Supporting Information

Palladacycle-catalyzed phosphonation of aryl halides in neat water

Kai Xu, Fan Yang, * Guodong Zhang, and Yangjie Wu*

The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, People's Republic of China. Fax:+86-371-67979408; E-mail: yangf@zzu.edu.cn wyj@zzu.edu.cn

Contents

Experimental Section

General

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. GC analysis was performed on Agilent 4890D gas chromatograph. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High-resolution mass spectra were measured on a MALDI-FTMS. Ethyl acetate and hexane (analytical grade) were used for column chromatography without purification. The palladacycles of cyclopalladated ferrocenylimines were synthesized according to the reported literature. [1] Other solvents were purified according to the standard methods. The other chemicals were bought from commercial sources and used as-received unless otherwise noted.

General procedure for the synthesis of cyclopalladated ferrocenylimines (palladacycle I)[1]

Ferrocenylimine and mole equivalent NaOAc were added to the MeOH solution of mole equivalent Li_2PdCl_4, and the resulting red solutions were stirred at room temperature for about 20 h. After the reaction was complete, the mixture was filtered and the solid cyclopalladated ferrocenylimines obtained were washed with MeOH.

General procedure for the synthesis of triphenylphosphine adduct (palladacycle II)[1]

A solution of palladacycle (I) (0.084 g, 0.092 mmol), and PPh_3 (0.058 g, 0.22 mmol) in dichloromethane (10 mL) was stirred at room temperature for 30 min. The mixture was filtered through Celite and evaporated to dryness. The crude product was recrystallized from dichloromethane-petroleum ether to afford the product as red crystal.

The palladacycle-catalyzed the cross-coupling of aryl iodides and bromides with diisopropyl H-phosphonate in water

Aryl iodide or bromide (0.4 mmol), diisopropyl H-phosphonate (0.6 mmol), KF (1.2 mmol), TBAB (0.4 mmol), ^{i}PrOH (1.2 mmol), and palladacycle **II** (1 mol%) were dissolved in H_2O (2 mL) in a 10 mL vial under nitrogen atmosphere. The mixture then refluxed for 16 h. After the reaction was complete, the mixture was filtered through a pad of Celite and washed with ethyl acetate. The mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent in vacuum, the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane) to give the pure product.

The palladacycle-catalyzed the cross-coupling of aryl chlorides with diisopropyl H-phosphonate in water

The mixture of aryl chloride (0.4 mmol), diisopropyl H-phosphonate (0.6 mmol), KF (1.7 mmol), TBAB (0.4 mmol), ^{i}PrOH (1.2 mmol), and palladacycle **I** (1 mol%)/X-Phos (4 mol%) was dissolved in H_2O (2 mL) in a 10 mL vial under nitrogen atmosphere. The mixture then refluxed for 16 h. After the reaction was complete, the mixture was filtered through a pad of Celite, and washed with ethyl acetate.

And the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent in vacuum, the residue was purified by flash chromatography on silica gel (ethyl acetate/hexane) to give the pure product.

The palladacycle-catalyzed the cross-coupling of aryl halides with diphenylphosphine oxide in water

The mixture of aryl halides (0.4 mmol), diphenylphosphine oxide (0.6 mmol), KF (1.2 mmol), TBAB (0.4 mmol), ^{i}PrOH (1.2 mmol), and palladacycle **II** (1 mol%) was dissolved in H_2O (2 mL) in a 10 mL vial under nitrogen atmosphere. The mixture then refluxed for 16 h. After the reaction was complete, the mixture was filtered through a pad of Celite, and washed with dichloromethane. And the mixture was added into H_2O (25 mL) and extracted with dichloromethane (10 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent in vacuum, the residue was purified by flash chromatography on silica gel (dichloromethane/ methanol) to give the pure product.

Diisopropyl (4-methoxyphenyl)phosphonate (3a) [2]

Oil, yield: 93% (Table 1, entry 7), 84% (Table 2, entry 3), 76% (Table 3, entry 6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J=12.6 Hz and 8.8 Hz, 2H), 6.89 (dd, J=8.8 Hz and 3.2 Hz, 2H), 4.64–4.52 (m, 2H), 3.78 (s, 3H), 1.30 (d, J=6.0 Hz, 6H), 1.15 (d, J=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.5 (d, J=3.3 Hz), 133.7 (d, J=11.3 Hz), 121.1 (d, J=194.0 Hz), 113.8 (d, J=15.9 Hz), 70.4 (d, J=5.3 Hz), 55.3, 24.1 (d, J=3.8 Hz), 23.8 (d, J=4.9 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 18.0.

Diisopropyl (*p*-tolyl)phosphonate (3b) [3]

Oil, yield: 94% (Table 2, entry 1), 60% (Table 2, entry 7), 99% (Table 4, entry 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J=13.2 Hz and 8.0 Hz, 2H), 7.26 (dd, J=7.6 Hz and 4.0 Hz, 2H), 4.72–4.60 (m, 2H), 2.39 (s, 3H), 1.36 (d, J=6.0 Hz, 6H), 1.22 (d, J=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.5 (d, J=3.2 Hz), 131.8 (d, J=10.2 Hz), 129.1 (d, J=15.3 Hz), 126.6 (d, J=189.5 Hz), 70.5 (d, J=5.4 Hz), 24.1 (d, J=3.8 Hz), 23.8 (d, J=4.9 Hz), 21.6; ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.9.

Diisopropyl (*o*-tolyl)phosphonate (3c) [4]

Oil, yield: 58% (Table 2, entry 2), 69% (Table 4, entry 3);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J=14.3 Hz and 7.5 Hz, 1H), 7.43 (t, J=7.3 Hz, 1H), 7.26–7.21 (m, 2H), 4.78–4.70 (m, 2H), 2.60 (s, 3H), 1.40 (d, J=6.1Hz, 6H), 1.26 (d, J=6.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.6 (d, J=9.9 Hz), 133.8 (d, J=10.4 Hz), 132.1 (d, J=2.9 Hz), 131.1 (d, J=14.8 Hz), 128.3 (d, J=183.6 Hz), 125.3 (d, J=14.9 Hz), 70.6 (d, J=5.7 Hz), 24.1 (d, J=3.9 Hz), 23.7 (d, J=4.6 Hz), 21.2 (d, J=3.4 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.6.

Diisopropyl (2-aminophenyl)phosphonate (3d) [5]

Oil, yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 1H), 7.26–7.21 (m, 1H), 6.71–6.61 (m, 2H), 5.20 (s, 2H), 4.69–4.60 (m, 2H), 1.37 (d, J=6.0 Hz, 6H), 1.23 (d, J=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3 (d, J=8.4 Hz), 133.9 (d, J=2.3 Hz), 133.8 (d, J=7.2 Hz), 117.1 (d, J=13.9 Hz), 116.5

(d, *J*=12.7 Hz), 110.0 (d, *J*=183.2 Hz), 71.0 (d, *J*=5.0 Hz), 24.5 (d, *J*=3.7 Hz), 24.1 (d, *J*=4.9 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 19.5.

Diisopropyl-(2-acetamidophenyl)phosphonate (3e)

Oil, yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.58 (t, *J*=7.2 Hz, 1H), 7.61–7.48 (m, 2H), 7.11 (t, *J*=5.6 Hz, 1H), 4.69–4.61 (m, 2H), 2.21 (s, 3H), 1.39 (d, *J*=6.0 Hz, 6H), 1.23 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.0, 142.4 (d, *J*=7.5 Hz), 133.7 (d, *J*=2.2 Hz), 132.6 (d, *J*=5.7 Hz), 122.8 (d, *J*=13.6 Hz), 120.6 (d, *J*=11.4 Hz), 115.1 (d, *J*=179.1 Hz), 71.6 (d, *J*=5.4 Hz), 25.2, 24.0 (d, *J*=3.8 Hz), 23.7 (d, *J*=5.0 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.9; HRMS: m/z 300.1365 ($[M+H]^+$, $C_{14}H_{23}NO_4P^+$ Calcd. 300.1365).

Diisopropyl phenylphosphonate (3f) [5]

Oil, yield: 99% (Table 2, entry 6), 68% (Table 2, entry 9), 88% (Table 4, entry 9); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.55–7.50 (m, 1H), 7.47–7.42 (m, 2H), 4.75–4.63 (m, 2H), 1.37 (d, *J*=6.4 Hz, 6H), 1.23 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 132.1 (d, *J*=3.0 Hz), 131.6 (d, *J*=9.8 Hz), 129.8 (d, *J*=187.4 Hz), 128.3 (d, *J*=14.8 Hz), 70.7 (d, *J*=5.5 Hz), 24.0 (d, *J*=3.9 Hz), 23.8 (d, *J*=4.8 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.1.

Diisopropyl (3-methoxyphenyl)phosphonate (3g)

Oil, yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.32 (m, 3H), 7.08–7.05 (m, 1H), 4.73–4.64 (m, 2H), 3.85 (s, 3H), 1.38 (d, *J*=6.4 Hz, 6H), 1.23 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.1 (d, *J*=18.7 Hz), 131.0 (d, 186.1 Hz), 129.5 (d, *J*=17.4 Hz), 123.9 (d, *J*=9.1 Hz), 118.3 (d, *J*=2.6 Hz), 116.2 (d, *J*=10.2 Hz), 70.7 (d, *J*=5.3 Hz), 55.3, 24.0 (d, *J*=3.6 Hz), 23.8 (d, *J*=4.7 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.0. HRMS: m/z ($[M+H]^+$, $C_{13}H_{22}O_4P^+$ Calcd. 273.125).

Diisopropyl naphthalen-2-ylphosphonate (3h) [2]

Oil, yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J*=15.6 Hz, 1H), 7.96–7.86 (m, 3H), 7.77 (t, *J*=9.6 Hz, 1H), 7.61–7.53 (m, 2H), 4.77–4.68 (m, 2H), 1.41 (d, *J*=6.4 Hz, 6H), 1.22 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.9 (d, *J*=2.6 Hz), 133.9 (d, *J*=10.2 Hz), 132.3 (d, *J*=16.6 Hz), 128.9, 128.2 (d, *J*=14.3 Hz), 128.1, 127.8, 126.9 (d, *J*=186.9 Hz), 126.8, 126.6 (d, *J*=9.7 Hz), 70.8 (d, *J*=5.3 Hz), 24.1 (d, *J*=3.8 Hz), 23.9 (d, *J*=4.8 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.4.

Diisopropyl (4-vinylphenyl)phosphonate (3i)

Oil, yield: 58%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J*=13.2 Hz and 8.0 Hz, 2H), 7.48 (dd, *J*=7.6 Hz and 3.6 Hz, 2H), 6.73 (dd, *J*=17.6 Hz and 10.8 Hz, 1H), 5.85 (d, *J*=17.6 Hz, 1H), 5.37 (d, *J*=10.8 Hz, 1H), 4.73–4.64 (m, 2H), 1.37 (d, *J*=6.4 Hz, 6H), 1.22 (d, *J*=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.1 (d, *J*=3.3 Hz), 136.0 (d, *J*=1.3 Hz), 132.0 (d, *J*=10.0 Hz), 128.8 (d, *J*=189.0 Hz), 126.0 (d, *J*=15.3 Hz), 116.3, 70.7 (d, *J*=5.4 Hz), 24.0 (d, *J*=3.9 Hz), 23.8 (d, *J*=4.8 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.1; HRMS: m/z 269.1310 ($[M+H]^+$, $C_{14}H_{22}O_3P^+$ Calcd. 269.1307).

Diisopropyl (4-methoxycarbonylphenyl)phosphonate (3j)

Oil, yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J*=7.8 Hz and 3.8 Hz, 2H), 7.90 (dd, *J*=12.8 and 8.0 Hz, 2H), 4.76–4.67 (m, 2H), 3.95 (s, 3H), 1.38 (d, *J*=6.0 Hz, 6H), 1.23 (d, *J*=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4, 134.9 (d, *J*=185.9 Hz), 133.2 (d, *J*=3.3 Hz), 131.8 (d, *J*=9.9 Hz), 129.3 (d, *J*=14.9 Hz), 71.2 (d, *J*=5.6 Hz), 52.5, 24.1 (d, *J*=3.9 Hz), 23.8 (d, *J*=4.7 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 15.3; HRMS: m/z 301.1206 ($[M+H]^+$, $C_{14}H_{22}O_5P^+$ Calcd. 301.1199).

Diisopropyl (benzo[b]thiophen-5-yl)phosphonate (3k)

Pale yellow solid, mp 104–105 ^{o}C; yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J*=14.4 Hz, 1H), 7.96 (dd, *J*=8.4 Hz and 3.6 Hz, 1H), 7.75–7.69 (m, 1H), 7.53 (d, *J*=5.6 Hz, 1H), 7.42 (d, *J*=5.2 Hz, 1H), 4.75–4.66 (m, 2H), 1.40 (d, *J*=6.4 Hz, 6H), 1.22 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.3 (d, *J*=3.3 Hz), 139.1 (d, *J*=17.0 Hz), 128.1 (d, *J*=10.9 Hz), 127.6, 126.3 (d, *J*=11.0 Hz), 125.5 (d, *J*=188.5 Hz), 124.2 (d, *J*=1.3 Hz), 122.6 (d, *J*=15.8 Hz), 70.7 (d, *J*=5.3 Hz), 24.1 (d, *J*=3.9 Hz), 23.9 (d, *J*=4.8 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 18.1; HRMS: m/z 299.0871 ($[M+H]^+$, $C_{14}H_{20}O_3PS^+$ Calcd. 299.0871).

Diisopropyl (*m*-tolyl)phosphonate (3l) [6]

Oil, yield: 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.57 (m, 2H), 7.35–7.32 (m, 2H), 4.72–4.63 (m, 2H), 2.39 (s, 3H), 1.37 (d, *J*=6.0 Hz, 6H), 1.23 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.1 (d, *J*=14.9 Hz), 132.9 (d, *J*=3.1 Hz), 132.3 (d, *J*=10.0 Hz), 129.6 (d, *J*=186.7 Hz), 128.7 (d, *J*=9.5 Hz), 128.2 (d, *J*=15.6 Hz), 70.6 (d, *J*=5.4 Hz), 24.1 (d, *J*=3.8 Hz), 23.9 (d, *J*=4.8 Hz), 21.3; ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.7.

Diisopropyl (3,4-dimethylphenyl)phosphonate (3m) [7]

Oil, yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J*=13.6 Hz, 1H), 7.56–7.50 (m, 1H), 7.21 (dd, *J*=7.6 Hz and 4.6 Hz, 1H), 4.70–4.61 (m, 2H), 2.30 (s, 6H), 1.37 (d, *J*=6.0 Hz, 6H), 1.22 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.2 (d, *J*=3.2 Hz), 136.6 (d, *J*=15.2 Hz), 132.7 (d, *J*=10.4 Hz), 129.5 (d, *J*=15.6 Hz), 129.2 (d, *J*=9.6 Hz), 126.7 (d, *J*=188.4 Hz), 70.3 (d, *J*=5.3 Hz), 24.0 (d, *J*=3.8 Hz), 23.8 (d, *J*=4.9 Hz), 19.9, 19.5; ^{31}P NMR ($CDCl_3$, 163 MHz) δ 18.2.

Diisopropyl (4-butylphenyl)phosphonate (3n)

Oil, yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J*=13.2 Hz and 8.0 Hz, 2H), 7.26 (dd, *J*=8.0 Hz and 4.0 Hz, 2H), 4.71–4.62 (m, 2H), 2.65 (t, *J*=7.6 Hz, 2H), 1.65–1.57 (m, 2H), 1.41–1.32 (m, 8H), 1.22 (d, *J*=6.4 Hz, 6H), 0.93 (t, *J*=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.3 (d, *J*=3.0 Hz), 131.7 (d, *J*=10.2 Hz), 128.3 (d, *J*=15.2 Hz), 126.6 (d, *J*=189.6 Hz), 70.4 (d, *J*=5.4 Hz), 35.6, 33.1, 24.0 (d, *J*=3.8 Hz), 23.7 (d, *J*=4.8 Hz), 22.2, 13.8; ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.9; HRMS: m/z 299.1771 ($[M+H]^+$, $C_{16}H_{28}O_3P^+$ Calcd. 299.1775).

Diisopropyl (4-methoxy-3-methylphenyl)phosphonate (3o)

Oil, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J*=12.4 Hz and 9.0 Hz, 1H), 7.57 (d, *J*=12.4 Hz, 1H) 6.87 (dd, *J*=8.2 Hz and 3.4 Hz, 1H), 4.69–4.60 (m, 2H), 3.86 (s, 3H), 3.09 (s, 3H), 1.37 (d, *J*=6.4 Hz, 6H), 1.22 (d, *J*=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.7 (d, *J*=3.4 Hz), 133.8 (d, 11.1 Hz), 131.4 (d, *J*=10.9 Hz), 126.6 (d, *J*=15.4 Hz), 120.3 (d, *J*=207.3 Hz), 109.3 (d, *J*=16.8 Hz), 70.2

(d, *J*=5.3 Hz), 55.2, 23.9 (d, *J*=3.8 Hz), 23.7 (d, *J*=4.8 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 18.6; HRMS: m/z 287.1407 ($[M+H]^+$, $C_{14}H_{24}O_4P^+$ Calcd. 287.1409).

Diisopropyl [3-(dimethylamino)phenyl]phosphonate (3p)

Oil, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.19–7.07 (m, 2H), 6.85 (dd, *J*=8.4Hz and 2.0 Hz, 1H), 4.71–4.62 (m, 2H), 2.98 (s, 6H), 1.37 (d, *J*=6.4 Hz, 6H), 1.23 (d, *J*=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.0 (d, *J*=16.8 Hz), 130.0 (d, *J*=184.3 Hz), 129.0 (d, *J*=17.2 Hz), 119.2 (d, *J*=9.0 Hz), 115.6 (d, *J*=3.0 Hz), 115.2 (d, *J*=12.5 Hz), 70.4 (d, *J*=5.2 Hz), 40.3, 24.0 (d, *J*=3.7 Hz), 23.7 (d, *J*=4.9 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 18.7; HRMS: m/z 286.1567 ($[M+H]^+$, $C_{14}H_{25}NO_3P^+$ Calcd. 286.1570).

Diisopropyl benzo[d][1,3]dioxol-5-ylphosphonate (3q) [5]

Oil, yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.35 (m, 1H), 7.21 (dd, *J*=12.8 Hz and 1.2 Hz, 1H), 6.87 (dd, *J*=8.0 Hz and 3.6 Hz, 1H), 6.02 (s, 2H), 4.70–4.61 (m, 2H), 1.37 (d, *J*=6.0 Hz, 6H), 1.23 (d, *J*=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.8 (d, *J*=3.3 Hz), 147.6 (d, *J*=22.4 Hz), 127.2 (d, *J*=11.0 Hz), 122.8 (d, *J*=192.8 Hz), 111.1 (d, *J*=12.1 Hz), 108.3 (d, *J*=18.5 Hz), 101.4, 70.5 (d, *J*=5.4 Hz), 23.9 (d, *J*=3.8 Hz), 23.7 (d, *J*=4.8 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.2.

Diisopropyl (naphthalen-1-yl)phosphonate (3r) [5]

Oil, yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J*=8.8 Hz, 1H), 8.29 (dd, *J*=16.6 Hz and 7.0 Hz, 1H), 8.01 (d, *J*=8.0 Hz, 1H), 7.87 (d, *J*=8.0 Hz, 1H), 7.61–7.48 (m, 3H), 4.77–4.68 (m, 2H), 1.41 (d, *J*=6.4 Hz, 6H), 1.14 (d, *J*=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.5 (d, *J*=9.3 Hz), 133.6 (d, *J*=12.5 Hz), 133.4 (d, *J*=3.2 Hz), 132.6 (d, *J*=10.6 Hz), 128.7 (d, *J*=1.7 Hz), 127.1, 127.0 (d, *J*= 4.1 Hz), 126.2, 126.0 (d, *J*= 181.9 Hz), 124.5 (d, *J*=16.5 Hz), 71.0 (d, *J*=5.3 Hz), 24.2 (d, *J*=3.8 Hz), 23.8 (d, *J*=4.9 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 17.2.

Diisopropyl (2-chlorophenyl)phosphonate (3s)

Oil, yield: 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J*=14.4 Hz and 7.2 Hz, 1H), 7.47–7.44 (m, 2H), 7.38–7.27 (m, 1H), 4.78–4.69 (m, 2H), 1.40 (d, *J*=6.0 Hz, 6H), 1.26 (d, *J*=6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.8 (d, *J*=2.8 Hz), 136.0 (d, *J*=8.0 Hz), 133.3 (d, *J*=2.5 Hz), 130.7 (d, *J*=10.1 Hz), 128.5 (d, *J*=189.1 Hz), 126.3 (d, *J*=13.7 Hz), 71.4 (d, *J*=5.6 Hz), 24.1 (d, *J*=4.1 Hz), 23.7 (d, *J*=4.8 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 12.5; HRMS: m/z 277.0762 ($[M+H]^+$, $C_{12}H_{19}ClO_3P^+$ Calcd. 277.0760).

1-Methyl-4-(diphenylphosphino)benzene (5a) [8]

White solid, mp 130–131 ^{o}C; yield: 97% (Table 5, entry 1), 99% (Table 5, entry 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.55 (m, 4H), 7.49–7.41 (m, 4H), 7.38–7.32 (m, 4H), 7.19–7.16 (m, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.5 (d, *J*=2.8 Hz), 131.7 (d, *J*=103.4 Hz), 131.1 (d, *J*=10.2 Hz), 131.0 (d, *J*=9.8 Hz), 130.8 (d, *J*=2.6 Hz), 128.3 (d, *J*=12.5 Hz), 128.0 (d, *J*=107.5 Hz), 127.4 (d, *J*=12.0 Hz), 20.6; ^{31}P NMR ($CDCl_3$, 163 MHz) δ 29.8.

Triphenylphosphine oxide (5b) [8]

White solid, mp 156–157 ^{o}C; yield: 94% (Table 5, entry 2), 92% (Table 5, entry 4), 35% (Table 5, entry 5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.64 (m, 6H), 7.55–7.50 (m, 3H), 7.47–7.41 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 131.4 (d, J=102.8 Hz), 131.0 (d, J=10.0 Hz), 131.0 (d, J=3.4 Hz), 127.5 (d, J=12.1 Hz); ^{31}P NMR ($CDCl_3$, 163 MHz) δ 29.7.

References

[1] S. Q. Huo, Y. J. Wu, C. X. Du, Y. Zhu, H. Z. Yuan and X. A. Mao, *J. Organomet. Chem.* 1994, **483**, 139.

[2] Y. Luo and J. Wu, *Organometallics* 2009, **28**, 6823.

[3] C. Huang, X. Tang, Y. Y. Jiang and Y. F. Zhao, *J. Org. Chem*. 2006, **71**, 5020.

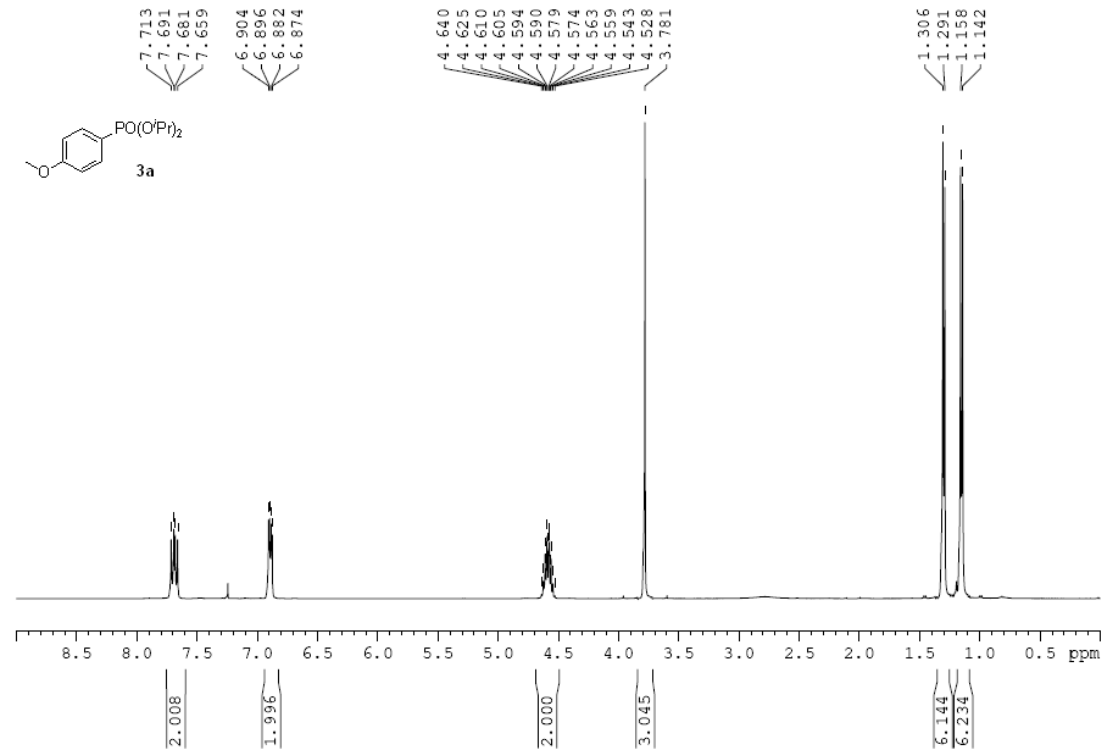
[4] H. Ohmori, S. Nakai and M. Masui, *J. Chem. Soc., Perkin Trans. 1: Org. Bio-Org. Chem.* 1979, 2023.

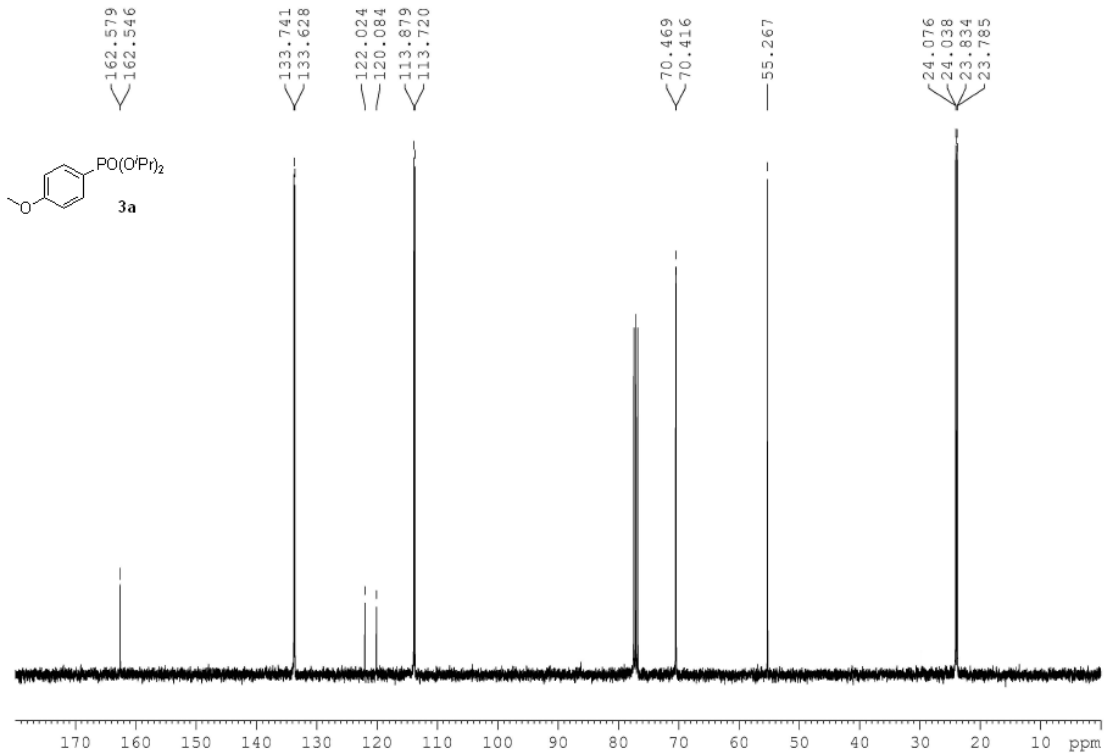
[5] Y. Belabassi, S. Alzghari and J. L. Montchamp, *J. Organomet. Chem.* 2008, **693**, 3171.

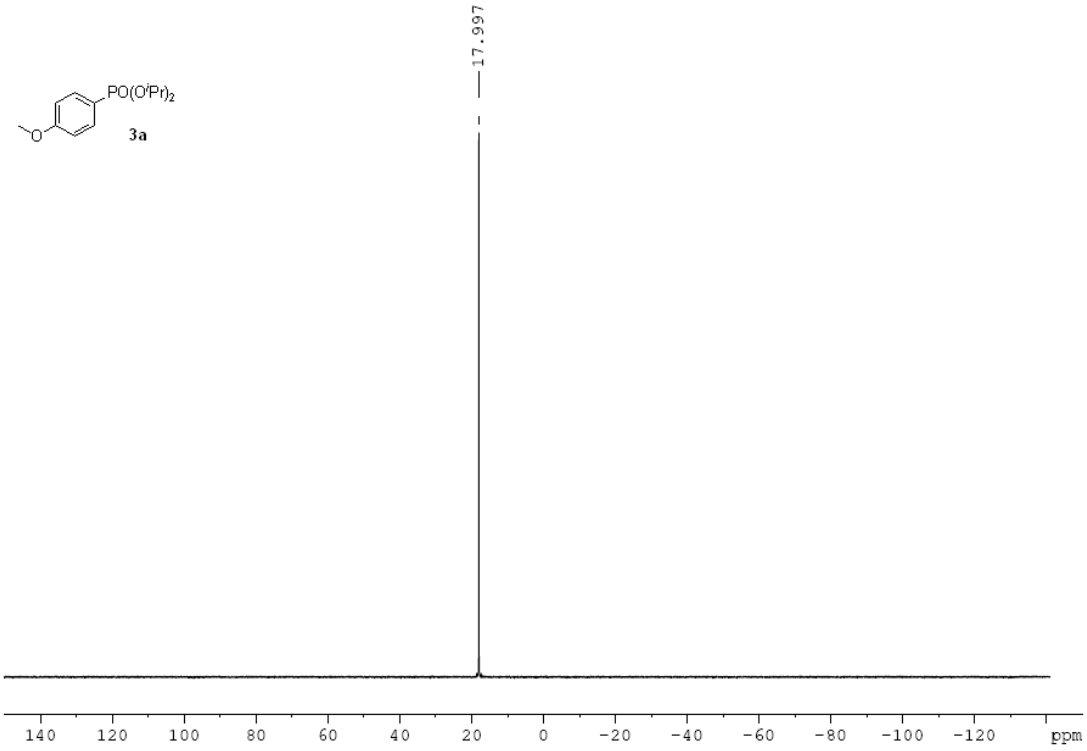
[6] E. V. Nikitin, A. S. Romakhin, O. V. Parakin, G. V. Romanov, Yu. M. Kargin and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1983, 626.

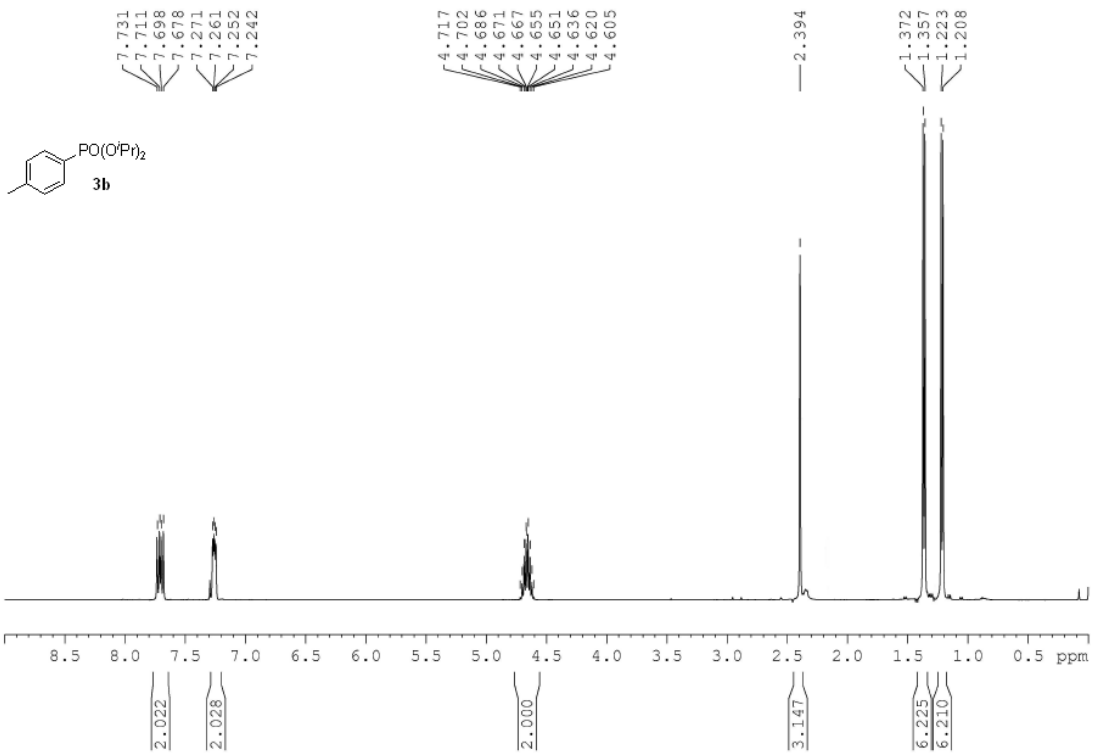
[7] M. Jonathan and S. Gordon, *Eur. Pat. Appl*. 233716, 1987.

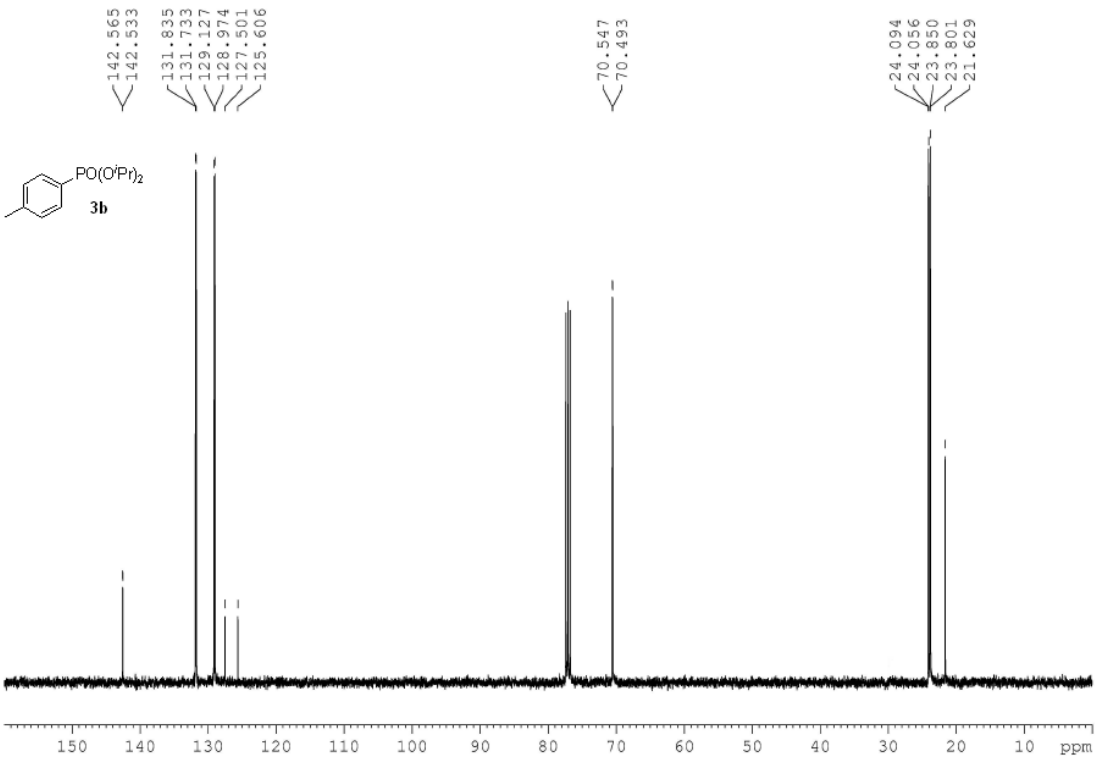
[8] X. H. Zhang, H. Z. Liu, X. M. Hu, G. Tang, J. Zhu and Y. F. Zhao, *Org. Lett.* 2011, **13**, 3478.

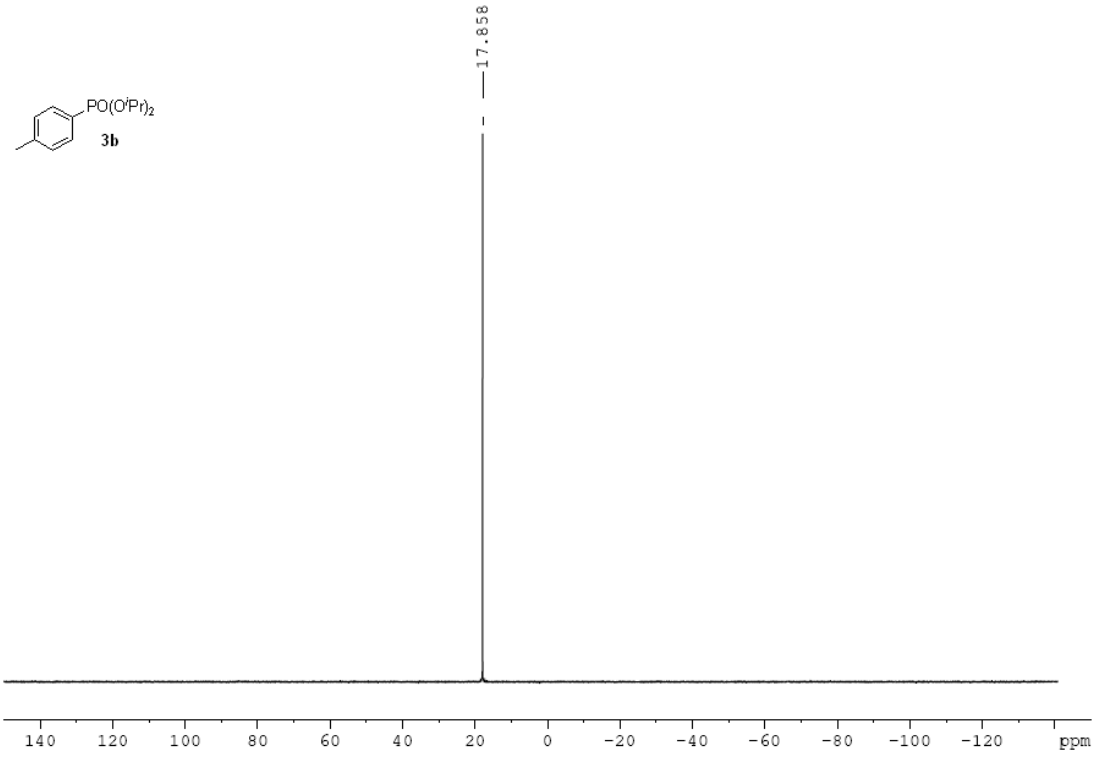


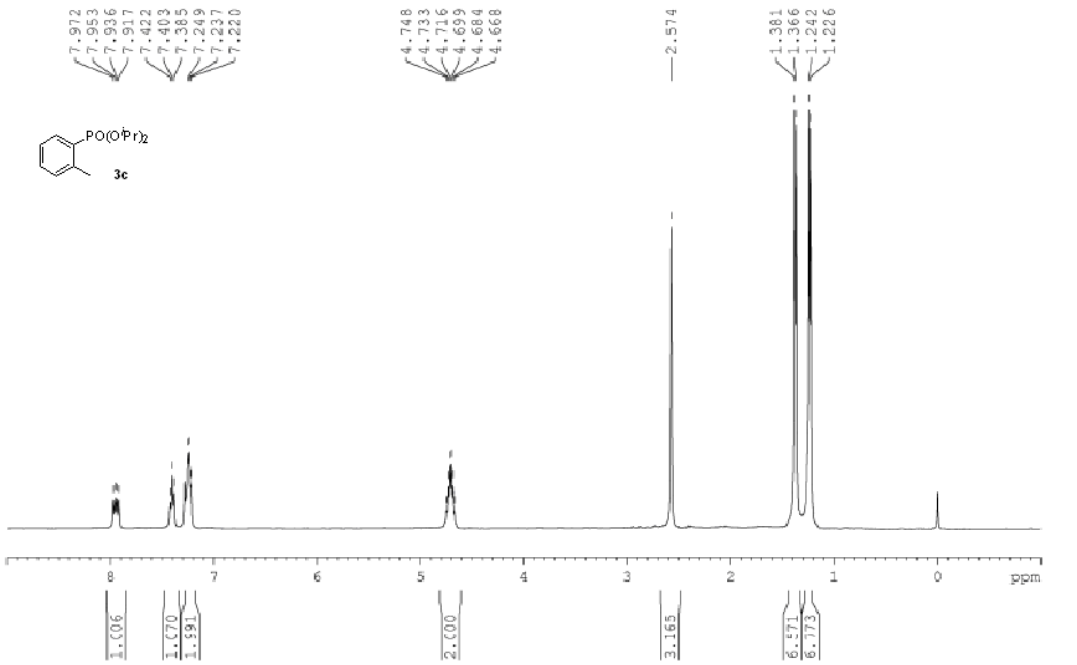


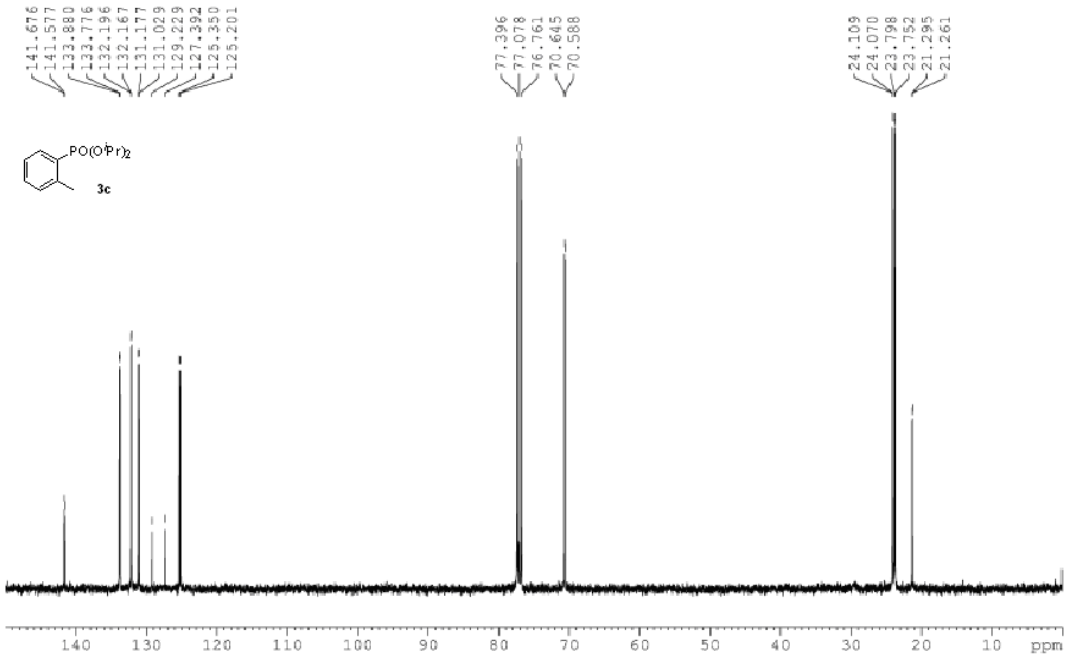

PO(O'Pr)2
3a
17.997
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

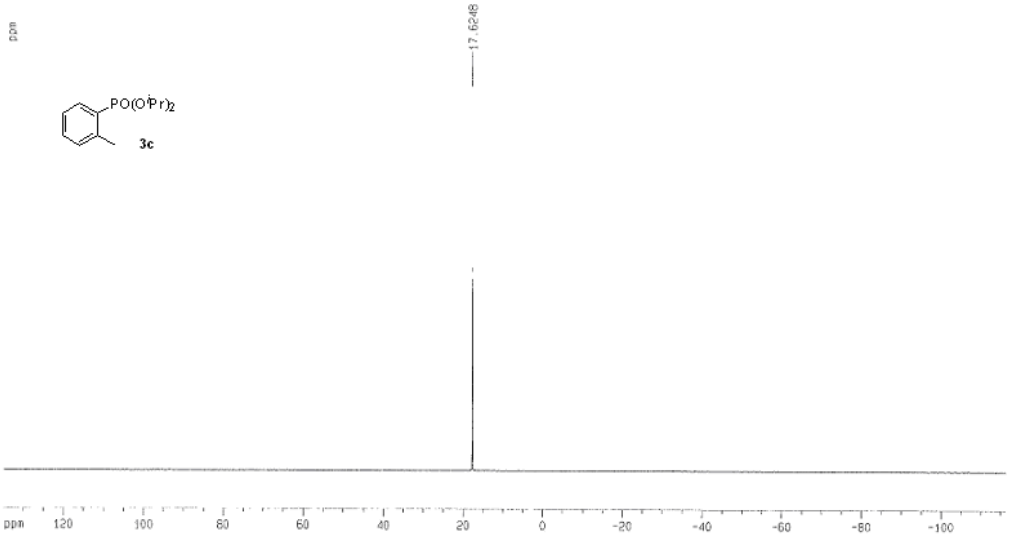

7.731
7.711
7.698
7.678
7.271
7.261
7.252
7.242
4.717
4.702
4.686
4.671
4.667
4.655
4.651
4.636
4.620
4.605
2.394
1.372
1.357
1.223
1.208
PO(O'Pr)2
3b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.022
2.028
2.000
3.147
6.225
6.210

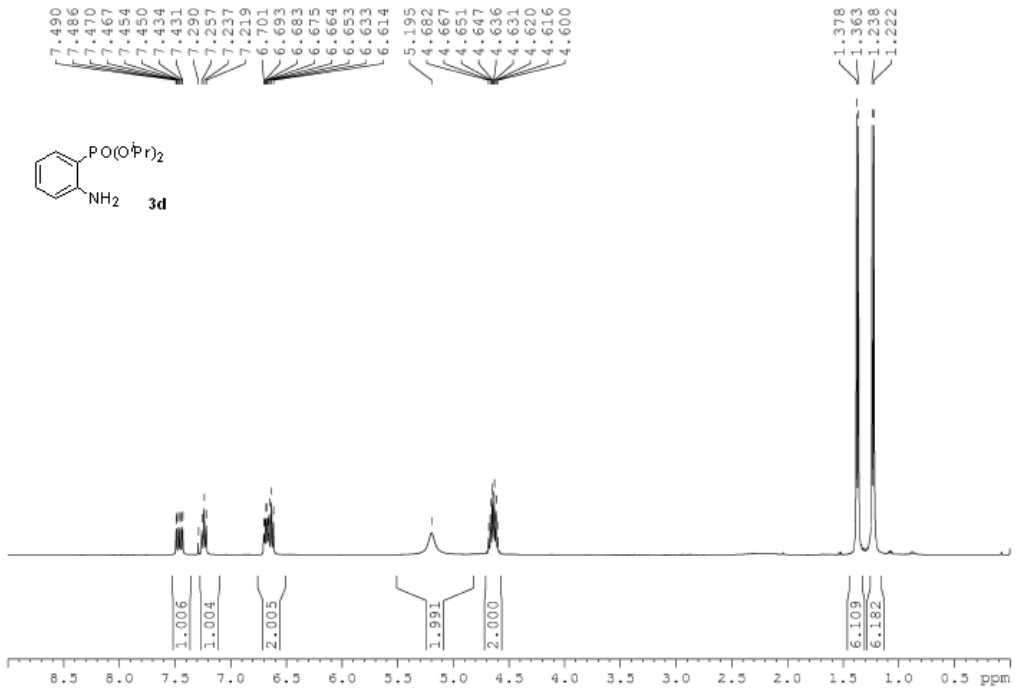


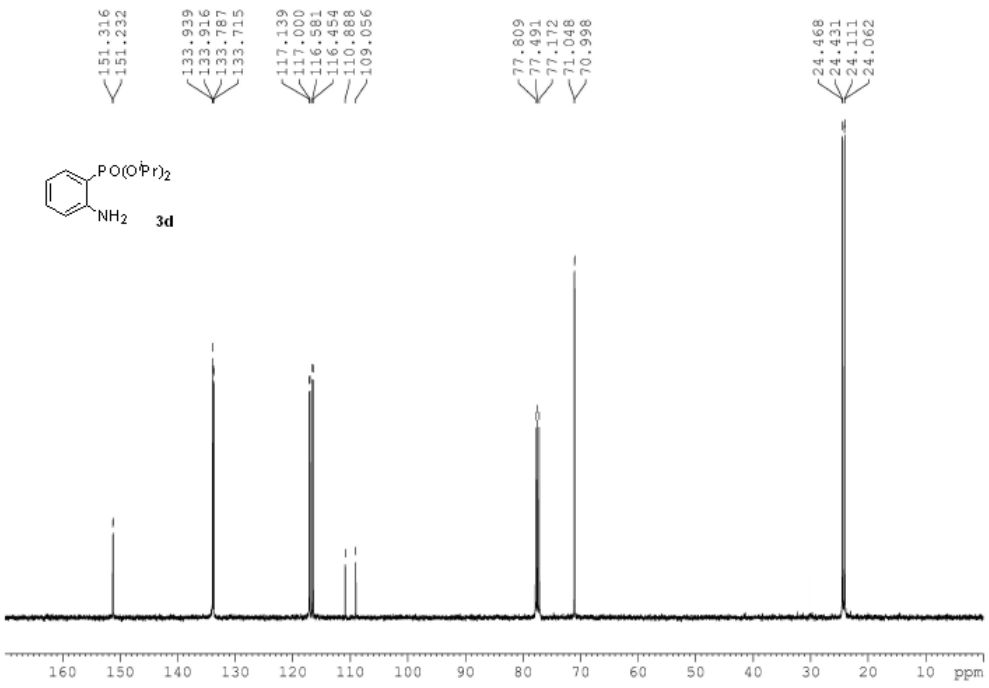


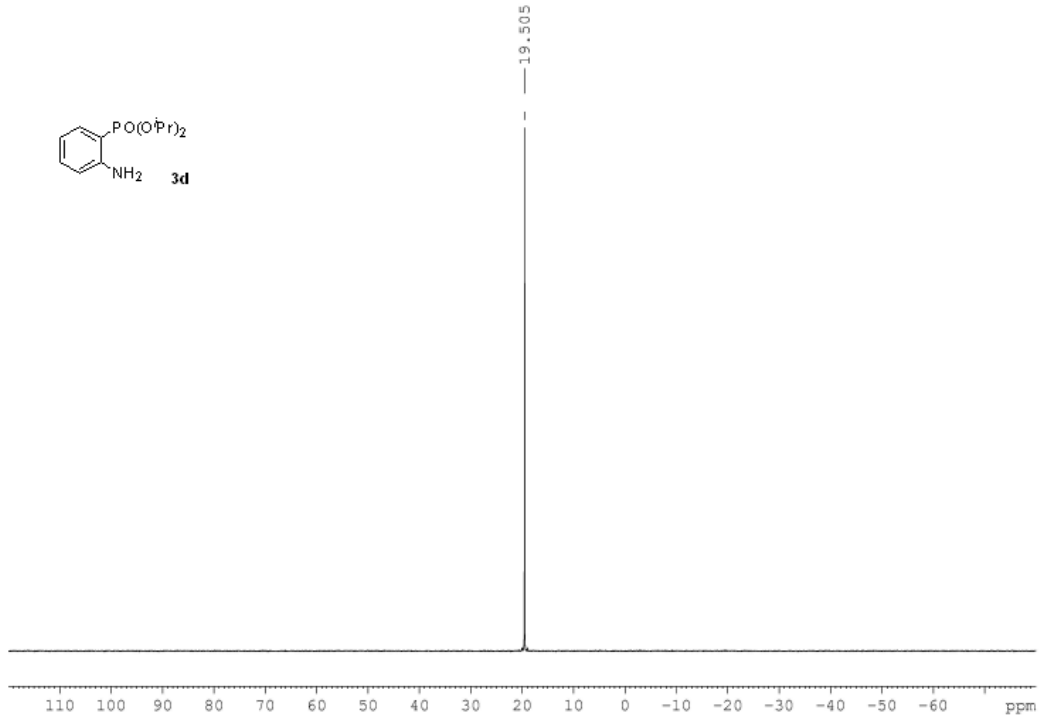


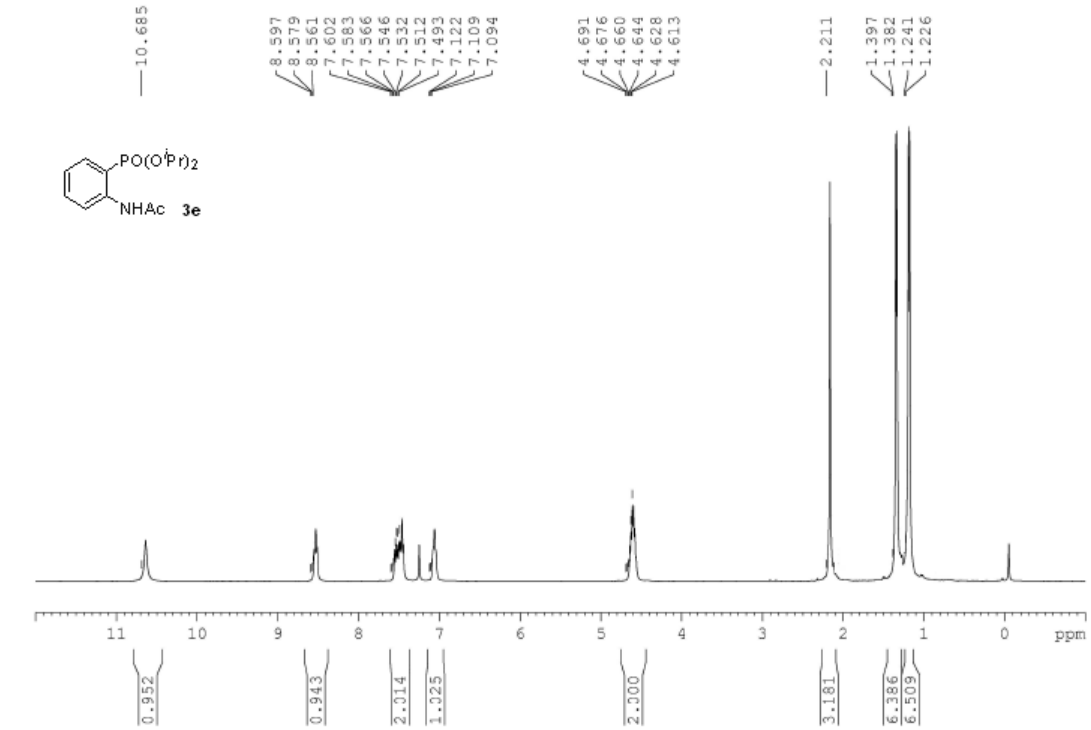


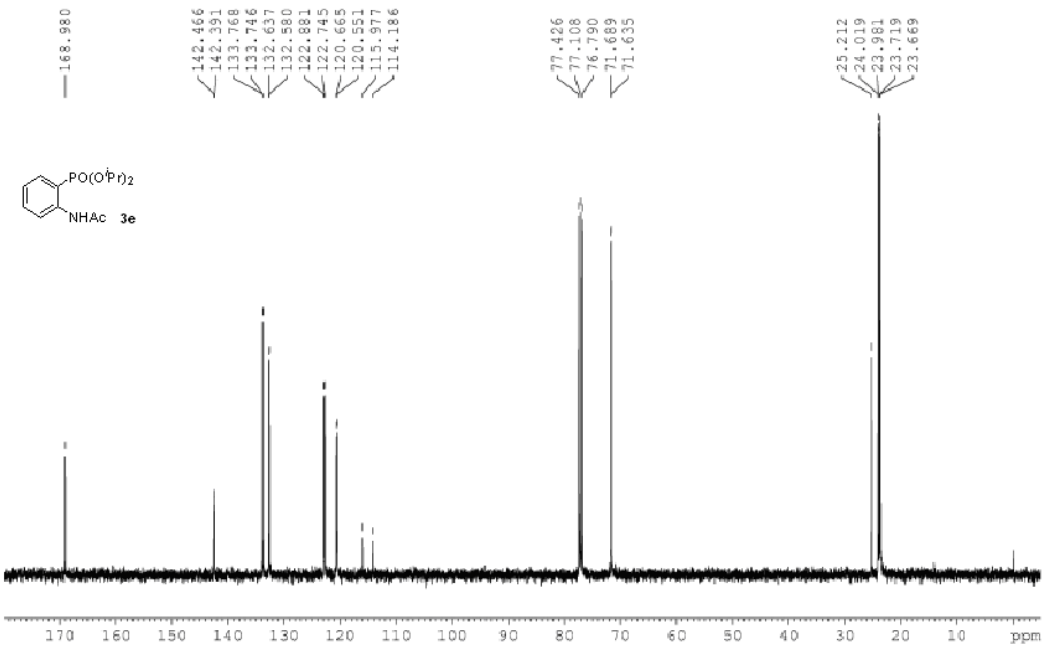

ppm
17.6248
PO(OiPr)2
3c
ppm 120 100 80 60 40 20 0 -20 -40 -60 -80 -100

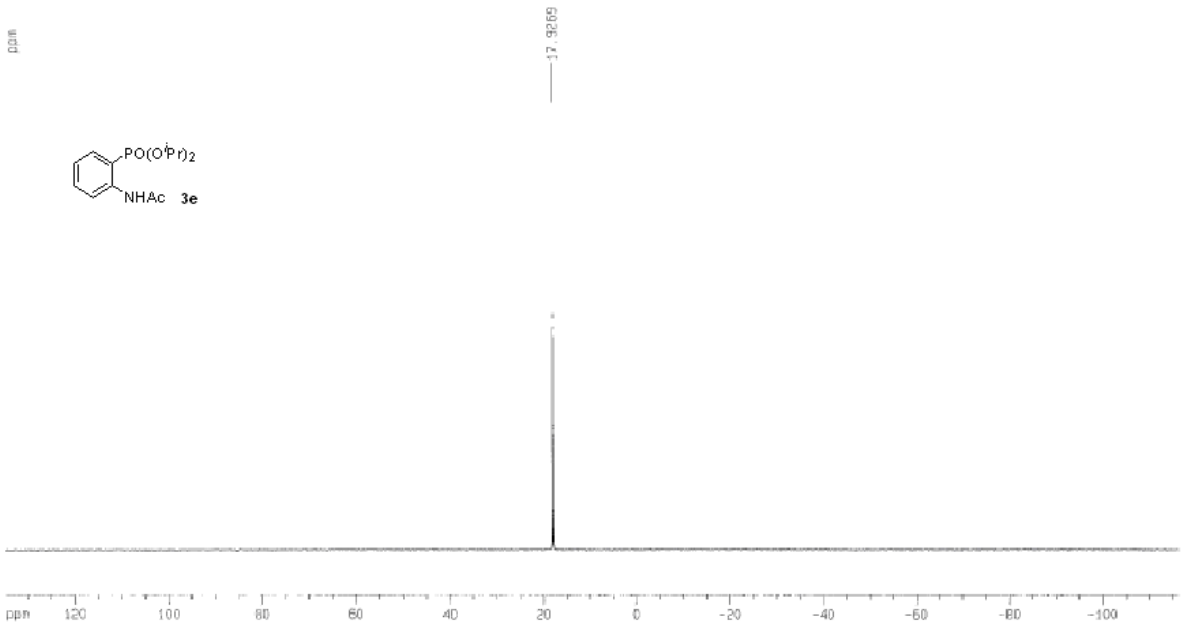

7.490
7.486
7.470
7.467
7.454
7.450
7.434
7.431
7.290
7.257
7.237
7.219
6.701
6.693
6.683
6.675
6.664
6.653
6.633
6.614
5.195
4.682
4.667
4.651
4.647
4.636
4.631
4.620
4.616
4.600
1.378
1.363
1.238
1.222
PO(OiPr)2
NH2
3d
1.006
1.004
2.005
1.991
2.000
6.109
6.182
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

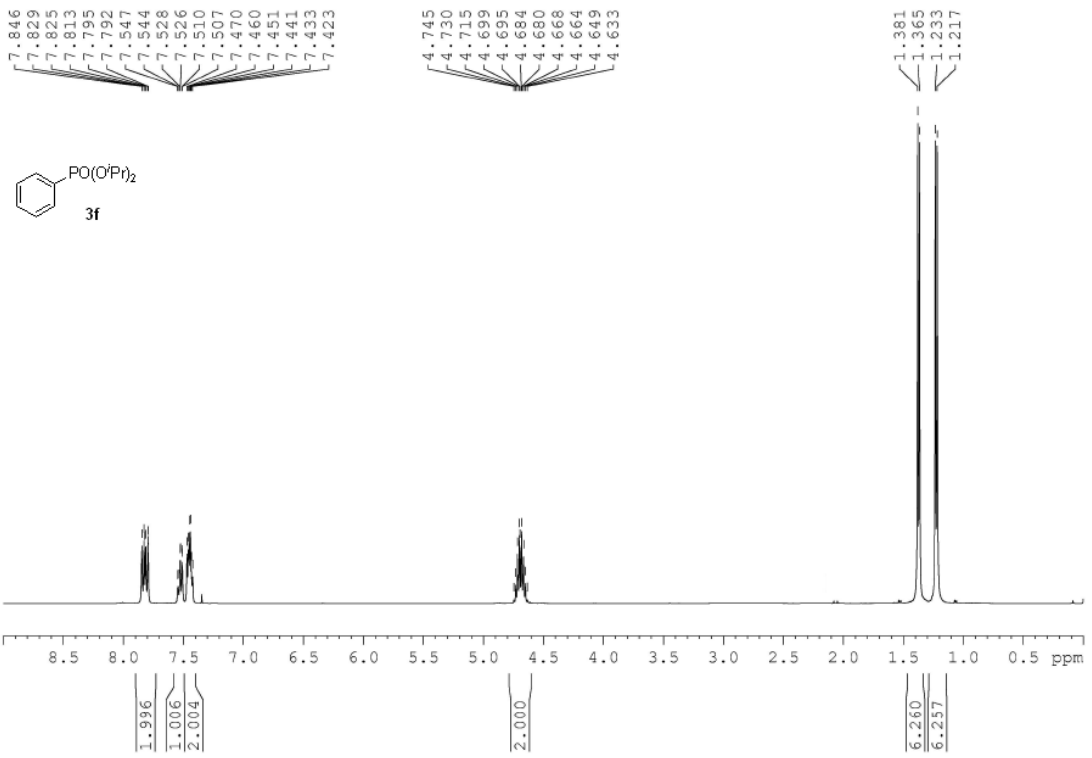

151.316
151.232
133.939
133.916
133.787
133.715
117.139
117.000
116.581
116.454
110.888
109.056
77.809
77.491
77.172
71.048
70.998
24.468
24.431
24.111
24.062
P(O)(OiPr)2
NH2
3d
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

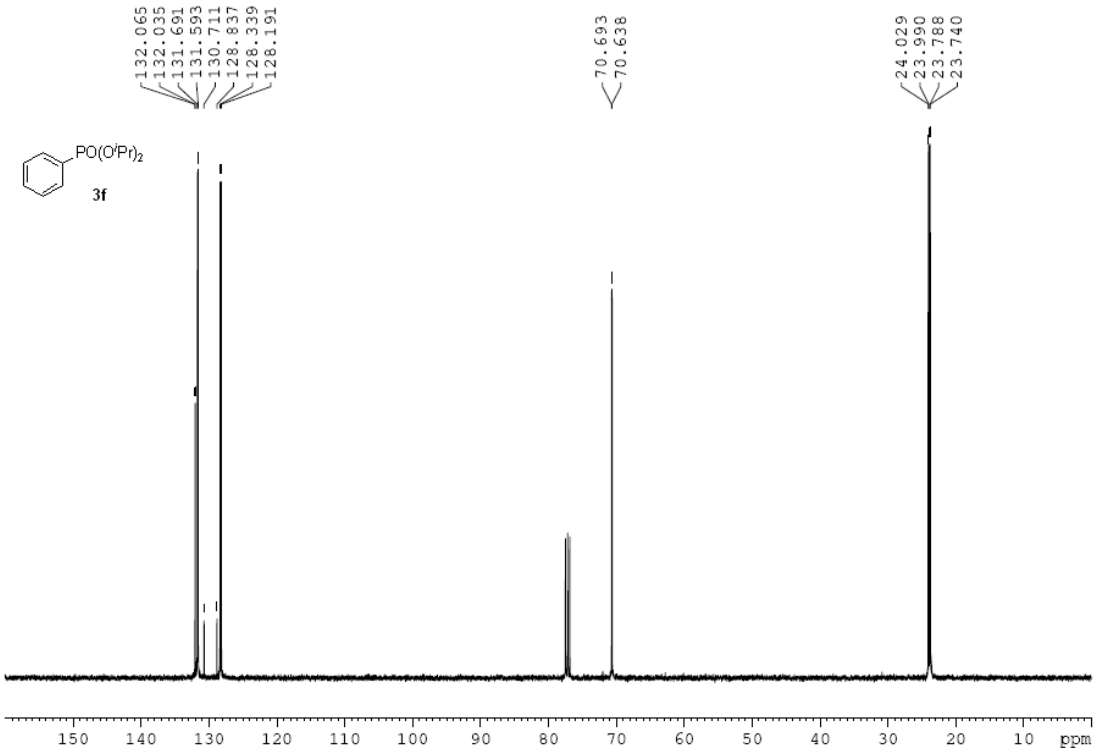

19.505
P(O)(OiPr)2
NH2
3d
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 ppm

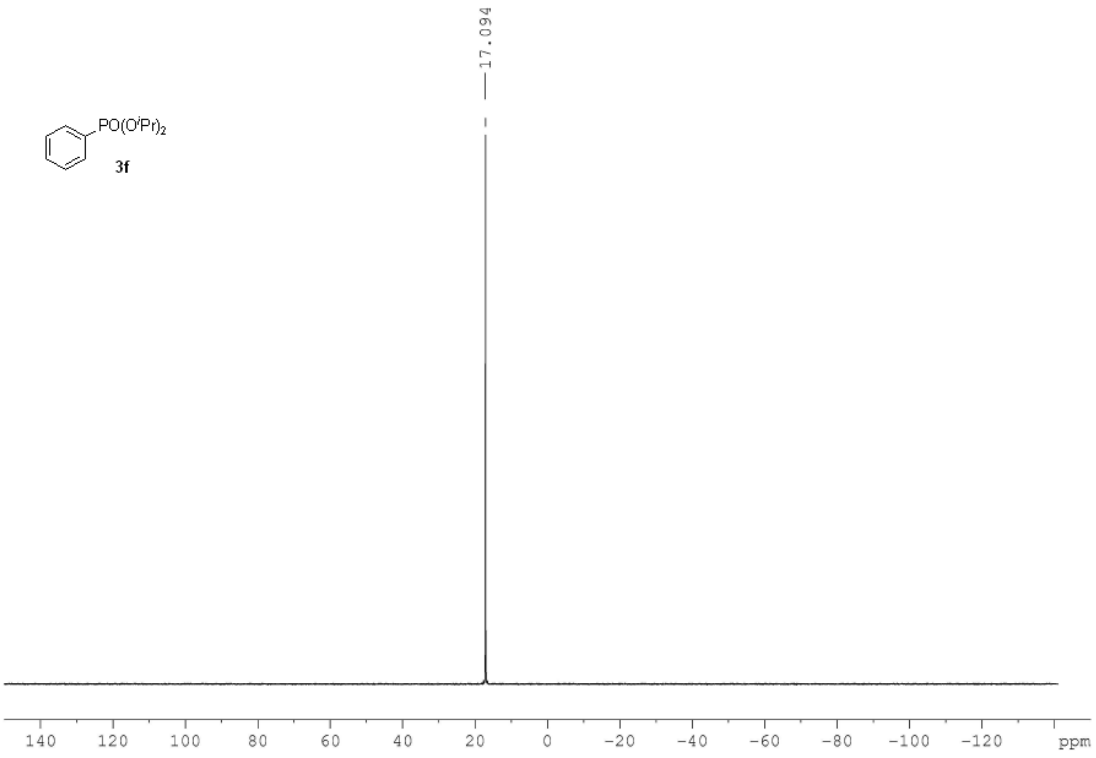

10.685
8.597
8.579
8.561
7.602
7.583
7.566
7.546
7.532
7.512
7.493
7.122
7.109
7.094
4.691
4.676
4.660
4.644
4.628
4.613
2.211
1.397
1.382
1.241
1.226
PO(OiPr)2
NHAc 3e
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.952
0.943
2.014
1.025
2.000
3.181
6.386
6.509

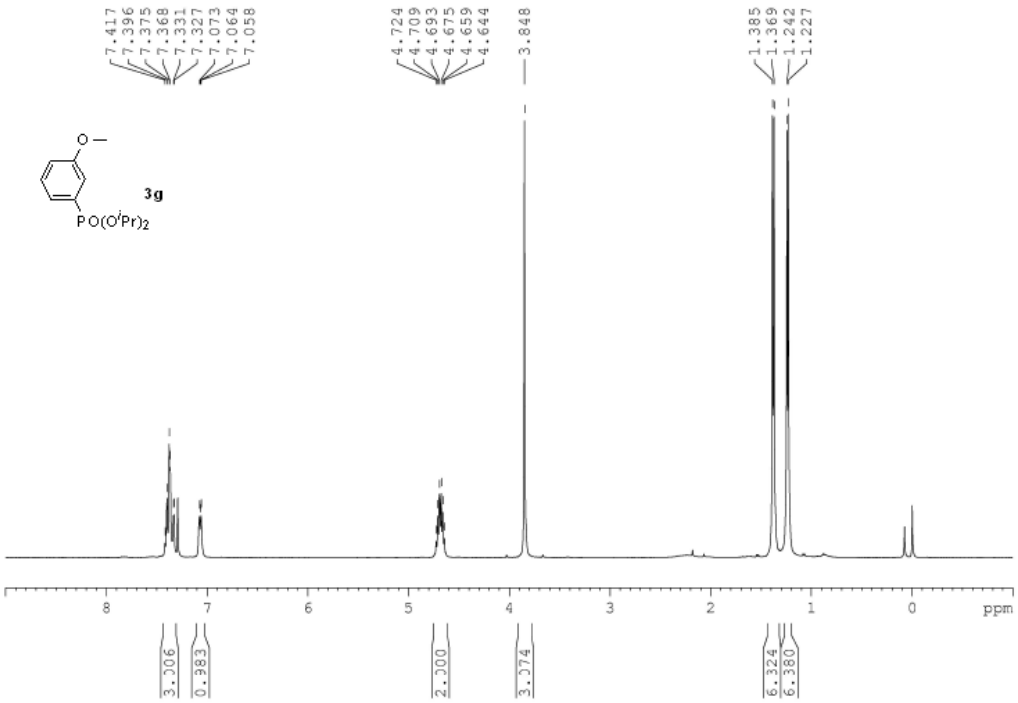

168.980
142.466
142.391
133.768
133.746
132.637
132.580
122.881
122.745
120.665
120.551
115.977
114.186
77.426
77.108
76.790
71.689
71.635
25.212
24.019
23.981
23.719
23.669
PO(OiPr)2
NHAc 3e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

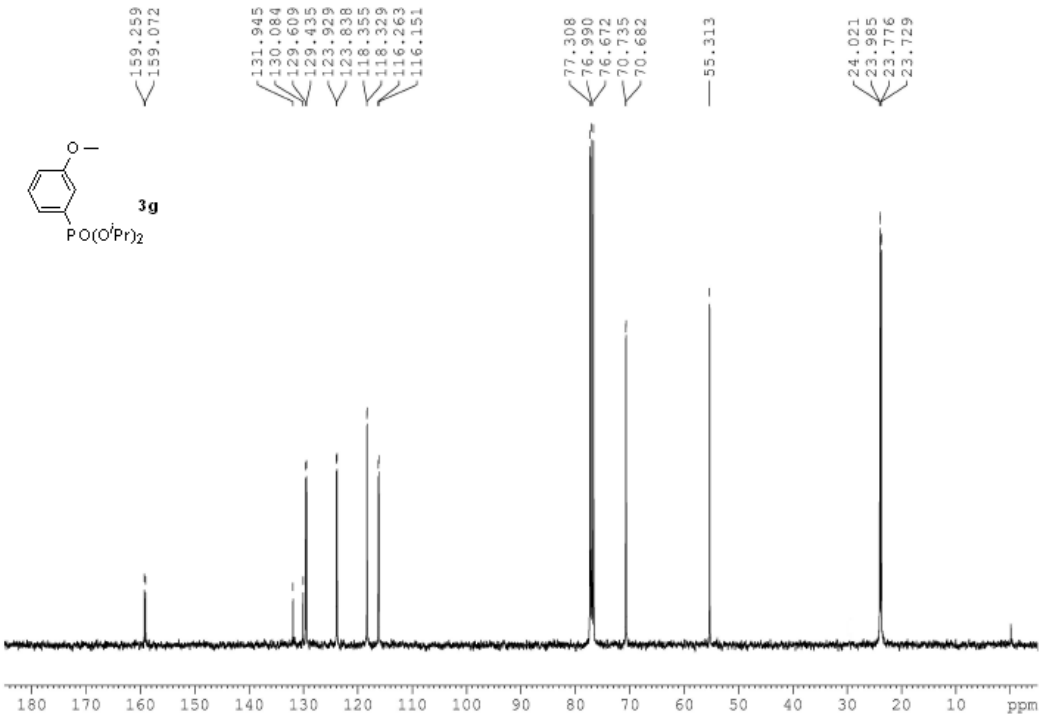

ppm
17.9269
PO(OiPr)2
NHAc
3e
ppm
120
100
80
60
40
20
0
-20
-40
-60
-80
-100

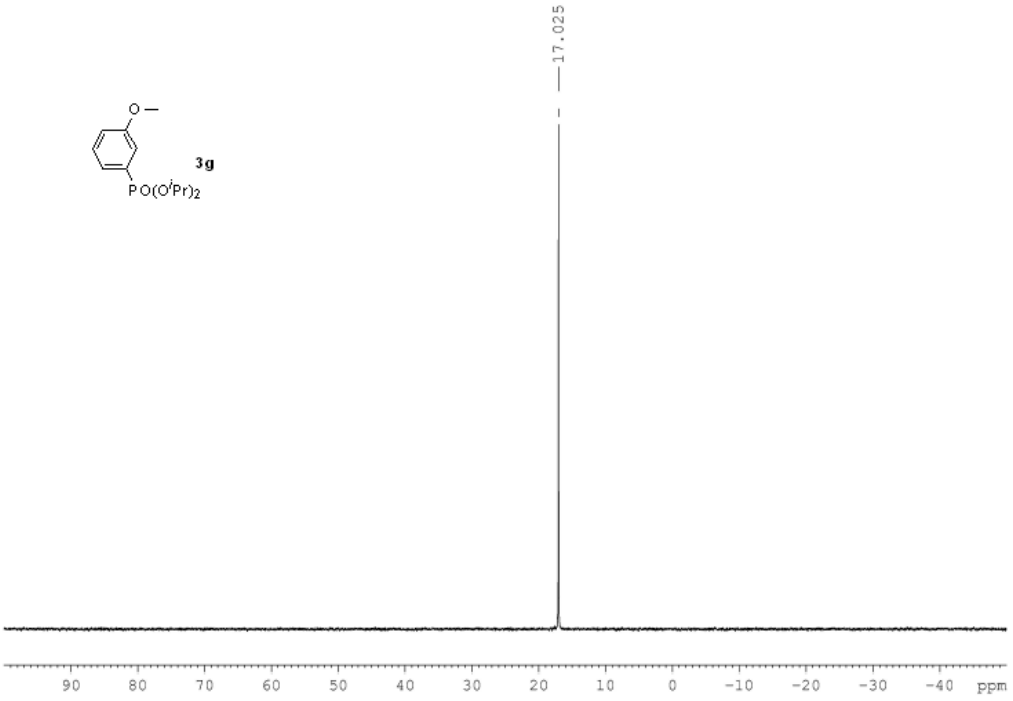

7.846
7.829
7.825
7.813
7.795
7.792
7.547
7.544
7.528
7.526
7.510
7.507
7.470
7.460
7.451
7.441
7.433
7.423
4.745
4.730
4.715
4.699
4.695
4.684
4.680
4.668
4.664
4.649
4.633
1.381
1.365
1.233
1.217
PO(OiPr)2
3f
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.996
1.006
2.004
2.000
6.260
6.257

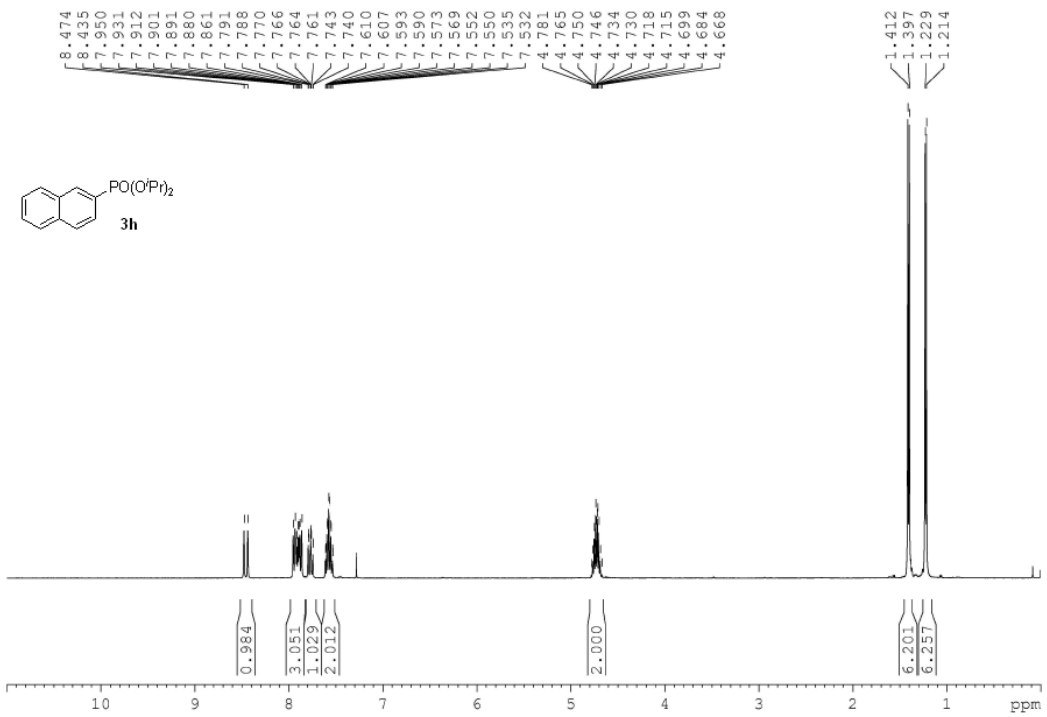


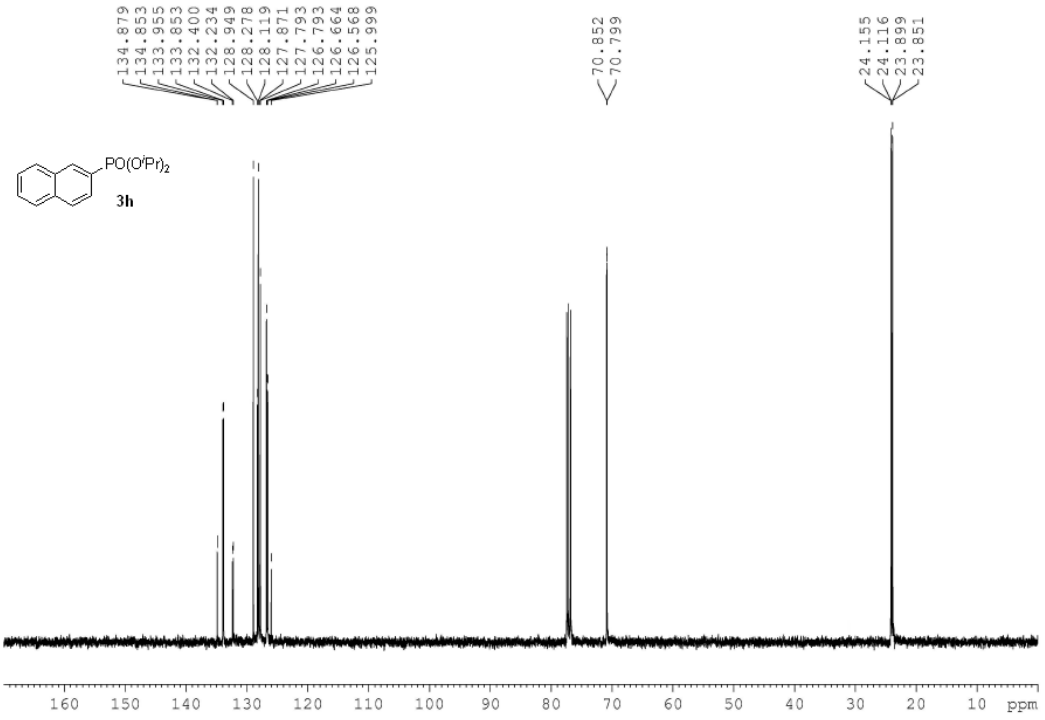


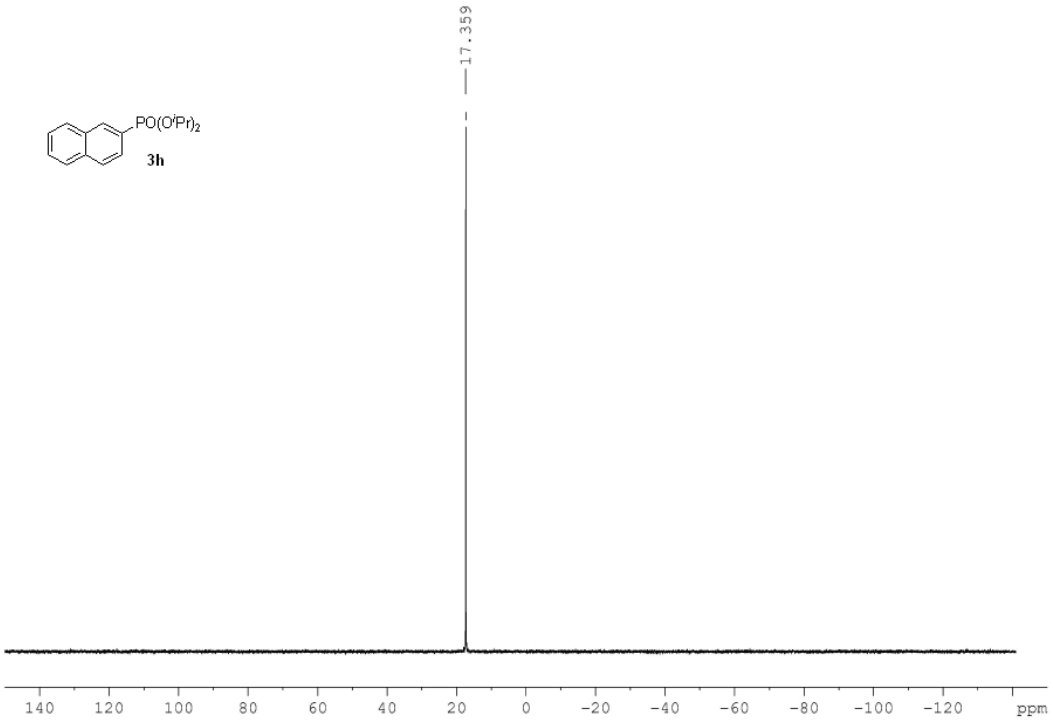

7.417
7.396
7.375
7.368
7.331
7.327
7.073
7.064
7.058
4.724
4.709
4.693
4.675
4.659
4.644
3.848
1.385
1.369
1.242
1.227
3g
PO(O^{i}Pr)$_2$
ppm
3.006
0.983
2.300
3.074
6.324
6.380

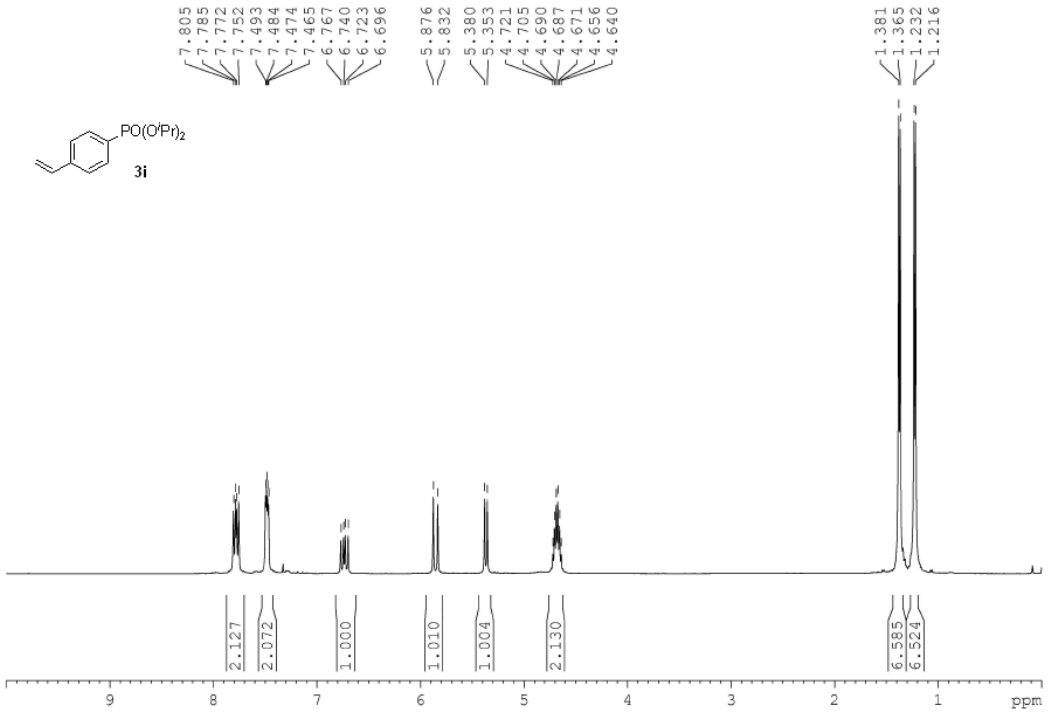

159.259
159.072
131.945
130.084
129.609
129.435
123.929
123.838
118.355
118.329
116.263
116.151
77.308
76.990
76.672
70.735
70.682
55.313
24.021
23.985
23.776
23.729
3g
PO(O^{i}Pr)$_2$
ppm

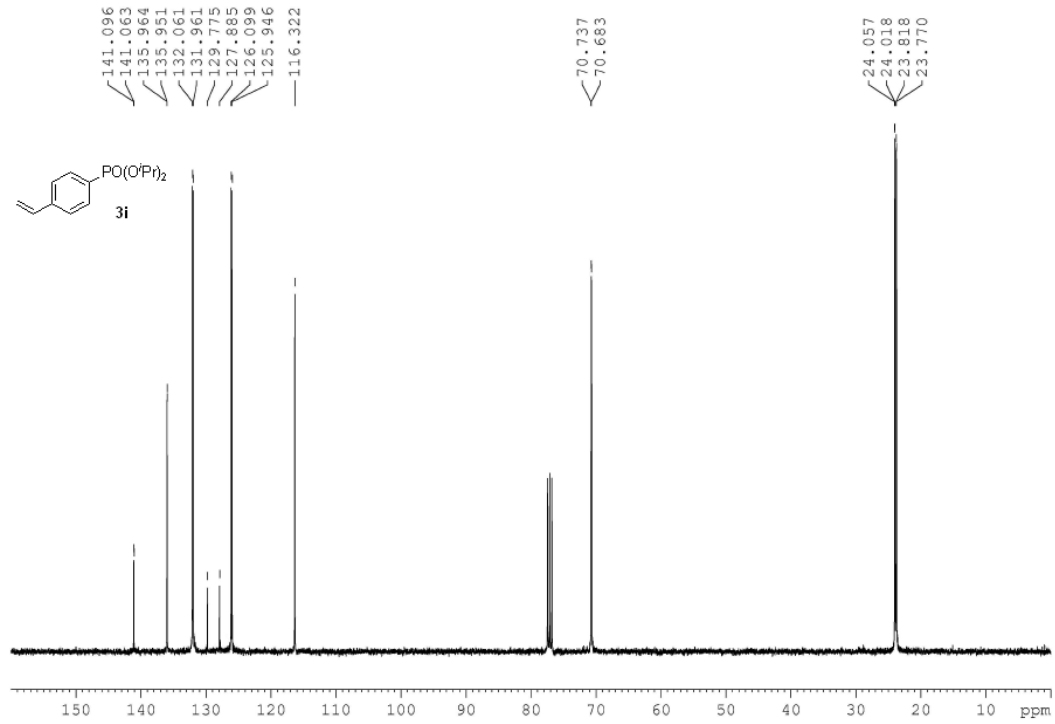


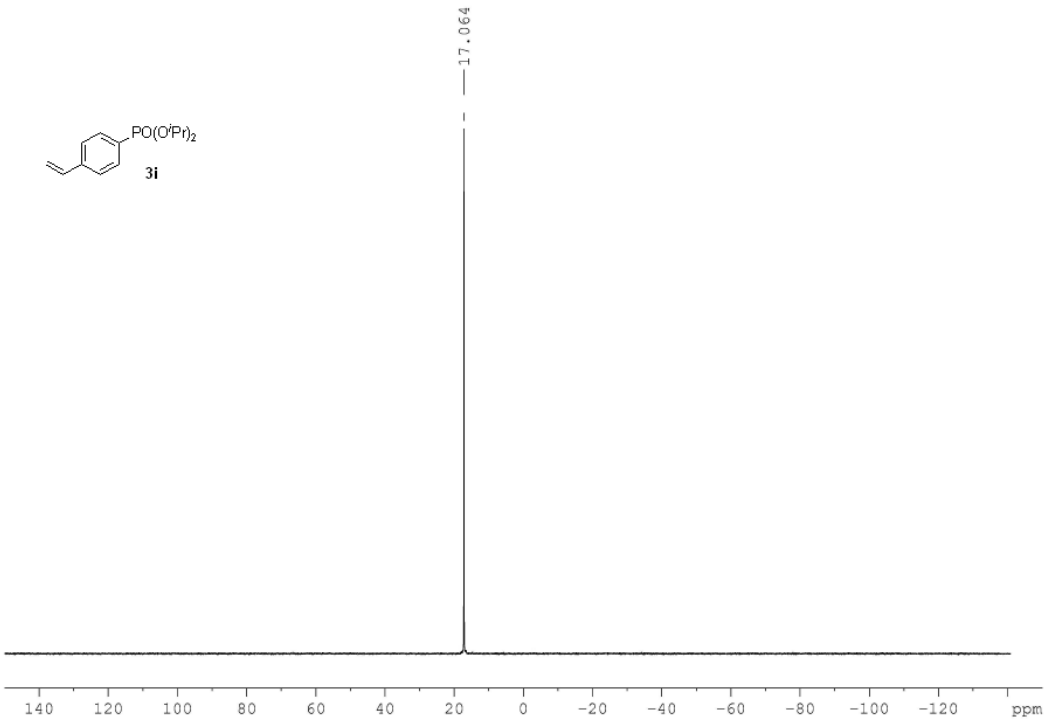


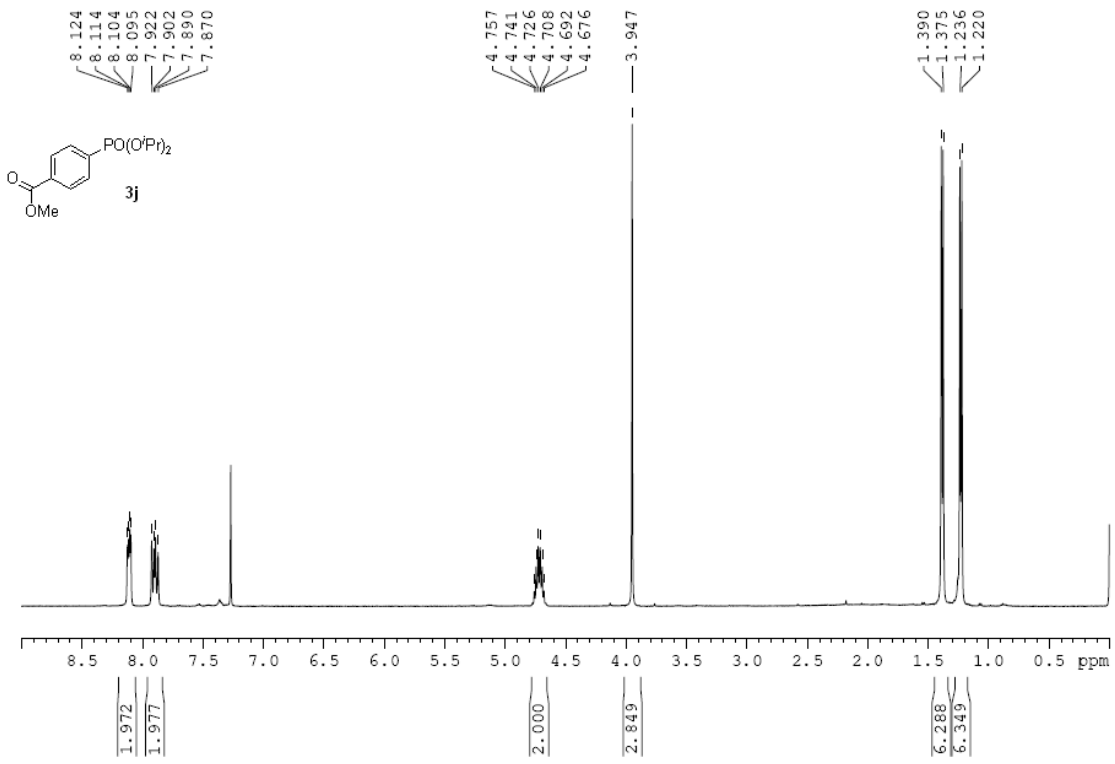


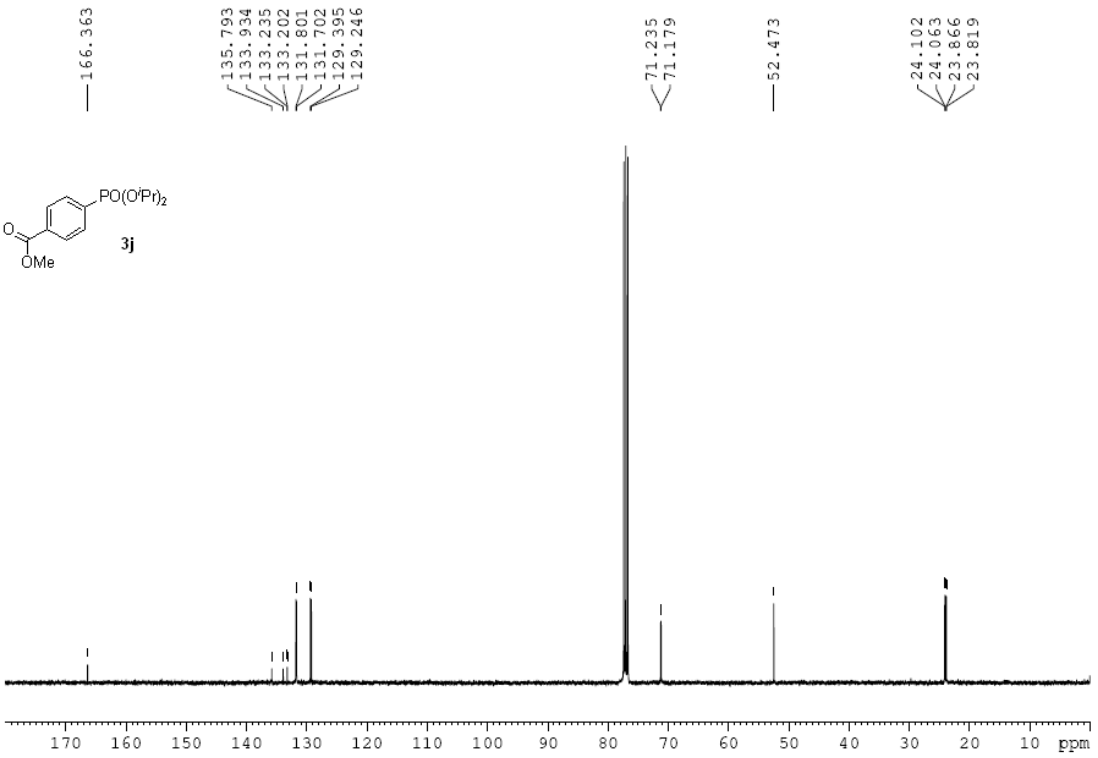


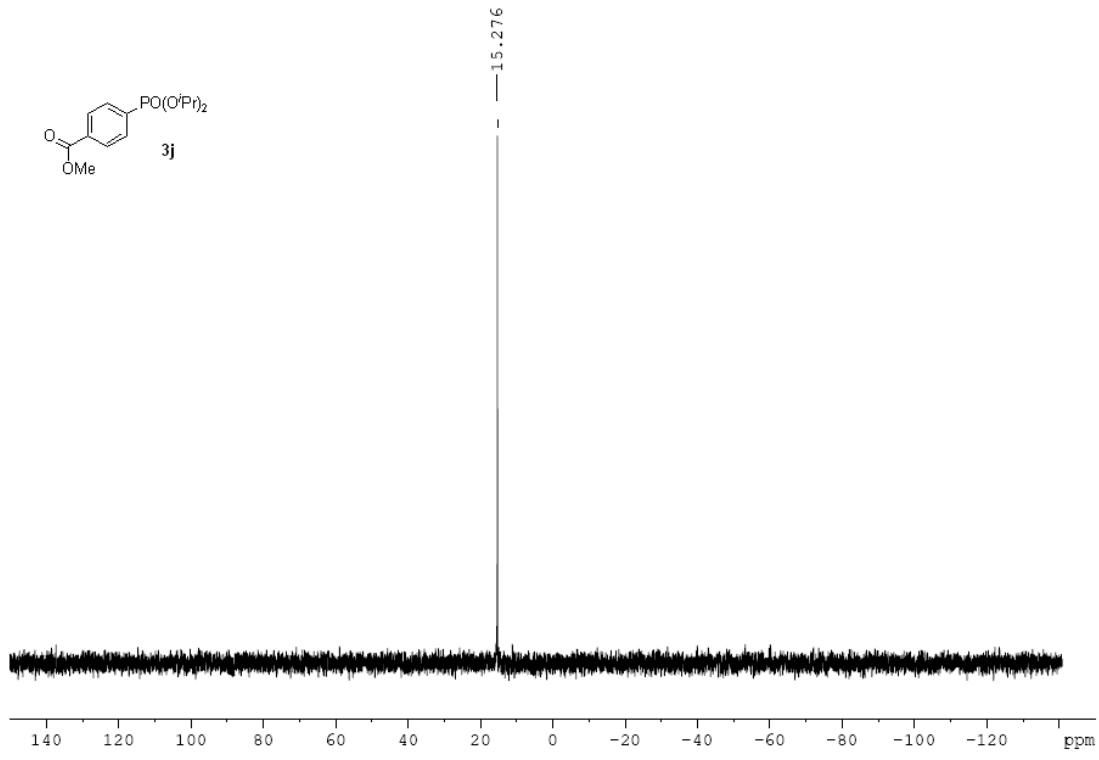


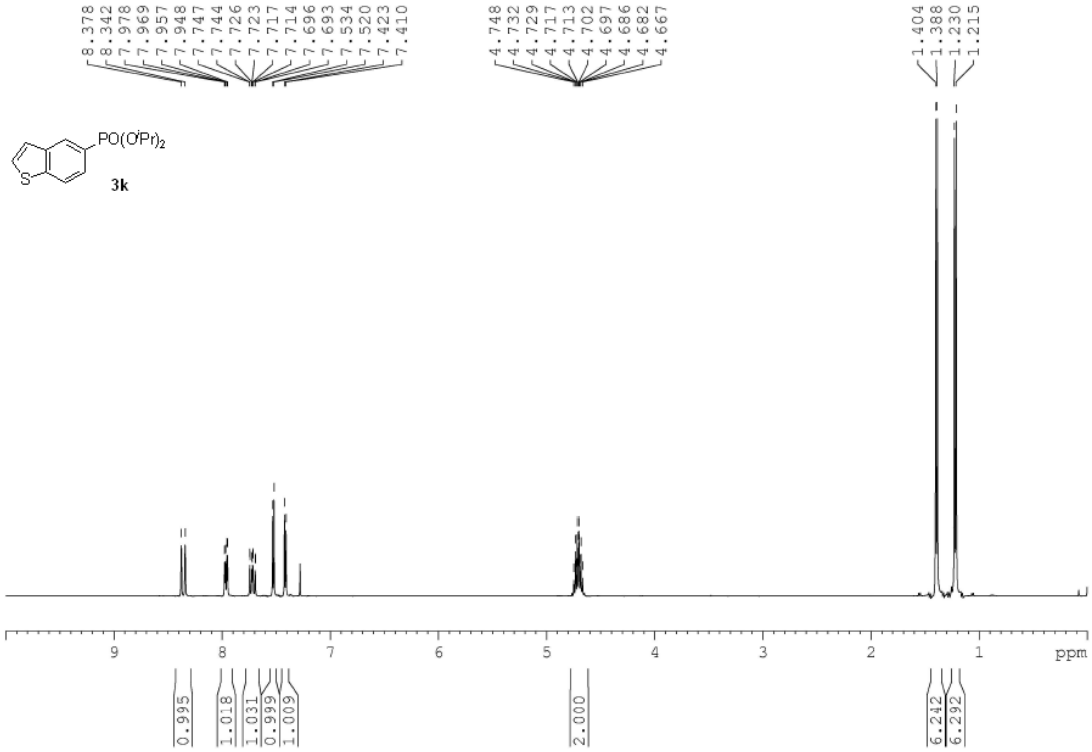


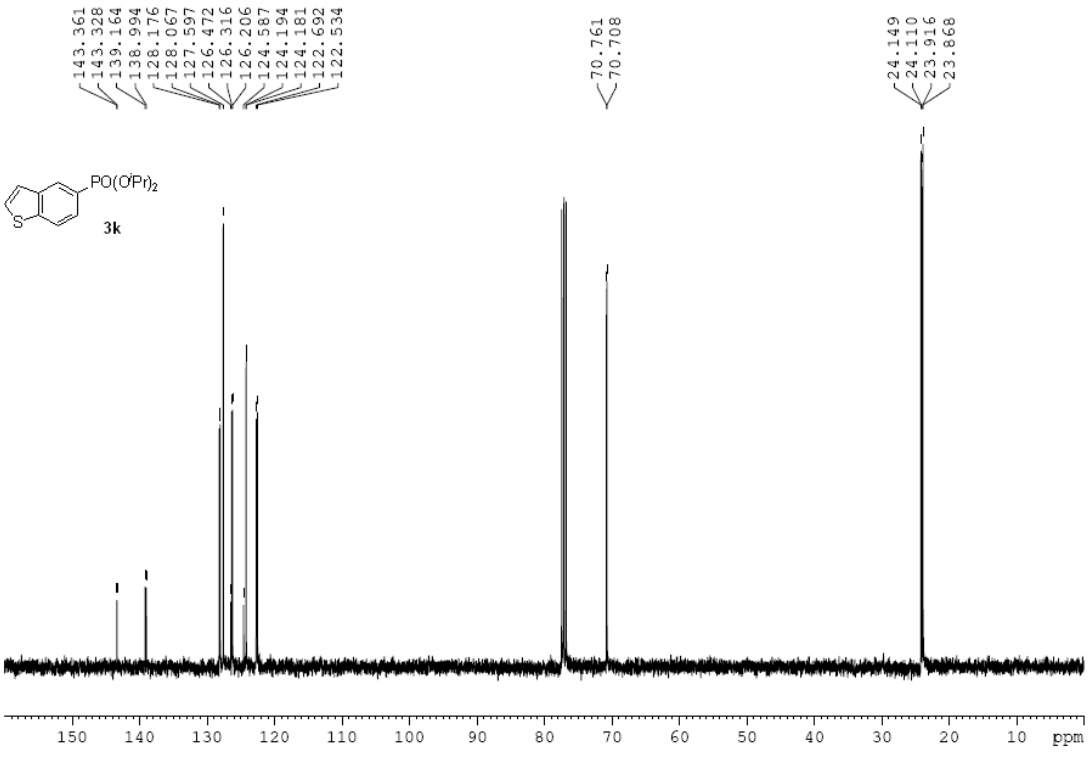


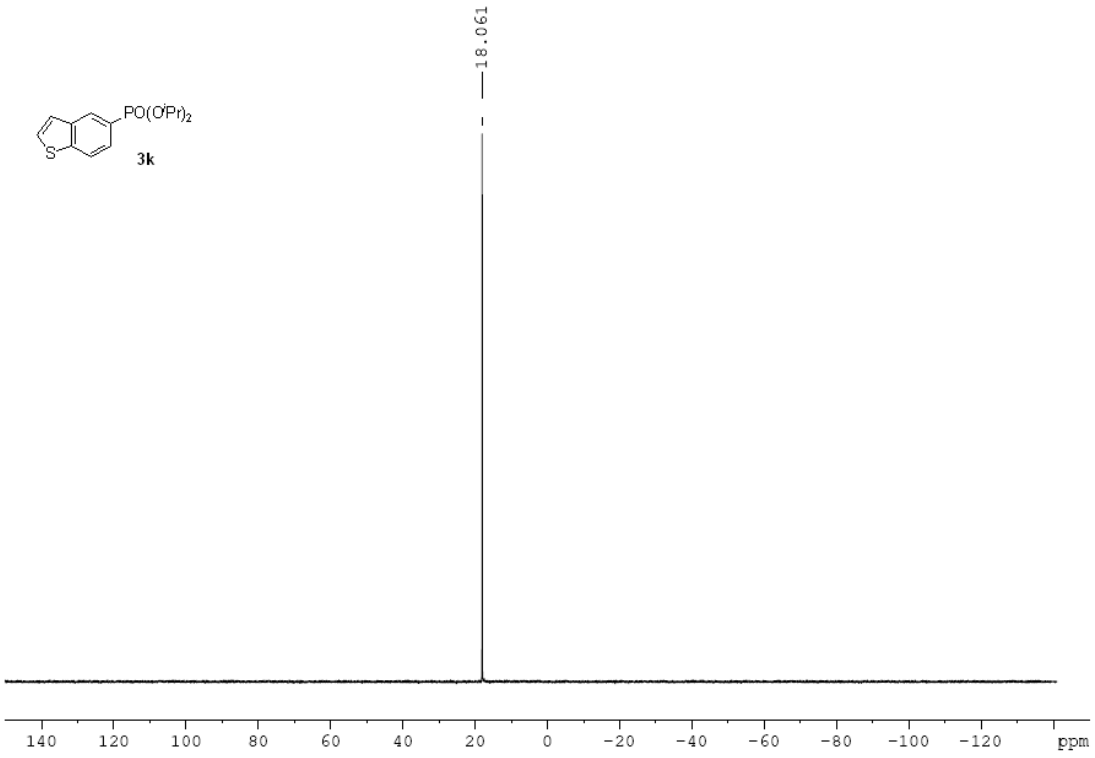


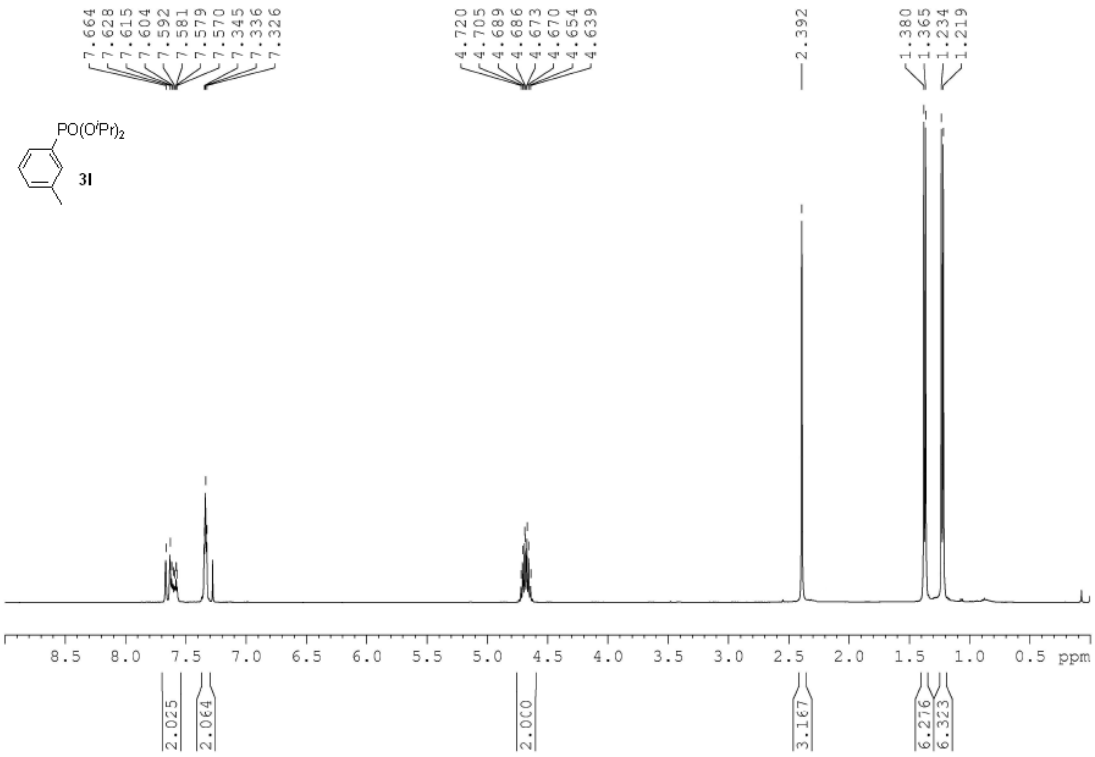


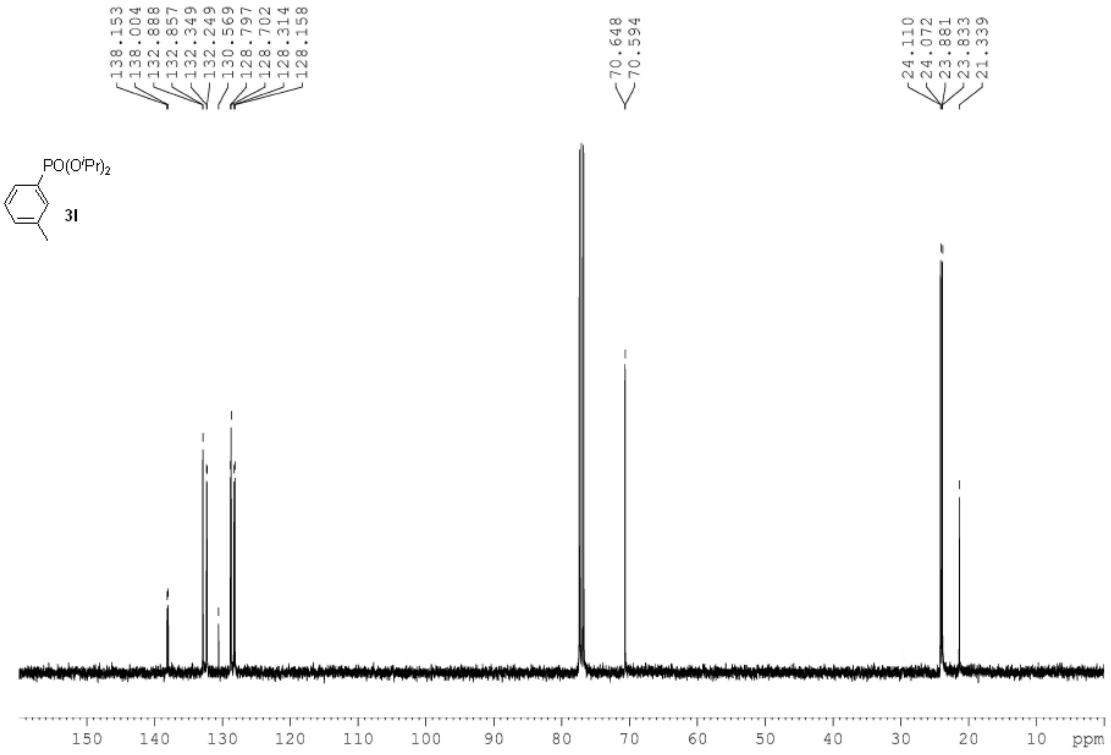


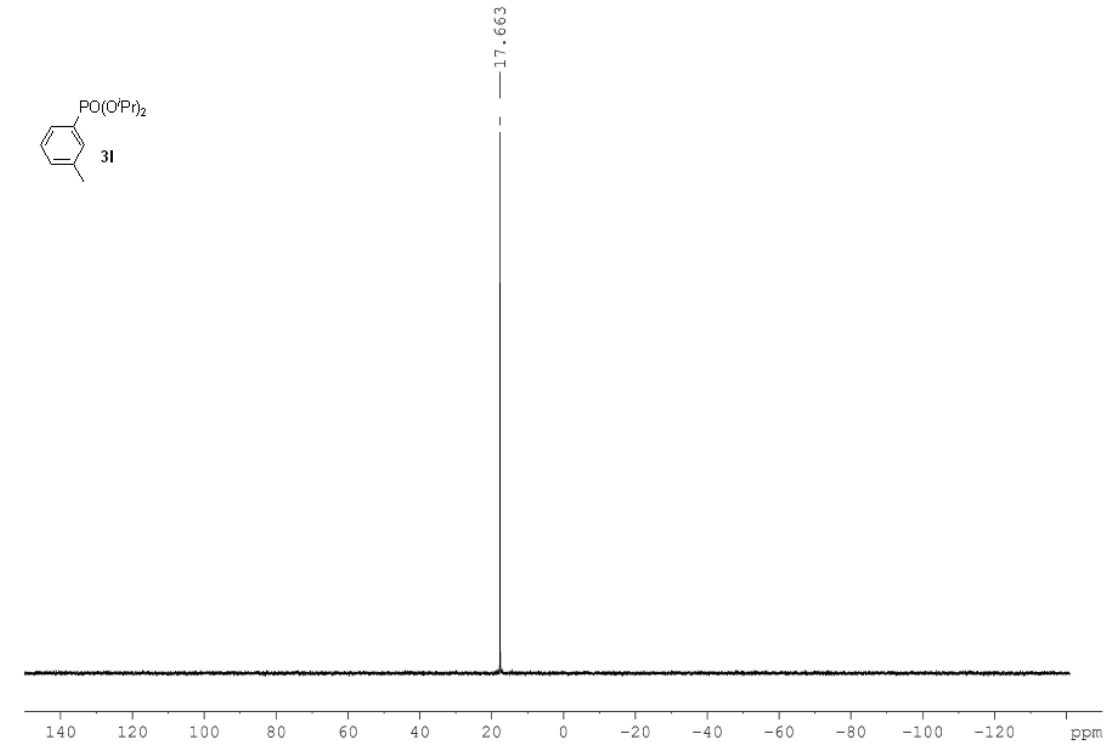


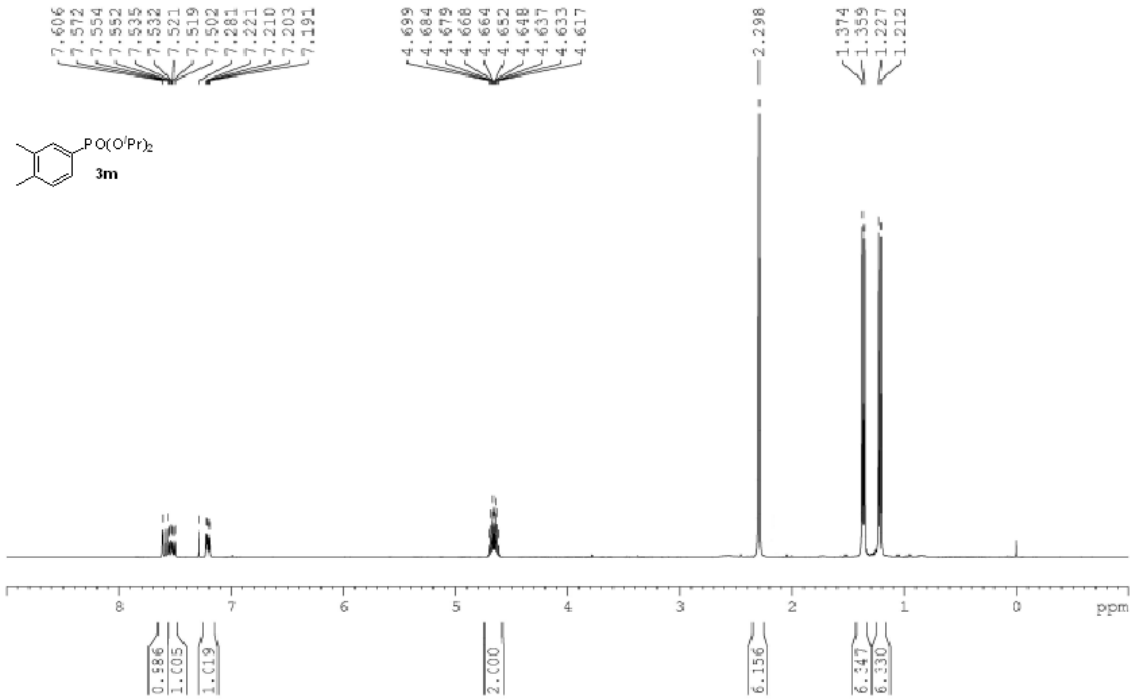


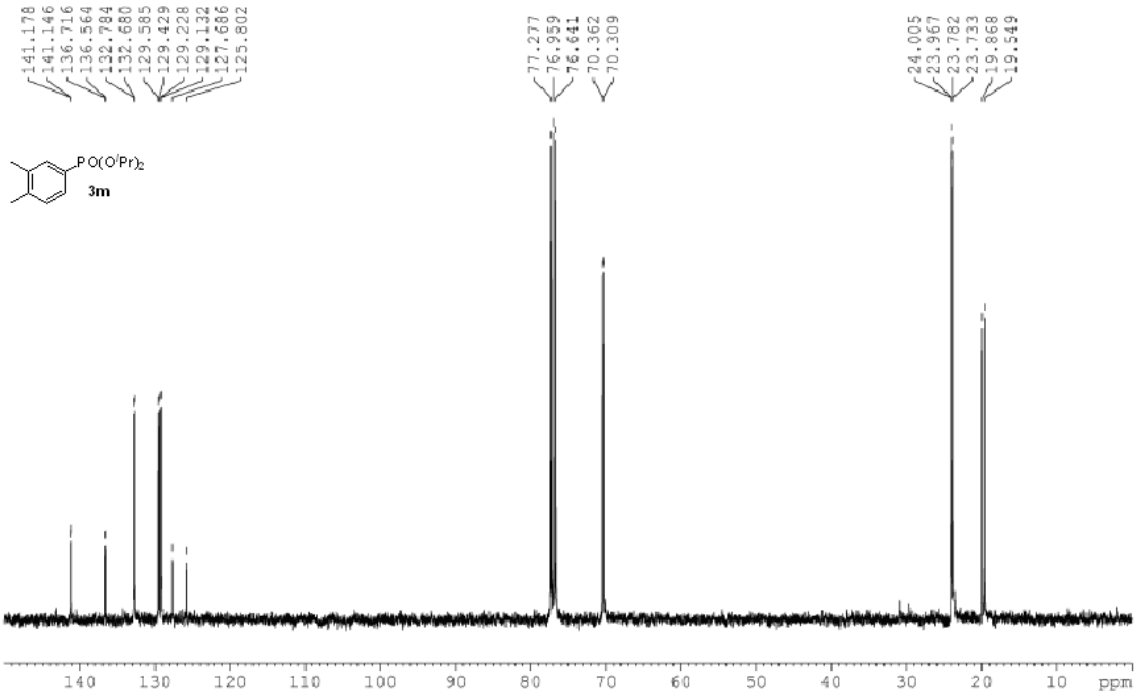


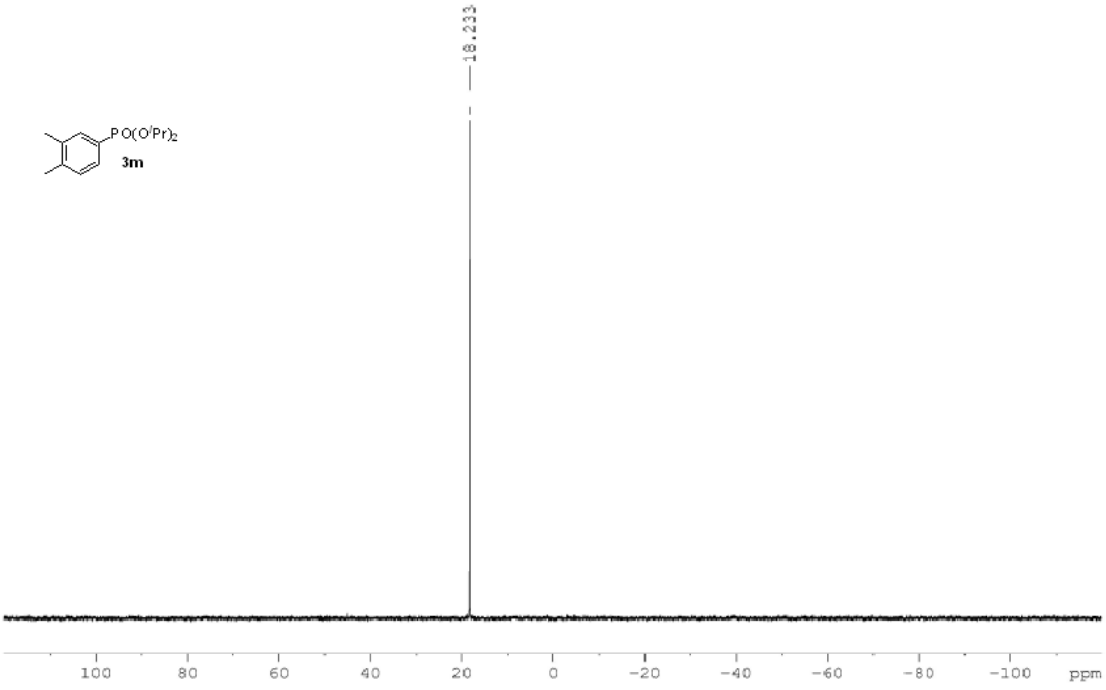


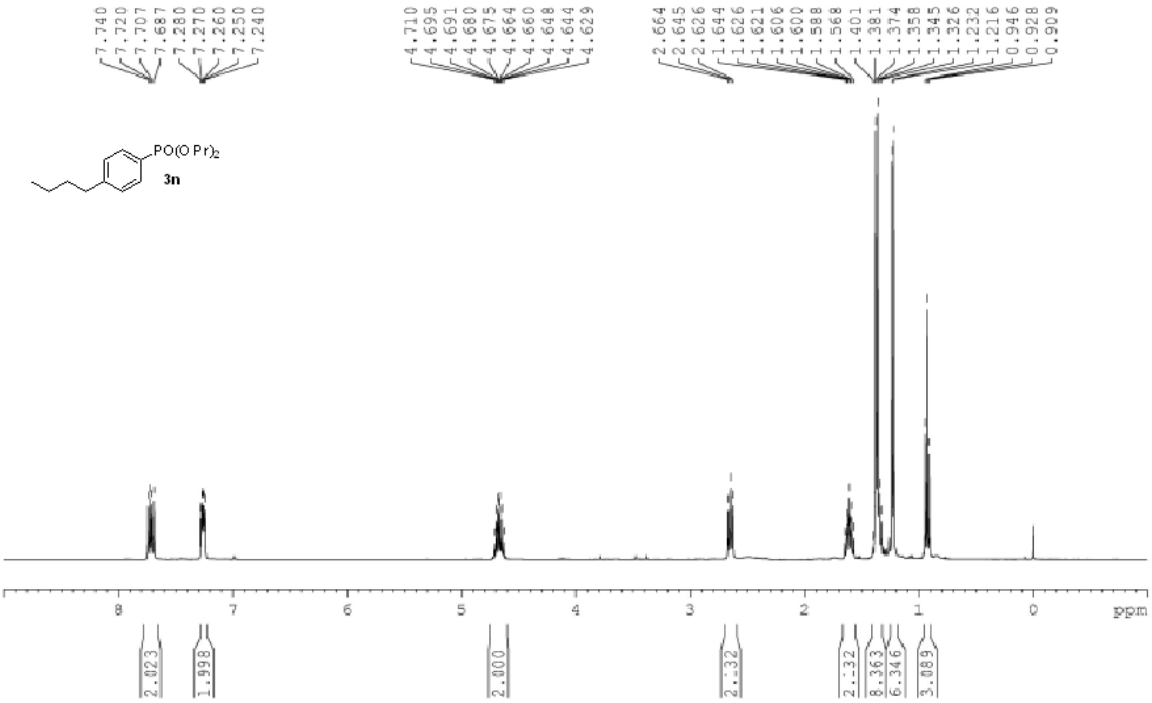

138.153
138.004
132.888
132.857
132.349
132.249
130.569
128.797
128.702
128.314
128.158
70.648
70.594
24.110
24.072
23.881
23.833
21.339
PO(O^{i}Pr)$_2$
3l
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

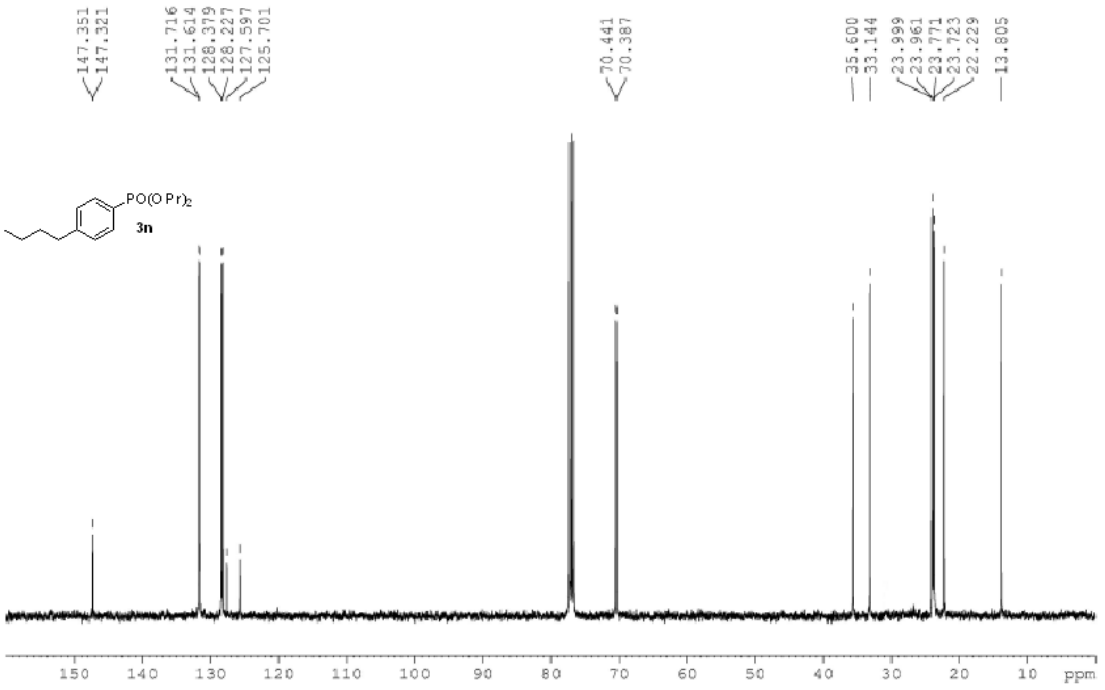

17.663
PO(O^{i}Pr)$_2$
3l
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

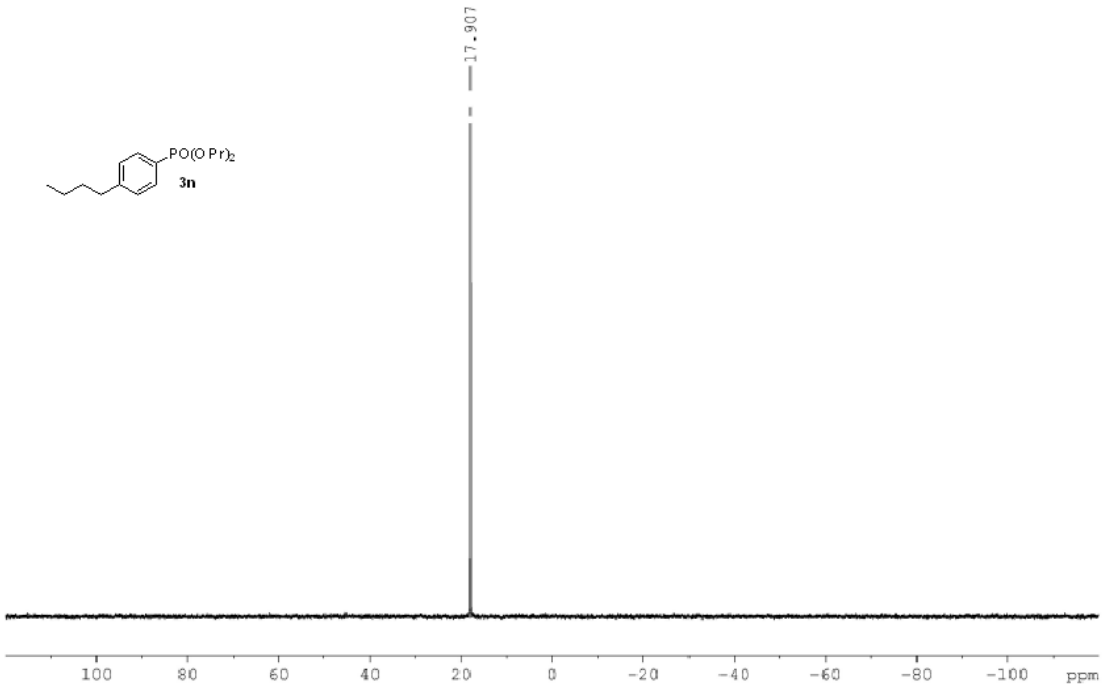

7.606
7.572
7.554
7.552
7.535
7.532
7.521
7.519
7.502
7.281
7.221
7.210
7.203
7.191
4.699
4.684
4.679
4.668
4.664
4.652
4.648
4.637
4.633
4.617
2.298
1.374
1.359
1.227
1.212
P O(O^{i}Pr)$_2$
3m
ppm
0.586
1.605
1.619
2.000
6.156
6.347
6.330

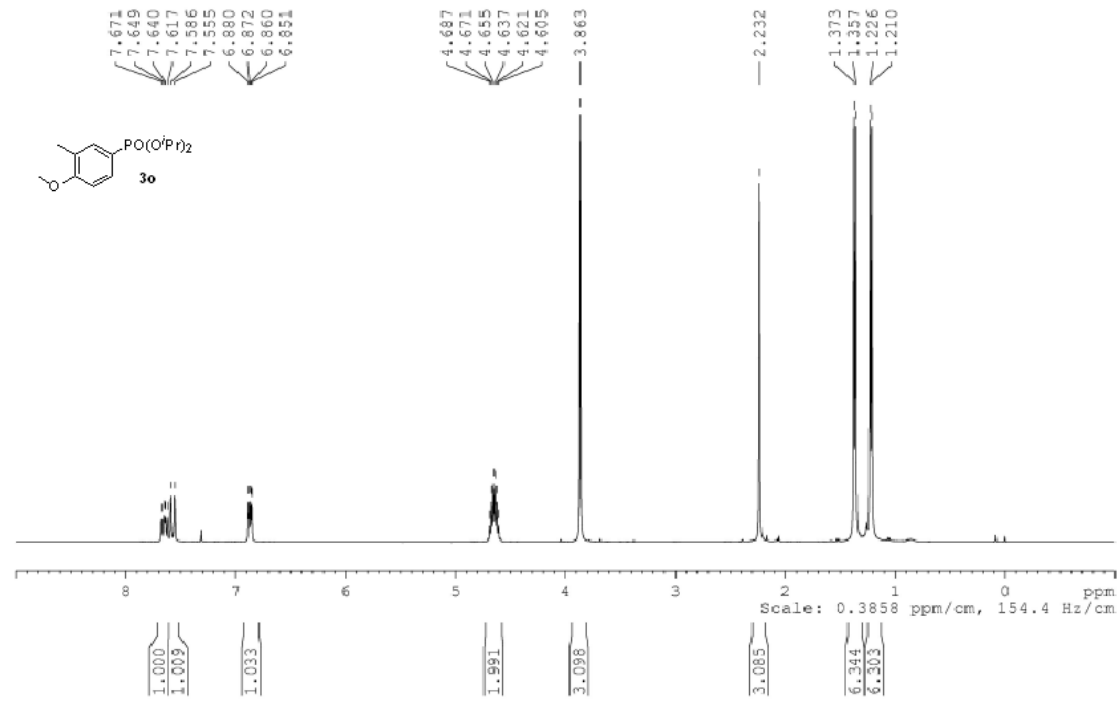

141.178
141.146
136.716
136.564
132.784
132.680
129.585
129.429
129.228
129.132
127.686
125.802
77.277
76.959
76.641
70.362
70.309
24.005
23.967
23.782
23.733
19.868
19.549
P O(O^{i}Pr)$_2$
3m
ppm

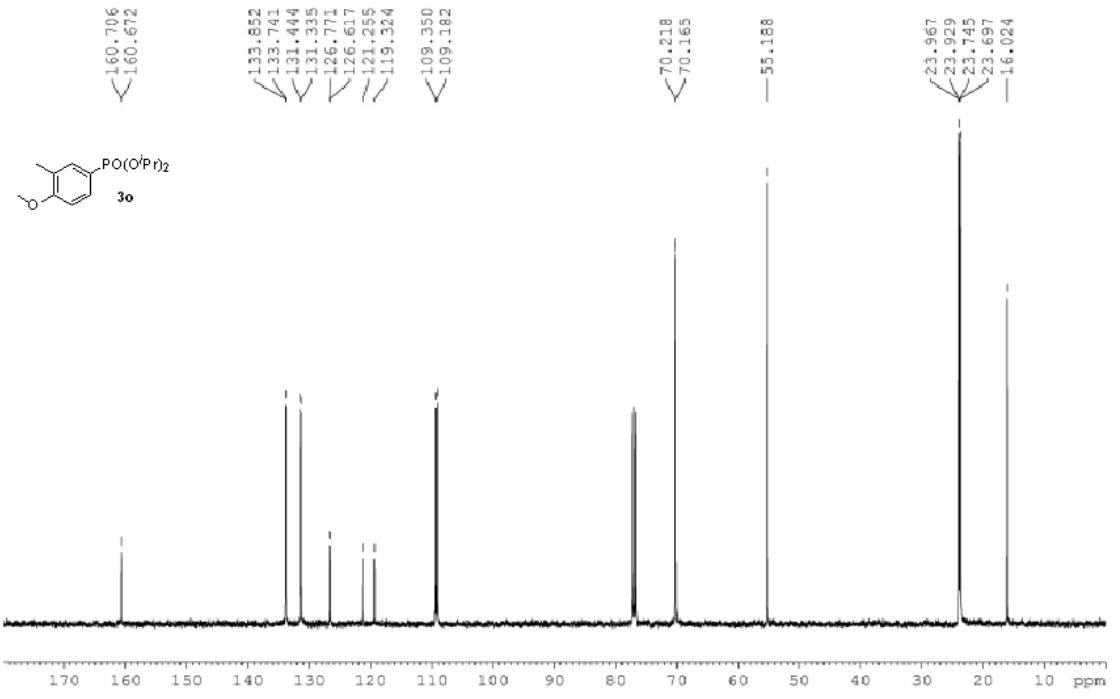

18.233
PO(O^{i}Pr)$_2$
3m
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

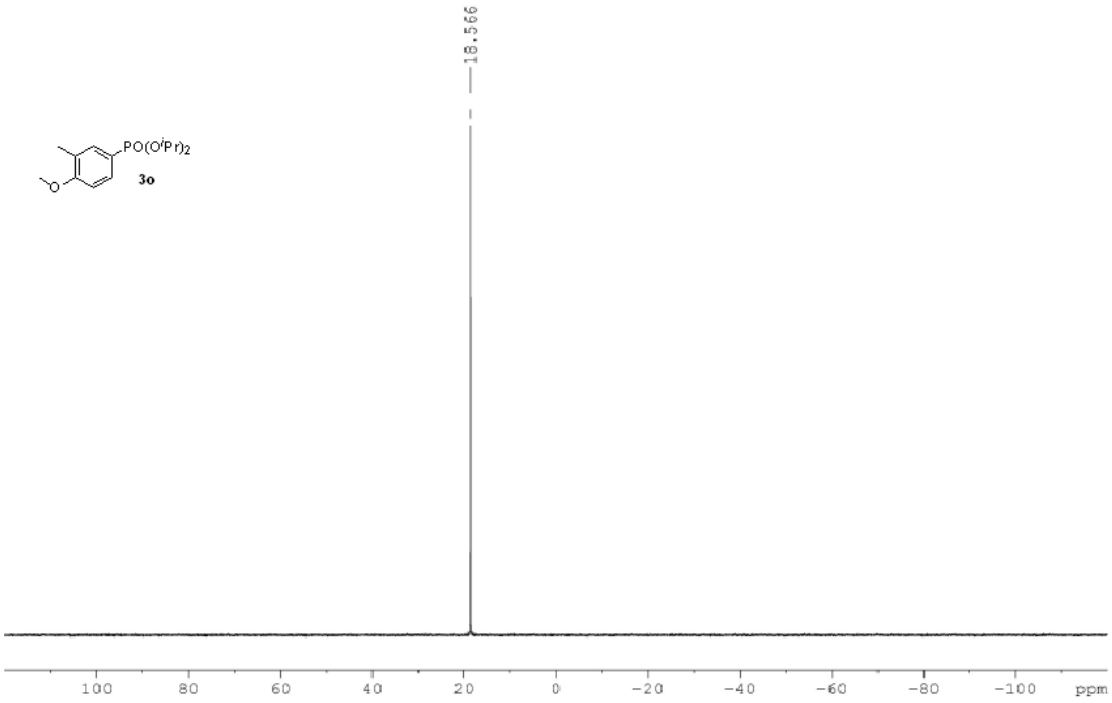

7.740
7.720
7.707
7.687
7.280
7.270
7.260
7.250
7.240
4.710
4.695
4.691
4.680
4.675
4.664
4.660
4.648
4.644
4.629
2.664
2.645
2.626
1.644
1.626
1.621
1.606
1.600
1.588
1.568
1.401
1.381
1.374
1.358
1.345
1.326
1.232
1.216
0.946
0.928
0.909
PO(O Pr)$_2$
3n
8
7
6
5
4
3
2
1
0
ppm
2.023
1.998
2.000
2.332
2.332
8.363
6.346
3.089

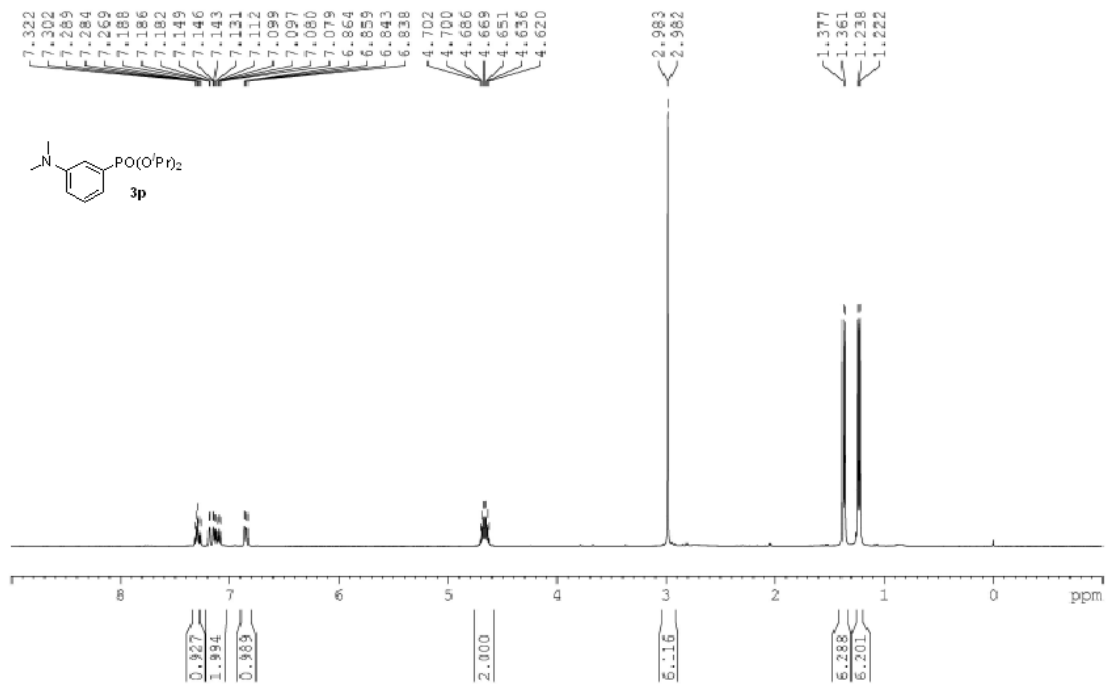


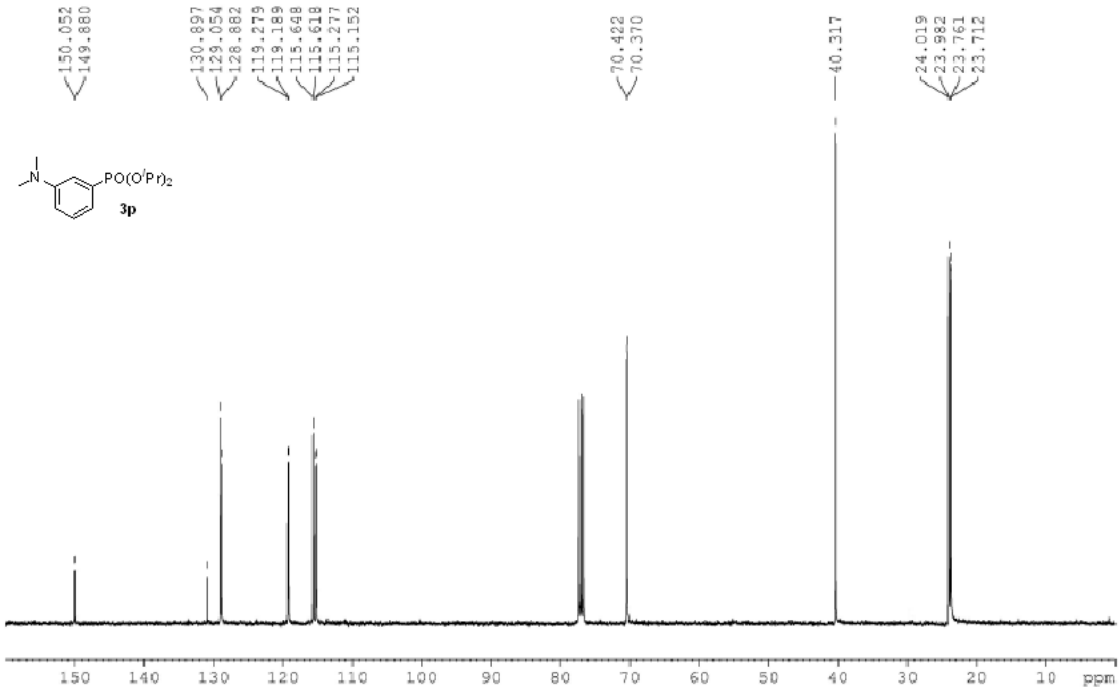


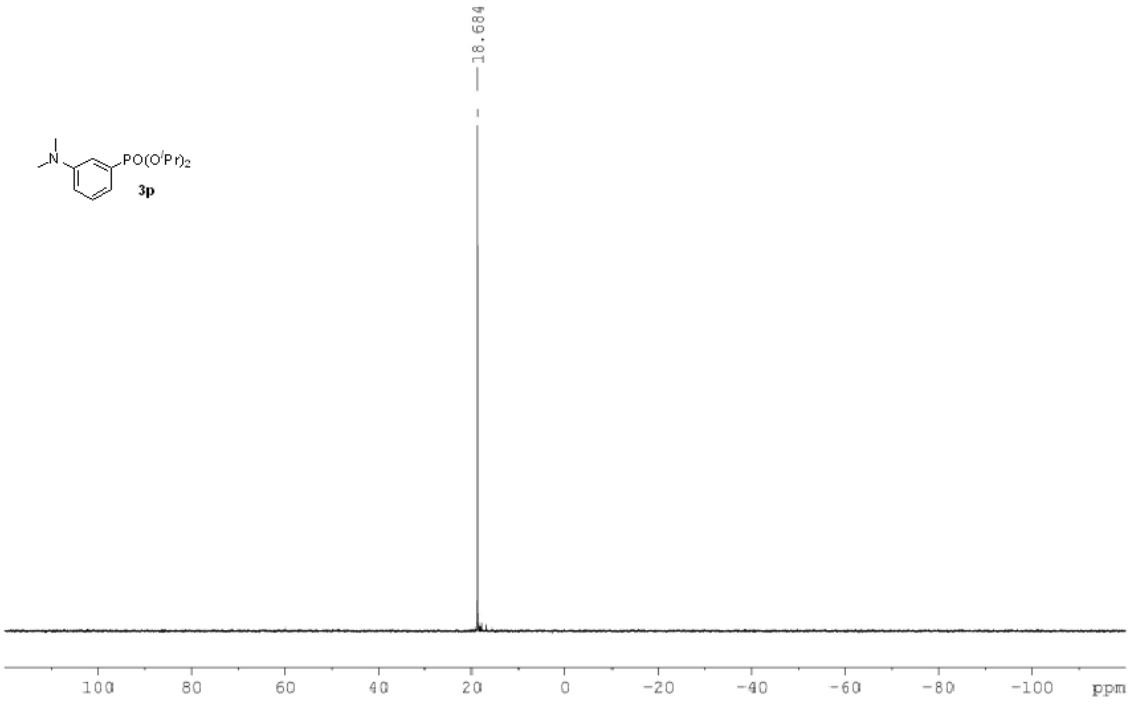

7.671
7.649
7.640
7.617
7.586
7.555
6.880
6.872
6.860
6.851
4.687
4.671
4.655
4.637
4.621
4.605
3.863
2.232
1.373
1.357
1.226
1.210
PO(OiPr)2
3o
8
7
6
5
4
3
2
1
0
ppm
Scale: 0.3858 ppm/cm, 154.4 Hz/cm
1.000
1.009
1.033
1.991
3.098
3.085
6.344
6.303

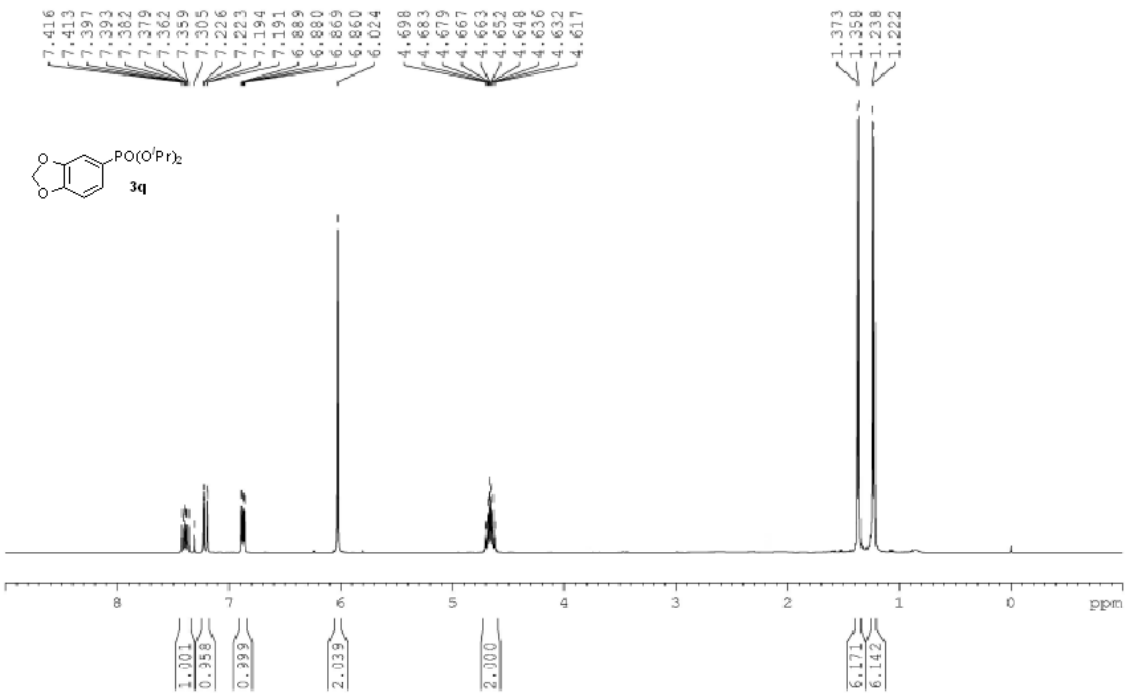

160.706
160.672
133.852
133.741
131.444
131.335
126.771
126.617
121.255
119.324
109.350
109.182
70.218
70.165
55.188
23.967
23.929
23.745
23.697
16.024
PO(OiPr)2
3o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

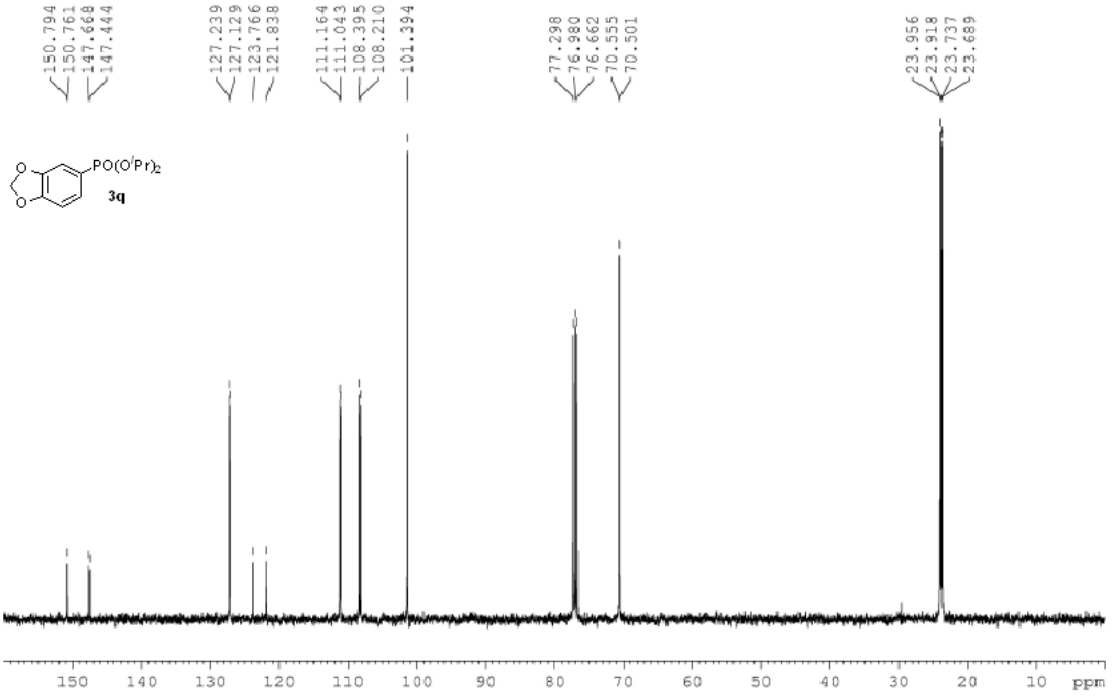


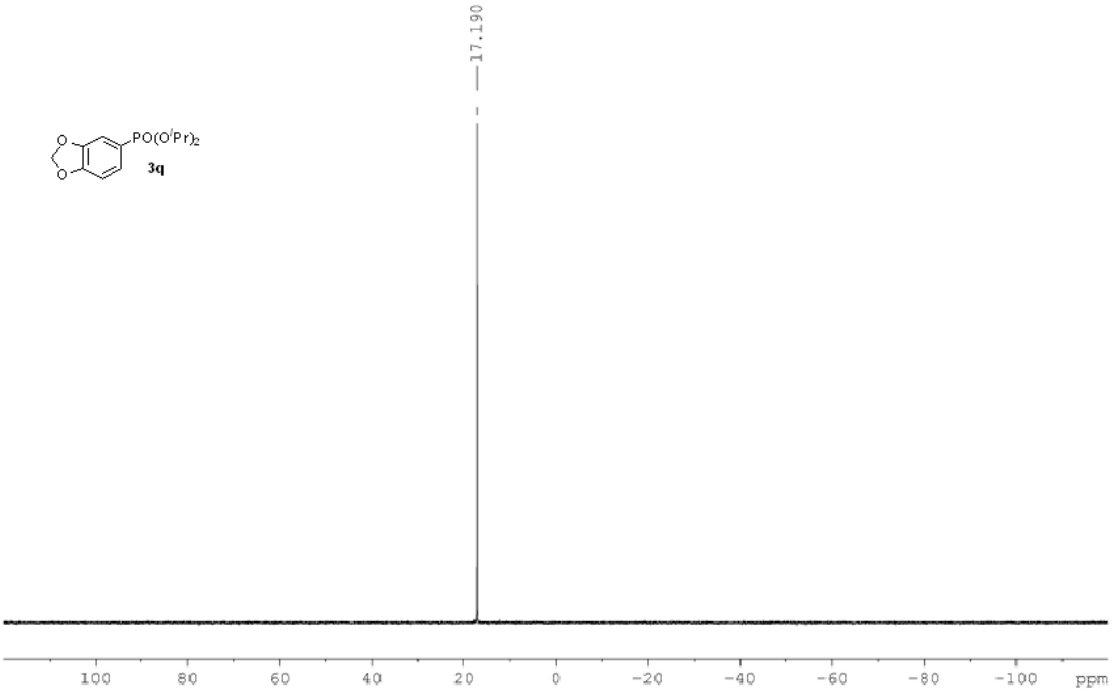


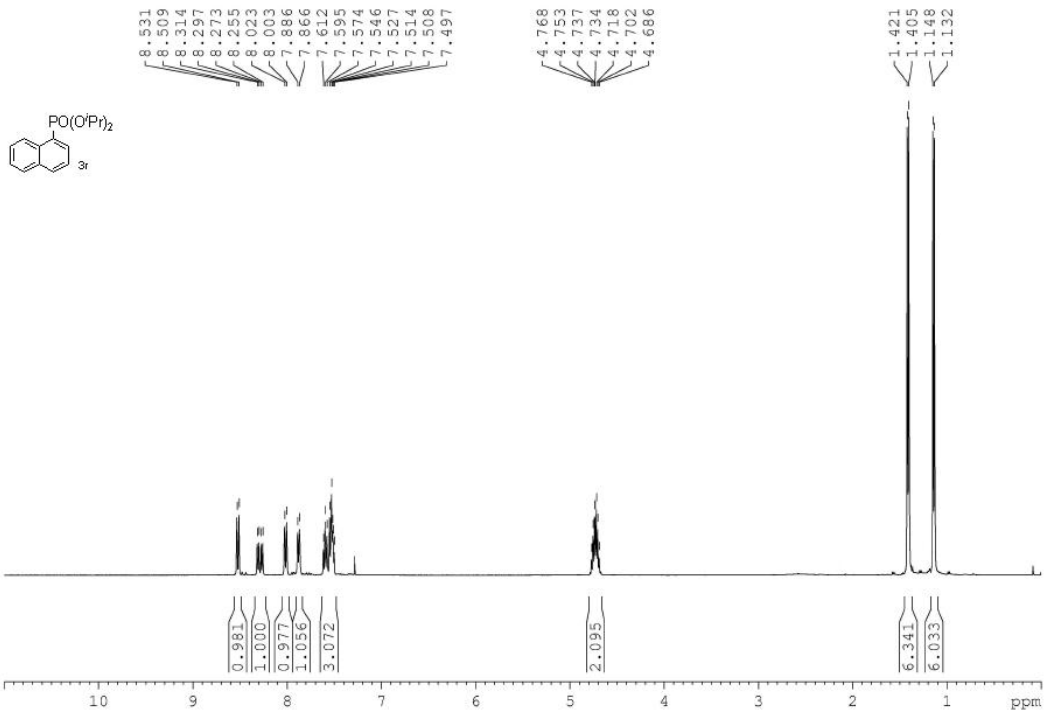

150.052
149.880
130.897
129.054
128.882
119.279
119.189
115.648
115.618
115.277
115.152
70.422
70.370
40.317
24.019
23.982
23.761
23.712
PO(O^{i}Pr)$_2$
3p
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

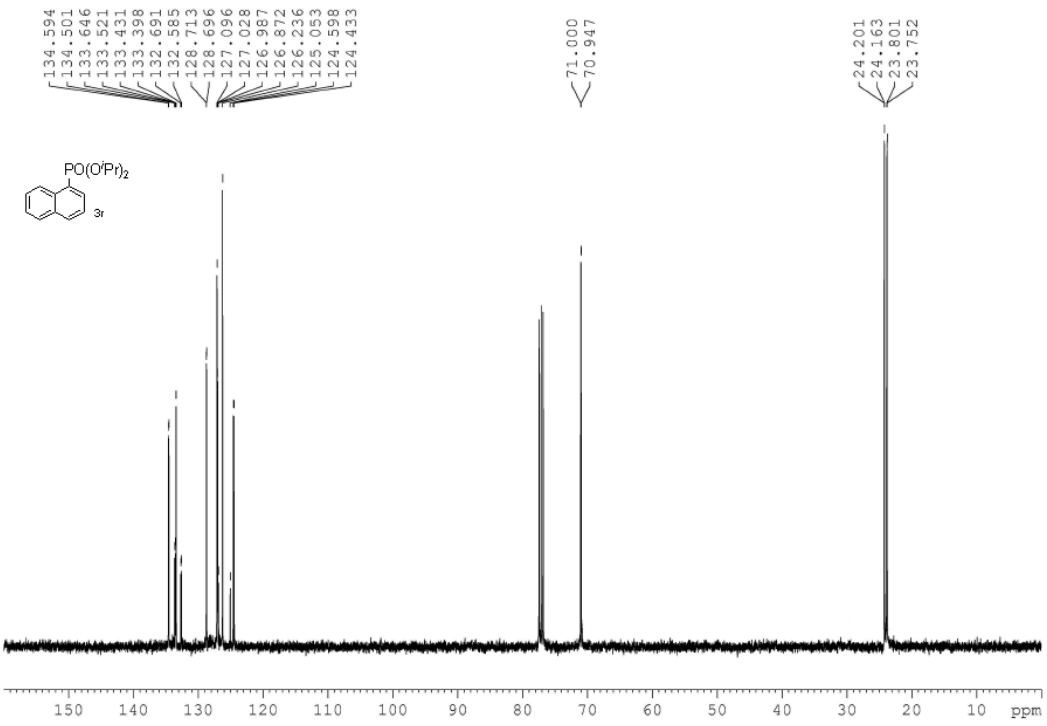

18.684
PO(O^{i}Pr)$_2$
3p
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

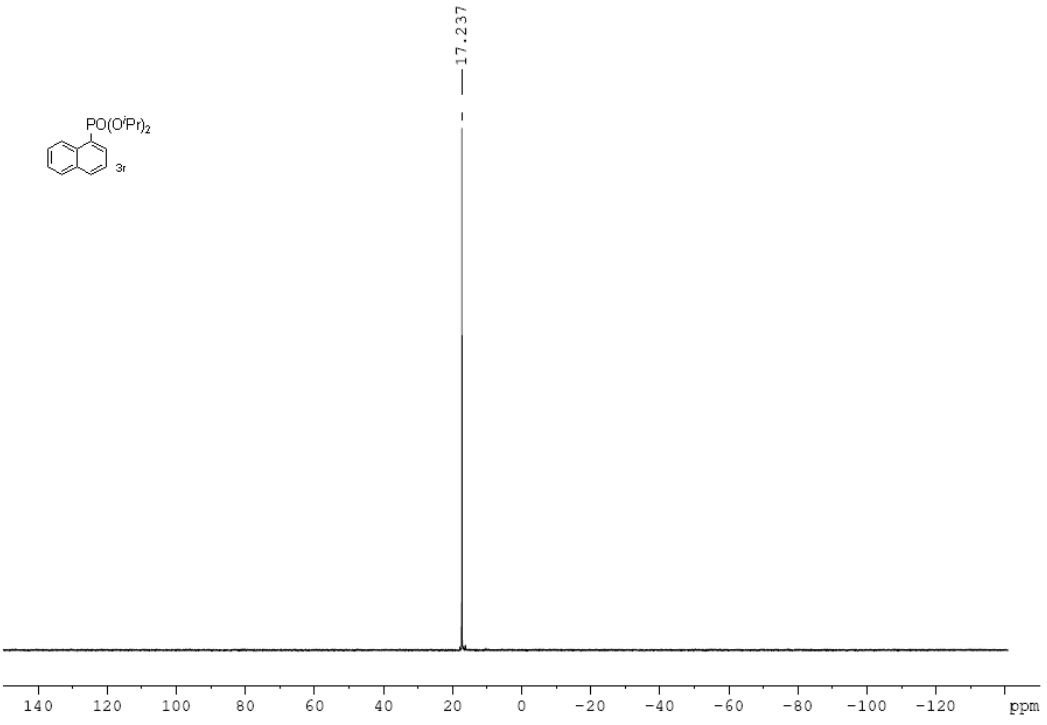


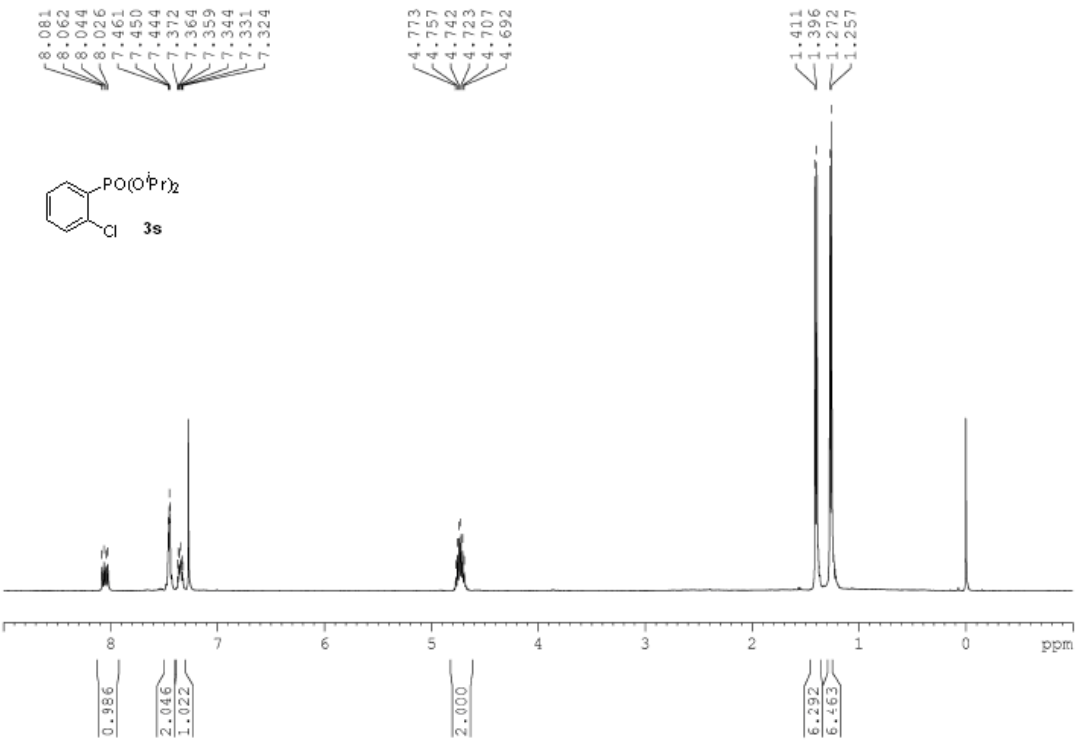


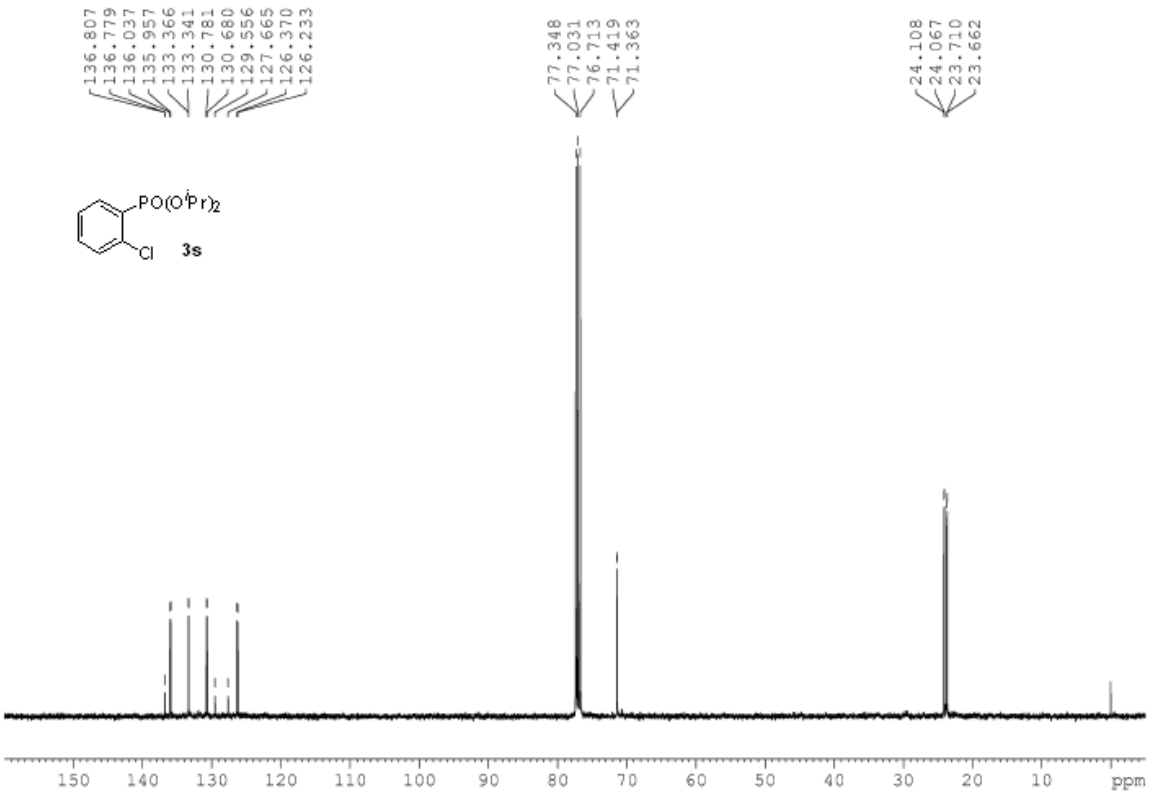

PO(O^{i}Pr)$_2$
3q
17.190
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

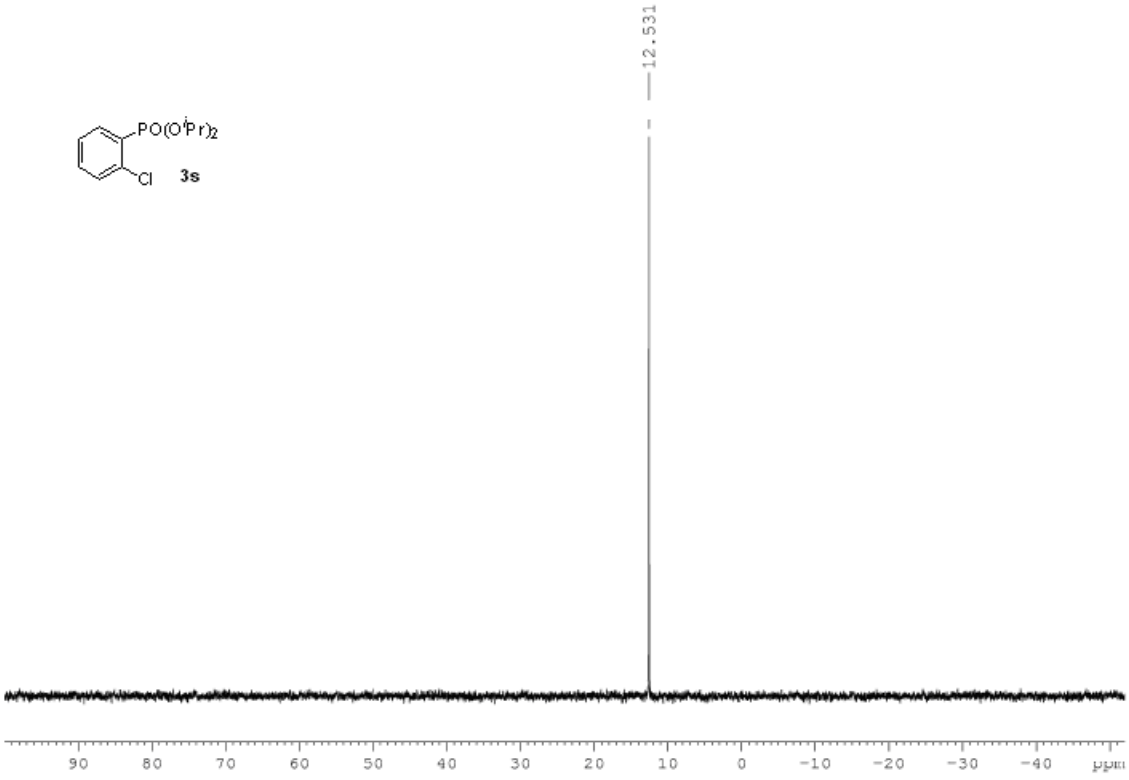

8.531
8.509
8.314
8.297
8.273
8.255
8.023
8.003
7.886
7.866
7.612
7.595
7.574
7.546
7.527
7.514
7.508
7.497
4.768
4.753
4.737
4.734
4.718
4.702
4.686
1.421
1.405
1.148
1.132
PO(O^{i}Pr)$_2$
0.981
1.000
0.977
1.056
3.072
2.095
6.341
6.033
10
9
8
7
6
5
4
3
2
1
ppm

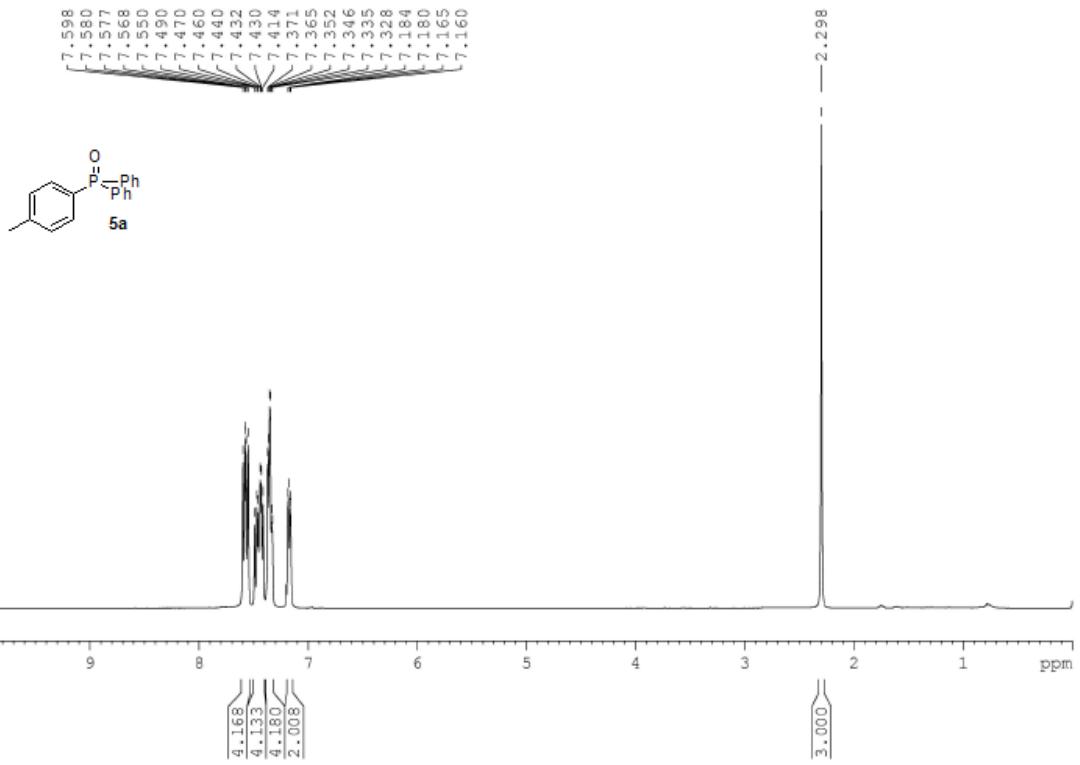


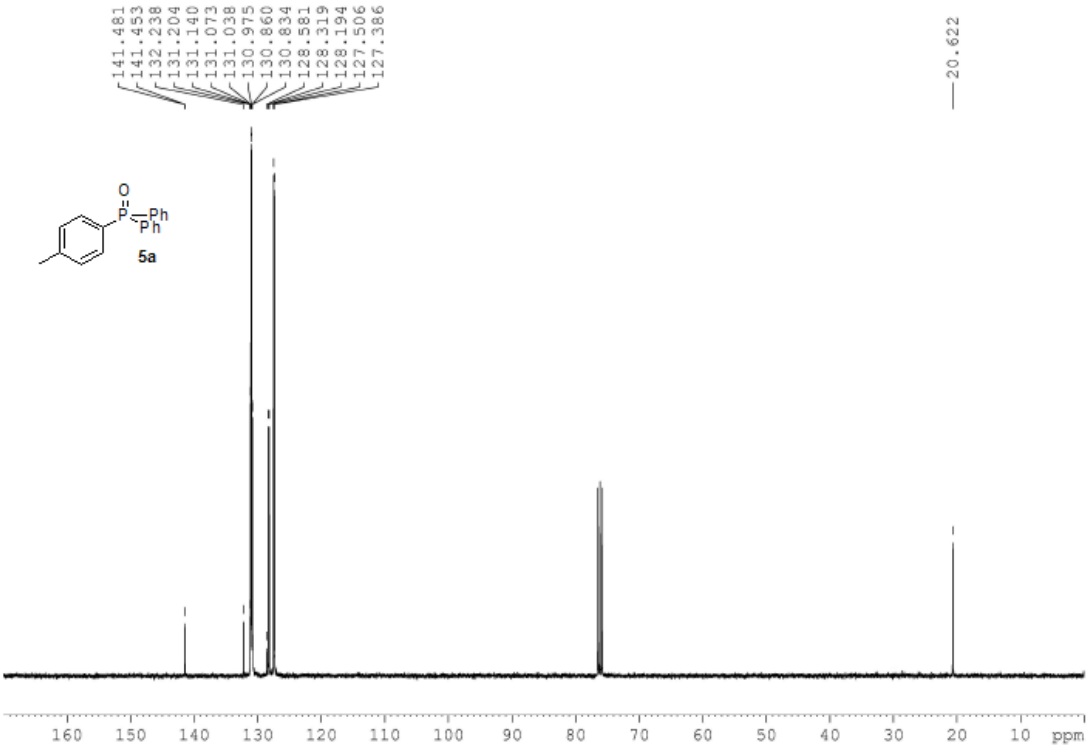


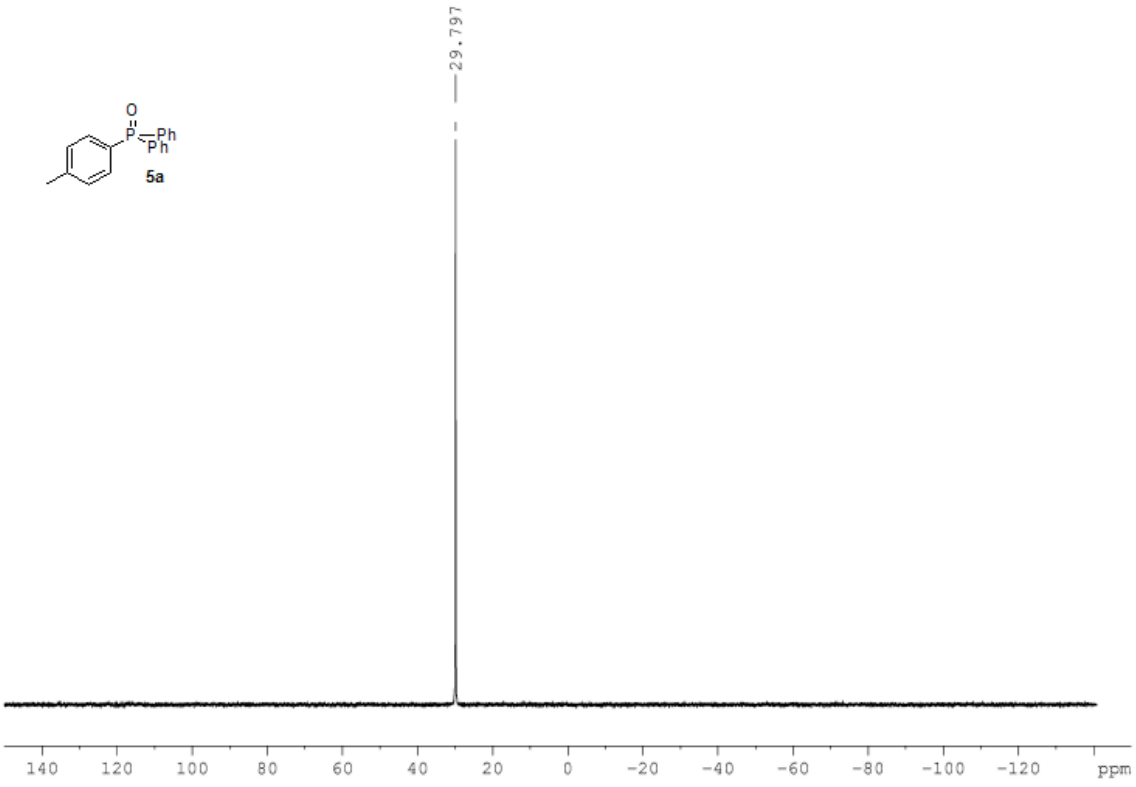


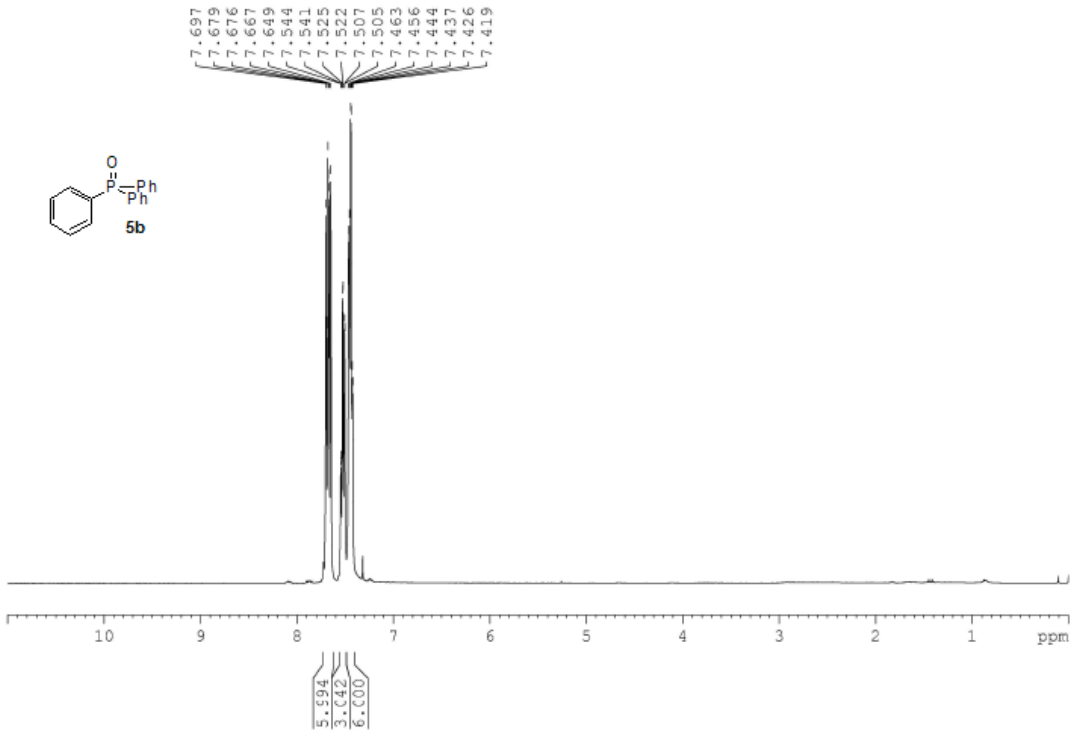


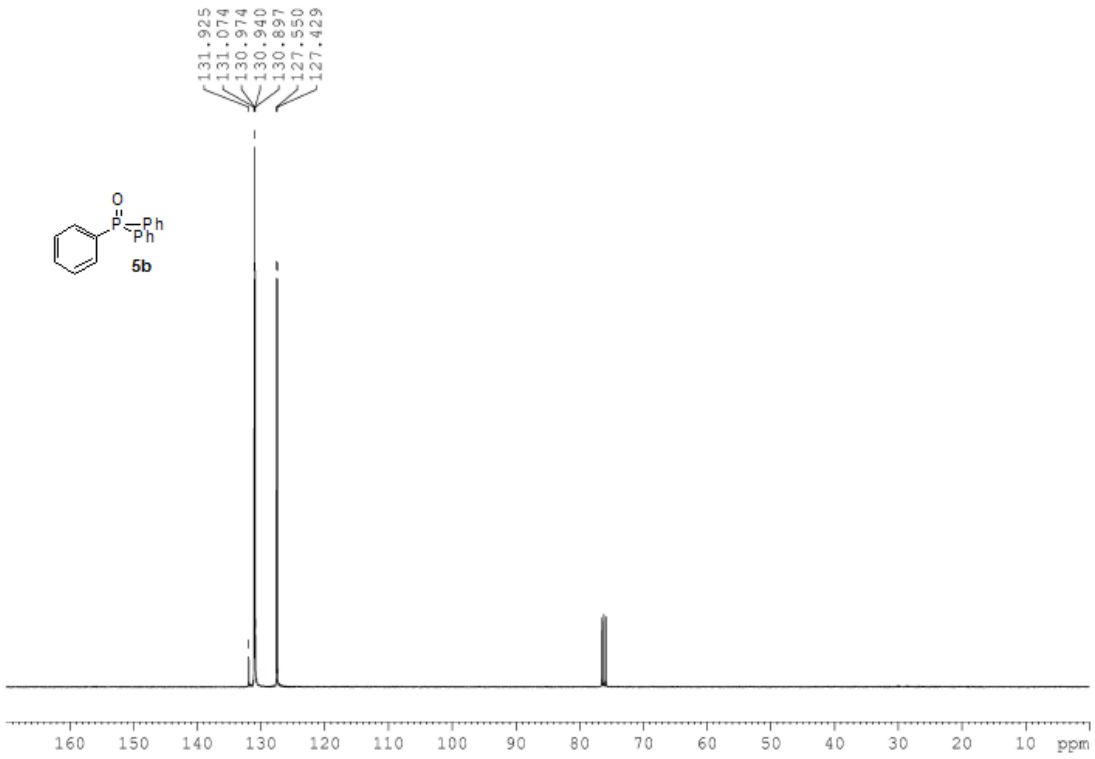

PO(OiPr)2
Cl
3s
12.531
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
ppm


7.598
7.580
7.577
7.568
7.550
7.490
7.470
7.460
7.440
7.432
7.430
7.414
7.371
7.365
7.352
7.346
7.335
7.328
7.184
7.180
7.165
7.160
O
P
Ph
Ph
5a
2.298
9
8
7
6
5
4
3
2
1
ppm
4.168
4.133
4.180
2.008
3.000






7.697
7.679
7.676
7.667
7.649
7.544
7.541
7.525
7.522
7.507
7.505
7.463
7.456
7.444
7.437
7.426
7.419
O
P
Ph
Ph
5b
10
9
8
7
6
5
4
3
2
1
ppm
5.594
3.642
6.000


131.925
131.074
130.974
130.940
130.897
127.550
127.429
O
P
Ph
Ph
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm