68 2.97
1.97 1.96 1.94 1.92 1.91 1.89 1.87 1.86 1.84 0.92 0.91 0.90 0.90
O
Bn
iBuO–P–NH
OiBu
5m
5.07 2.00 4.04 1.00 2.07 12.04
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)


139.68
139.61
128.50
127.29
127.24
77.32
77.00
76.68
72.37
72.31
45.33
29.08
29.01
18.73
O
Bn
iBuO–P–NH
OiBu
5m
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.44
O
Bn
iBuO–P–NH
OiBu
5m
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -9
f1 (ppm)