

Supporting Information

**NaIO₄/air-Initiated Phosphorylation of Alcohols with H-phosphine Oxides for
the Construction of P(O)-O Bonds in Water**

Huabin Wang,^a Lianhua Xu,^a Xiongwei Liu,^a Yang Shi,^a Zhen Yao,^a Ying Zhou,^{*,a} Qiang
Huang^{*,b,c}

^a *College of Pharmacy, Guizhou University of Traditional Chinese Medicine, Guiyang
550025, P. R. China.*

^b *School of Pharmacy, Zunyi Medical University, Zunyi 563006, P. R. China.*

^c *Key Laboratory of Basic Pharmacology of Ministry of Education and Joint
International Research Laboratory of Ethnomedicine of Ministry of Education, Zunyi
Medical University, Zunyi 563006, P. R. China.*

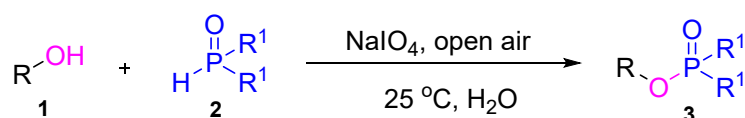
E-mail: huangqiang65@sina.com; yingzhou71@sina.com

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. 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). ¹H NMR spectra were recorded in DMSO-*d*₆ on a Bruker 400 (400 MHz) spectrometer. ¹³C NMR spectra were recorded in DMSO-*d*₆ on a Bruker 400 (101 MHz) spectrometer. ³¹P NMR spectra were recorded in DMSO-*d*₆ on a Bruker 400 (243 MHz) spectrometer. Chemical shifts were reported relative to DMSO-*d*₆ (δ 2.50 ppm) for ¹H NMR and DMSO-*d*₆ (δ 39.52 ppm) for ¹³C NMR. High-resolution mass spectra (HRMS) were recorded on a Q-Exactive Orbitrap mass spectrometer (Thermo, CA).

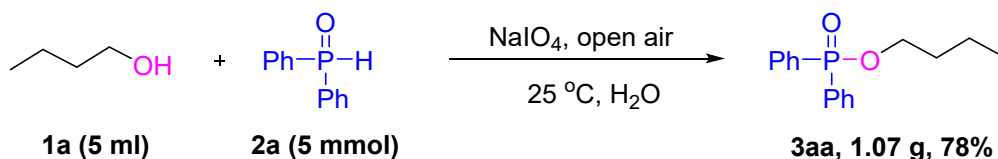
2. Experimental Section

1) General procedure for the synthesis of compound 3



To a solution of alcohols **1** (0.5 ml) and diarylphosphine oxide **2** (101 mg, 0.5 mmol) in water (2 mL) was added NaIO₄ (215 mg, 1 mmol) under air, the reaction mixture was stirred at 25 °C for 6 h. After completion of reaction, the solution of 20% NaHCO₃ was added into the mixture, and then the solution was extracted three times with EA (3 × 20 mL). The combined organic phase was concentrated and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford diarylphosphinate **3**. The structures of isolated products were identified by NMR and HRMS.

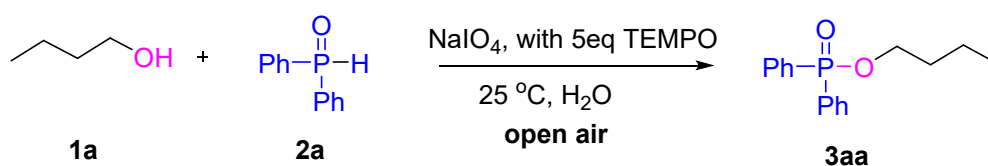
2) Large-Scale Synthesis



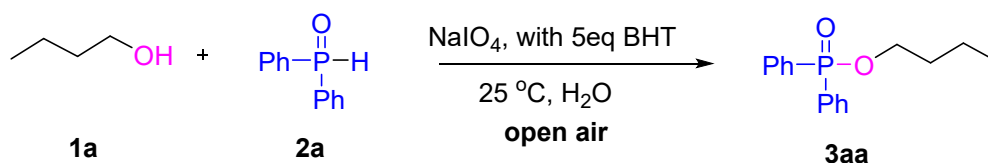
To a solution of alcohols **1a** (5 ml) and diarylphosphine oxide **2a** (1.01 g, 5 mmol)

in water (20 mL) was added NaIO₄ (2.15 g, 10 mmol) under air, the reaction mixture was stirred at 25 °C for 6 h. After completion of reaction, the solution of 20% NaHCO₃ was added into the mixture, and then the solution was extracted three times with EA (3 × 50 mL). The combined organic phase was concentrated and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford diarylphosphinate **3aa** with the yield of 78%.

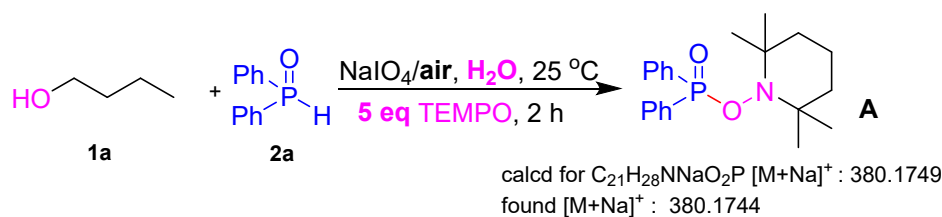
3) Mechanistic Studies



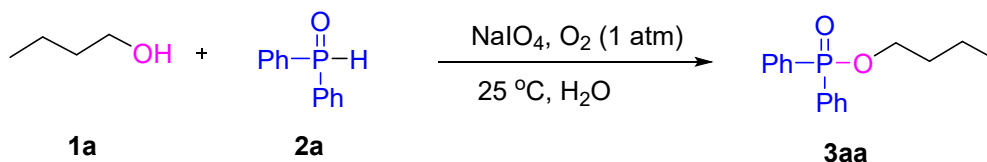
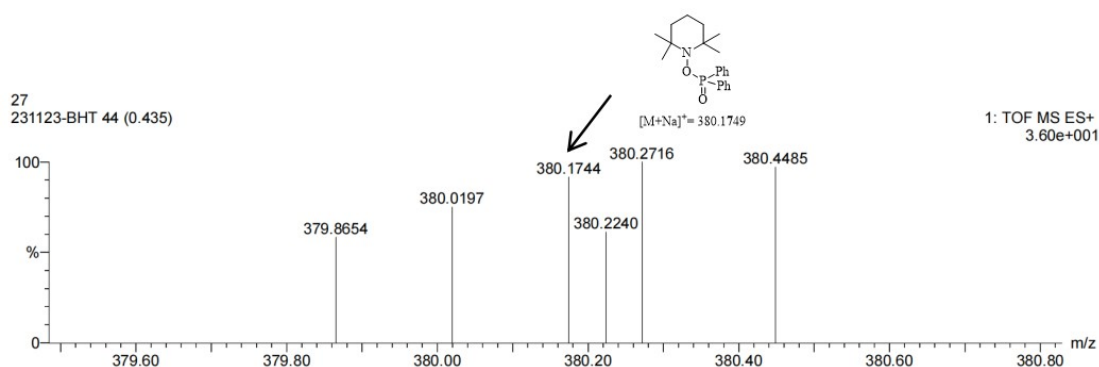
To a solution of alcohols **1a** (0.5 ml) and diarylphosphine oxide **2a** (101 mg, 0.5 mmol) and TEMPO (391 mg, 2.5 mmol) in water (2 mL) was added NaIO₄ (215 mg, 1 mmol) under air, the reaction mixture was stirred at 25 °C for 6 h. After completion of reaction, the solution of 20% NaHCO₃ was added into the mixture, and then the solution was extracted three times with EA (3 × 20 mL). The combined organic phase was concentrated and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford diarylphosphinate **3aa** with the yield of 12%.



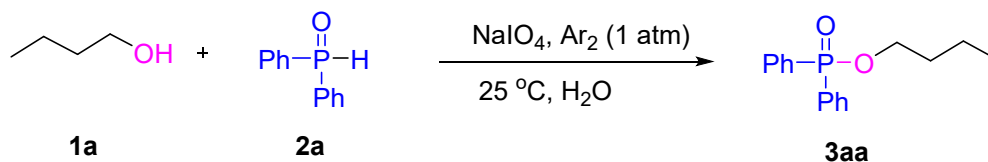
To a solution of alcohols **1a** (0.5 ml) and diarylphosphine oxide **2a** (101 mg, 0.5 mmol) and BHT (551 mg, 2.5 mmol) in water (2 mL) was added NaIO₄ (215 mg, 1 mmol) under air, the reaction mixture was stirred at 25 °C for 6 h. After completion of reaction, the solution of 20% NaHCO₃ was added into the mixture, and then the solution was extracted three times with EA (3 × 20 mL). The combined organic phase was concentrated and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford diarylphosphinate **3aa** with the yield of 18%.



To a solution of alcohols **1a** (0.5 ml) and diarylphosphine oxide **2a** (101 mg, 0.5 mmol) and TEMPO (391 mg, 2.5 mmol) in water (2 mL) was added $NaIO_4$ (215 mg, 1 mmol) under air, the reaction mixture was stirred at 25 °C for 2 h, and then analyzed by LC-HRMS to capture the intermediates. The intermediate **A** was found at 380.1744 of m/s, which was consistent with the molecular ion peak of $[M+Na]^+$.



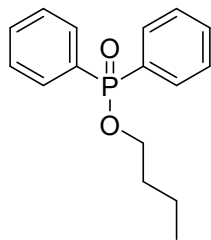
To a solution of alcohols **1a** (0.5 ml) and diarylphosphine oxide **2a** (101 mg, 0.5 mmol) in water (2 mL) was added $NaIO_4$ (215 mg, 1 mmol) under O_2 atmosphere (1 atm), the reaction mixture was stirred at 25 °C for 6 h. After completion of reaction, the solution of 20% $NaHCO_3$ was added into the mixture, and then the solution was extracted three times with EA (3×20 mL). The combined organic phase was concentrated and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford diarylphosphinate **3aa** with the yield of 89%.



To a solution of alcohols **1a** (0.5 ml) and diarylphosphine oxide **2a** (101 mg, 0.5 mmol) in water (2 mL) was added NaIO₄ (215 mg, 1 mmol) under argon atmosphere (1 atm), the reaction mixture was stirred at 25 °C for 6 h. After completion of reaction, the solution of 20% NaHCO₃ was added into the mixture, and then the solution was extracted three times with EA (3 × 20 mL). The combined organic phase was concentrated and no product of diarylphosphinate **3aa** was found.

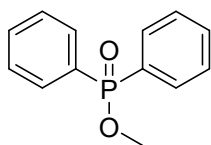
3. NMR data of products 3

Butyl Diphenylphosphinate (3aa)



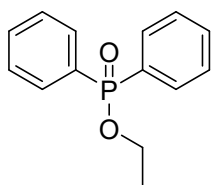
Colorless oil (116 mg, 85%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.80 – 7.74 (m, 4H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 4H), 3.91 (q, 6.4 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.41 – 1.32 (m, 2H), 0.85 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.49 (d, $J = 2.8$ Hz), 132.00 (d, $J = 135.4$ Hz), 131.44 (d, $J = 10.1$ Hz), 129.03 (d, $J = 13.0$ Hz), 64.36 (d, $J = 6.0$ Hz), 32.21 (d, $J = 6.4$ Hz), 18.56, 13.64; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.29. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 275.1195, found 275.1197.

Methyl Diphenylphosphinate (3ab)



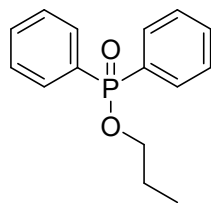
Colorless oil (103 mg, 89%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.79 – 7.74 (m, 4H), 7.63 – 7.59 (m, 2H), 7.56 – 7.51 (m, 4H), 3.65 (d, $J = 11.2$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.65 (d, $J = 2.8$ Hz), 131.55 (d, $J = 10.1$ Hz), 131.44 (d, $J = 135.8$ Hz), 129.13 (d, $J = 12.5$ Hz), 51.61 (d, $J = 5.9$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 31.66. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 233.0726, found 233.0722

Ethyl Diphenylphosphinate (3ac)



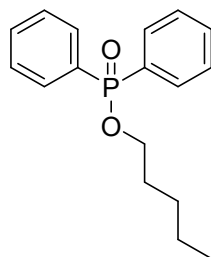
Colorless oil (103 mg, 84%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.80 – 7.74 (m, 4H), 7.62 – 7.57 (m, 2H), 7.55 – 7.50 (m, 4H), δ 4.02 – 3.95 (m, 2H), 1.27 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.48 (d, $J = 2.8$ Hz), 132.03 (d, $J = 135.4$ Hz), 131.45 (d, $J = 9.7$ Hz), 129.01 (d, $J = 12.6$ Hz), 60.99 (d, $J = 5.8$ Hz), 16.53 (d, $J = 6.0$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.18. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 247.0882, found 247.0881.

Propyl Diphenylphosphinate (3ad)



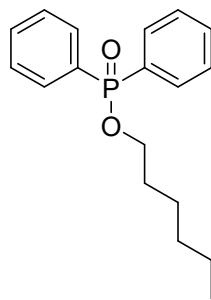
Colorless oil (114 mg, 88%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.80 – 7.74 (m, 4H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 4H), 3.87 (q, $J = 6.7$ Hz, 2H), 1.69 – 1.61 (m, 2H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.49 (d, $J = 2.9$ Hz), 132.01 (d, $J = 135.3$ Hz), 131.45 (d, $J = 9.8$ Hz), 129.03 (d, $J = 12.9$ Hz), 66.24 (d, $J = 5.9$ Hz), 23.63 (d, $J = 6.5$ Hz), 10.30; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 29.69. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 261.1039, found 261.1035.

Pentyl Diphenylphosphinate (3ae)



Colorless oil (128 mg, 89%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.79 – 7.71 (m, 4H), 7.61 – 7.50 (m, 6H), 3.90 (q, 6.5 Hz, 4H), 1.67 – 1.60 (m, 2H), 1.36 – 1.21 (m, 2H), 0.83 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 133.98 (d, $J = 3.1$ Hz), 132.32 (d, $J = 10.2$ Hz), 131.76 (d, $J = 137.1$ Hz), 130.19 (d, $J = 12.9$ Hz), 66.35 (d, $J = 6.4$ Hz), 30.56 (d, $J = 6.1$ Hz), 28.29, 22.66, 14.87. ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 31.77. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 289.1352, found 289.1353.

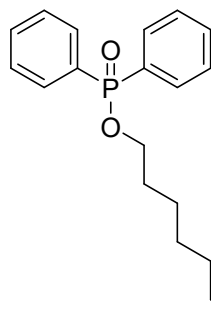
Octyl diphenylphosphinate (3af)



Colorless oil (125 mg, 83%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.78 – 7.73 (m, 4H), 7.61 – 7.49 (m, 6H), 3.90 (q, $J = 6.7$ Hz, 2H), 1.66 – 1.59 (m, 2H),

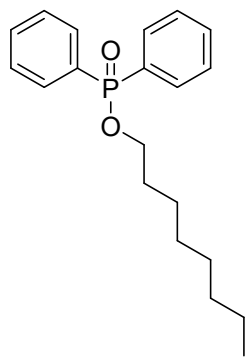
1.36 – 1.28 (m, 2H), 1.28 – 1.16 (m, 4H), 0.82 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.24 (d, $J = 3.3$ Hz), 131.80 (d, $J = 135.1$ Hz), 131.21 (d, $J = 9.7$ Hz), 128.78 (d, $J = 12.5$ Hz), 64.44 (d, $J = 5.9$ Hz), 30.70, 29.88 (d, $J = 6.0$ Hz), 24.71, 21.94, 13.83; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 29.45. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 303.1508, found 303.1508.

Heptyl Diphenylphosphinate (3ag)



Colorless oil (122 mg, 77%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.78 – 7.73 (m, 4H), 7.61 – 7.49 (m, 6H), 3.90 (q, $J = 6.7$ Hz, 2H), 1.66 – 1.59 (m, 2H), 1.36 – 1.29 (m, 2H), 1.25 – 1.15 (m, 6H), 0.86 – 0.79 (m, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.71 (d, $J = 2.8$ Hz), 132.27 (d, $J = 135.5$ Hz), 131.67 (d, $J = 10.1$ Hz), 129.25 (d, $J = 12.8$ Hz), 64.90 (d, $J = 5.9$ Hz), 31.57, 30.38 (d, $J = 6.0$ Hz), 28.63, 25.48, 22.47, 14.36; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 29.45. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 317.1665, found 317.1665.

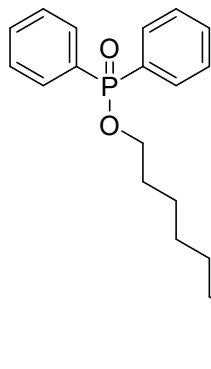
Hexyl Diphenylphosphinate (3ah)



Colorless oil (130 mg, 79%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.78 – 7.73 (m, 4H), 7.61 – 7.49 (m, 6H), 3.90 (q, $J = 6.7$ Hz, 2H), 1.66 – 1.59 (m, 2H), 1.36 – 1.28 (m, 2H), 1.25 – 1.17 (m, 8H), 0.83 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.44 (d, $J = 2.4$ Hz), 132.01 (d, $J = 133.5$ Hz), 131.41 (d, $J = 9.7$ Hz), 128.98 (d, $J = 12.5$ Hz), 64.63 (d, $J = 5.9$ Hz), 31.39, 30.11 (d, $J = 6.4$ Hz),

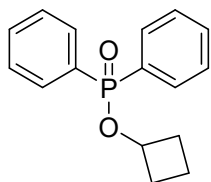
28.70 (d, $J = 8.7$ Hz), 25.25, 22.25, 14.12; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 29.44.
HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 331.1821, found 331.1824.

Nonyl Diphenylphosphinate (3ai)



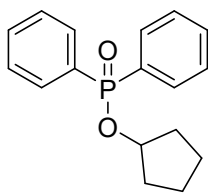
Colorless oil (133 mg, 77%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.78 – 7.72 (m, 4H), 7.62 – 7.57 (m, 2H), 7.54 – 7.50 (m, 4H), 3.90 (q, $J = 6.7$ Hz, 2H), 1.66 – 1.60 (m, 2H), 1.35 – 1.29 (m, 2H), 1.27 – 1.22 (m, 10H), 0.84 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{Chloroform-}d$) δ 132.27 (d, $J = 2.9$ Hz), 131.80 (d, $J = 135.2$ Hz), 131.21 (d, $J = 10.1$ Hz), 128.80 (d, $J = 12.9$ Hz), 64.45 (d, $J = 5.9$ Hz), 31.24, 29.89 (d, $J = 6.0$ Hz), 28.82, 28.54 (d, $J = 12.3$ Hz), 25.03, 22.09, 13.94; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{29}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 345.1978, found 345.1978.

Cyclobutyl Diphenylphosphinate (3aj)



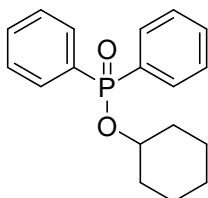
Colorless oil (71 mg, 52%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.78 – 7.72 (m, 4H), 7.61 – 7.56 (m, 2H), 7.55 – 7.49 (m, 4H), 4.68 – 4.58 (m, 1H), 2.21 – 2.06 (m, 4H), 1.69 – 1.60 (m, 1H), 1.48 – 1.34 (m, 1H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.53 (d, $J = 2.9$ Hz), 132.21 (d, $J = 135.3$ Hz), 131.46 (d, $J = 9.7$ Hz), 129.00 (d, $J = 12.5$ Hz), 68.83 (d, $J = 7.3$ Hz), 32.08 (d, $J = 4.5$ Hz), 12.61; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 28.93. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 273.1039, found 273.1036.

Cyclopentyl Diphenylphosphinate (3ak)



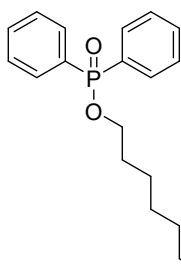
Colorless oil (83 mg, 58%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.78 – 7.72 (m, 4H), 7.61 – 7.56 (m, 2H), 7.54 – 7.49 (m, 4H), 4.75 – 4.69 (m, 1H), 1.86 – 1.67 (m, 6H), 1.58 – 1.48 (m, 2H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.57 (d, $J = 135.8$ Hz), 132.37 (d, $J = 2.8$ Hz), 131.44 (d, $J = 10.1$ Hz), 128.97 (d, $J = 12.9$ Hz), 78.48 (d, $J = 6.0$ Hz), 33.99 (d, $J = 4.3$ Hz), 22.85; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 28.43. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 287.1195, found 287.1192.

Cyclohexyl Diphenylphosphinate (3a)



Colorless oil (84 mg, 56%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.79 – 7.73 (m, 4H), 7.61 – 7.56 (m, 2H), 7.54 – 7.49 (m, 4H), 4.29 – 4.21 (m, 1H), 1.83 – 1.77 (m, 2H), 1.70 – 1.62 (m, 2H), 1.58 – 1.50 (m, 2H), 1.44 – 1.37 (m, 1H), 1.28 – 1.23 (m, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 132.75 (d, $J = 135.8$ Hz), 132.42 (d, $J = 2.8$ Hz), 131.42 (d, $J = 10.1$ Hz), 128.99 (d, $J = 12.5$ Hz), 74.42 (d, $J = 6.0$ Hz), 33.50 (d, $J = 3.9$ Hz), 24.92, 23.11; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 28.62. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 301.1352, found 301.1353.

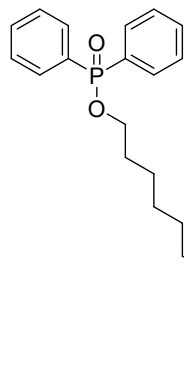
6-bromohexyl diphenylphosphinate (3am)



Colorless oil (153 mg, 81%): ^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.73 (m, 4H), 7.54 – 7.47 (m, 2H), 7.46 – 7.38 (m, 4H), 4.00 (q, $J = 6.5$ Hz, 2H), 3.36 (t, $J = 6.7$ Hz, 2H), 1.87 – 1.77 (m, 2H), 1.78 – 1.67 (m, 2H), 1.46 – 1.35 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.18, 132.16, 131.67, 131.57, 130.85, 128.63, 128.50, 64.77 (d, $J = 5.9$ Hz), 33.76, 32.58, 30.36 (d, $J = 6.6$ Hz), 27.69, 24.87. ^{31}P NMR (162

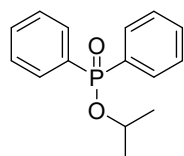
MHz, CDCl₃) δ 31.35. HRMS (ESI) calcd for C₁₈H₂₂BrNaO₂P [M+Na]⁺: 403.0433, found 403.0437.

6-bromohexyl diphenylphosphinate (3an)



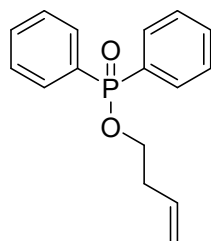
Colorless oil (136 mg, 65%): ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.74 (m, 4H), 7.52 – 7.46 (m, 2H), 7.45 – 7.39 (m, 4H), 3.99 (q, J = 6.7 Hz, 2H), 3.37 (t, J = 6.8 Hz, 2H), 1.86 – 1.76 (m, 2H), 1.74 – 1.65 (m, 2H), 1.41 – 1.32 (m, 4H), 1.30 – 1.22 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 132.31, 132.13, 132.10, 131.68, 131.58, 130.95, 128.60, 128.46, 65.00 (d, J = 6.1 Hz), 34.05, 32.77, 30.51 (d, J = 6.7 Hz), 29.26, 29.01, 28.64, 28.10, 25.56. ³¹P NMR (162 MHz, CDCl₃) δ 31.17. HRMS (ESI) calcd for C₂₁H₂₉BrO₂P [M+H]⁺: 423.1083, found 423.1086.

Isopropyl diphenylphosphinate (3ao)



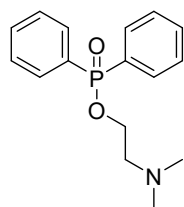
Colorless oil (58 mg, 45%): ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.76 (m, 4H), 7.53 – 7.46 (m, 2H), 7.46 – 7.38 (m, 4H), 4.66 (td, J = 12.6, 6.2 Hz, 1H), 1.33 (d, J = 6.2 Hz, 6H). ¹³C NMR (101 MHz, cdcl₃) δ 132.96, 132.06, 131.84, 131.65, 131.55, 128.38, 128.23, 70.25 (dd, J = 11.9, 6.1 Hz), 24.31 (dd, J = 14.2, 4.3 Hz). ³¹P NMR (162 MHz, CDCl₃) δ 29.88. HRMS (ESI) calcd for C₁₅H₁₈O₂P [M+H]⁺: 261.1039, found 261.1036.

But-3-en-1-yl Diphenylphosphinate (3ap)



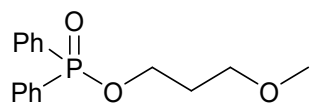
Colorless oil (34 mg, 25%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.79 – 7.73 (m, 4H), 7.62 – 7.57 (m, 2H), 7.56 – 7.50 (m, 4H), 5.87 – 5.77 (m, 1H), 5.16 – 5.15 (m, 1H), 5.12 – 5.06 (m, 1H), 4.00 – 3.94 (m, 2H), 2.44 – 2.39 (m, 2H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 134.53, 132.53 (d, $J = 2.5$ Hz), 131.85 (d, $J = 134.0$ Hz), 131.45 (d, $J = 10.1$ Hz), 129.03 (d, $J = 12.9$ Hz), 117.70, 63.79 (d, $J = 5.8$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.06. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 273.1039, found 273.1031.

2-(dimethylamino)ethyl diphenylphosphinate (3aq)



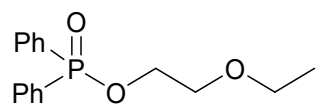
Colorless oil (49 mg, 34%): ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.78 (m, 4H), 7.54 – 7.48 (m, 2H), 7.48 – 7.40 (m, 4H), 4.15 – 4.07 (m, 2H), 2.68 (t, $J = 5.9$ Hz, 2H), 2.27 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.22, 132.10, 131.71, 131.60, 128.68 (d, $J = 13.1$ Hz), 128.41 (d, $J = 13.4$ Hz), 62.57, 59.08, 45.62. ^{31}P NMR (162 MHz, CDCl_3) δ 32.34. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2\text{P}$ $[\text{M}+\text{H}]^+$: 290.1304, found 290.1301.

3-methoxypropyl diphenylphosphinate (3ar)



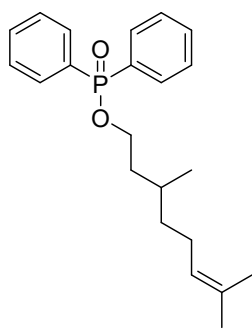
Colorless oil (96 mg, 66%): ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.73 (m, 1H), 7.52 – 7.45 (m, 1H), 7.45 – 7.38 (m, 1H), 4.09 (q, $J = 6.4$ Hz, 1H), 3.48 (t, $J = 6.1$ Hz, 1H), 3.28 (s, 1H), 1.96 (p, $J = 6.2$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.33, 132.07, 131.91, 131.63, 131.53, 130.55, 128.69 (d, $J = 12.4$ Hz), 128.41 (d, $J = 13.5$ Hz), 68.64, 62.16 (d, $J = 5.9$ Hz), 58.65 (d, $J = 18.1$ Hz), 30.75 (d, $J = 6.6$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 31.72. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 291.1145, found 291.1142.

2-ethoxyethyl diphenylphosphinate (3av)



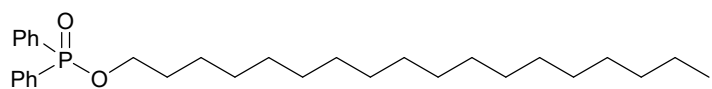
Colorless oil (106 mg, 73%): ^1H NMR (400 MHz, CDCl_3) δ 7.88 – 7.77 (m, 4H), 7.54 – 7.47 (m, 2H), 7.46 – 7.38 (m, 4H), 4.20 – 4.12 (m, 2H), 3.67 (t, $J = 4.8$ Hz, 2H), 3.48 (q, $J = 7.0$ Hz, 2H), 1.17 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.35, 132.11, 131.76, 131.64, 130.45, 128.45, 128.31, 69.58 (d, $J = 6.7$ Hz), 66.57, 64.06 (d, $J = 6.0$ Hz), 15.12 (d, $J = 13.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 32.60. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 291.1145, found 291.1141.

3,7-dimethyloct-6-en-1-yl diphenylphosphinate (3aw)



Colorless oil (94 mg, 53%): ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.75 (m, 4H), 7.53 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 5.04 (t, $J = 7.0$ Hz, 1H), 4.11 – 3.99 (m, 2H), 2.00 – 1.87 (m, 2H), 1.80 – 1.71 (m, 1H), 1.65 (s, 3H), 1.63 – 1.58 (m, 1H), 1.56 (s, 3H), 1.53 – 1.44 (m, 1H), 1.29 – 1.25 (m, 1H), 1.19 – 1.09 (m, 1H), 0.86 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.24, 132.13, 132.11, 131.68, 131.58, 131.33, 130.88, 128.59, 128.46, 124.54, 63.40 (d, $J = 6.0$ Hz), 37.42 (d, $J = 6.6$ Hz), 36.90, 29.06, 25.72, 25.33, 19.33, 17.66. ^{31}P NMR (162 MHz, CDCl_3) δ 31.31. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 357.1978, found 357.1982.

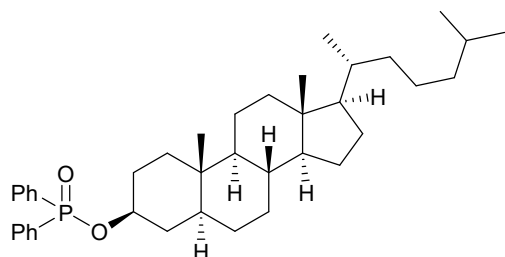
Octadecyl diphenylphosphinate (3ay)



Colorless oil (190 mg, 81%): ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.75 (m, 4H), 7.55 – 7.47 (m, 2H), 7.47 – 7.40 (m, 4H), 4.01 (q, $J = 6.4$ Hz, 2H), 1.76 – 1.61 (m, 3H), 1.43 – 1.16 (m, 28H), 0.86 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.40, 132.07 (d, $J = 2.7$ Hz), 131.70, 131.60, 131.04, 128.57, 128.44, 65.06 (d, $J = 6.0$ Hz), 31.94, 30.59, 30.53,

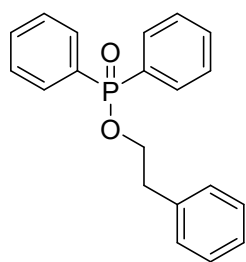
29.71, 29.58, 29.51, 29.37, 29.16, 25.63, 22.70, 14.13. ^{31}P NMR (162 MHz, CDCl_3) δ 31.15. HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{48}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 471.3386, found 471.3389.

(3S,5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl diphenylphosphinate (3az)



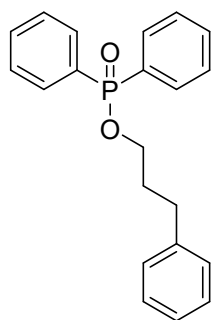
Colorless oil (94 mg, 53%): ^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.74 (m, 4H), 7.52 – 7.46 (m, 2H), 7.46 – 7.37 (m, 4H), 4.37 – 4.24 (m, 1H), 1.95 – 1.38 (m, 14H), 1.35 – 1.16 (m, 11H), 1.13 – 0.92 (m, 9H), 0.84 (d, $J = 6.6$ Hz, 6H), 0.80 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 133.23, 131.93 (d, $J = 1.9$ Hz), 131.86, 131.71, 131.65, 131.61, 131.55, 128.48, 128.35, 76.19 (d, $J = 6.4$ Hz), 56.39, 56.25, 54.15, 44.71, 42.58, 39.96, 39.52, 36.85, 36.62, 36.16, 35.79, 35.44, 35.28, 31.95, 30.09 (d, $J = 3.7$ Hz), 29.72, 28.50, 28.23, 28.01, 24.19, 23.83, 22.82, 22.57, 21.19, 18.66, 12.27, 12.06. ^{31}P NMR (162 MHz, CDCl_3) δ 29.95. HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{57}\text{NaO}_2\text{P}$ $[\text{M}+\text{Na}]^+$: 611.3988, found 611.3992.

Phenethyl Diphenylphosphinate (3bc)



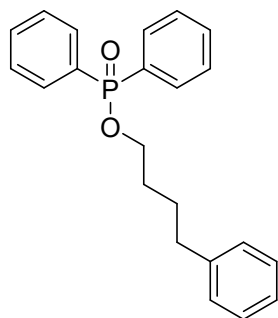
Colorless oil (81 mg, 50%): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.67 – 7.61 (m, 4H), 7.60 – 7.54 (m, 2H), 7.50 – 7.45 (m, 4H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 3H), 4.10 (q, $J = 6.6$ Hz, 2H), 2.97 (t, $J = 6.5$ Hz, 2H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 138.06, 132.55 (d, $J = 2.9$ Hz), 131.74 (d, $J = 135.5$ Hz), 131.42 (d, $J = 9.9$ Hz), 129.30, 129.02, 128.70 (d, $J = 4.9$ Hz), 126.73, 65.40 (d, $J = 5.9$ Hz), 36.43 (d, $J = 6.7$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO}-d_6$) δ 29.96. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 323.1195, found 323.1197.

3-phenylpropyl Diphenylphosphinate (3bd)



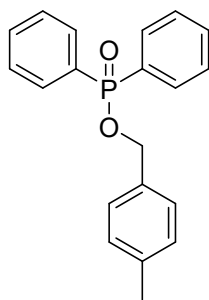
Colorless oil (82 mg, 49%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.81 – 7.74 (m, 4H), 7.62 – 7.57 (m, 2H), 7.55 – 7.49 (m, 4H), 7.28 – 7.23 (m, 2H), 7.21 – 7.14 (m, 2H), 3.94 – 3.89 (m, 2H), 2.68 (t, $J = 8.5$ Hz, 2H), 2.00 – 1.92 (m, 2H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 141.29, 131.92 (d, $J = 135.6$ Hz), 132.52, 131.44, 129.05 (d, $J = 12.9$ Hz), 128.56, 128.32, 126.10, 125.94, 64.06 (d, $J = 5.9$ Hz), 31.85 (d, $J = 6.4$ Hz), 31.38; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 29.86. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 337.1352, found 337.1354.

4-phenylbutyl Diphenylphosphinate (3be)



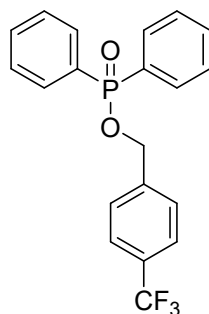
Colorless oil (138 mg, 79%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.78 – 7.73 (m, 4H), 7.60 – 7.47 (m, 6H), 7.27 – 7.23 (m, 2H), 7.17 – 7.14 (m, 2H), 3.96 – 3.91 (m, 2H), 2.57 – 2.53 (m, 2H), 1.67 – 1.62 (m, 4H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 141.84, 132.25 (d, $J = 2.9$ Hz), 131.78 (d, $J = 135.2$ Hz), 131.26, 131.16, 128.79 (d, $J = 12.9$ Hz), 128.28, 128.25, 125.70, 64.28 (d, $J = 6.2$ Hz), 34.53, 29.53 (d, $J = 6.4$ Hz), 26.95; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 29.54. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 337.1352, found 337.1353.

4-methylbenzyl diphenylphosphinate (3bf)



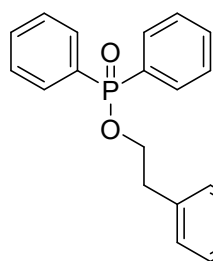
Colorless oil (92 mg, 57%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.81 – 7.75 (m, 4H), 7.62 – 7.58 (m, 2H), 7.56 – 7.50 (m, 4H), 7.29 (d, $J = 8.20$ Hz, 2H), 7.18 (d, $J = 7.8$ Hz, 2H), 4.94 (d, $J = 7.5$ Hz, 2H), 2.29 (s, 1H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 137.69, 133.59 (d, $J = 6.1$ Hz), 132.58 (d, $J = 2.8$ Hz), 131.55 (d, $J = 135.1$ Hz), 131.40 (d, $J = 10.2$ Hz), 129.17, 129.03 (d, $J = 13.0$ Hz), 128.02, 65.83 (d, $J = 5.7$ Hz), 20.89; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.52. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 322.1123, found 322.1124.

4-(Trifluoromethyl)benzyl Diphenylphosphinate (3bg)



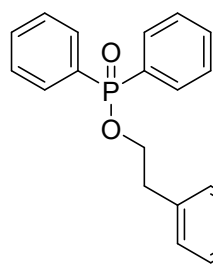
Colorless oil (111 mg, 59%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.86 – 7.80 (m, 4H), 7.74 – 7.72 (m, 2H), 7.66 – 7.58 (m, 4H), 7.56 – 7.51 (m, 4H), 5.12 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 141.60 (d, $J = 6.5$ Hz), 132.74 (d, $J = 2.9$ Hz), 131.53 (d, $J = 10.1$ Hz), 131.47 (d, $J = 135.3$ Hz), 129.13 (d, $J = 13.0$ Hz), 128.27, 125.55 (q, $J = 3.9$ Hz), 123.05, 65.07 (d, $J = 5.2$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 31.66. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{16}\text{F}_3\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 377.0913, found 377.0912.

4-methylphenethyl Diphenylphosphinate (3bh)



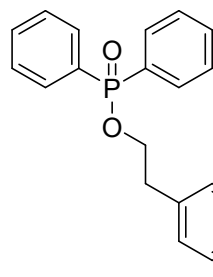
Colorless oil (84 mg, 50%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.66 – 7.55 (m, 6H), 7.50 – 7.45 (m, 4H), 7.13 – 7.09 (m, 4H), 4.06 (q, $J = 6.6$ Hz, 2H), 2.92 (t, $J = 6.6$ Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 135.53, 134.69, 132.35 (d, $J = 2.7$ Hz), 131.54 (d, $J = 135.2$ Hz), 131.23 (d, $J = 10.1$ Hz), 128.98, 128.96, 128.83 (d, $J = 13.0$ Hz), 65.32 (d, $J = 5.9$ Hz), 35.84 (d, $J = 6.7$ Hz), 31.17; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.62. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{21}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 337.1351, found 337.1351.

4-fluorophenethyl Diphenylphosphinate (3bi)



Colorless oil (80 mg, 47%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.68 – 7.62 (m, 4H), 7.58 – 7.54 (m, 2H), 7.50 – 7.45 (m, 4H), 7.30 – 7.24 (m, 2H), 7.14 – 7.08 (m, 2H), 4.09 (q, $J = 6.5$ Hz, 2H), 2.96 (t, $J = 6.4$ Hz, 2H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 161.14 (d, $J = 242.0$ Hz), 134.04 (d, $J = 3.3$ Hz), 132.35 (d, $J = 2.8$ Hz), 131.50 (d, $J = 135.2$ Hz), 131.21 (d, $J = 10.1$ Hz), 130.91 (d, $J = 8.0$ Hz), 128.82 (d, $J = 12.9$ Hz), 115.07 (d, $J = 21.1$ Hz), 65.15 (d, $J = 5.9$ Hz), 35.34 (d, $J = 7.0$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.31; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{FO}_2\text{P}$ $[\text{M}+\text{H}]^+$: 341.1101, found 341.1104.

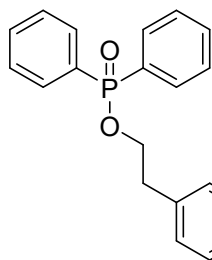
4-chlorophenethyl Diphenylphosphinate (3bj)



Colorless oil (93 mg, 52%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.81 – 7.75 (m, 4H), 7.62 – 7.50 (m, 6H), 7.31 – 7.28 (m, 2H), 7.19 – 7.17 (m, 2H),

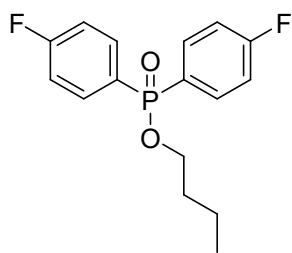
4.94 (d, $J = 7.5$ Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 136.97, 132.31, 132.30 (d, $J = 2.5$ Hz), 131.47 (d, $J = 135.3$ Hz), 131.17 (d, $J = 9.8$ Hz), 130.93, 128.77 (d, $J = 12.6$ Hz), 128.27, 64.91 (d, $J = 5.8$ Hz), 35.44 (d, $J = 6.7$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.63. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{ClO}_2\text{P}$ $[\text{M}+\text{H}]^+$: 357.0806, found 357.0808.

4-bromophenethyl Diphenylphosphinate (3bk)



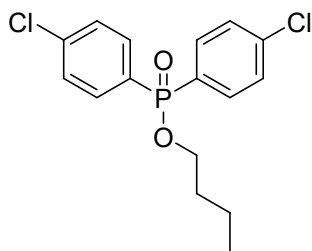
Colorless oil (122 mg, 61%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.65 – 7.55 (m, 6H), 7.50 – 7.45 (m, 6H), 7.24 – 7.20 (m, 2H), 4.10 (q, $J = 6.4$ Hz, 2H), 2.95 (t, $J = 6.3$ Hz, 2H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 137.49, 132.38 (d, $J = 2.8$ Hz), 131.45 (d, $J = 135.3$ Hz), 131.40, 131.20 (d, $J = 10.2$ Hz), 130.78, 128.84 (d, $J = 13.0$ Hz), 119.67, 64.91 (d, $J = 6.0$ Hz), 35.51 (d, $J = 6.7$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.63. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{18}\text{BrO}_2\text{P}$ $[\text{M}+\text{H}]^+$: 401.0301, found 401.0304.

Butyl bis(4-fluorophenyl)phosphinate (3ca)



Colorless oil (116 mg, 75%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.86 – 7.78 (m, 4H), 7.40 – 7.33 (m, 4H), 3.91 (q, $J = 7.4, 6.3$ Hz, 2H), 1.64 – 1.57 (m, 2H), 1.40 – 1.28 (m, 2H), 0.83 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 164.59 (dd, $J = 251.0, 3.4$ Hz), 134.24 (dd, $J = 11.5, 8.9$ Hz), 127.95 (dd, $J = 139.9, 3.3$ Hz), 116.20 (dd, $J = 21.6, 13.9$ Hz), 64.45 (d, $J = 5.9$ Hz), 31.98 (d, $J = 6.3$ Hz), 18.35, 13.42; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 28.79; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{F}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 311.1007, found 311.1006.

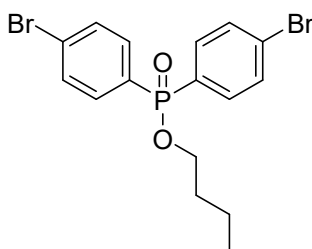
Butyl bis(4-chlorophenyl)phosphinate (3cb)



Colorless oil (130 mg, 76%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$)

δ 7.79 – 7.73 (m, 4H), 7.62 – 7.58 (m, 4H), 3.92 (q, $J = 7.5, 6.4$ Hz, 2H), 1.65 – 1.58 (m, 2H), 1.40 – 1.31 (m, 2H), 0.84 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 137.75 (d, $J = 3.6$ Hz), 133.24 (d, $J = 11.0$ Hz), 130.22 (d, $J = 138.1$ Hz), 129.15 (d, $J = 13.6$ Hz), 64.68 (d, $J = 6.1$ Hz), 31.96 (d, $J = 6.4$ Hz), 18.33, 13.44; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 28.29. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{Cl}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 343.0416, found 343.0417.

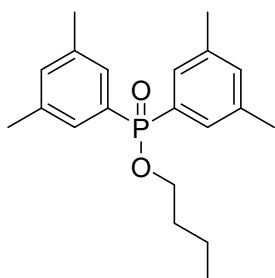
Butyl bis(4-bromophenyl)phosphinate (3cc)



Colorless oil (159 mg, 74%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$)

δ 7.75 – 7.73 (m, 4H), 7.70 – 7.65 (m, 4H), 3.92 (q, $J = 6.7$ Hz, 2H), 1.64 – 1.57 (m, 2H), 1.39 – 1.30 (m, 2H), 0.83 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 133.29 (d, $J = 10.9$ Hz), 132.05 (d, $J = 13.1$ Hz), 130.55 (d, $J = 138.0$ Hz), 126.80 (d, $J = 3.6$ Hz), 64.67 (d, $J = 5.9$ Hz), 31.96 (d, $J = 6.3$ Hz), 18.32, 13.43; ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 28.60. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{Br}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 430.9406, found 430.9408.

Butyl bis(3,5-dimethylphenyl)phosphinate (3cd)

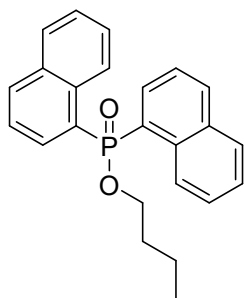


Colorless oil (122 mg, 74%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$)

δ 7.81 – 7.76 (m, 2H), 7.52 – 7.47 (m, 2H), 7.40 – 7.34 (m, 2H), 7.29 – 7.26 (m, 2H), 3.90 (q, $J = 6.5$ Hz, 2H), 2.25 (t, $J = 1.4$ Hz, 1H), 1.67 – 1.60 (m, 2H), 1.42 – 1.27 (m,

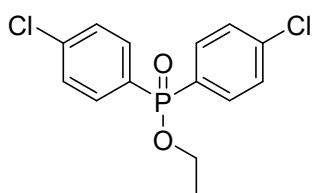
2H), 0.86 (t, $J = 7.4$ Hz, 3H)¹³C NMR (101 MHz, DMSO- d_6) δ 140.83 (d, $J = 10.9$ Hz), 132.89 (d, $J = 9.6$ Hz), 131.51 (d, $J = 12.3$ Hz), 130.08 (d, $J = 131.3$ Hz), 125.85 (d, $J = 12.3$ Hz), 63.73 (d, $J = 5.8$ Hz), 32.04 (d, $J = 6.5$ Hz), 20.58 (d, $J = 3.8$ Hz), 18.53, 13.49; ³¹P NMR (243 MHz, DMSO- d_6) δ 30.80. HRMS (ESI) calcd for C₂₀H₂₇O₂P [M+H]⁺: 331.1821, found 331.1824.

Butyl di(naphthalen-1-yl)phosphinate (3ce)



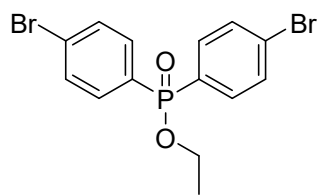
Colorless oil (139 mg, 74%): ¹H NMR (600 MHz, DMSO- d_6) δ 8.52 (d, $J = 13.9$ Hz, 2H), 8.09 (d, $J = 8.1$ Hz, 2H), 8.03 (dd, $J = 8.4, 3.2$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.83 – 7.79 (m, 2H), 7.62 – 7.57 (m, 5H), 4.00 (q, $J = 6.7$ Hz, 2H), 1.68 – 1.63 (m, 2H), 1.42 – 1.33 (m, 2H), 0.82 (t, $J = 7.4$ Hz, 3H); ¹³C NMR (101 MHz, DMSO- d_6) δ 134.46 (d, $J = 2.4$ Hz), 133.21 (d, $J = 9.9$ Hz), 132.15 (d, $J = 14.6$ Hz), 129.74, 129.05, 128.63 (d, $J = 3.0$ Hz), 128.38, 128.02 (d, $J = 150.9$ Hz), 127.88, 126.33 (d, $J = 10.7$ Hz), 64.61 (d, $J = 5.9$ Hz), 32.17 (d, $J = 5.9$ Hz), 18.47, 13.56; ³¹P NMR (243 MHz, DMSO- d_6) δ 29.66. HRMS (ESI) calcd for C₂₄H₂₃O₂P [M+H]⁺: 375.1508, found 375.1504.

Ethyl bis(4-chlorophenyl)phosphinate (3cf)



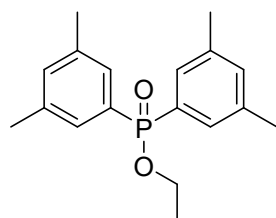
Colorless oil (113 mg, 72%): ¹H NMR (400 MHz, DMSO- d_6) δ 7.80 – 7.73 (m, 4H), 7.63 – 7.58 (m, 4H), 4.03 – 3.96 (m, 2H), 1.27 (t, $J = 7.0$ Hz, 3H); ¹³C NMR (101 MHz, DMSO- d_6) δ 137.90 (d, $J = 3.5$ Hz), 133.43 (d, $J = 11.3$ Hz), 130.46 (d, $J = 138.1$ Hz), 129.31 (d, $J = 13.3$ Hz), 61.49 (d, $J = 5.8$ Hz), 16.49 (d, $J = 6.3$ Hz); ³¹P NMR (243 MHz, DMSO- d_6) δ 28.03. HRMS (ESI) calcd for C₁₄H₁₃Cl₂O₂P [M+H]⁺: 315.0103, found 315.0106.

Ethyl bis(4-bromophenyl)phosphinate (3cg)



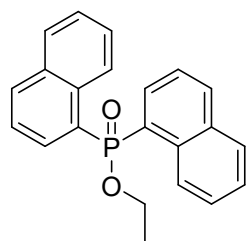
Colorless oil (140 mg, 70%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.77 – 7.72 (m, 4H), 7.72 – 7.66 (m, 4H), 4.04 – 3.97 (m, 2H), 1.27 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 133.49 (d, $J = 10.9$ Hz), 132.22 (d, $J = 13.6$ Hz), 130.80 (d, $J = 137.5$ Hz), 126.96 (d, $J = 3.6$ Hz), 61.49 (d, $J = 5.8$ Hz), 16.49 (d, $J = 6.0$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 28.35. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{13}\text{Br}_2\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 402.9093, found 402.9095.

Ethyl bis(3,5-dimethylphenyl)phosphinate (3ch)



Colorless oil (107 mg, 71%): ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.39 – 7.33 (m, 4H), 7.20 (s, 2H), 3.98 – 3.91 (m, 2H), 2.29 (s, 12H), 1.27 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 138.23 (d, $J = 13.2$ Hz), 133.80 (d, $J = 3.2$ Hz), 132.07 (d, $J = 133.8$ Hz), 128.91 (d, $J = 9.6$ Hz), 60.76 (d, $J = 5.8$ Hz), 21.01, 16.60 (d, $J = 6.3$ Hz); ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ 30.56. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 303.1508, found 303.1507.

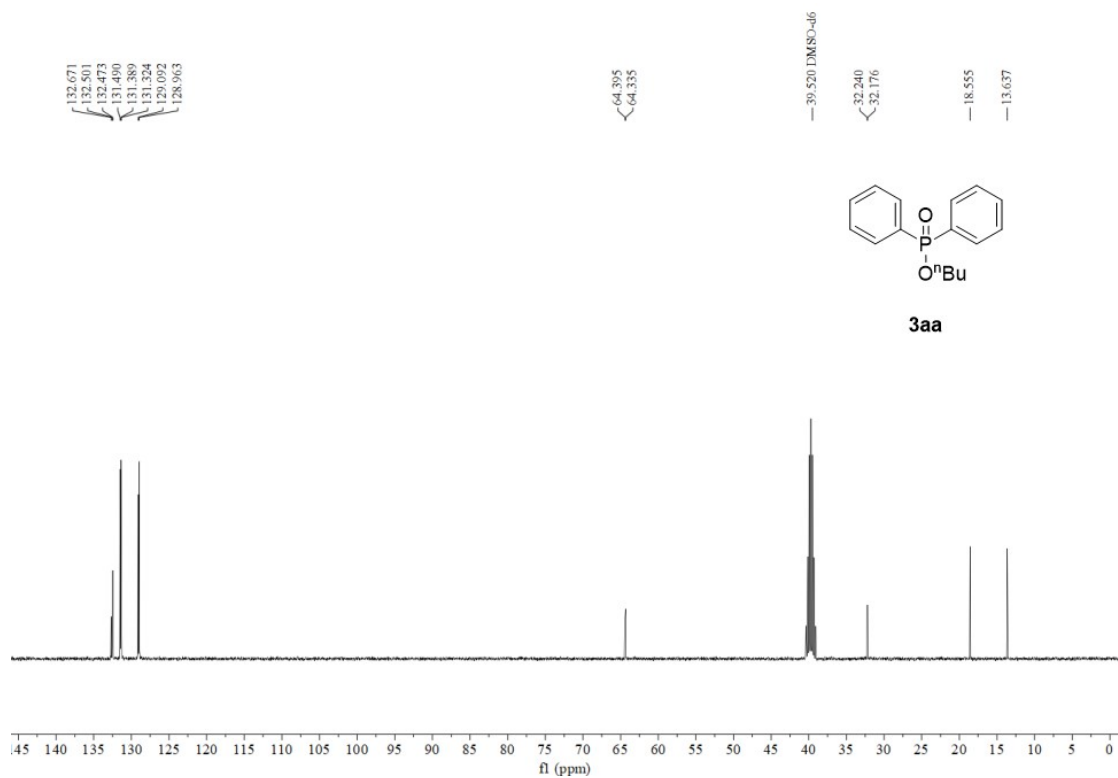
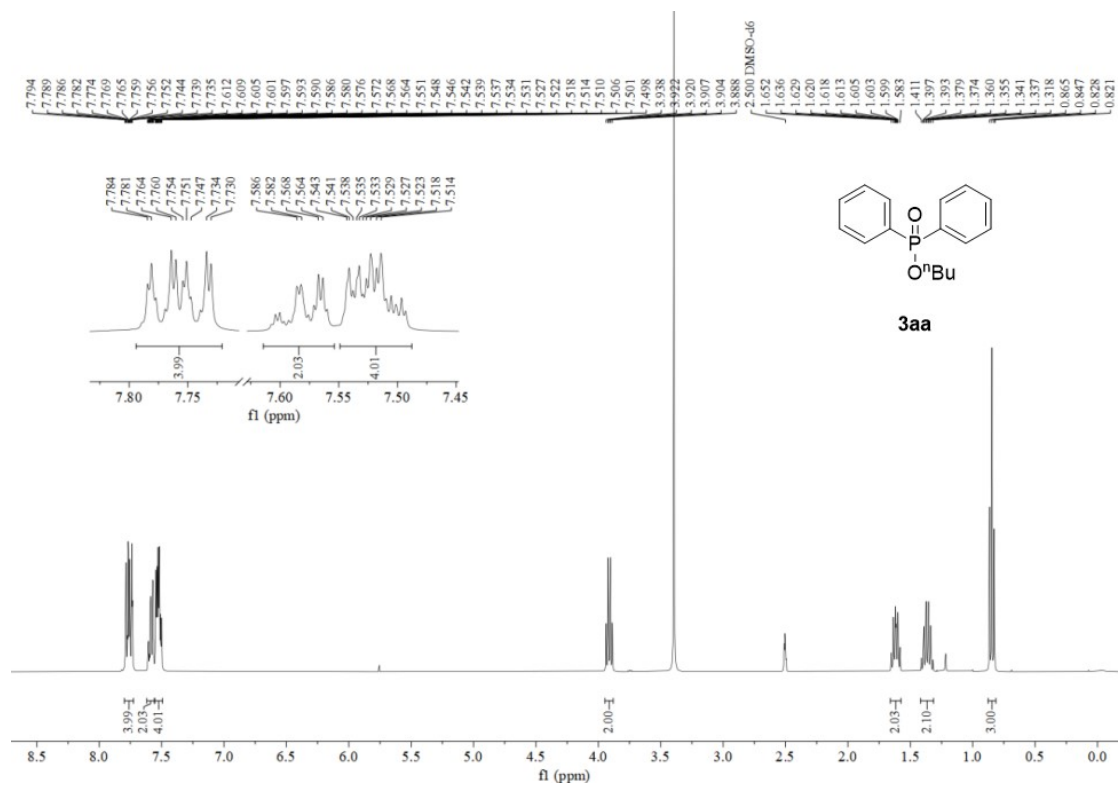
Ethyl di(naphthalen-1-yl)phosphinate (3ci)

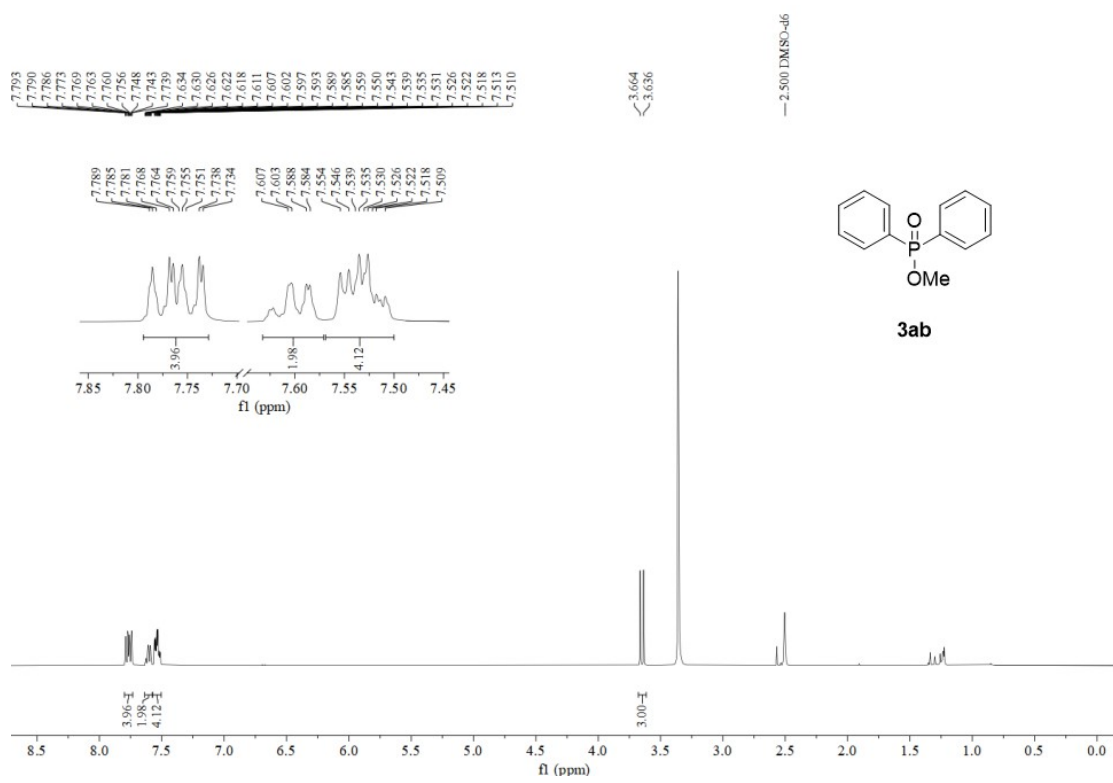
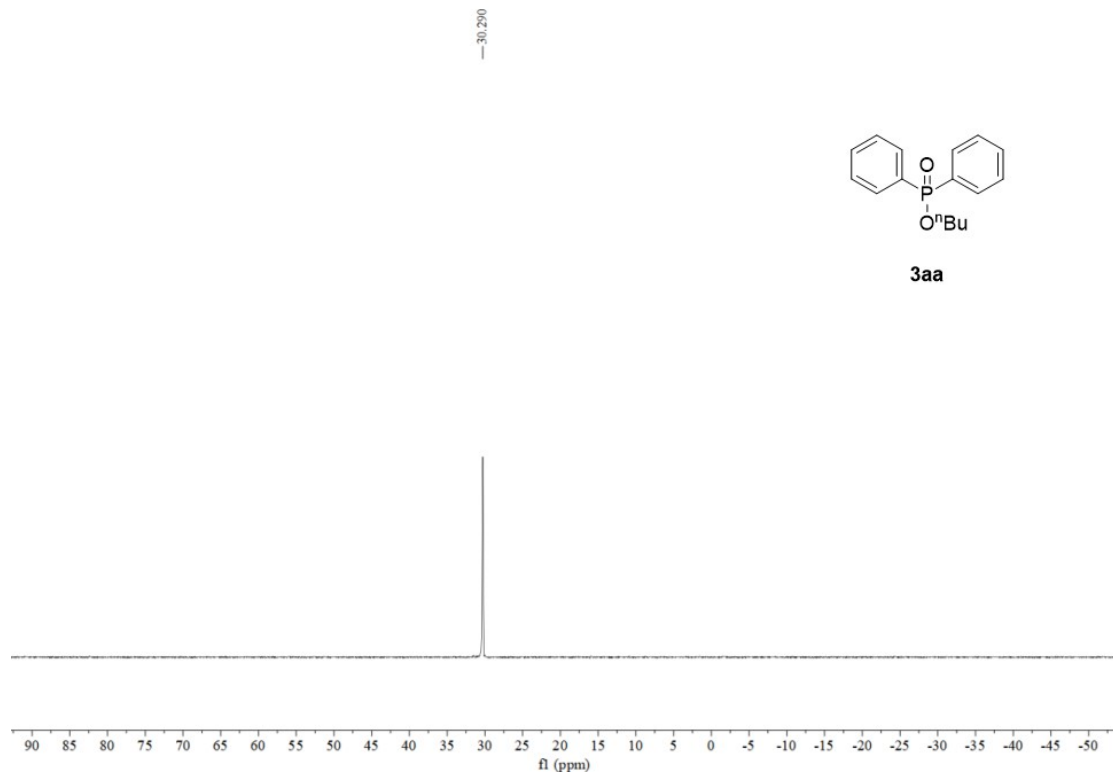


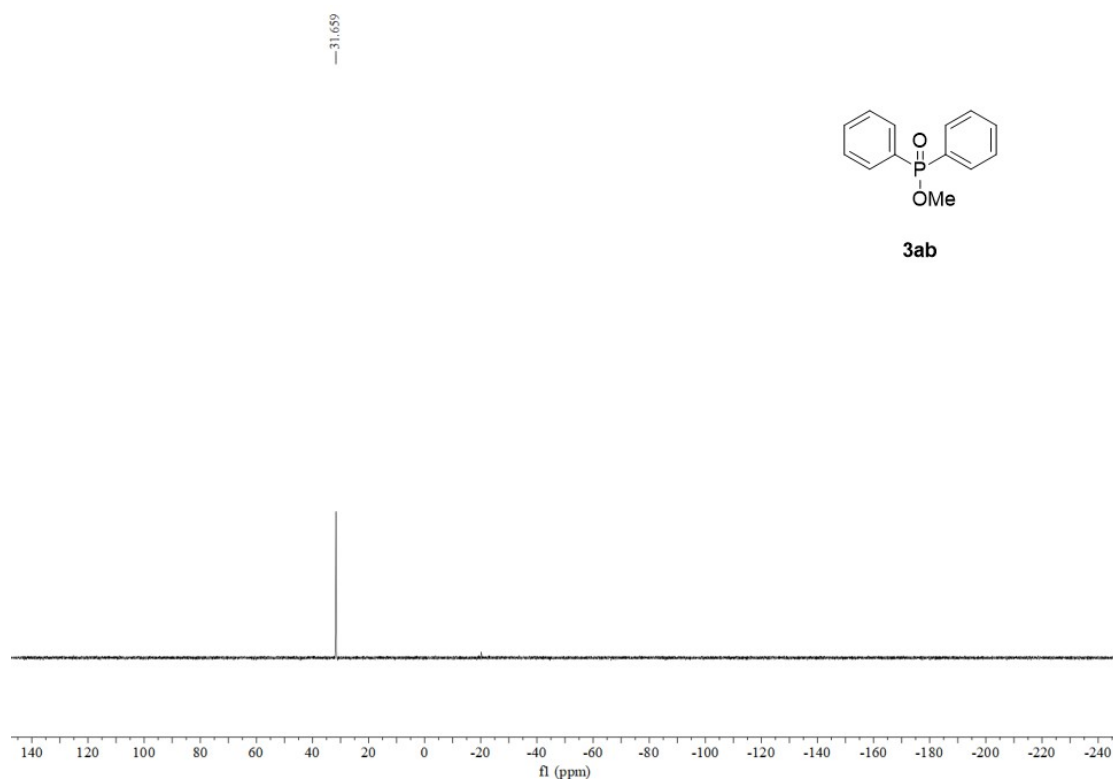
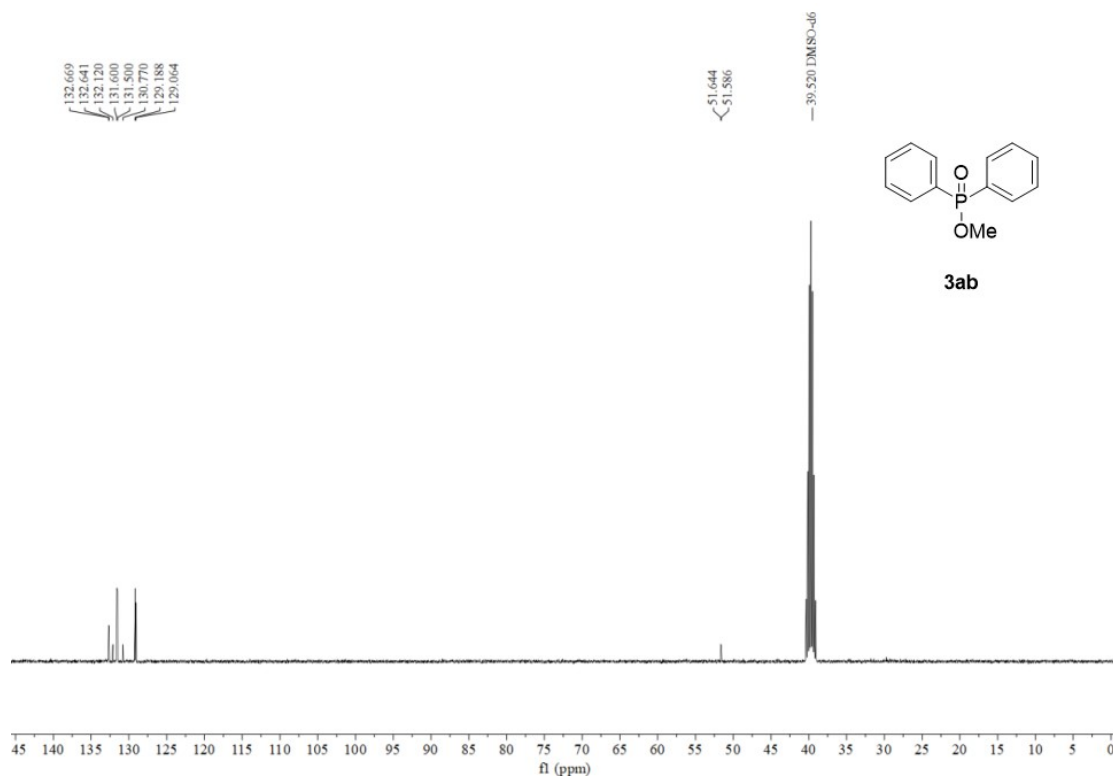
Colorless oil (118 mg, 68%): ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 8.52 (d, $J = 13.9$ Hz, 2H), 8.09 (d, $J = 8.1$ Hz, 2H), 8.03 (dd, $J = 8.4, 3.2$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.83 – 7.79 (m, 2H), 7.62 – 7.57 (m, 5H), 4.00 (q, $J = 6.7$ Hz, 2H), 1.68 – 1.63 (m, 2H), 1.42 – 1.33 (m, 2H), 0.82 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 133.68 (d, $J = 3.3$ Hz), 133.56, 133.43 (d, $J = 10.4$ Hz), 132.27 (d, $J = 10.5$ Hz), 129.24, 127.99 (d, $J = 132.0$ Hz), 127.53, 126.63, 125.95 (d, $J = 4.9$ Hz), 125.18 (d, $J = 14.5$ Hz), 61.32 (d, $J = 5.8$ Hz), 16.43 (d, $J = 6.4$ Hz); ^{31}P NMR (243

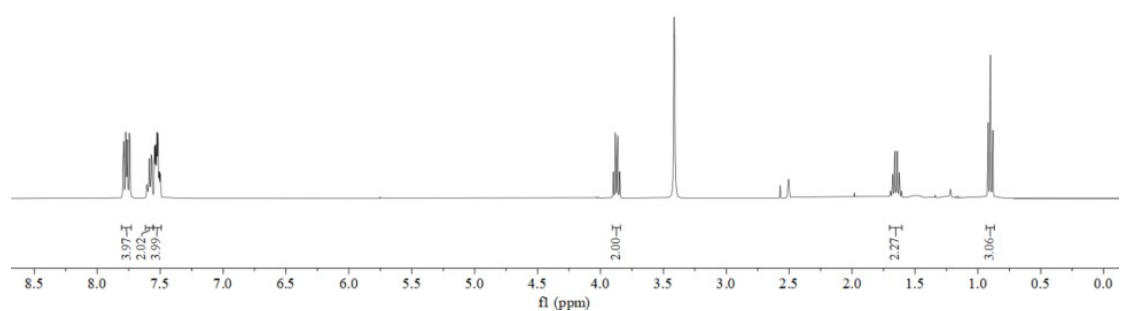
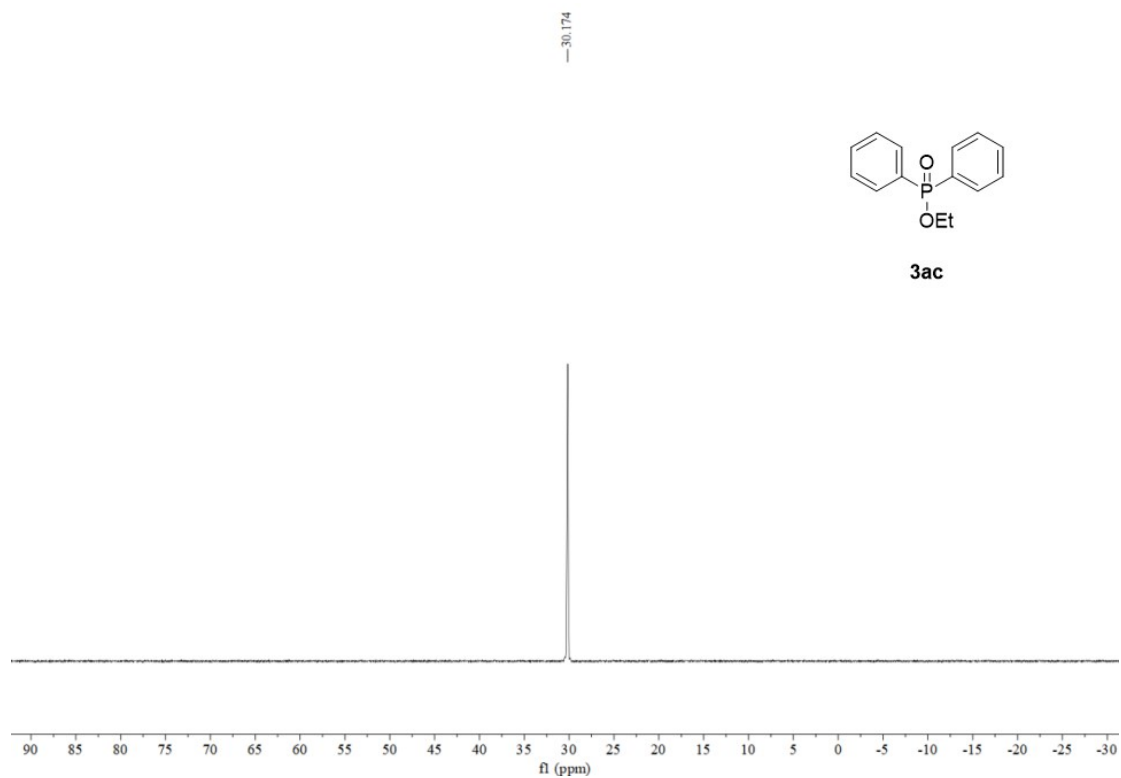
MHz, DMSO-*d*₆) δ 31.46. HRMS (ESI) calcd for C₂₂H₁₉O₂P [M+H]⁺: 347.1195, found 347.1198.

4. NMR Spectra for Products







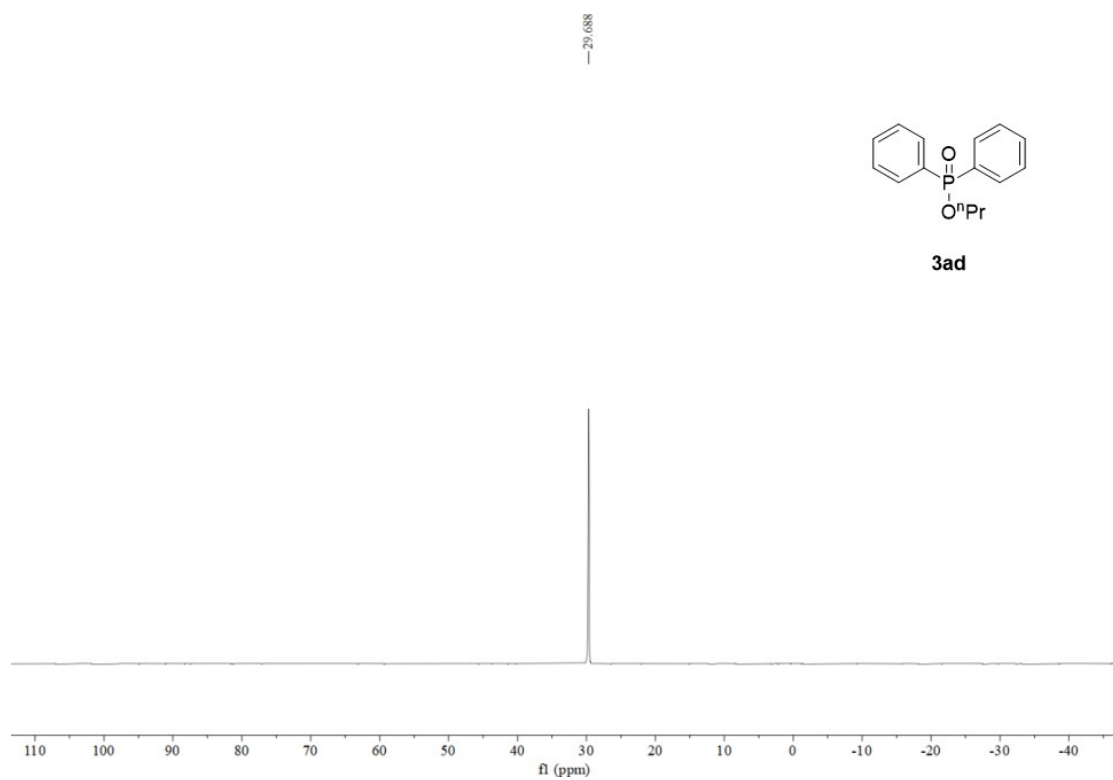
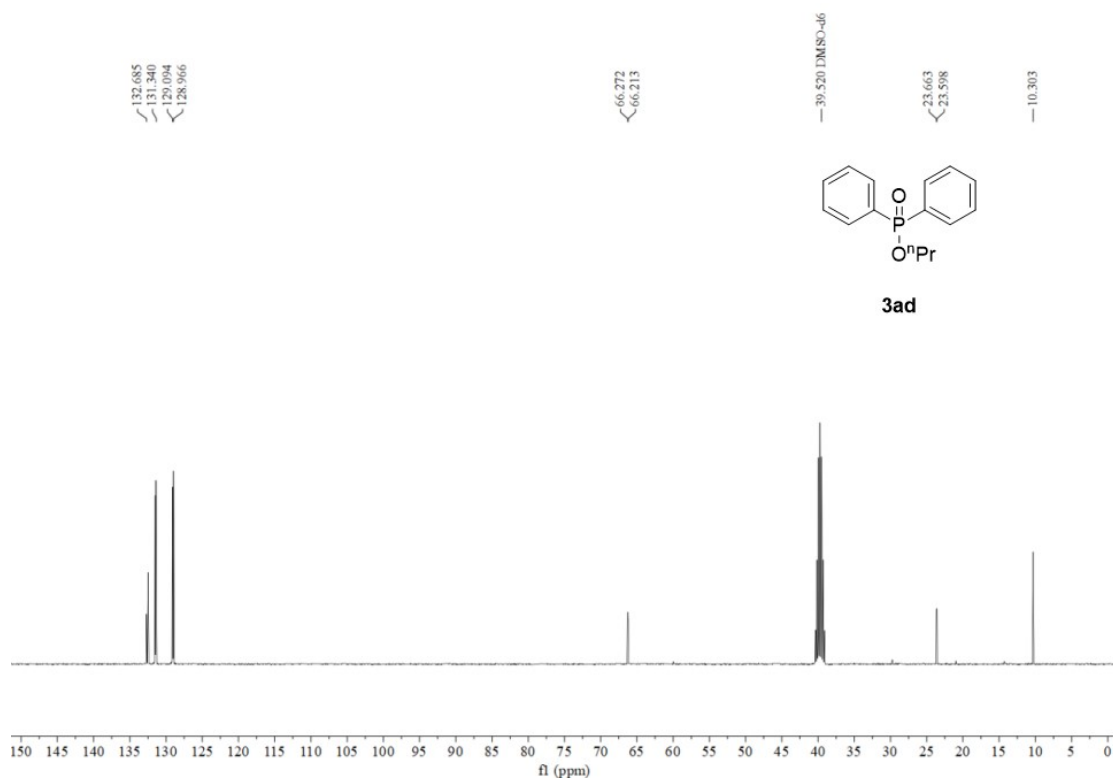


7.799
7.794
7.791
7.787
7.779
7.774
7.770
7.764
7.761
7.757
7.749
7.744
7.740
7.610
7.606
7.603
7.599
7.595
7.588
7.584
7.578
7.574
7.570
7.566
7.562
7.545
7.540
7.530
7.526
7.521
7.517
7.512
7.508
7.504
7.500
7.496

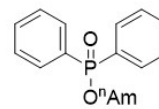
3.897
3.881
3.864
3.847

—2.500 DMSO-d6

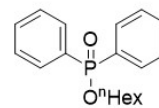
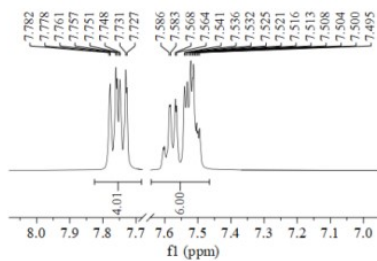
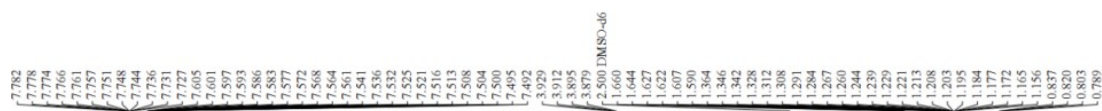
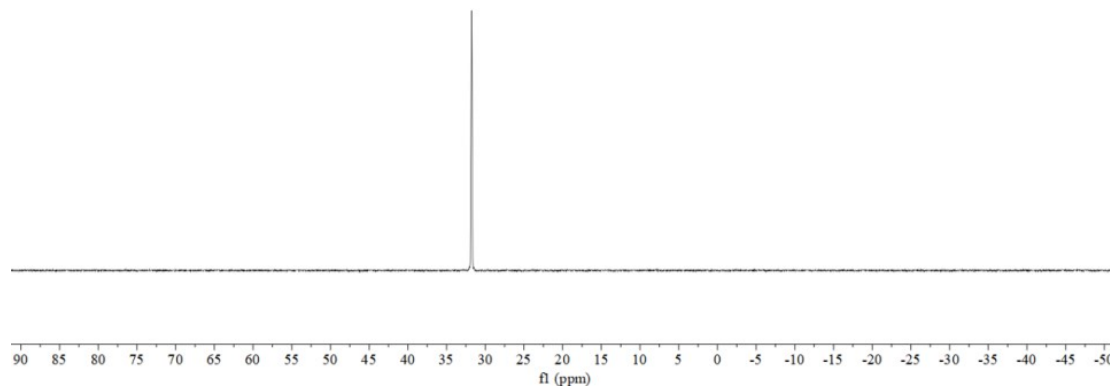
1.694
1.677
1.659
1.642
1.624
1.607
0.919
0.900
0.882



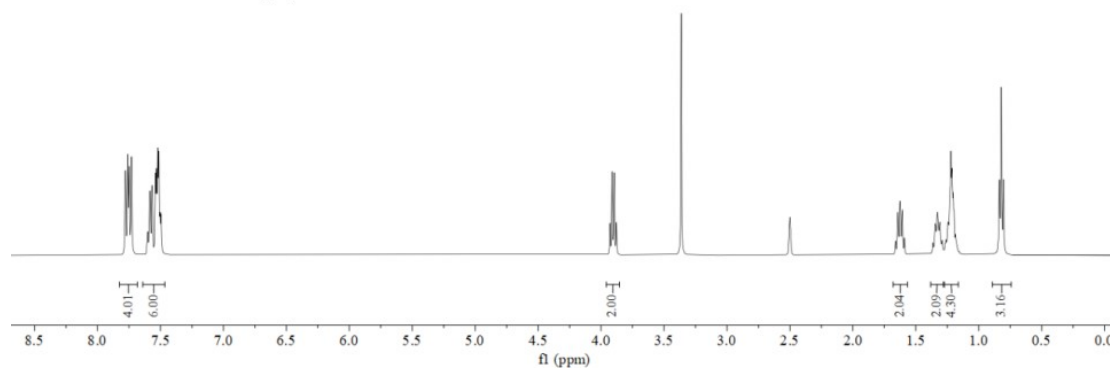
-31.771

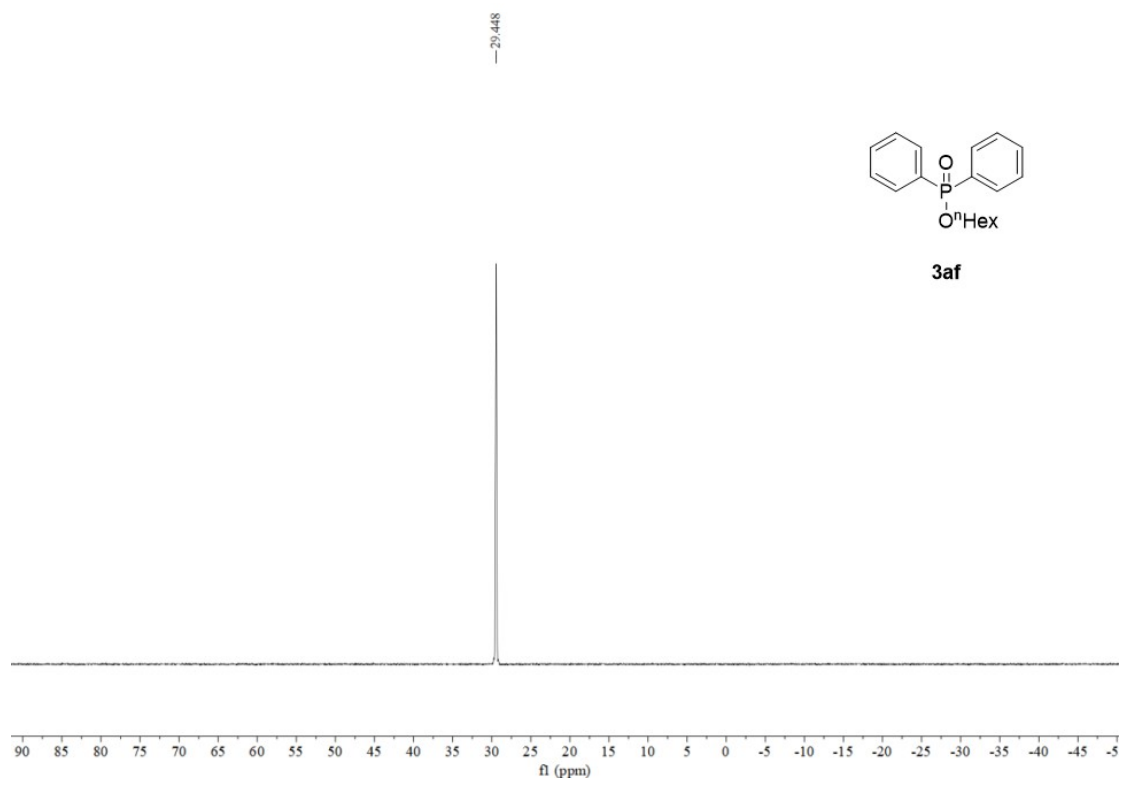
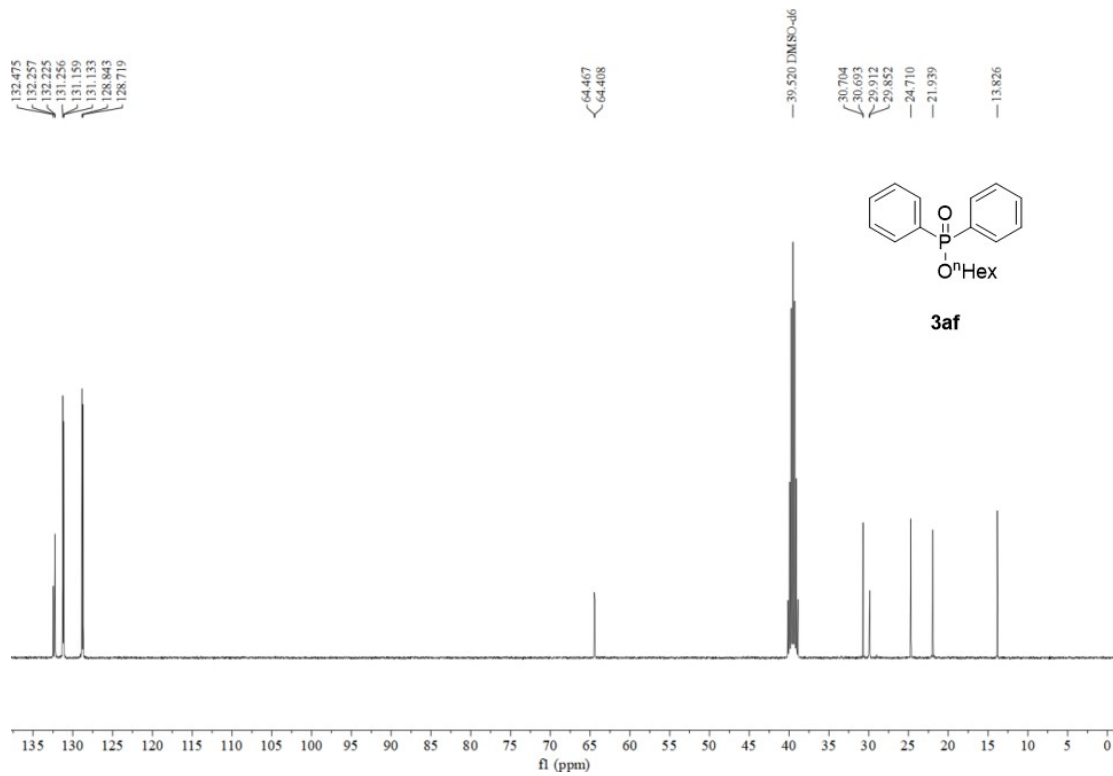


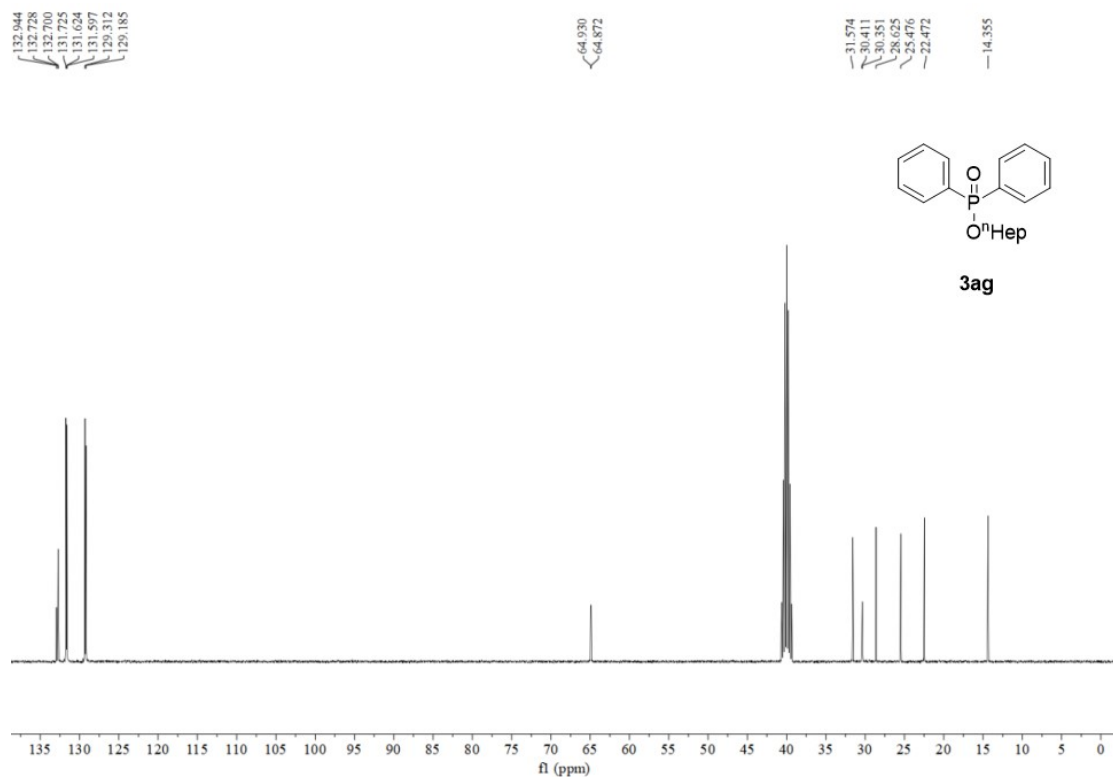
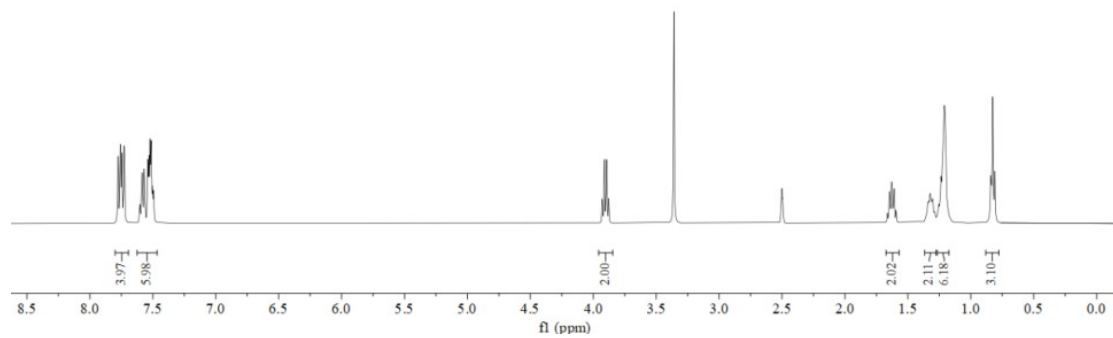
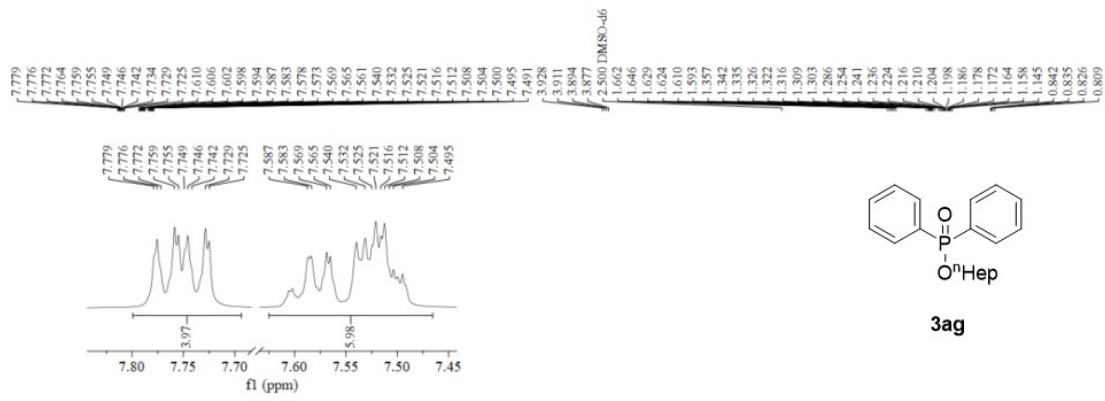
3ae

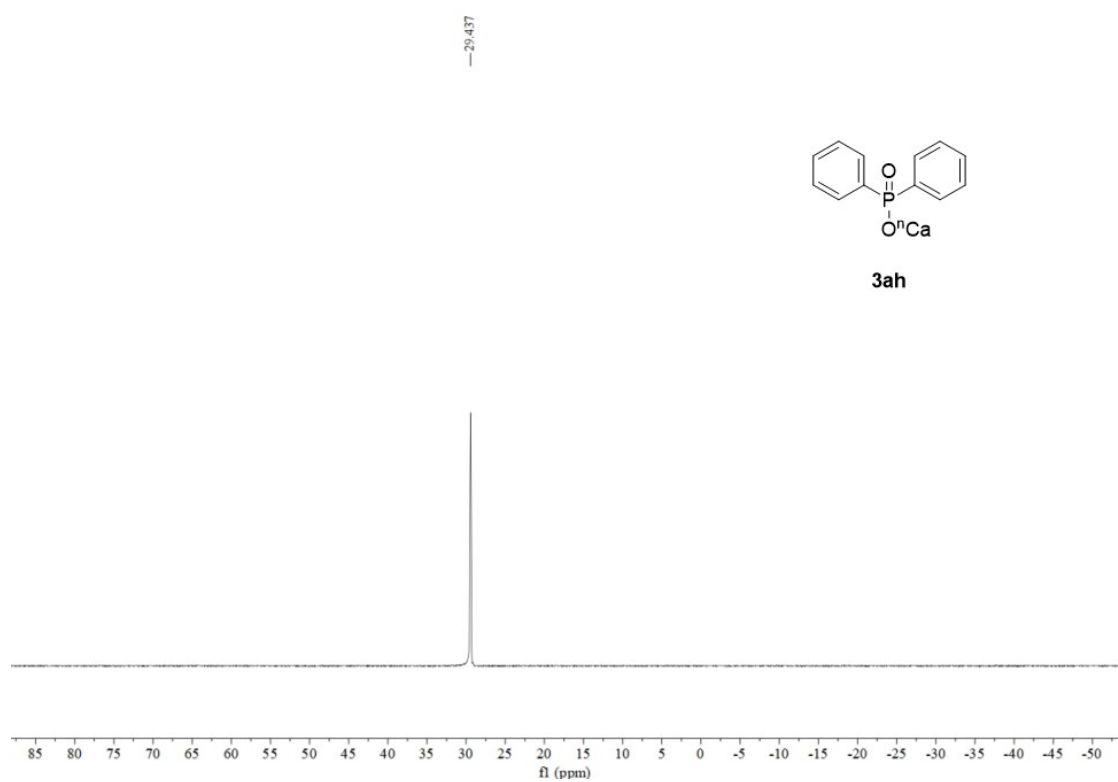
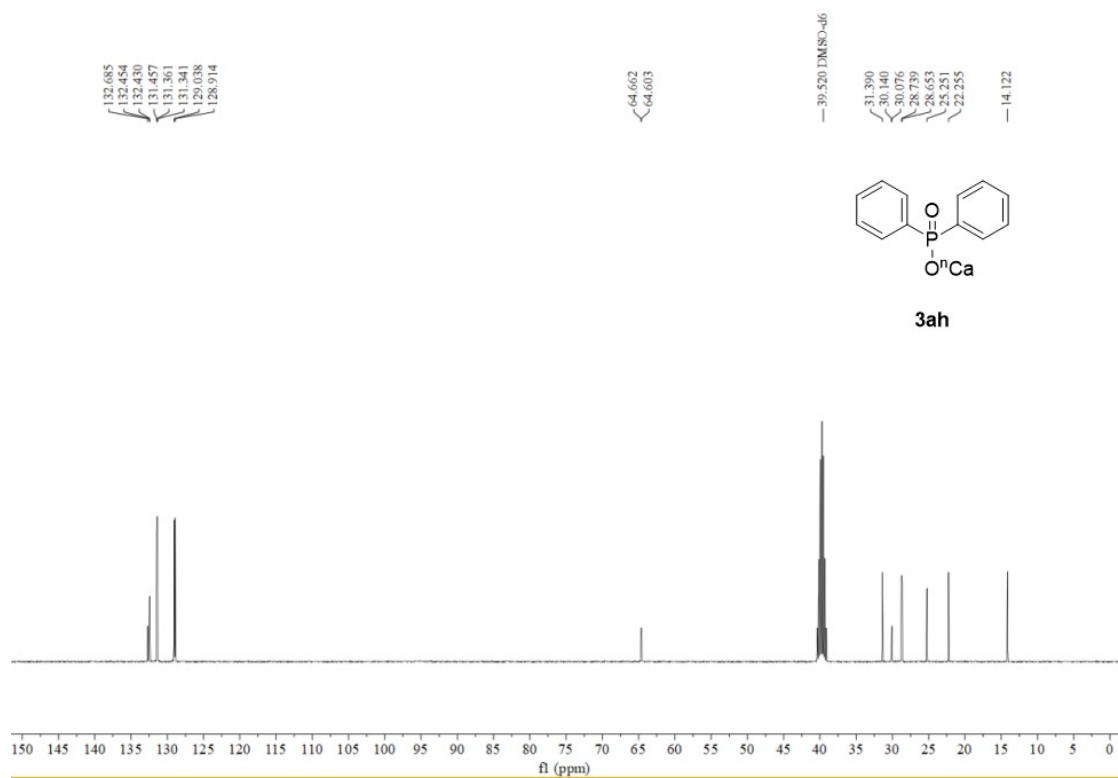


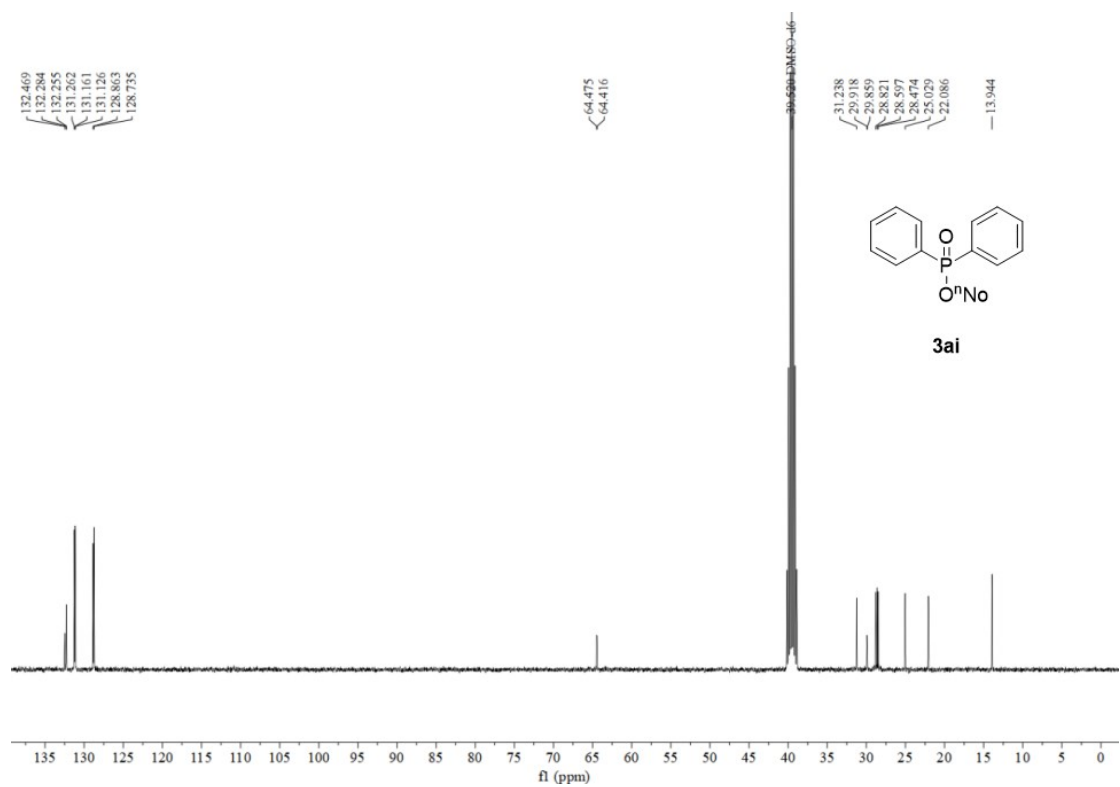
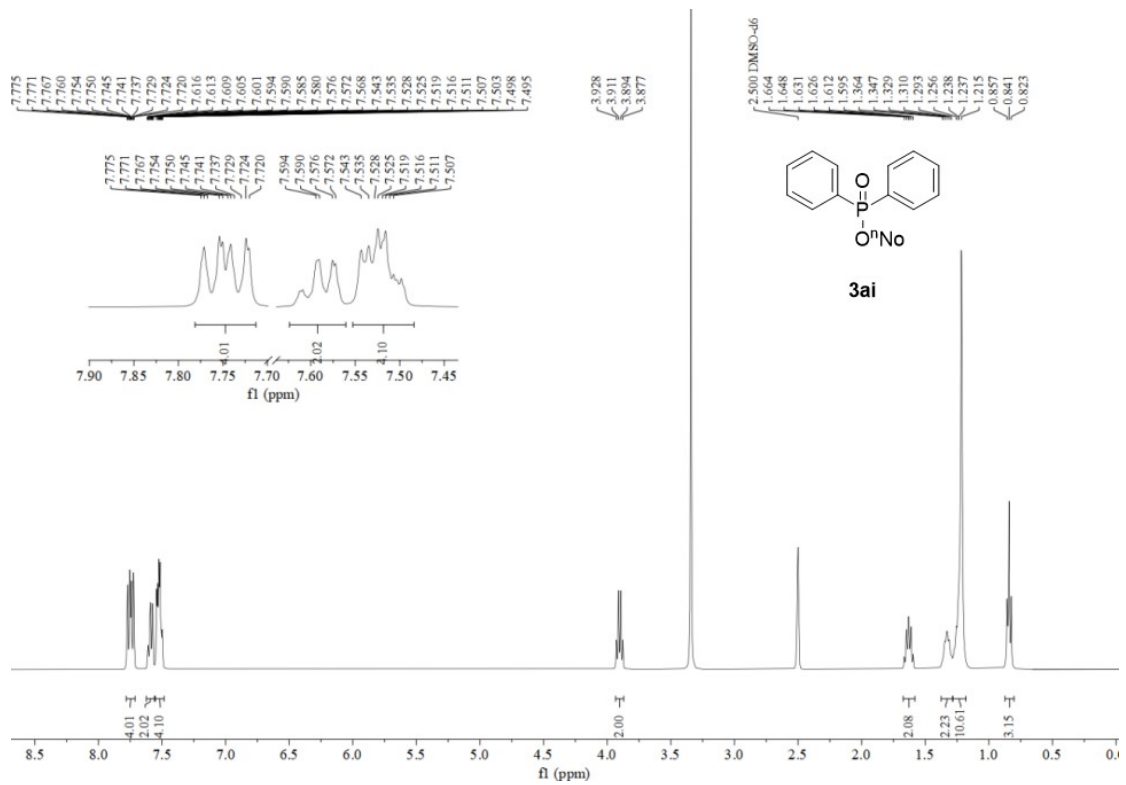
3af

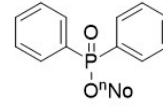




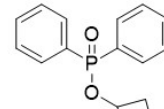
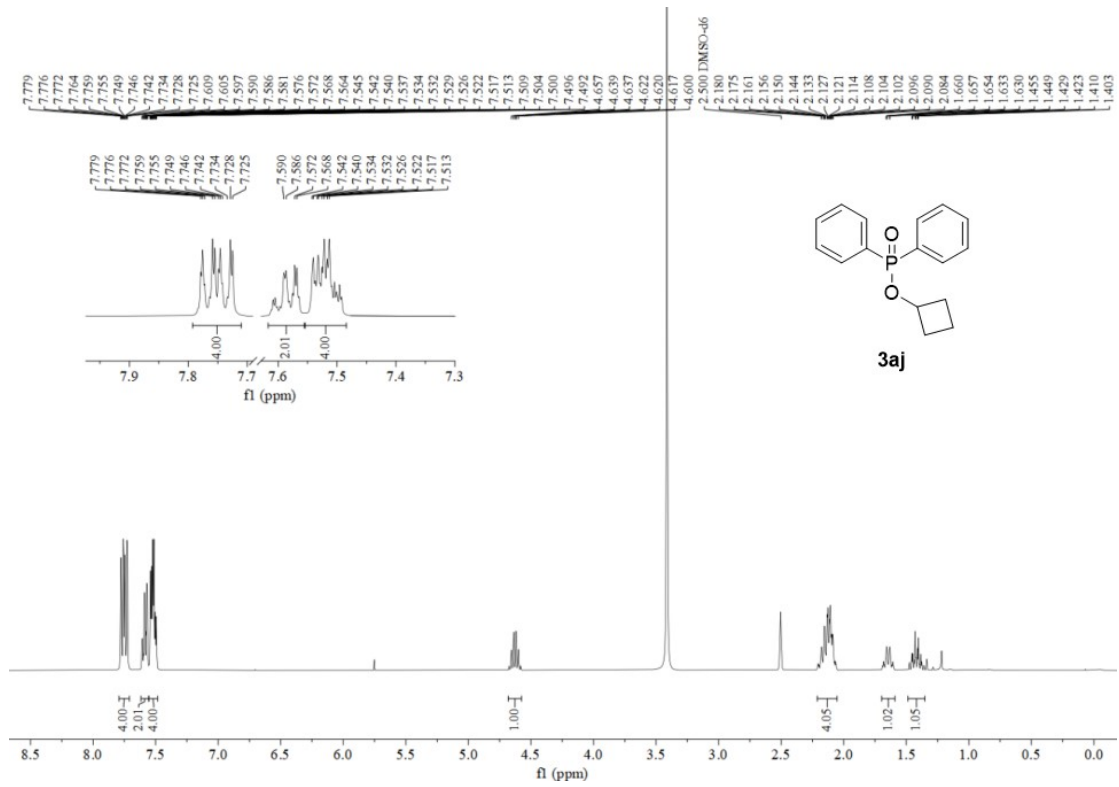
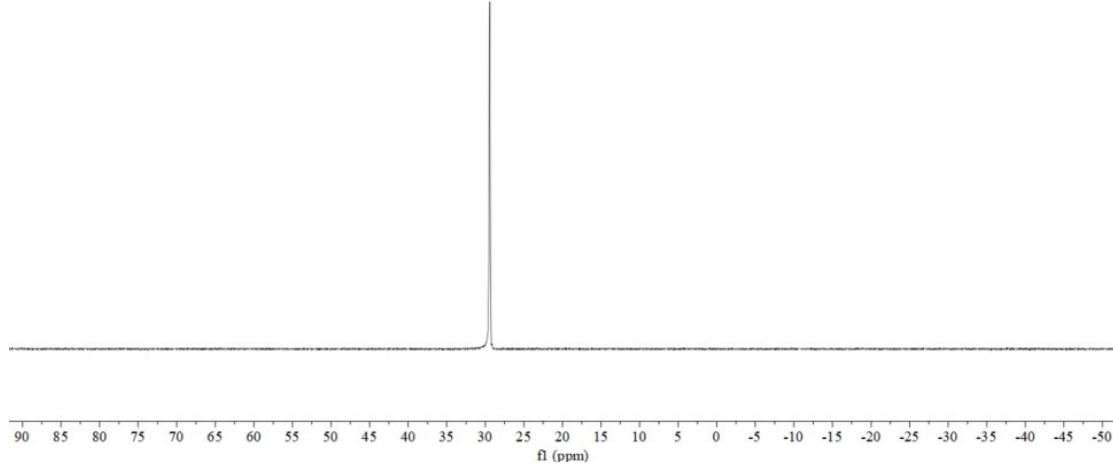




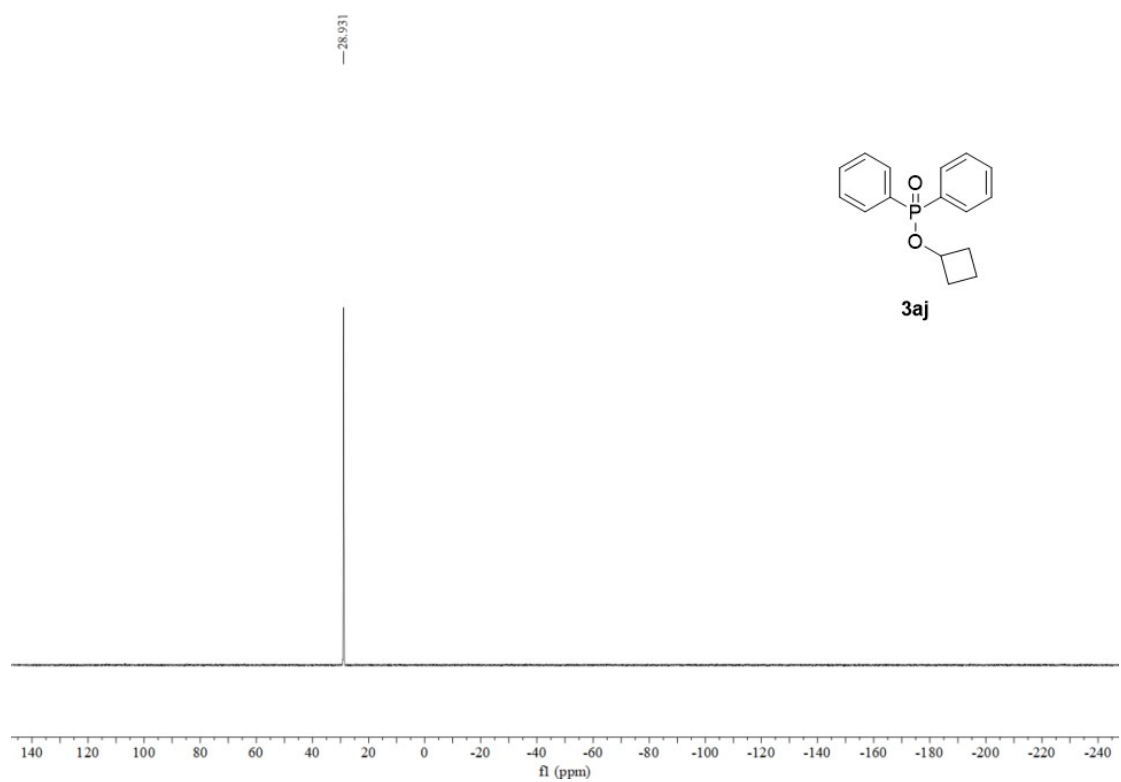
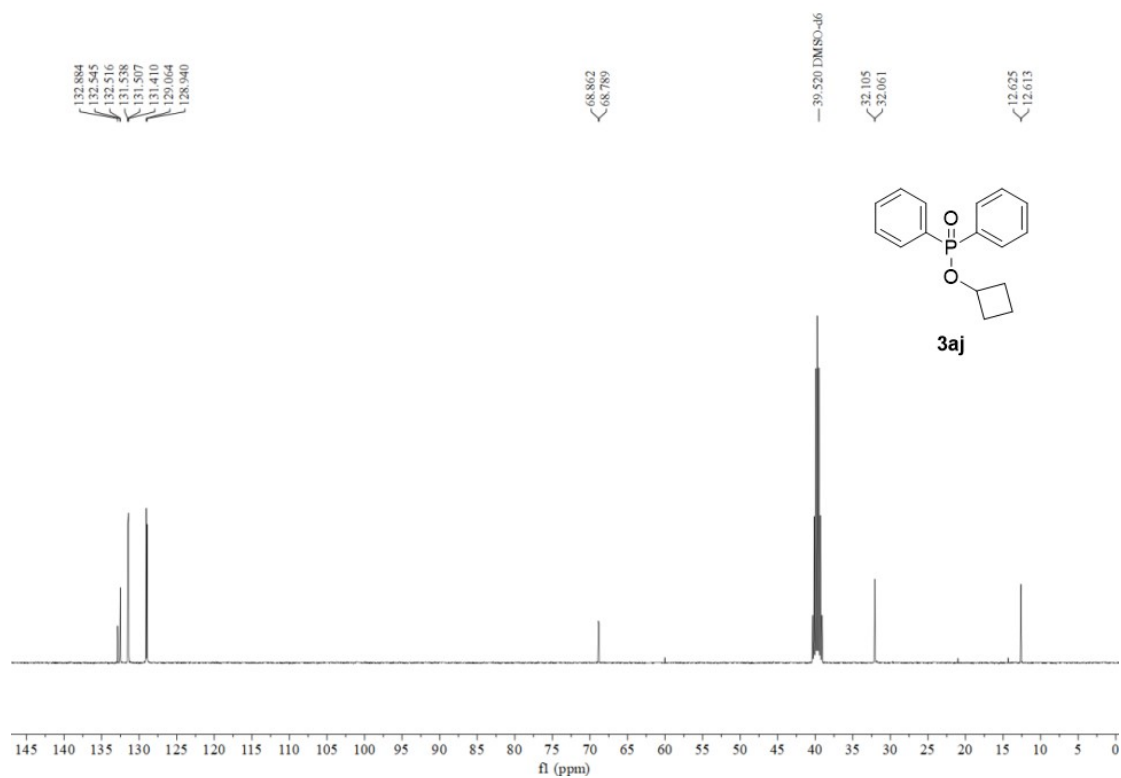


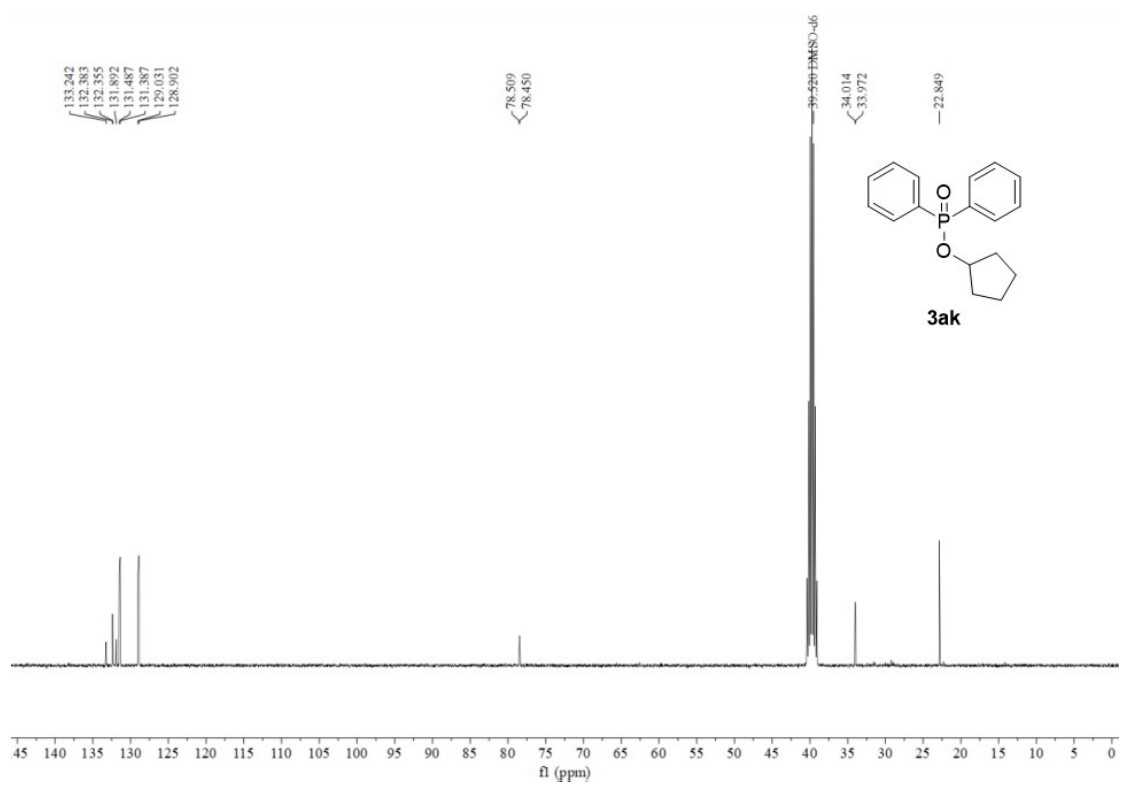
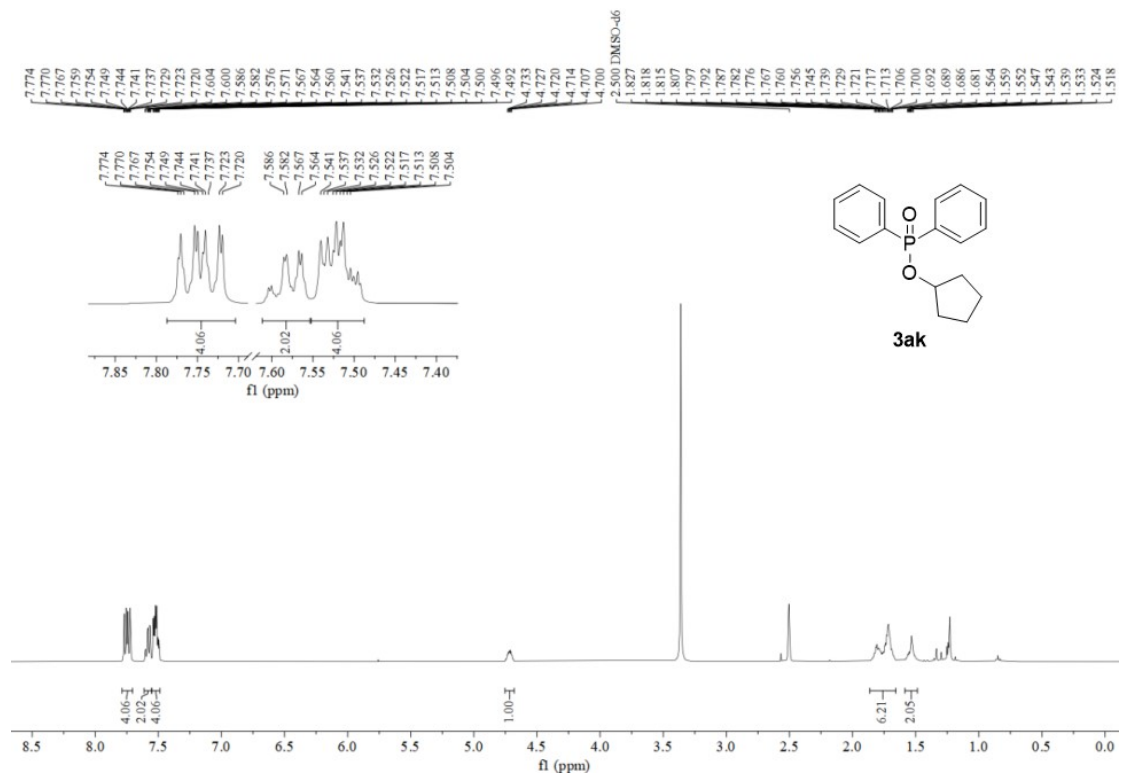


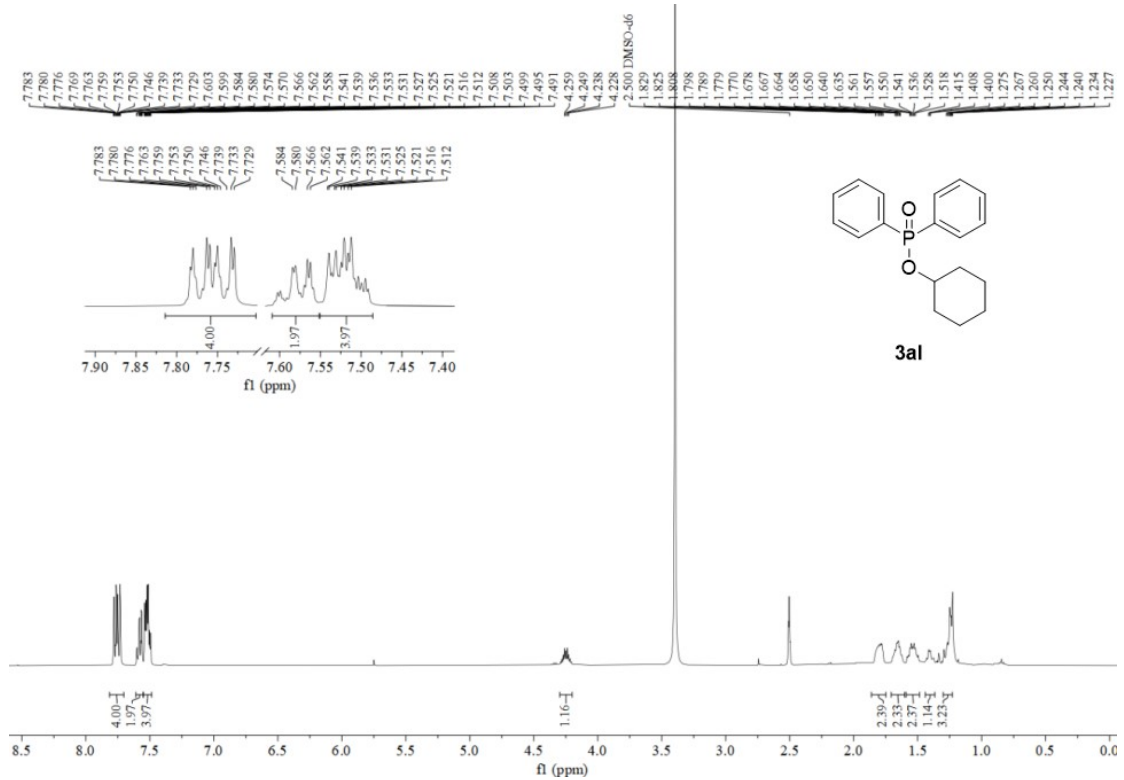
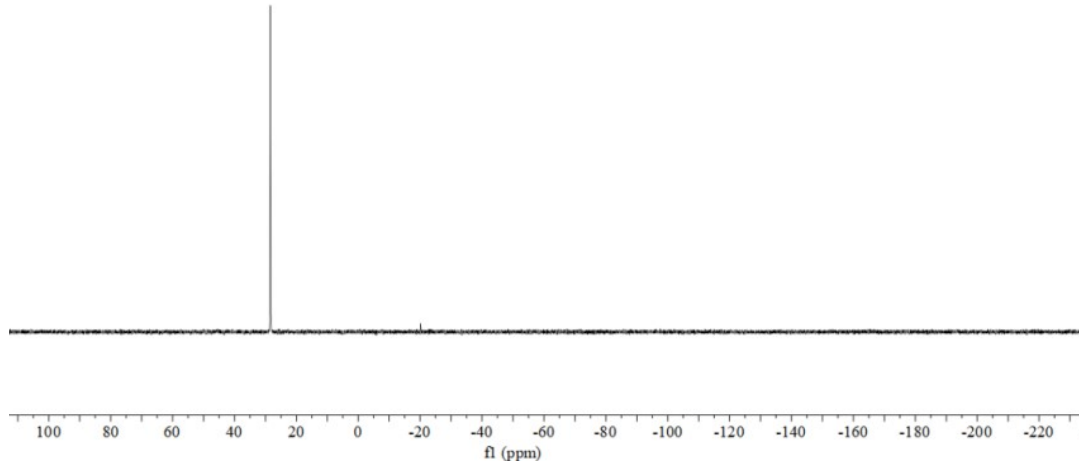
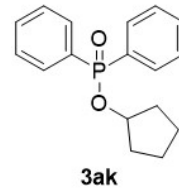
3ai

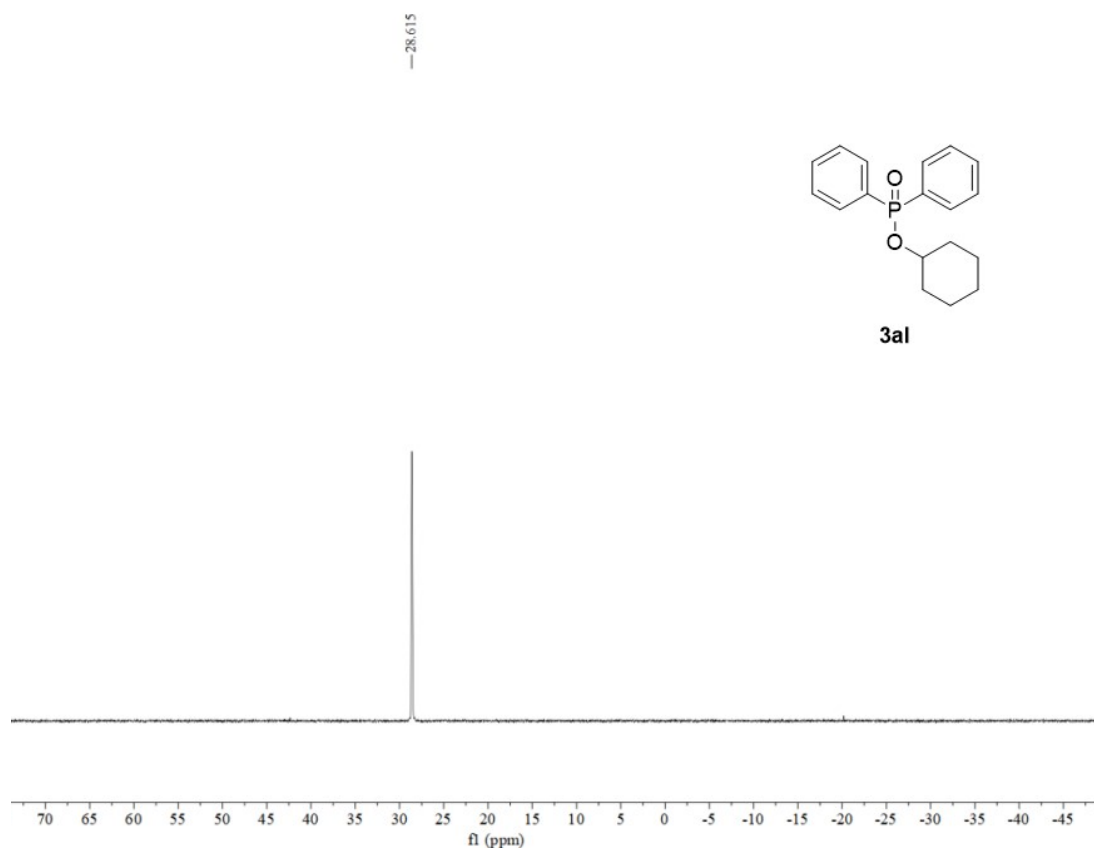
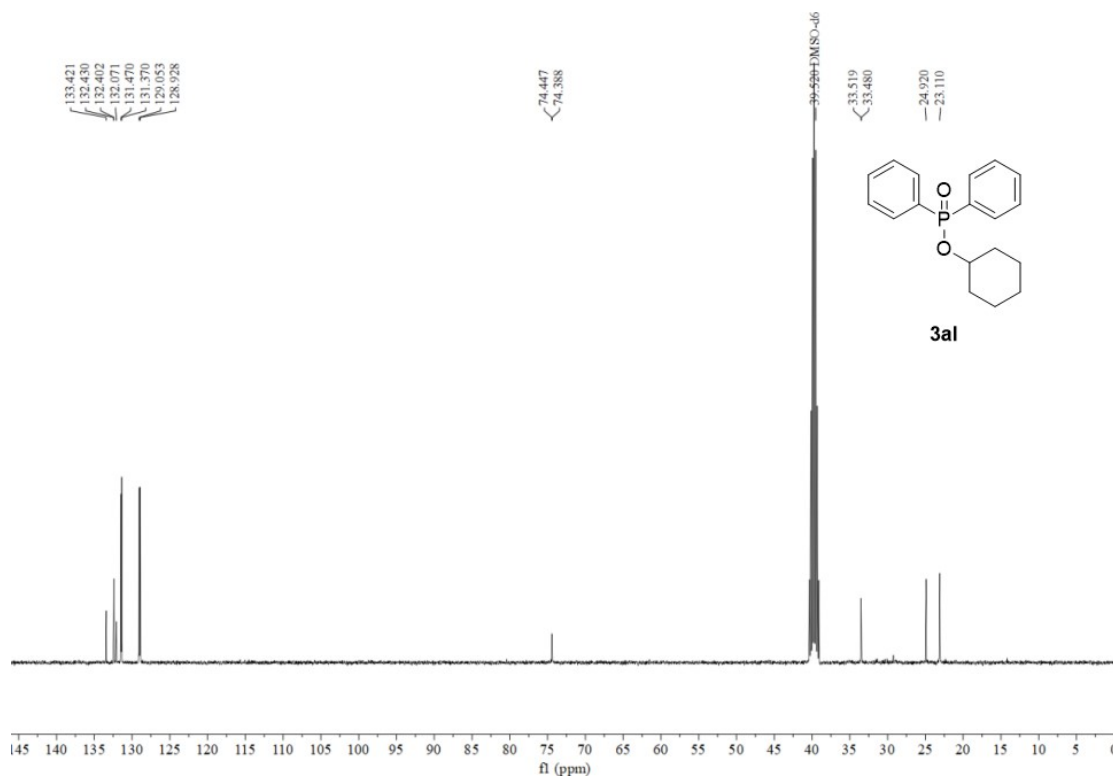


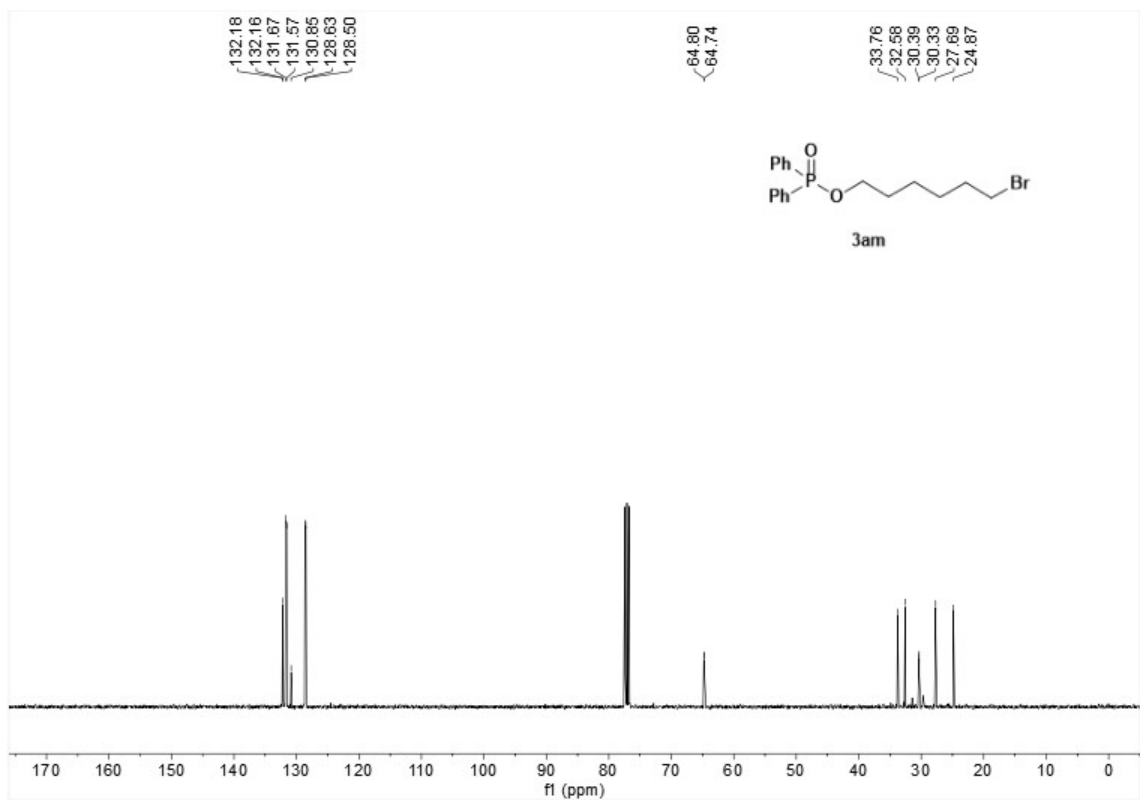
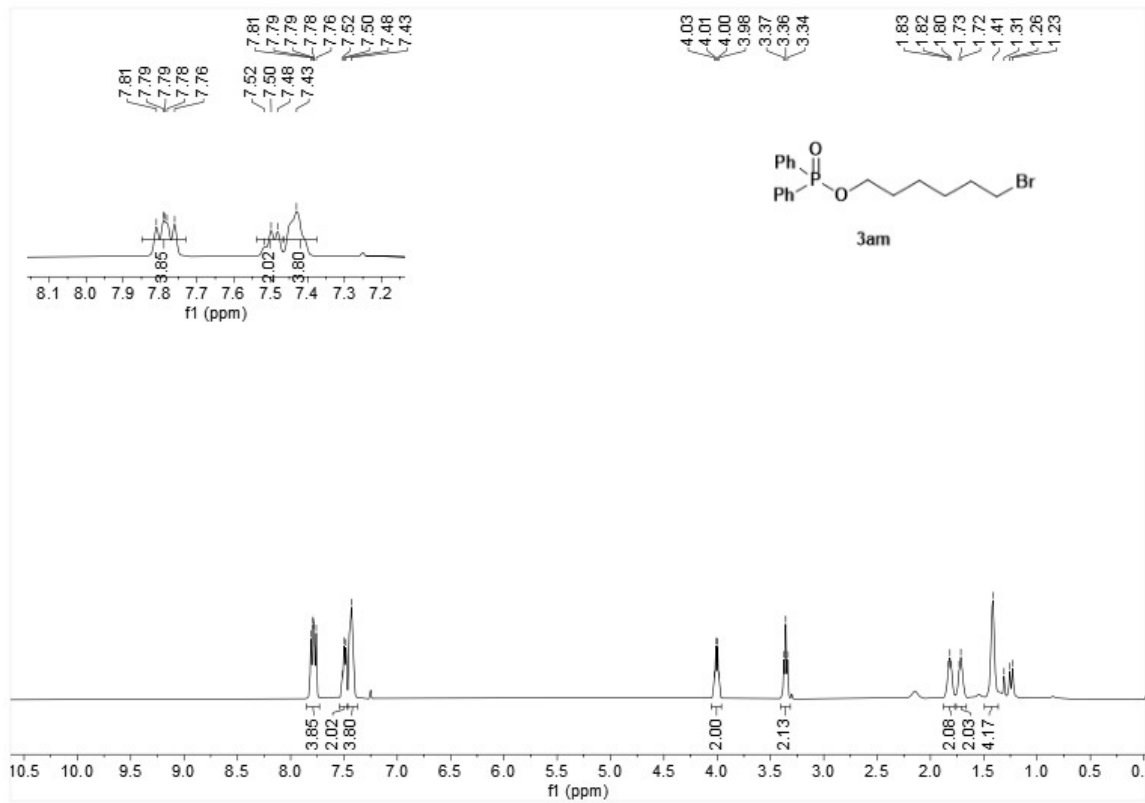
3aj

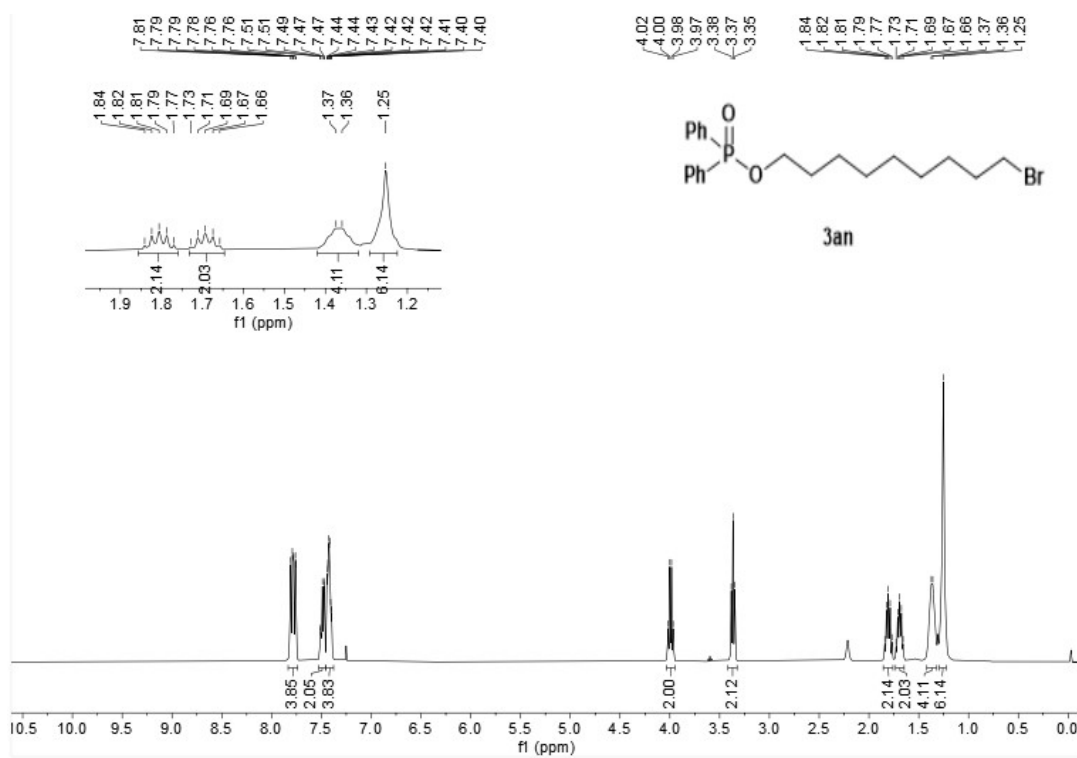
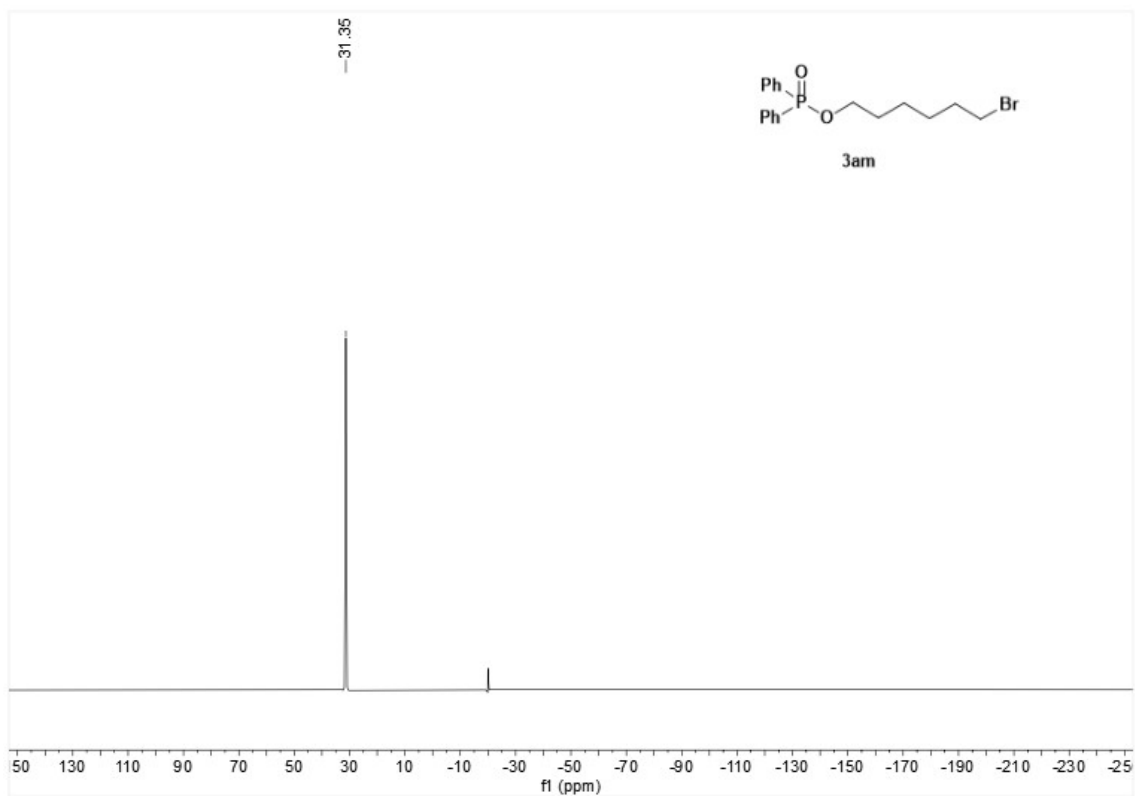


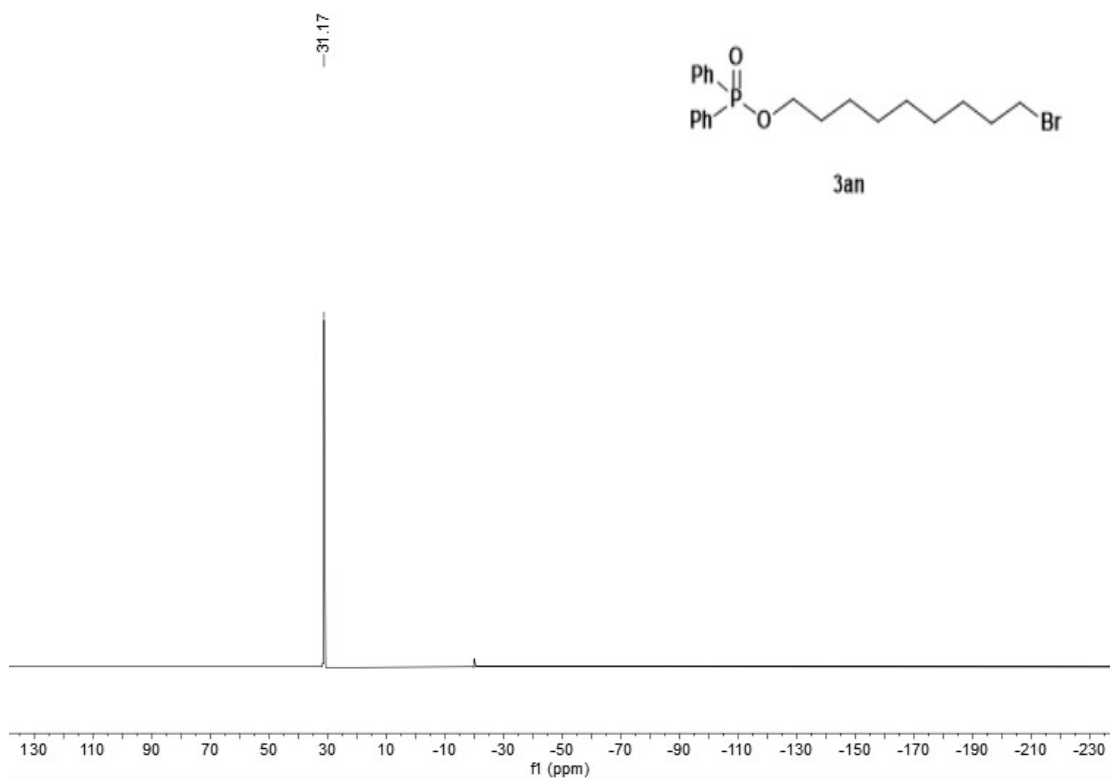
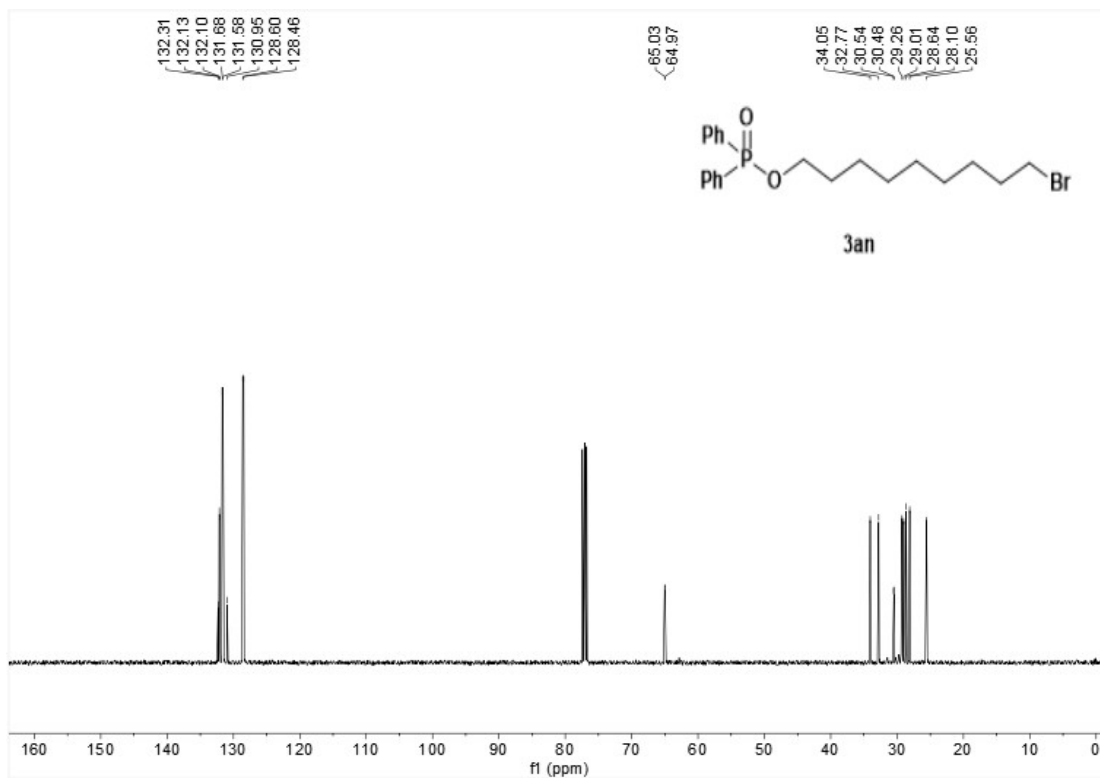


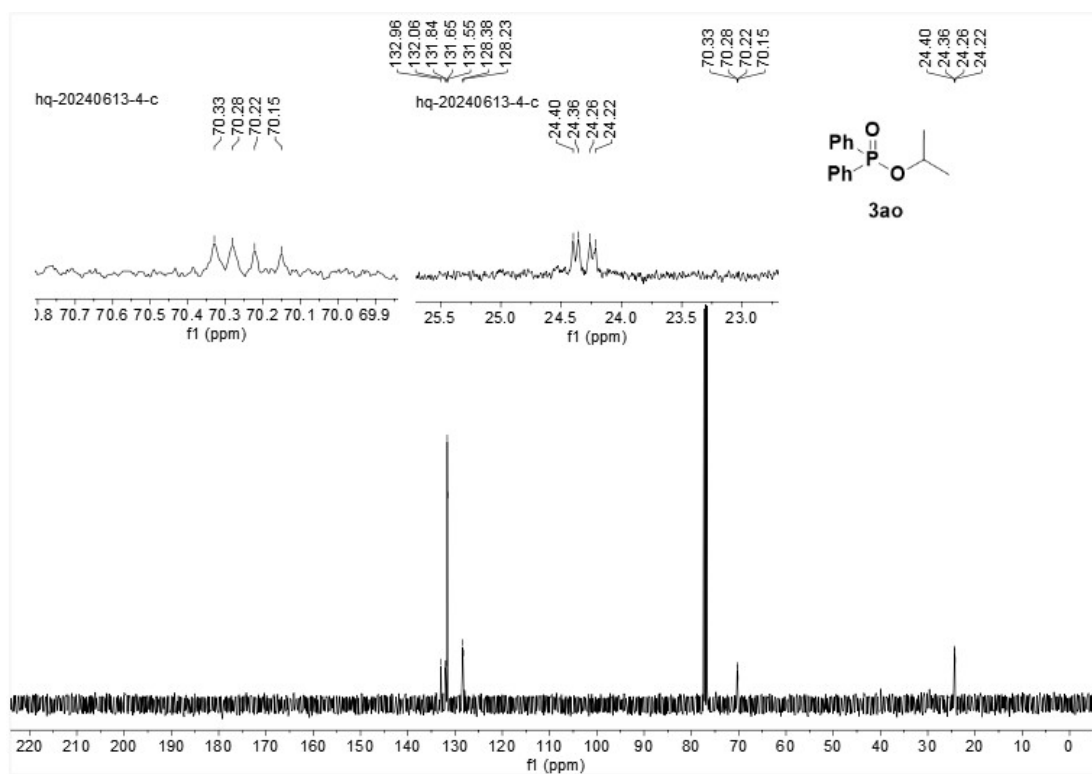
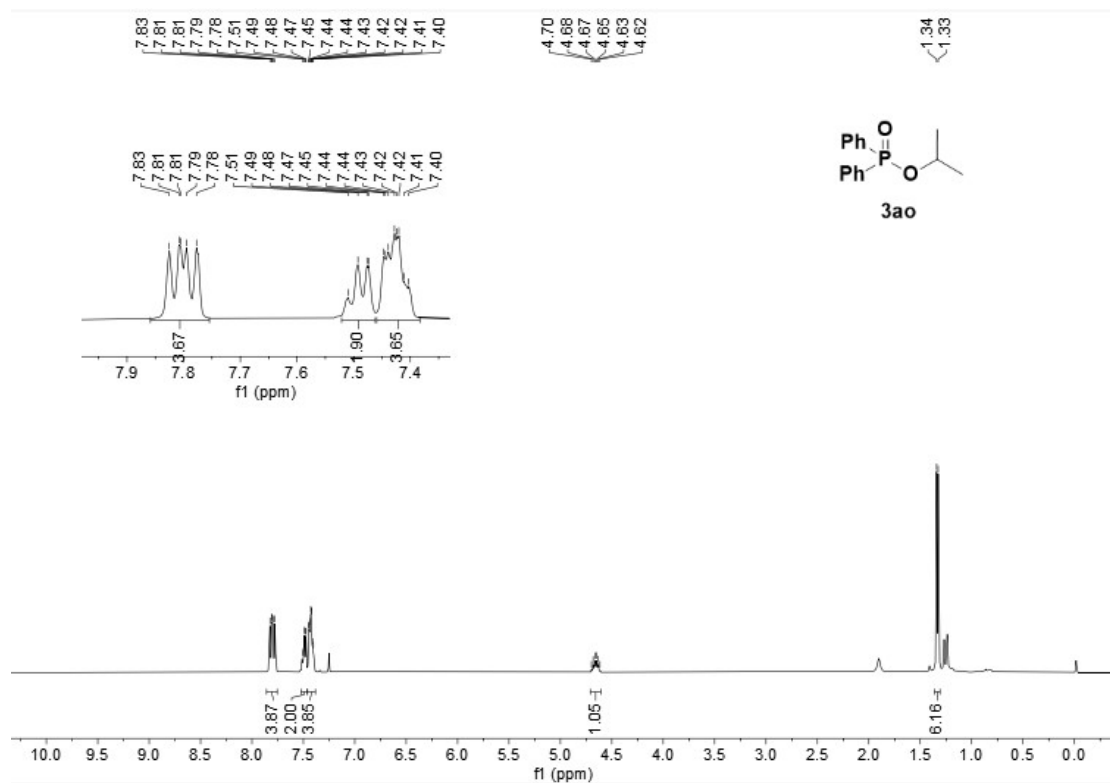


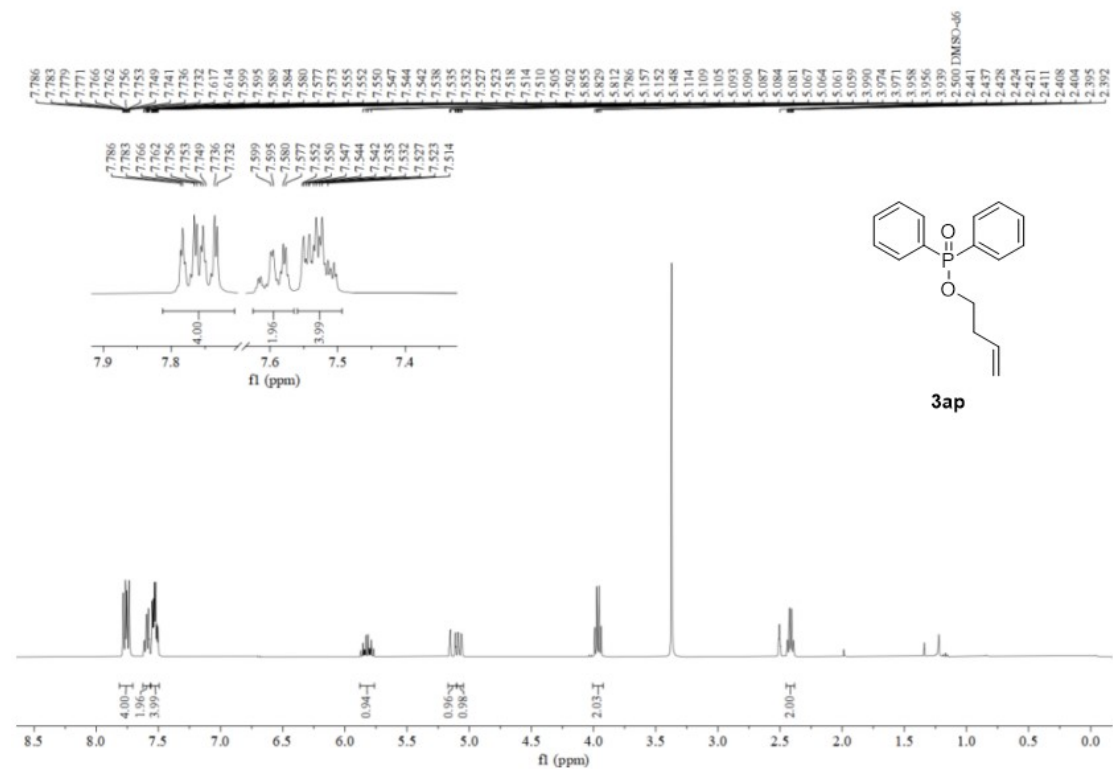
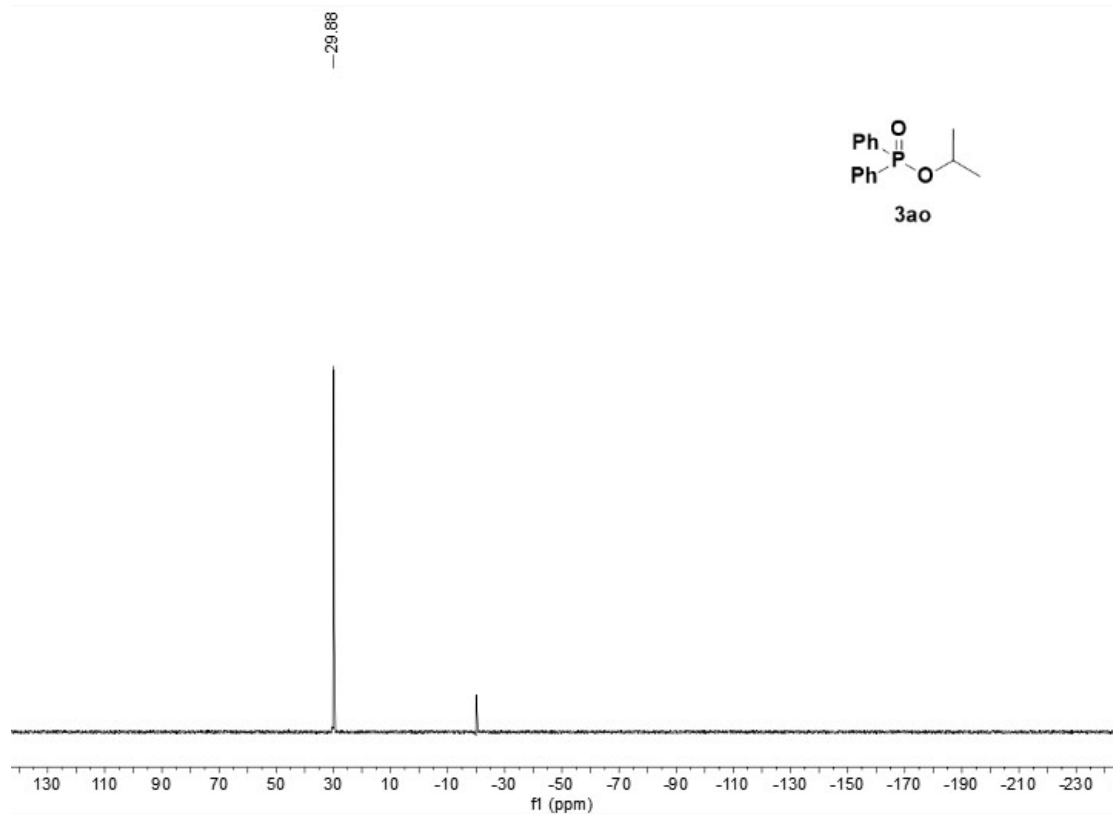


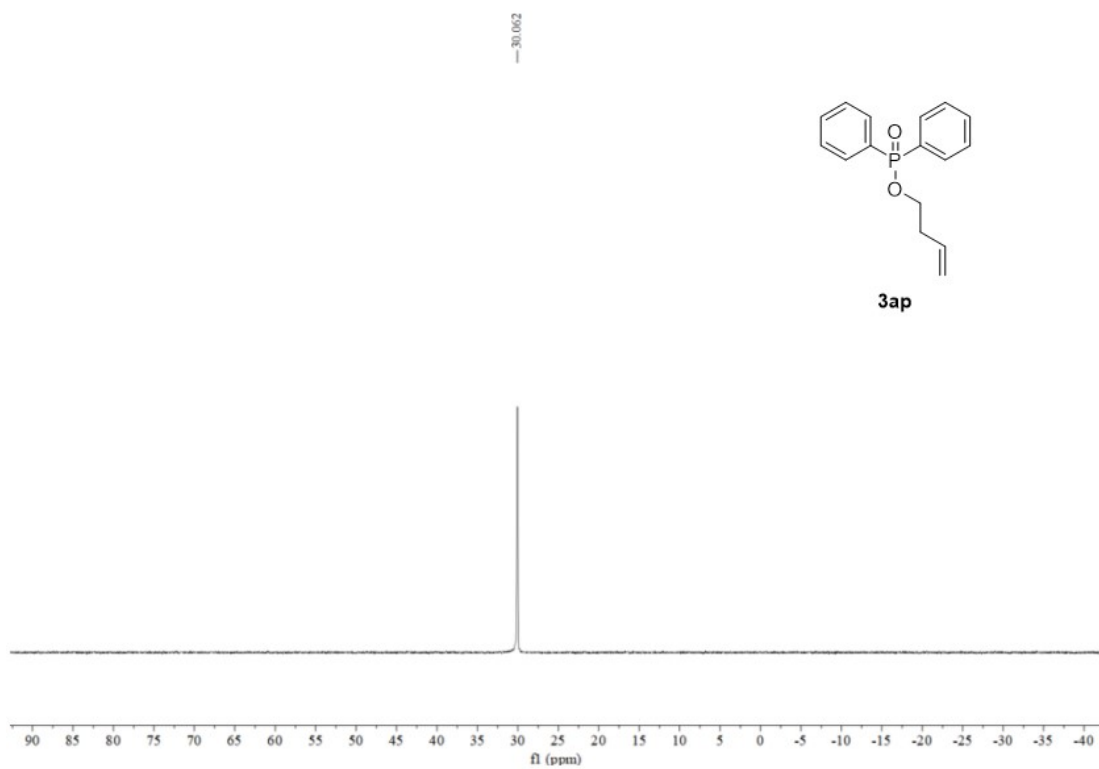
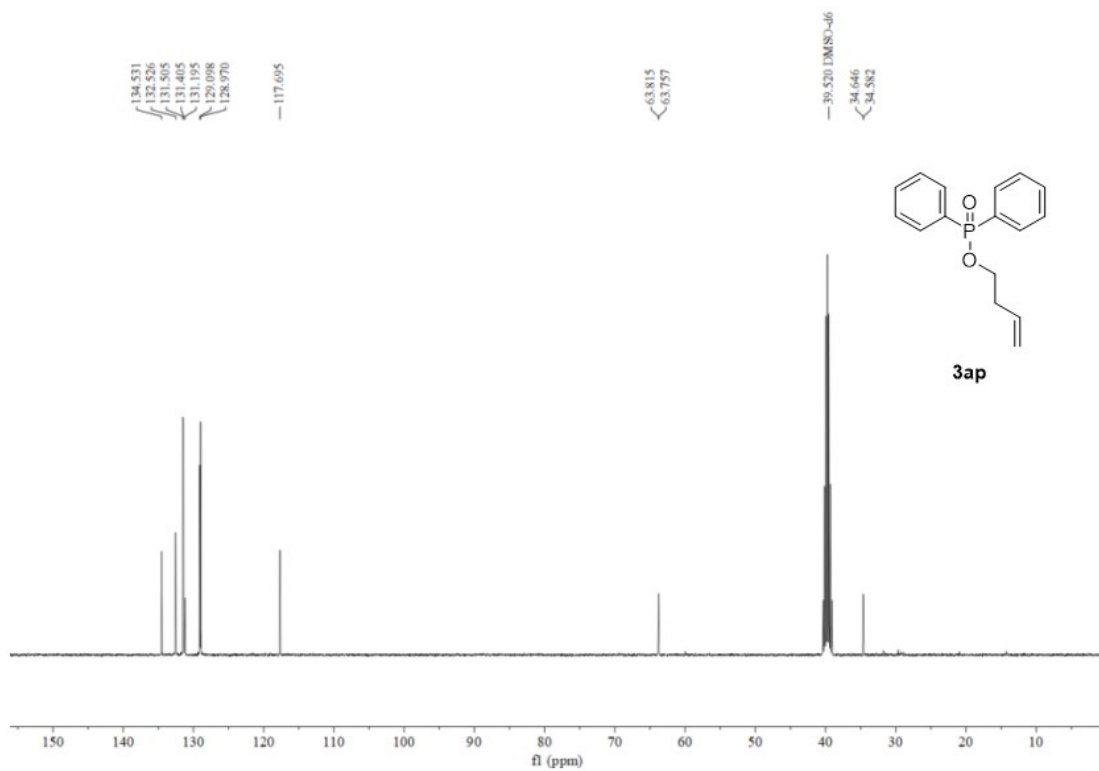


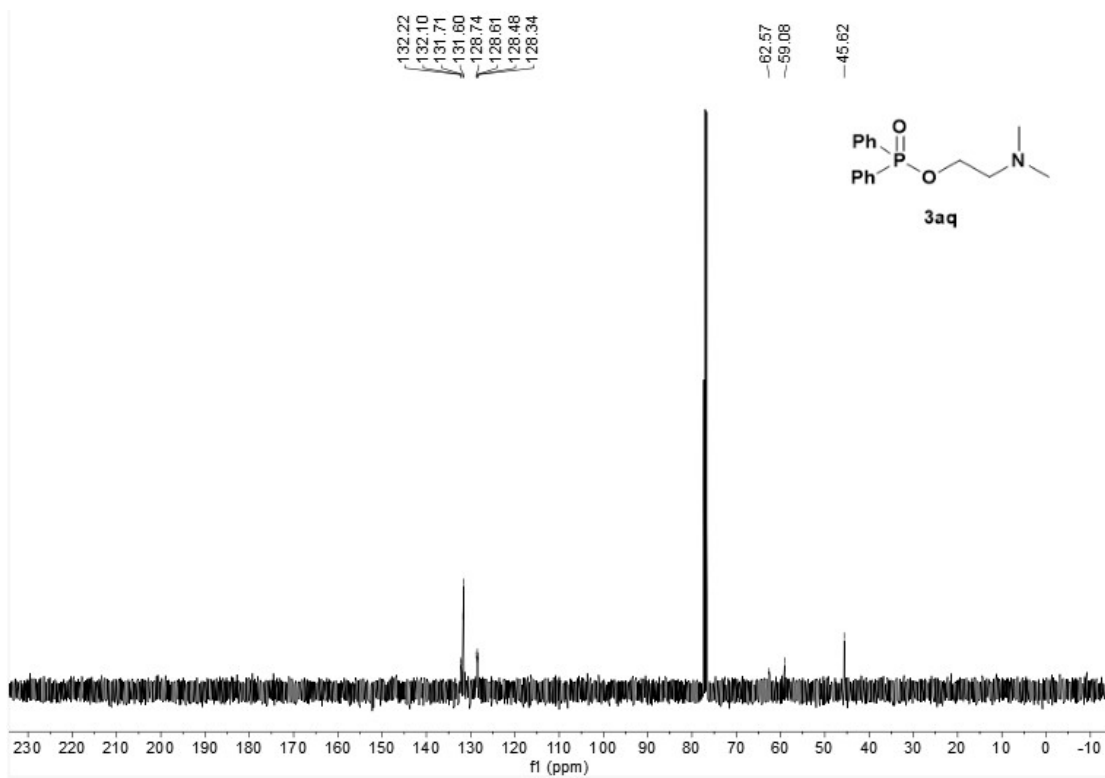
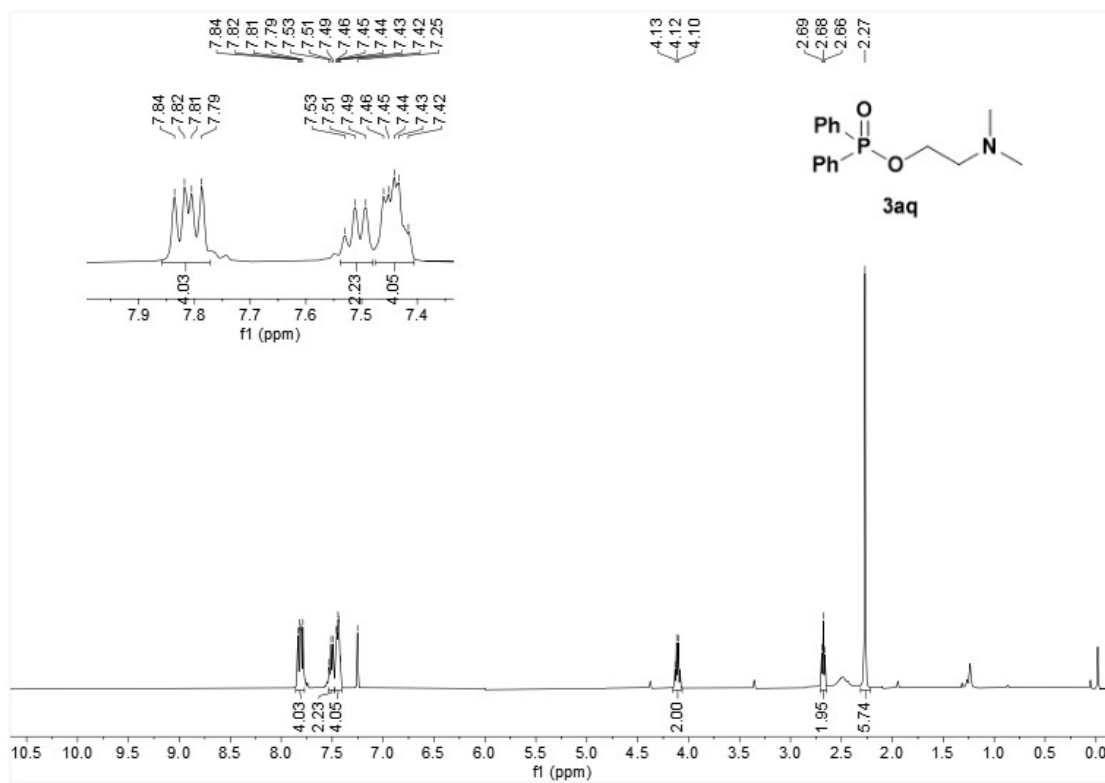


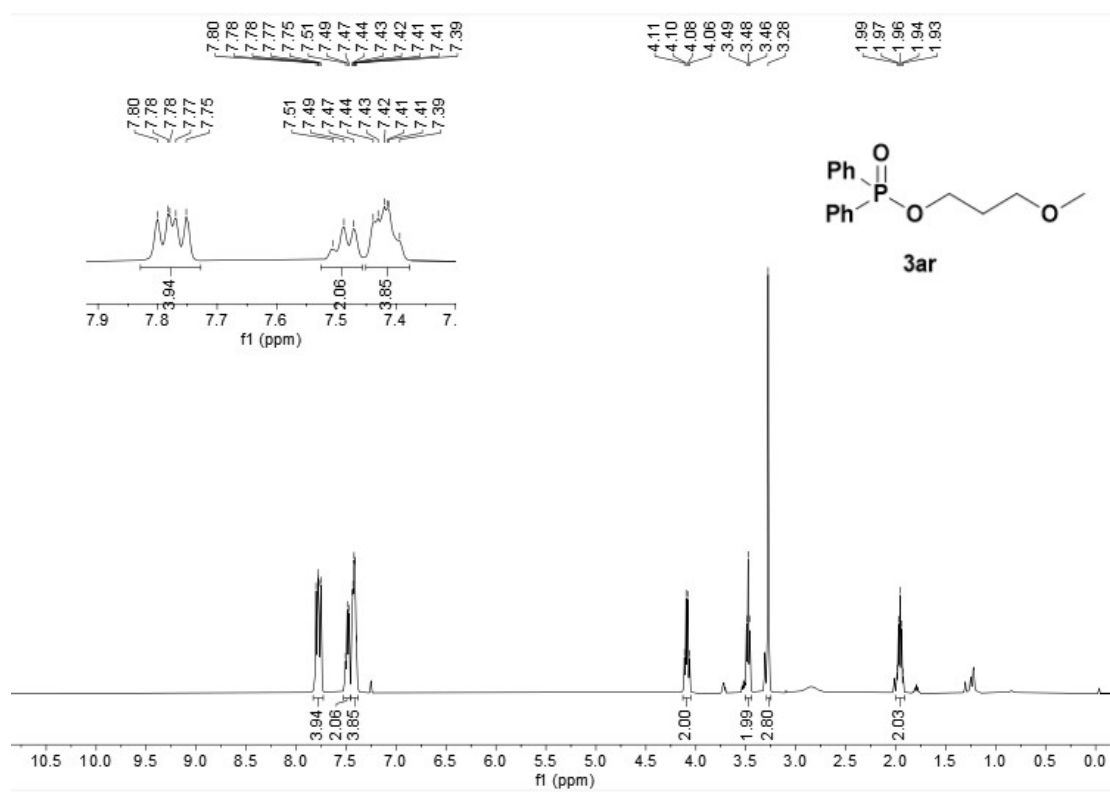
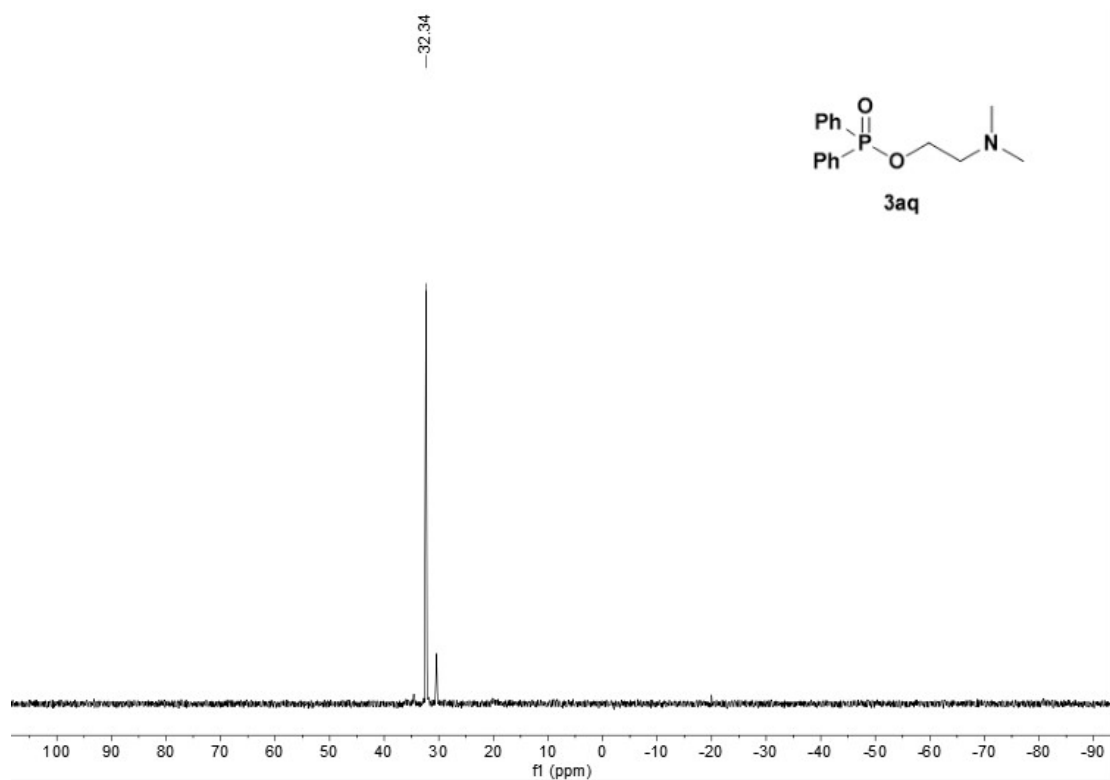


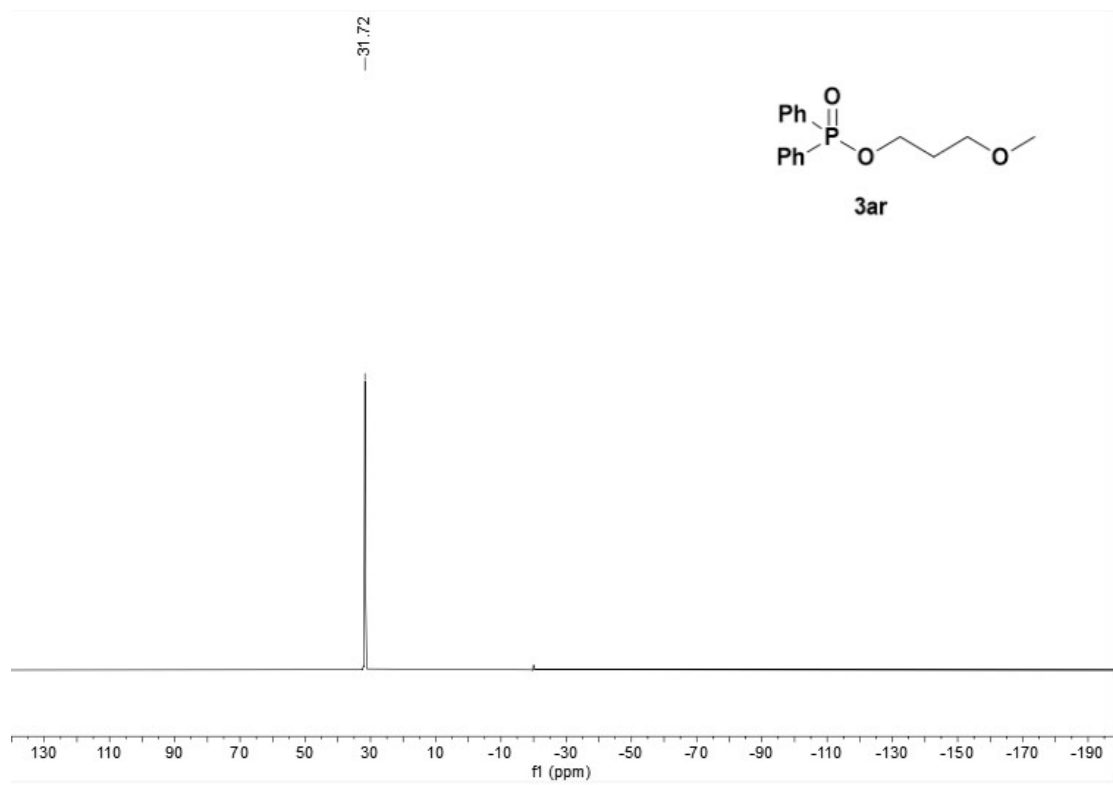
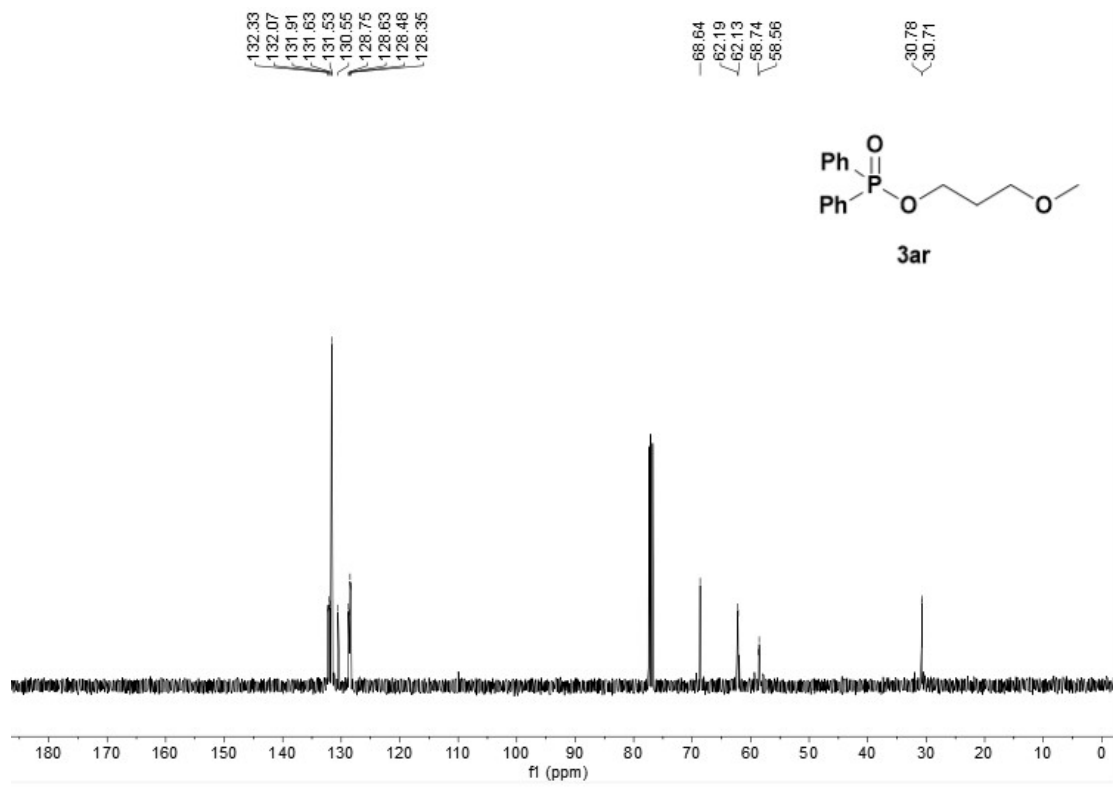


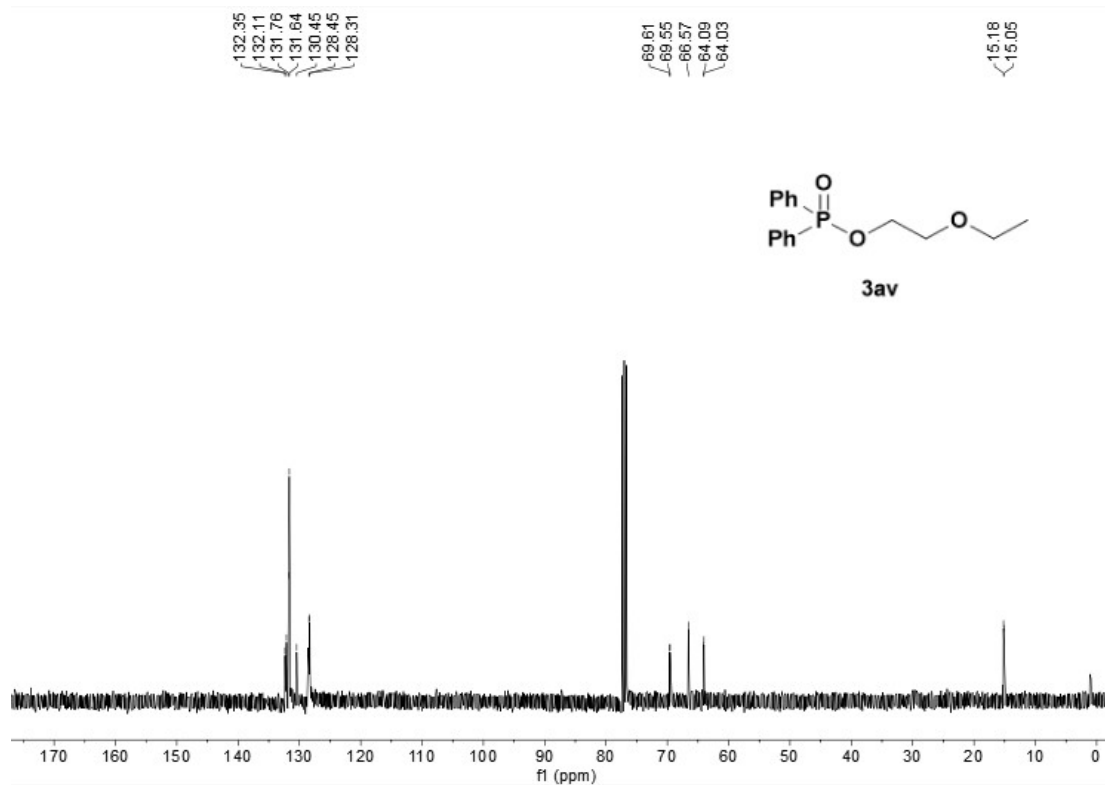
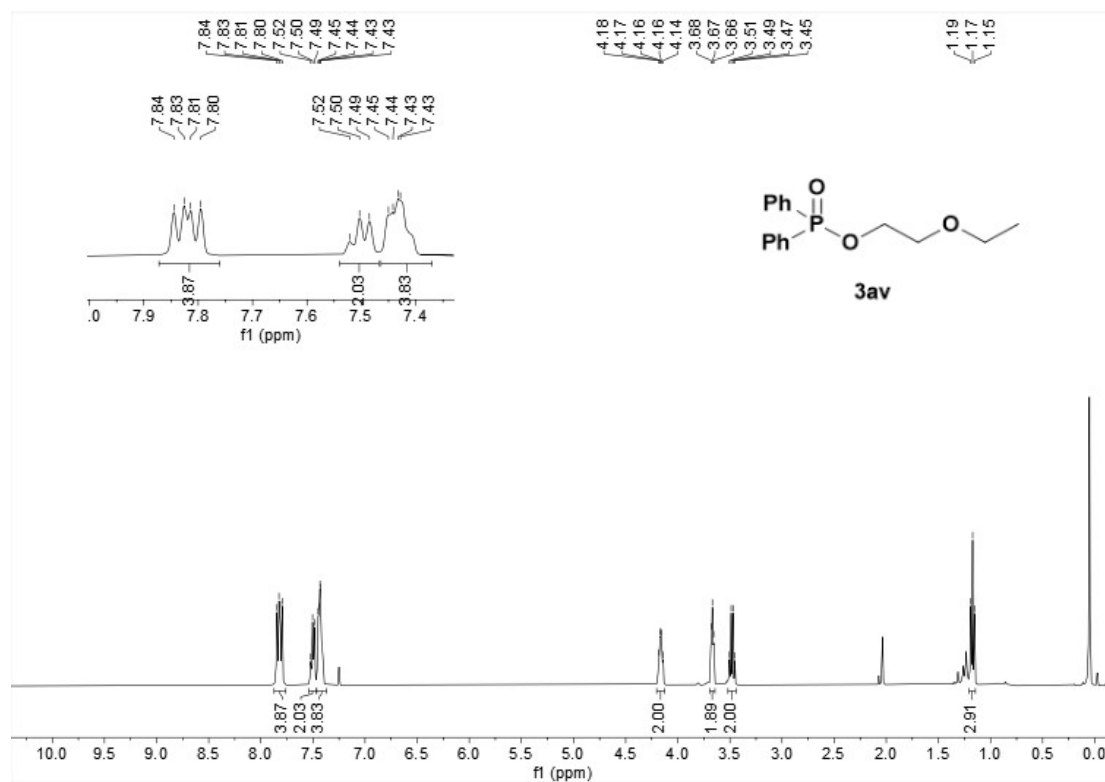


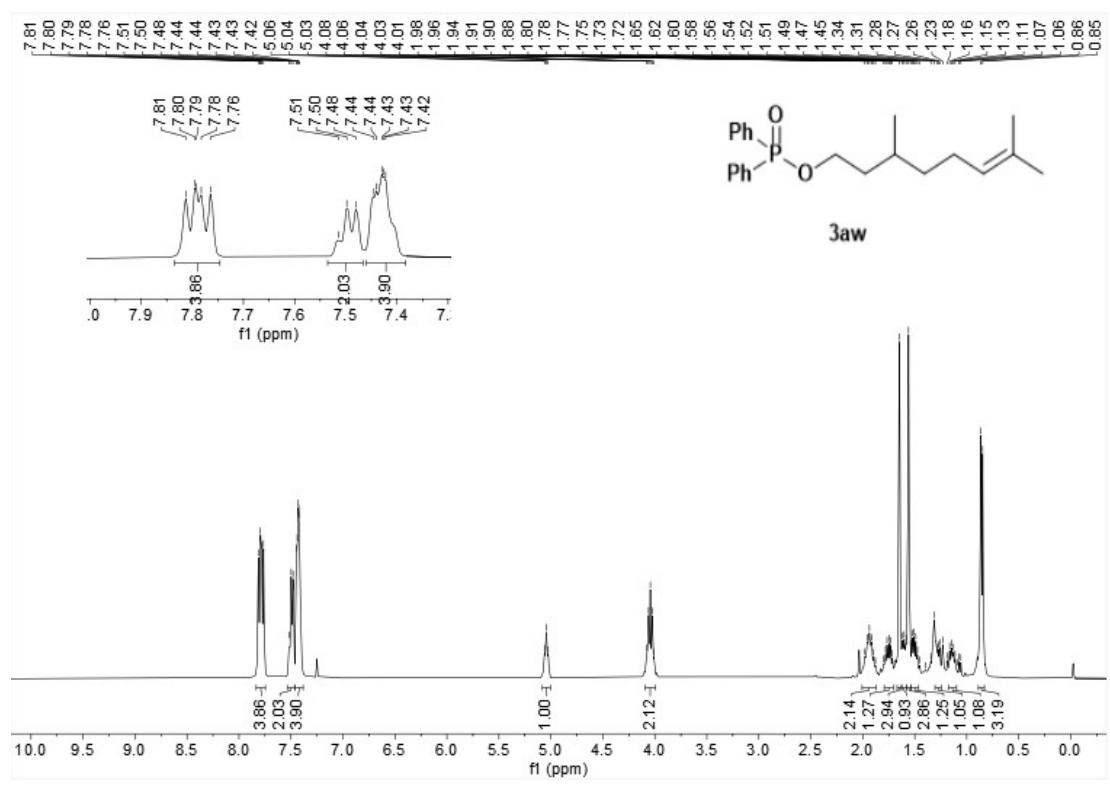
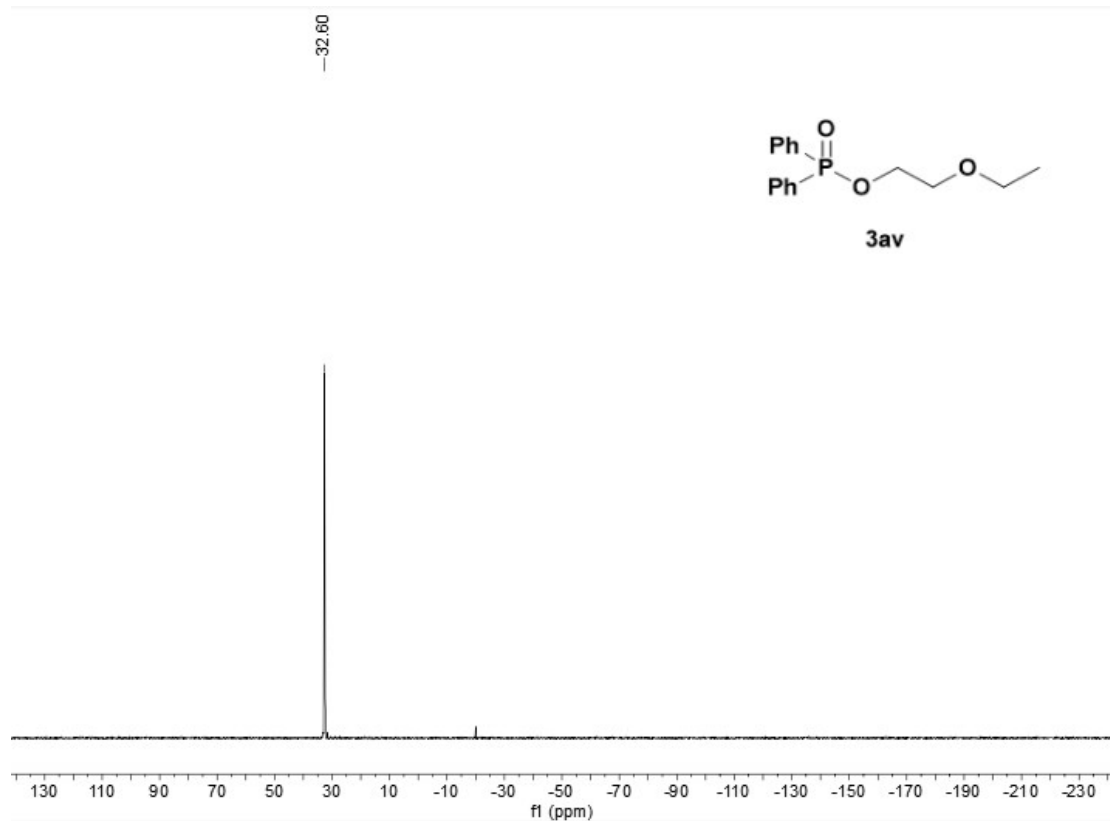


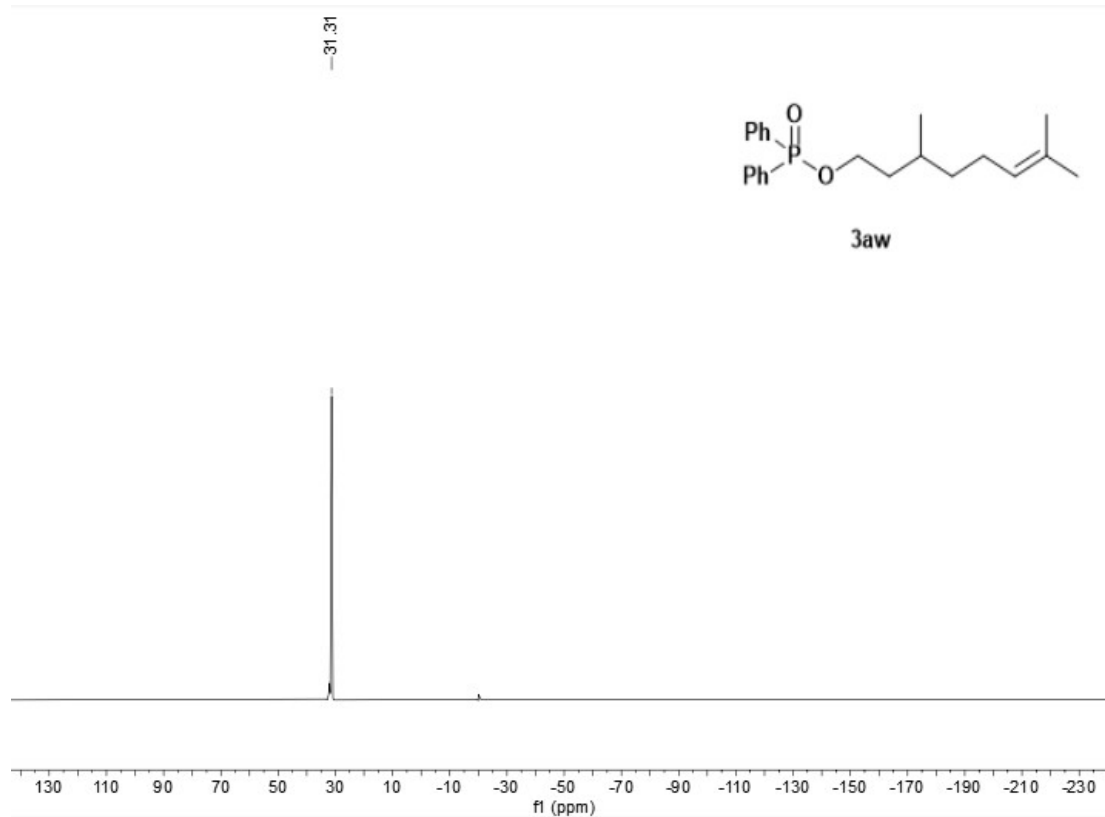
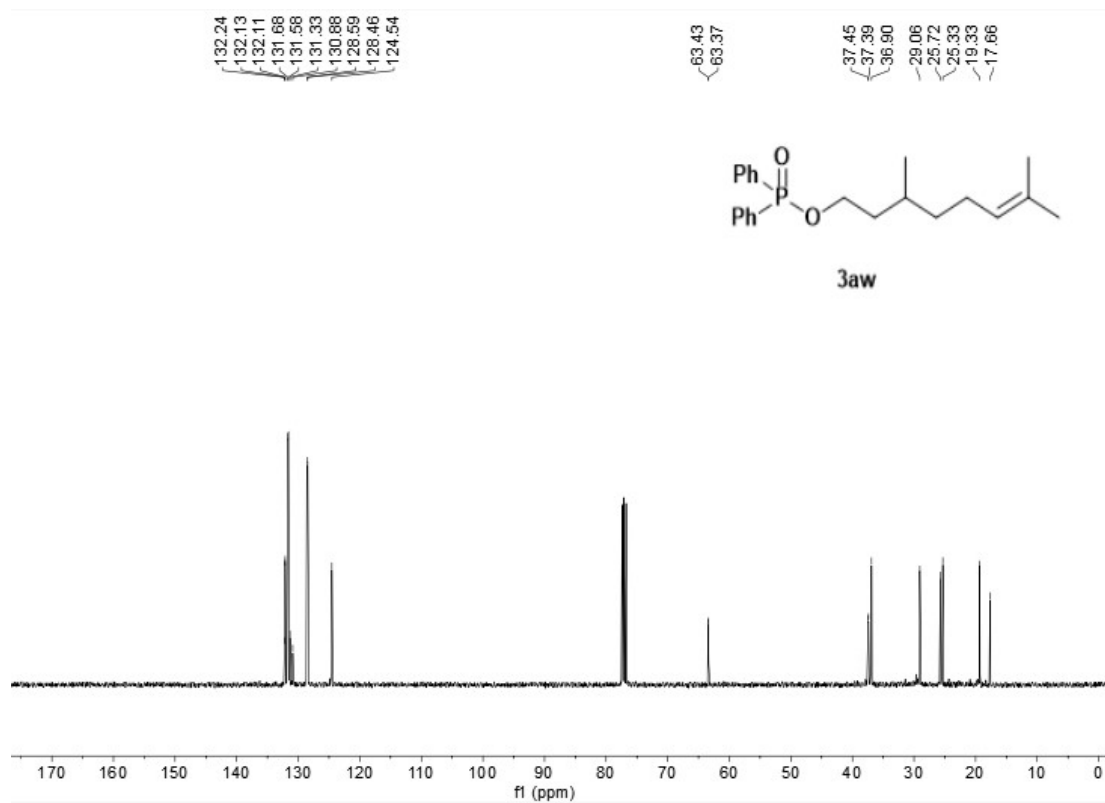


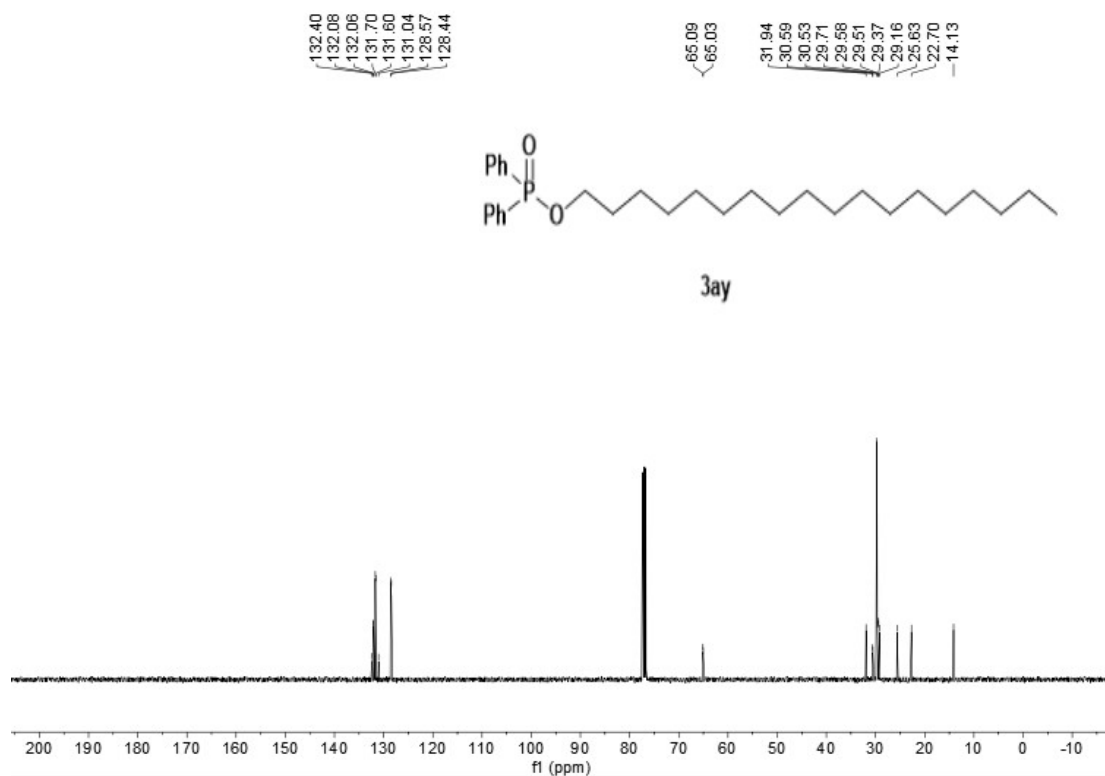
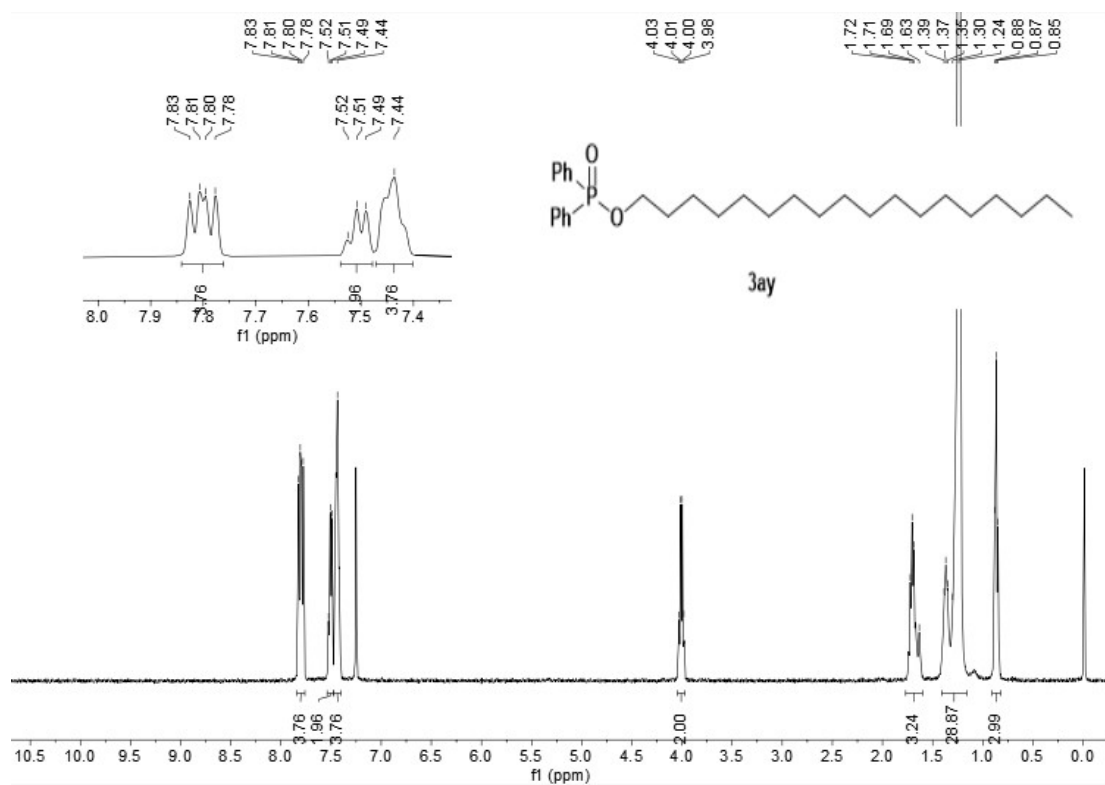




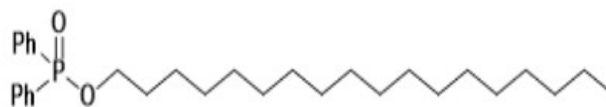




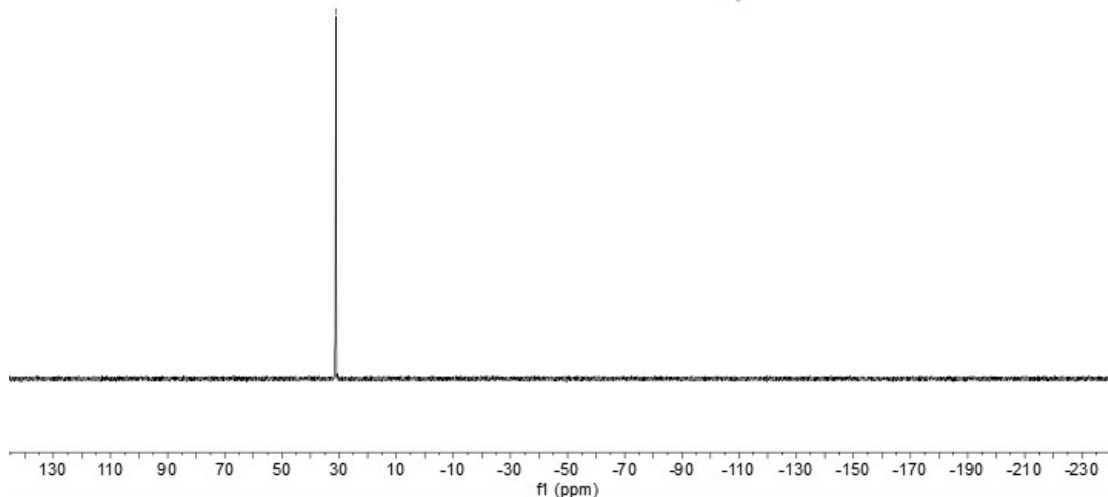




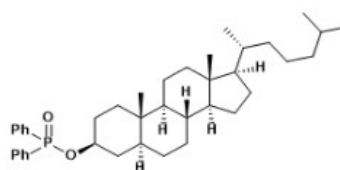
-31.15



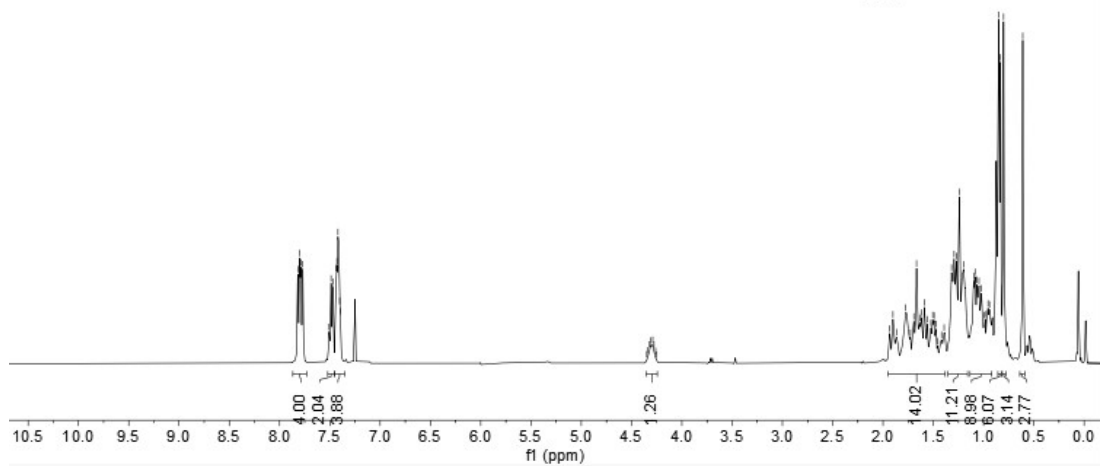
3ay

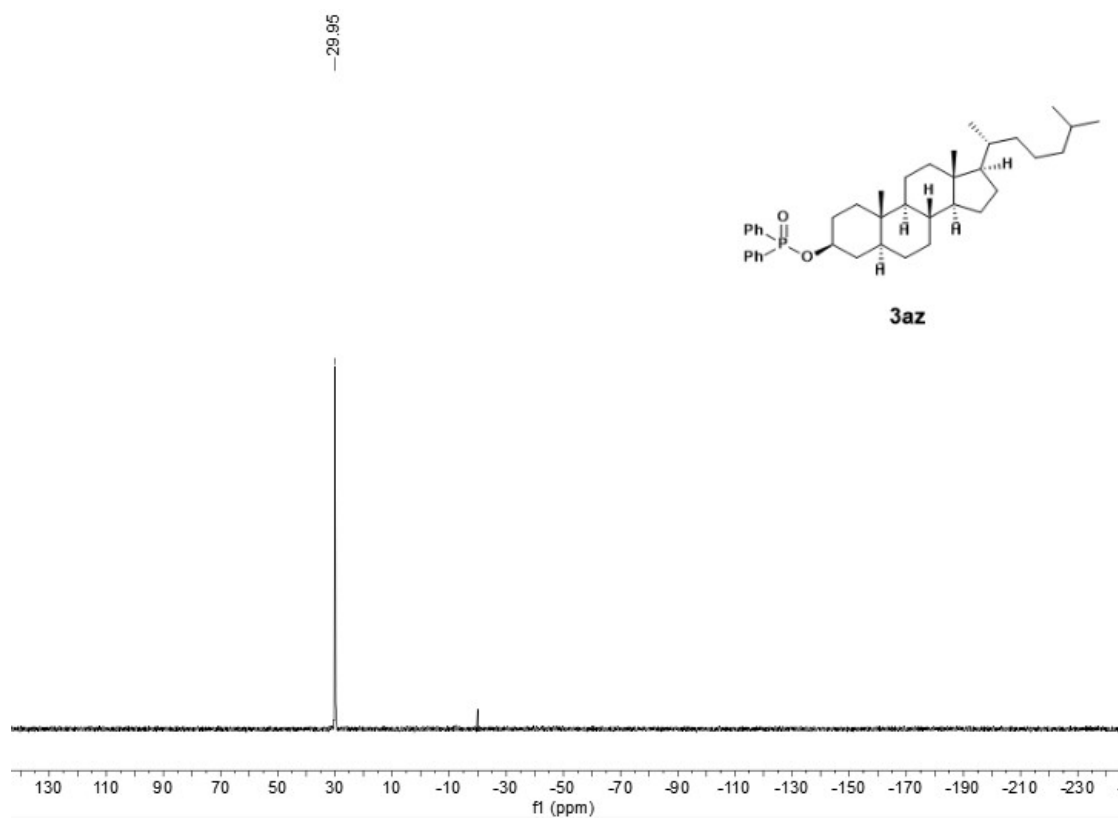
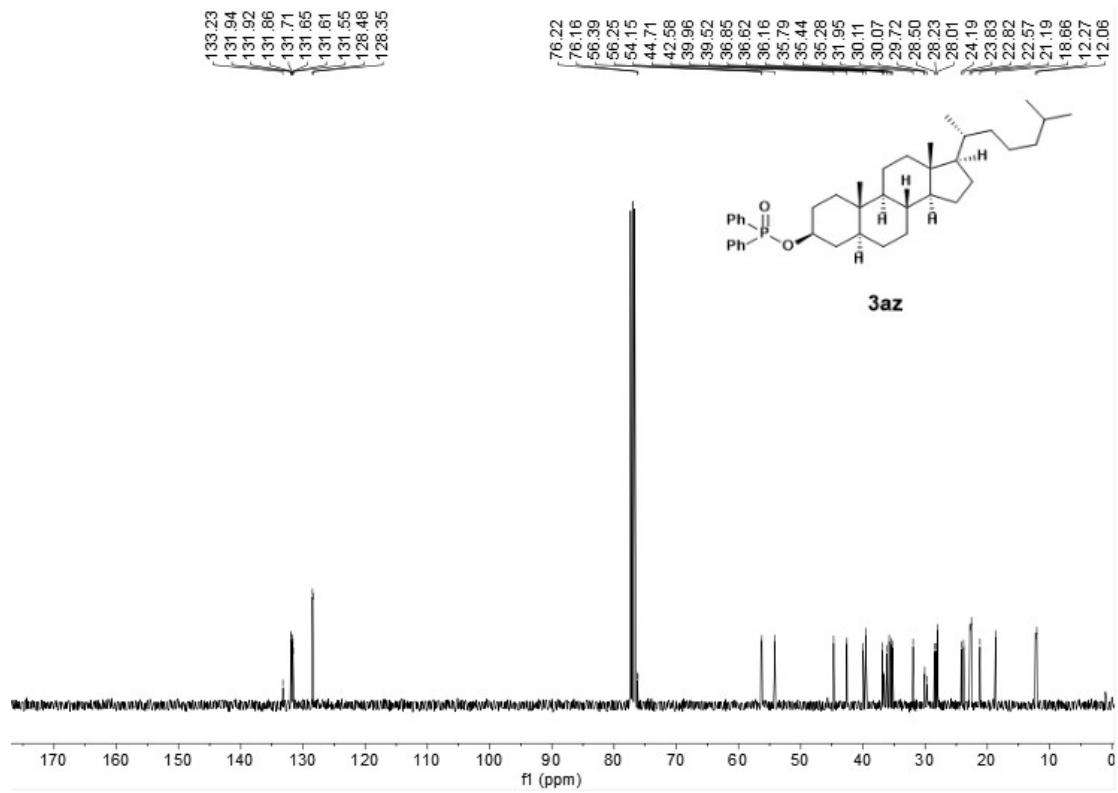


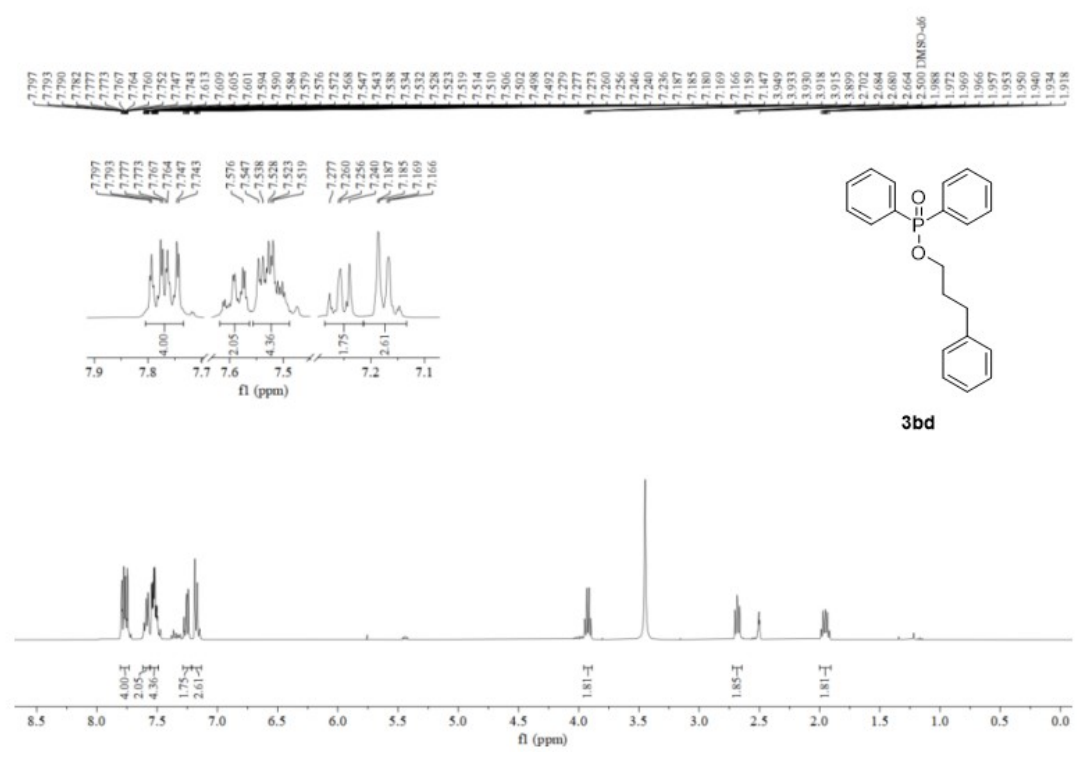
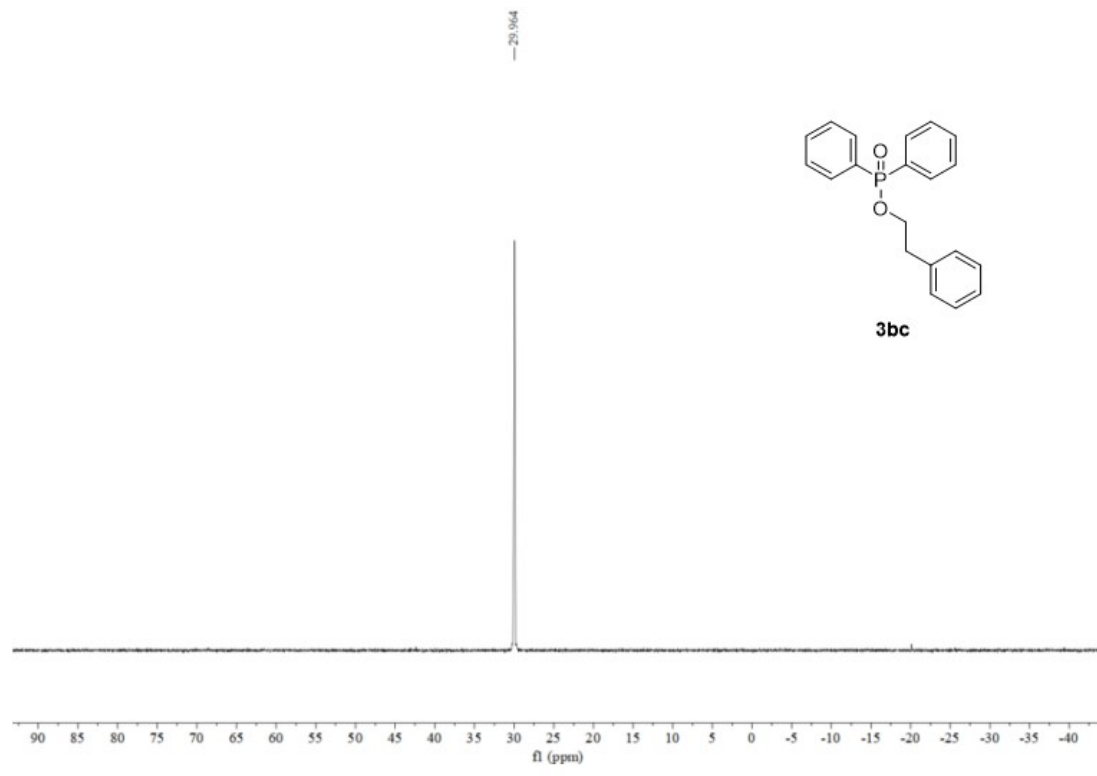
7.82
7.80
7.79
7.77
7.51
7.49
7.47
7.44
7.43
7.42
7.40
7.39
4.35
4.34
4.32
4.31
4.29
4.28
4.26
4.25
1.93
1.90
1.87
1.77
1.73
1.69
1.67
1.63
1.62
1.59
1.56
1.52
1.51
1.49
1.48
1.46
1.42
1.39
1.32
1.29
1.27
1.24
1.20
1.10
1.08
1.07
1.05
1.02
1.00
0.98
0.96
0.94
0.85
0.83
0.80
0.61

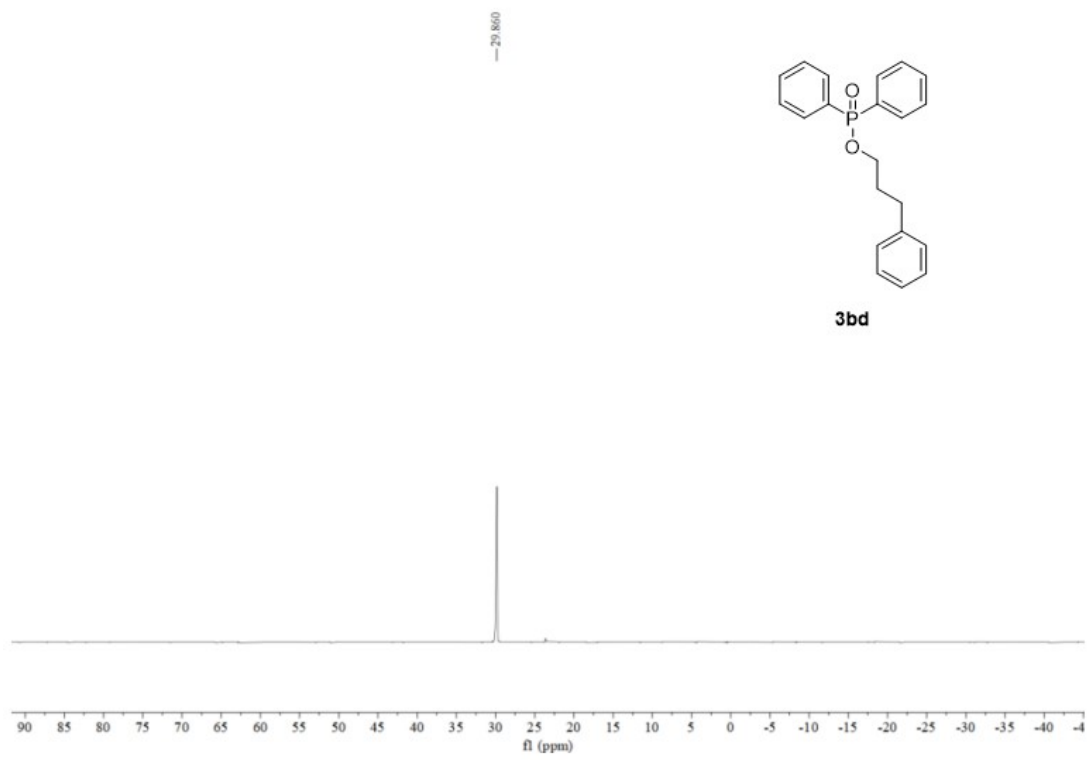
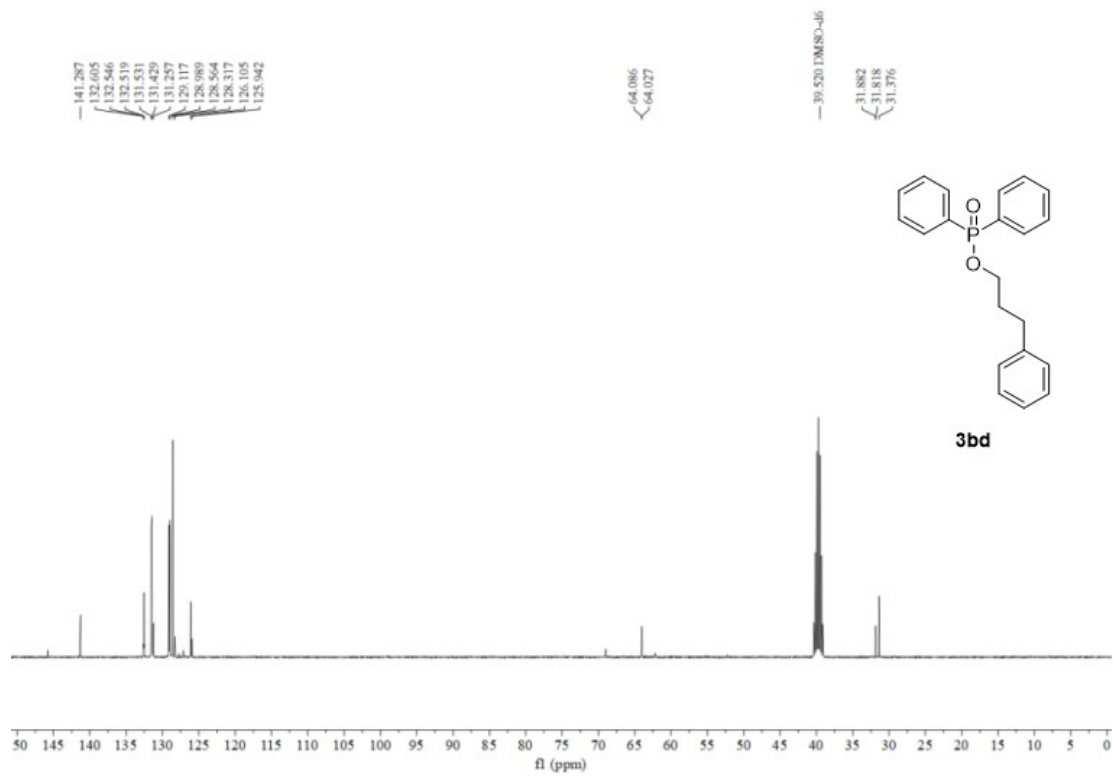


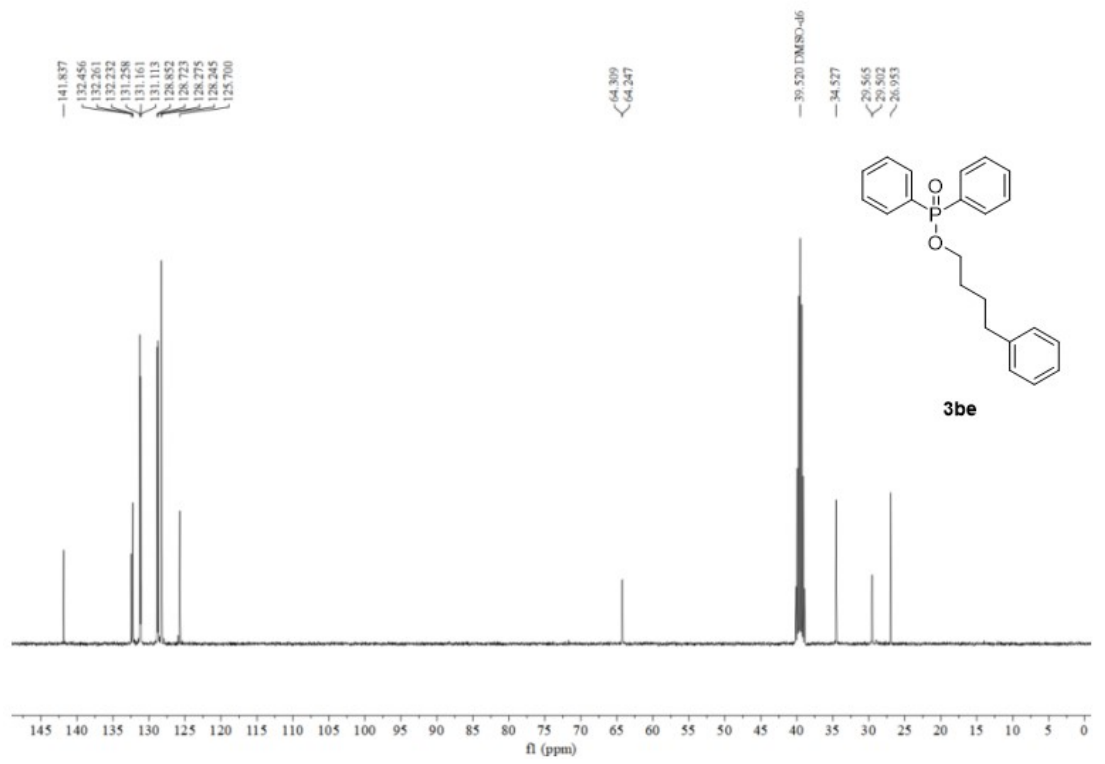
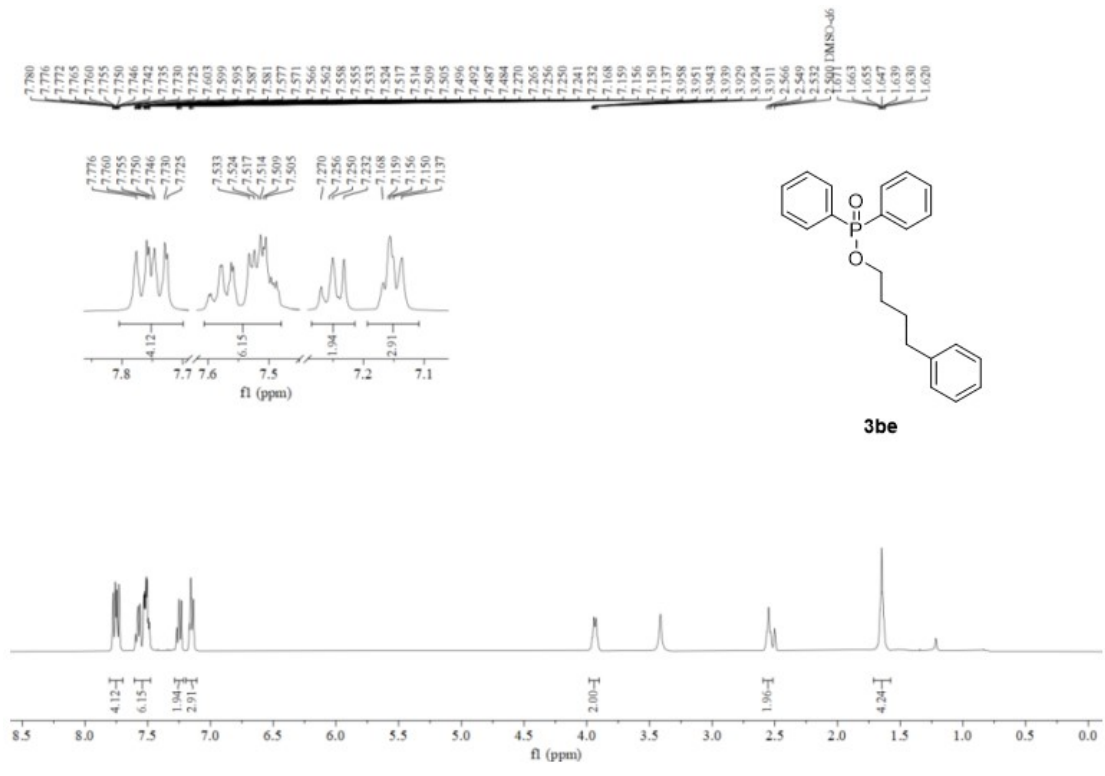
3az

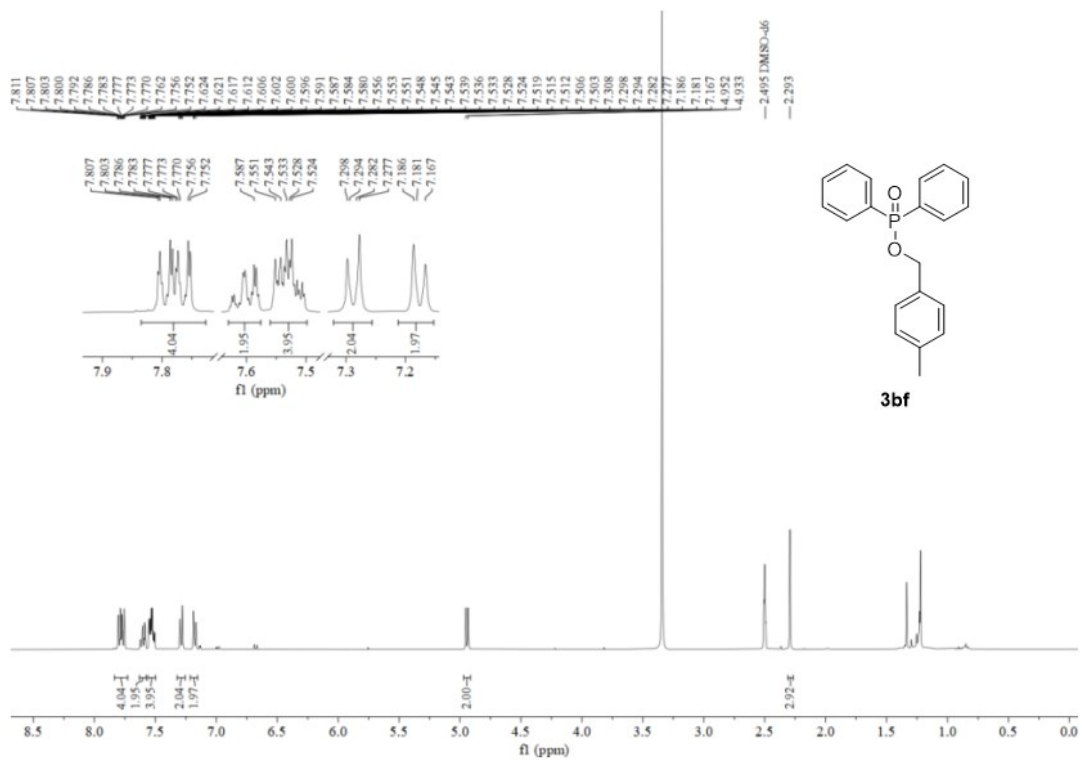
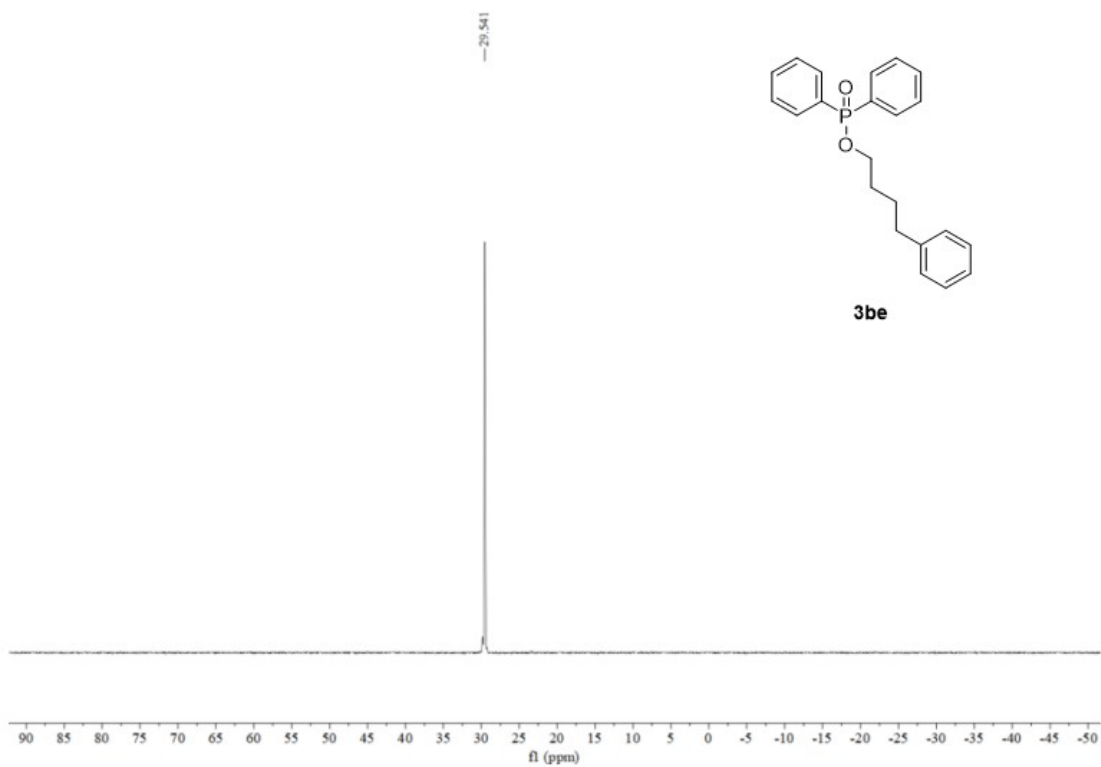


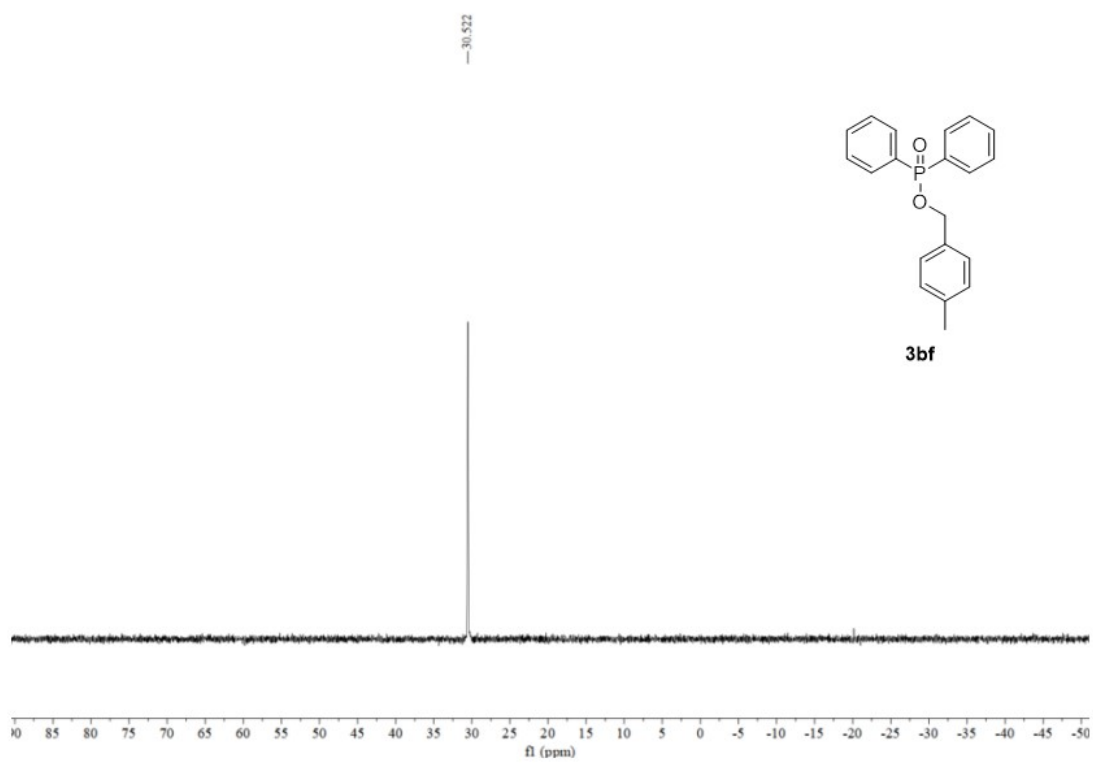
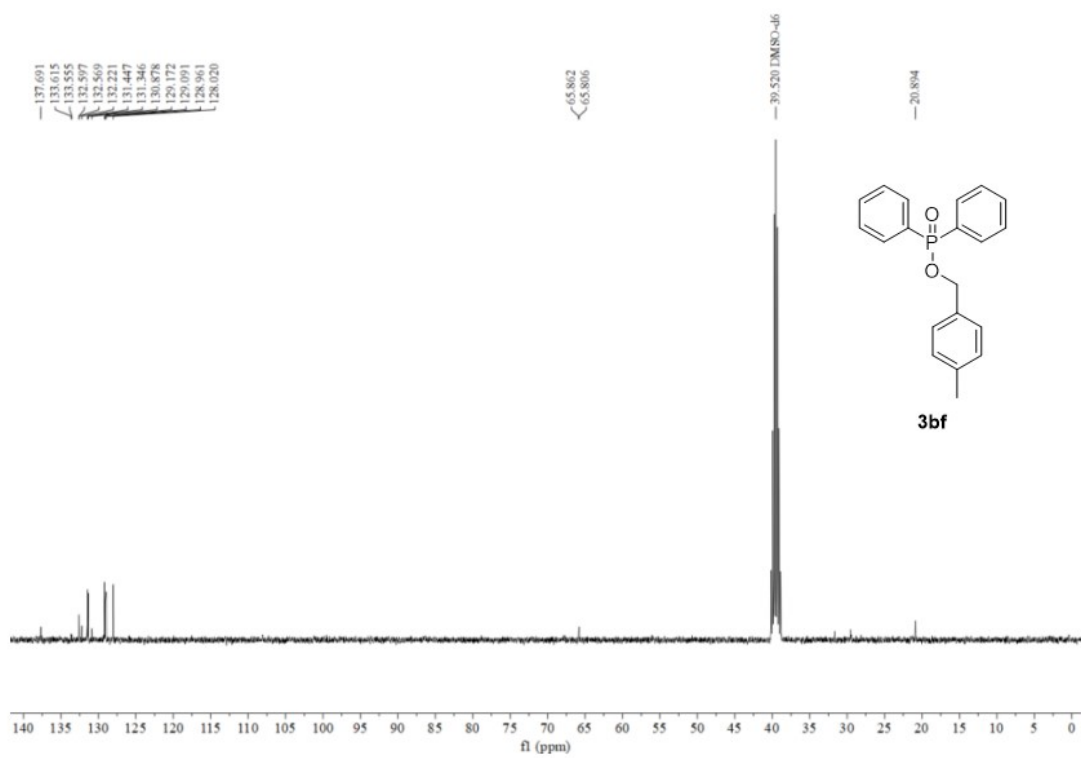


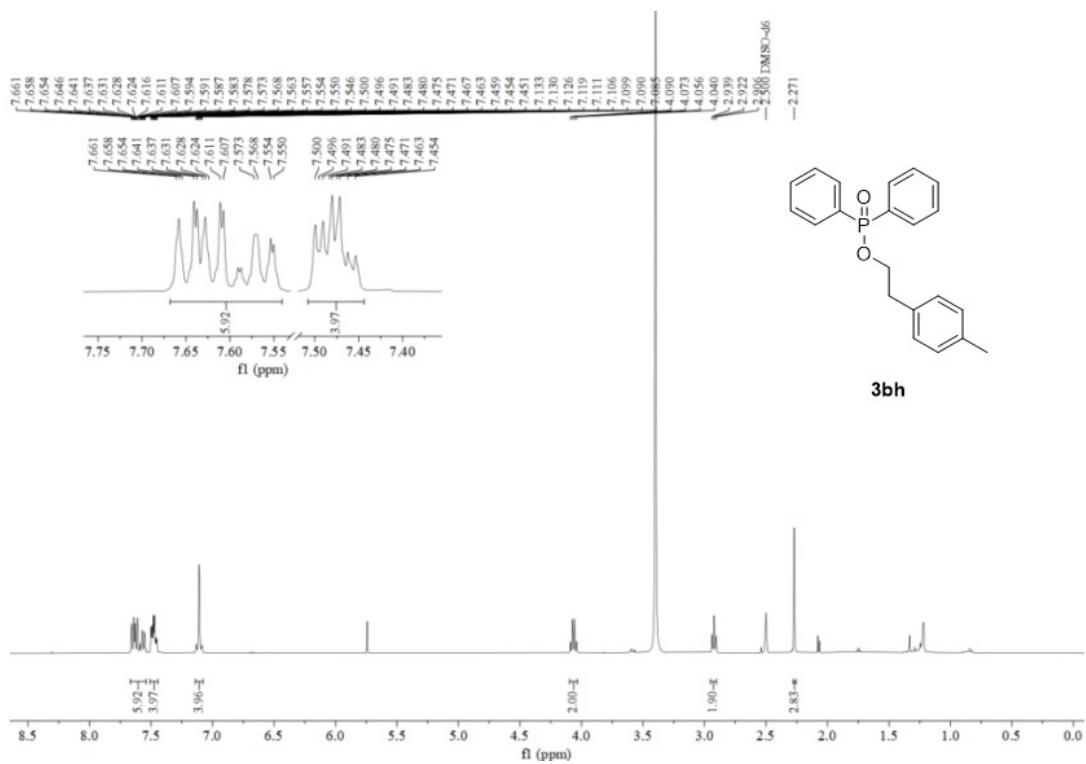
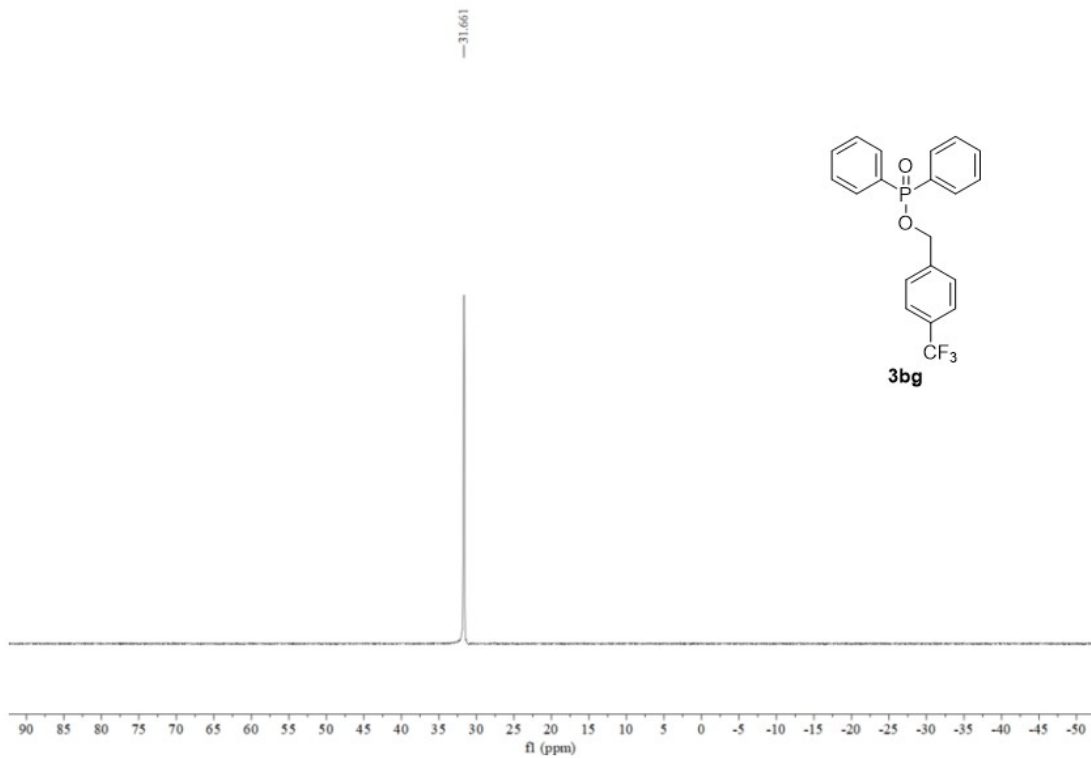


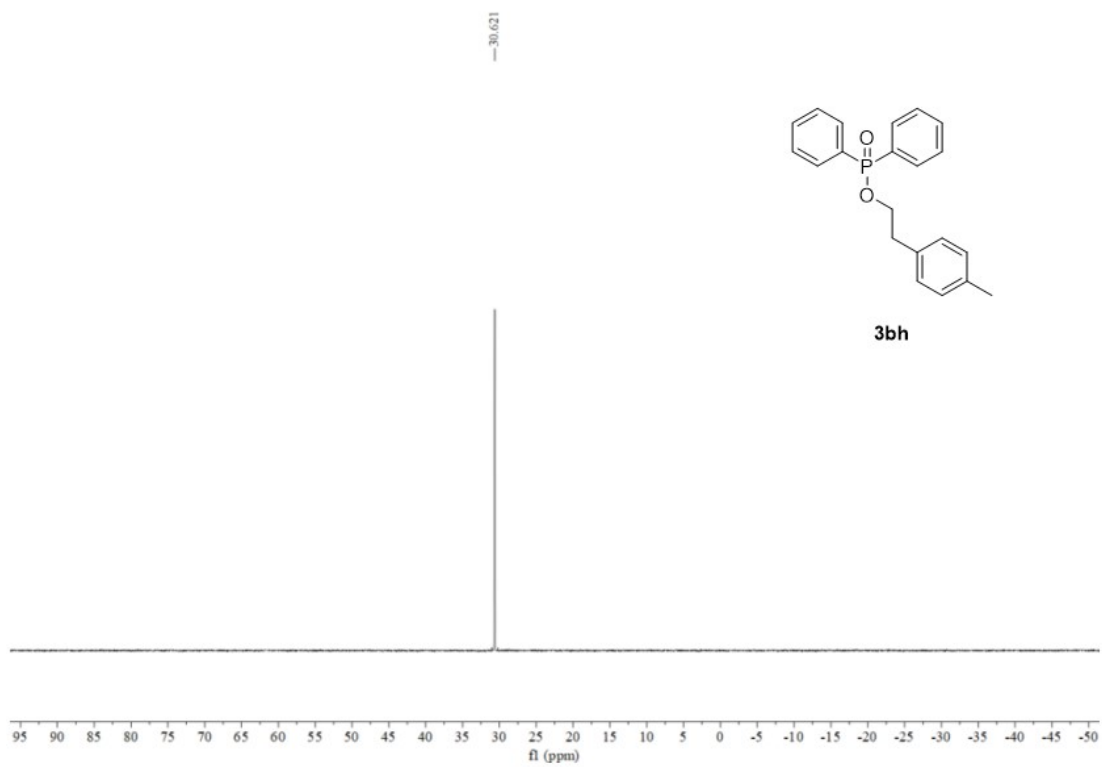
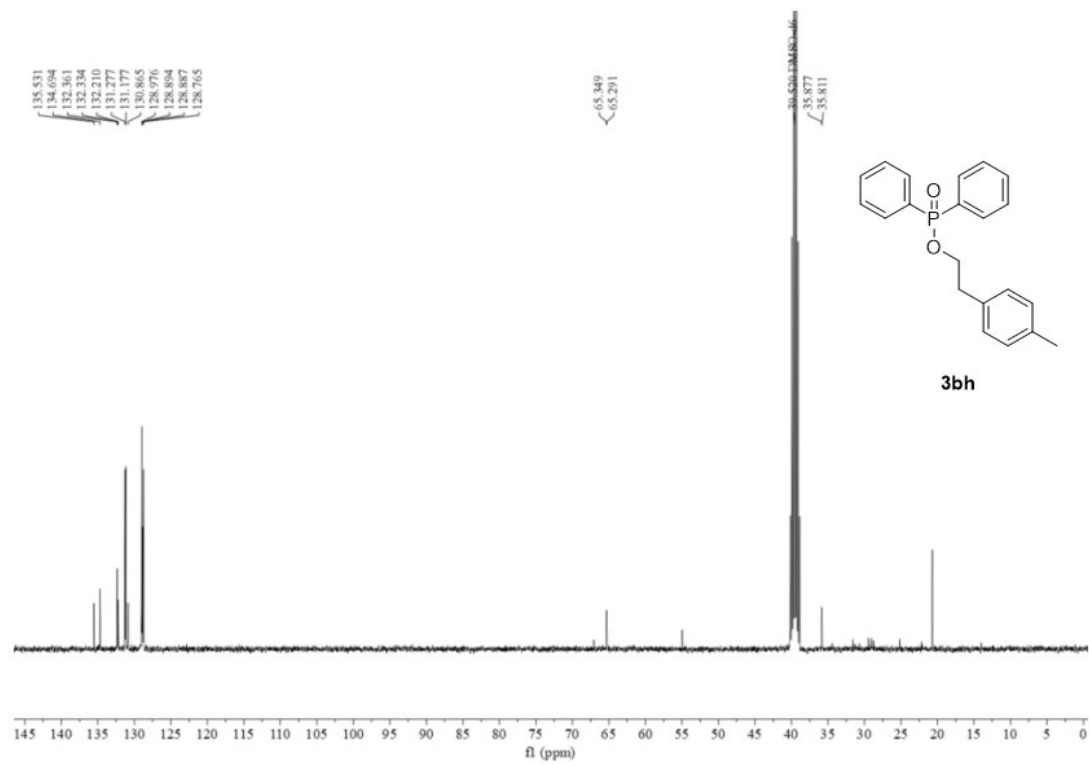


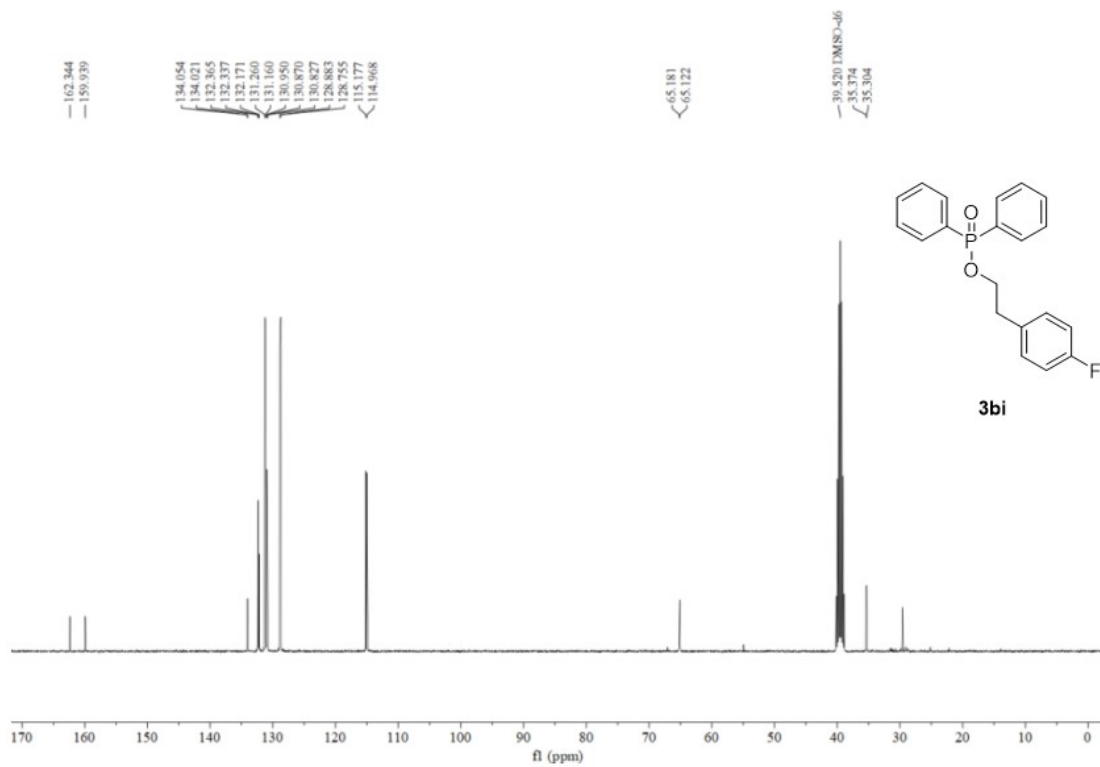
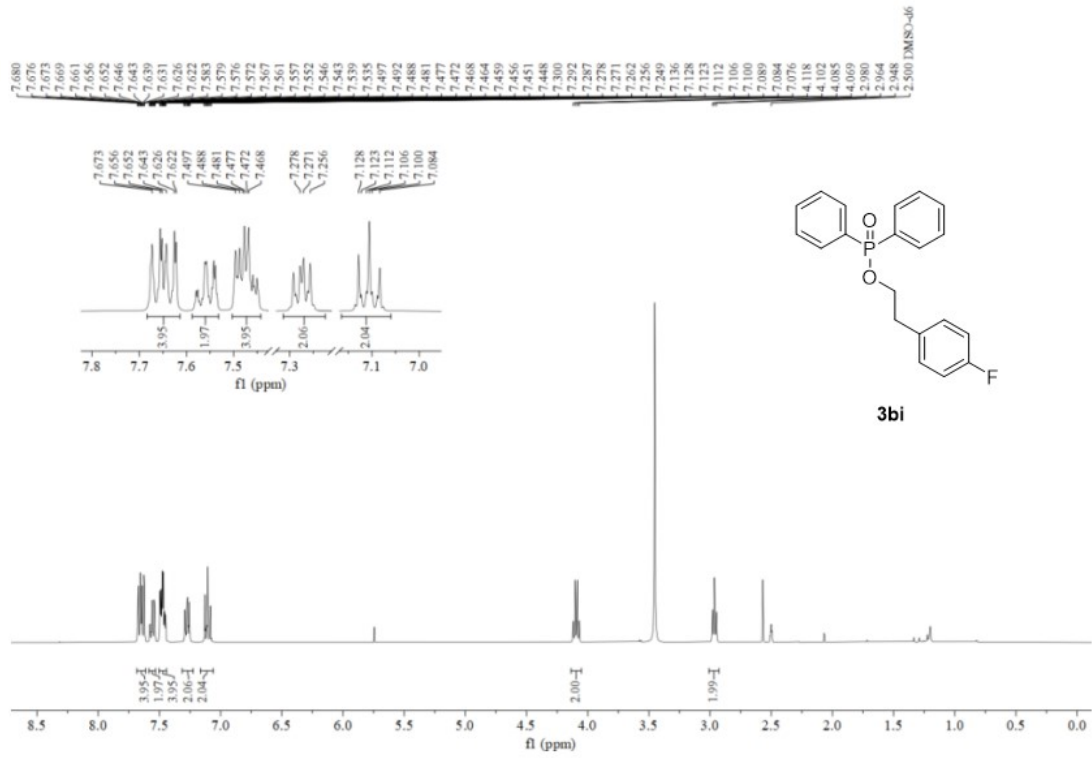


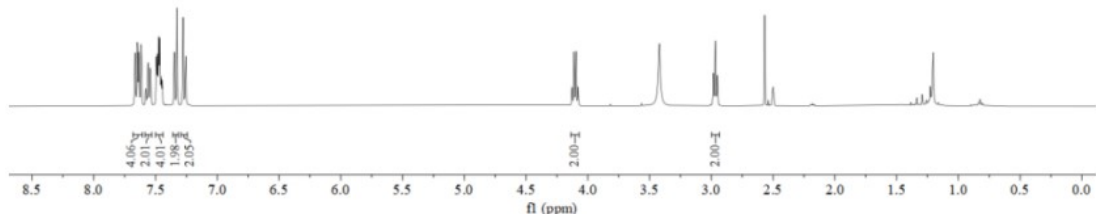
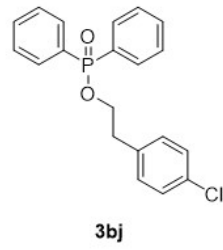
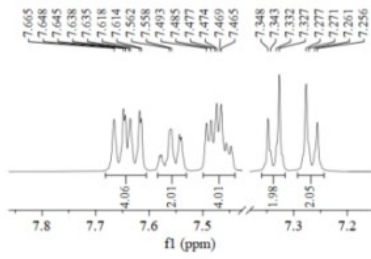
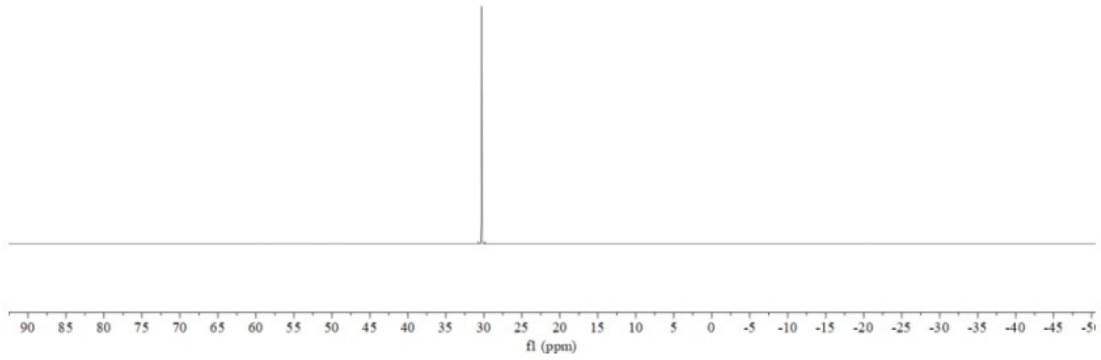
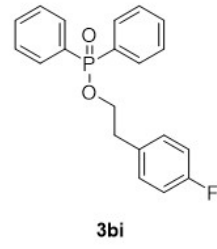


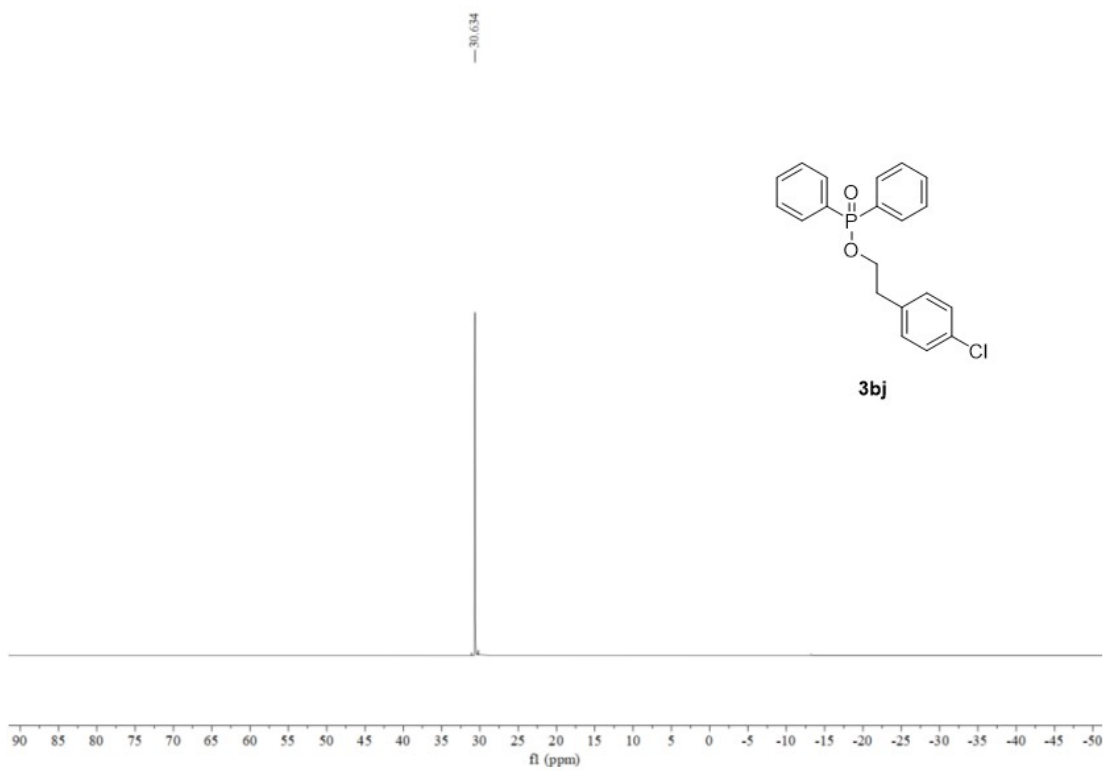
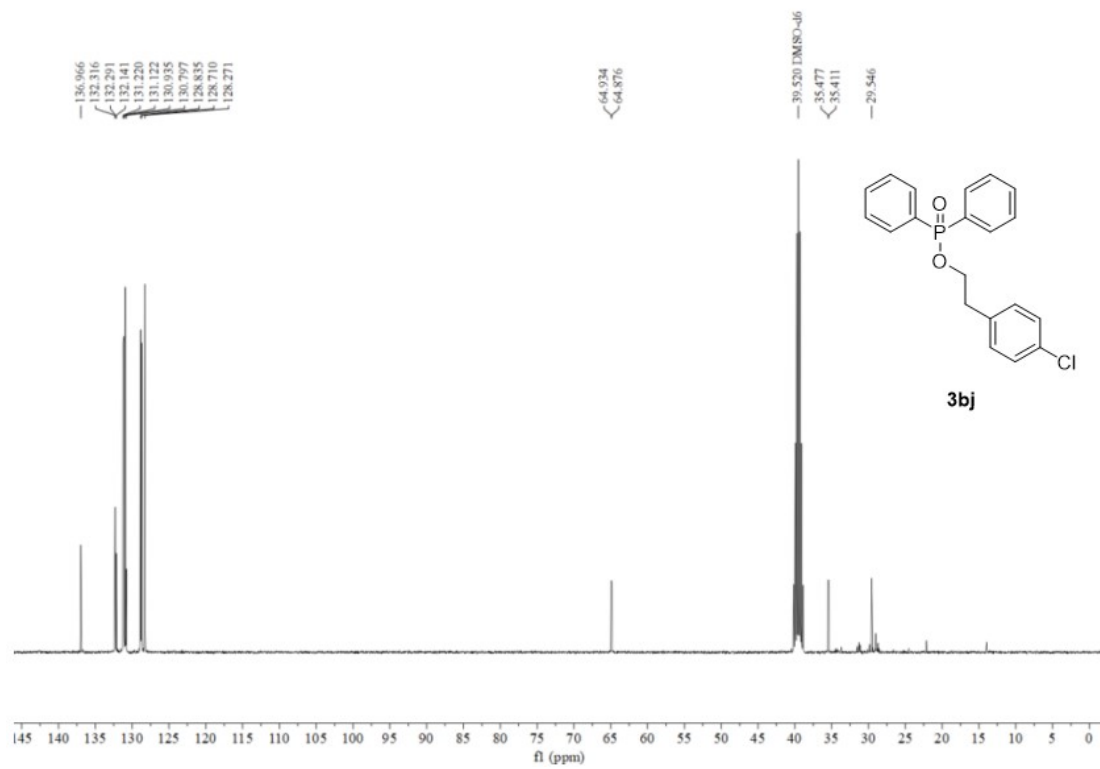


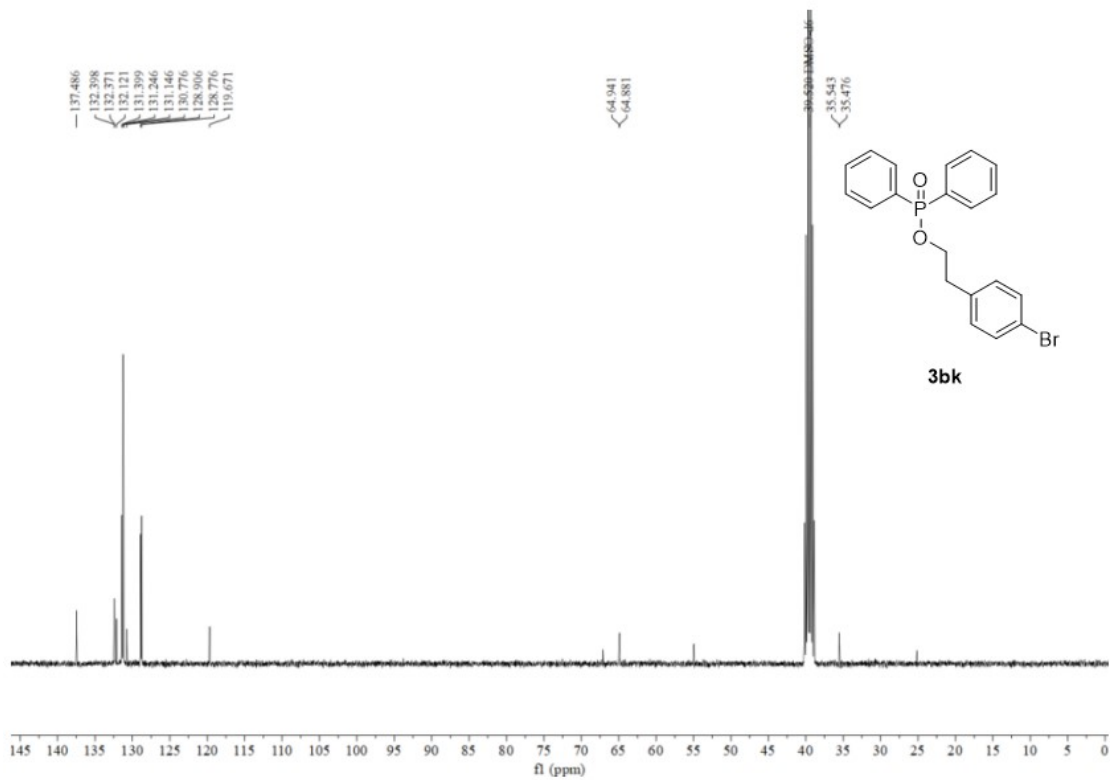
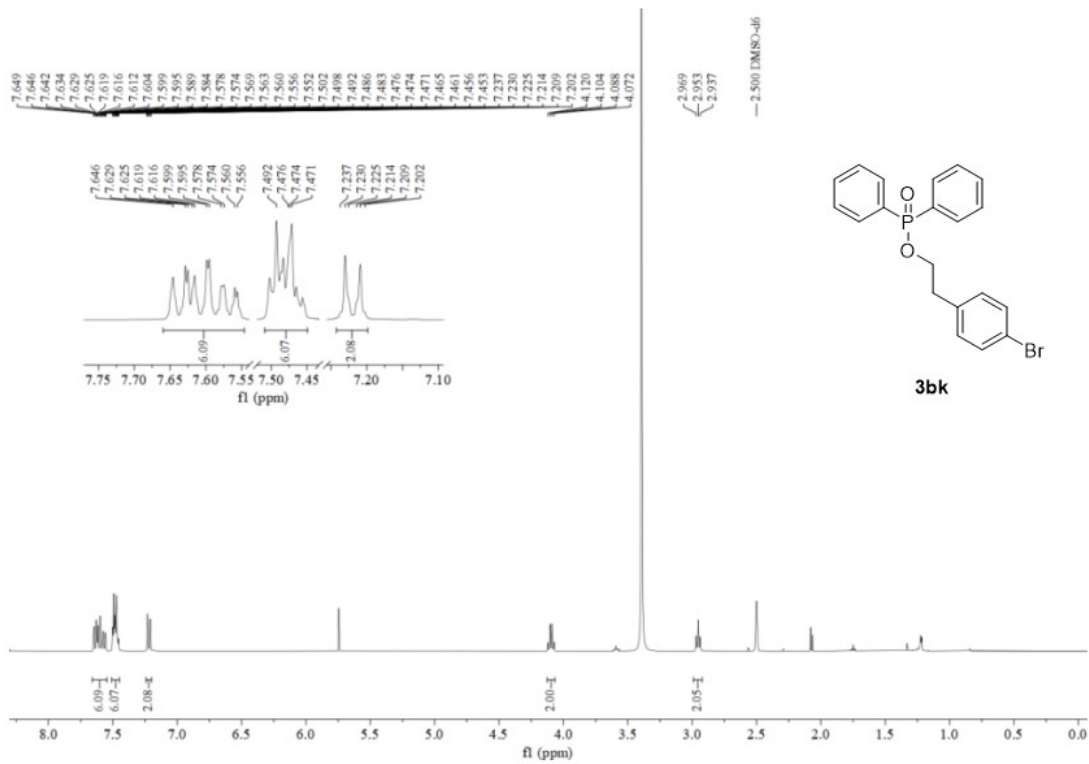


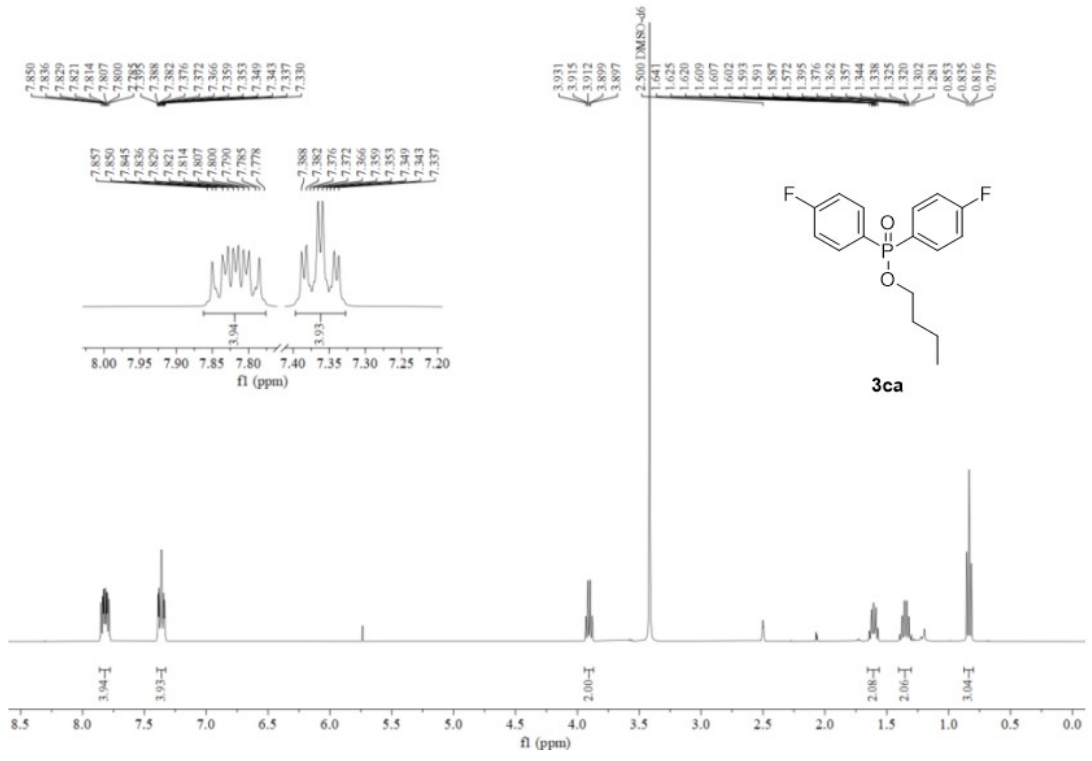
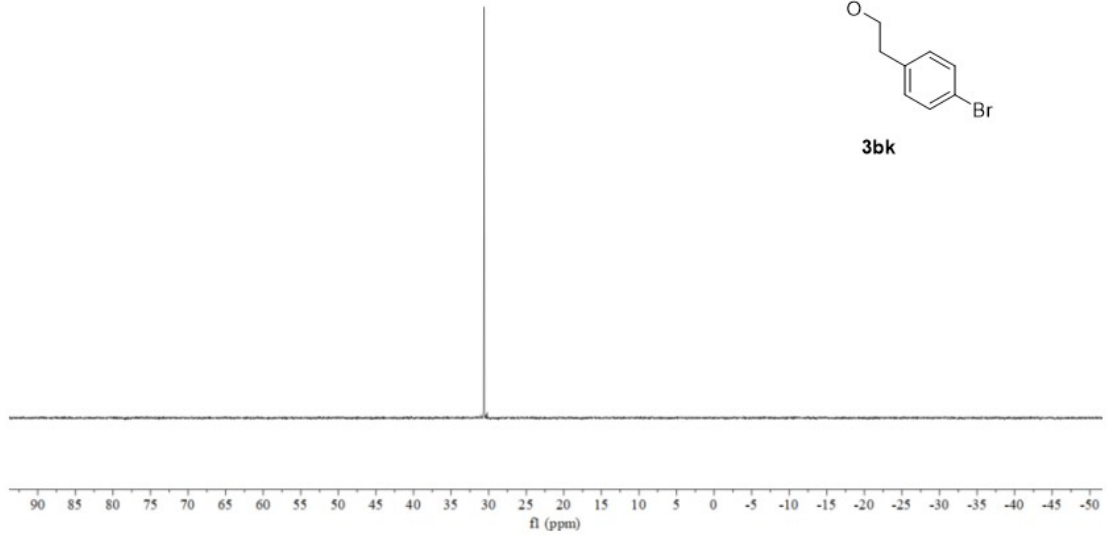
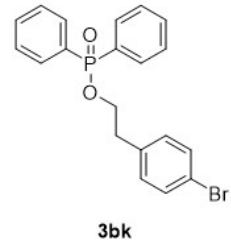


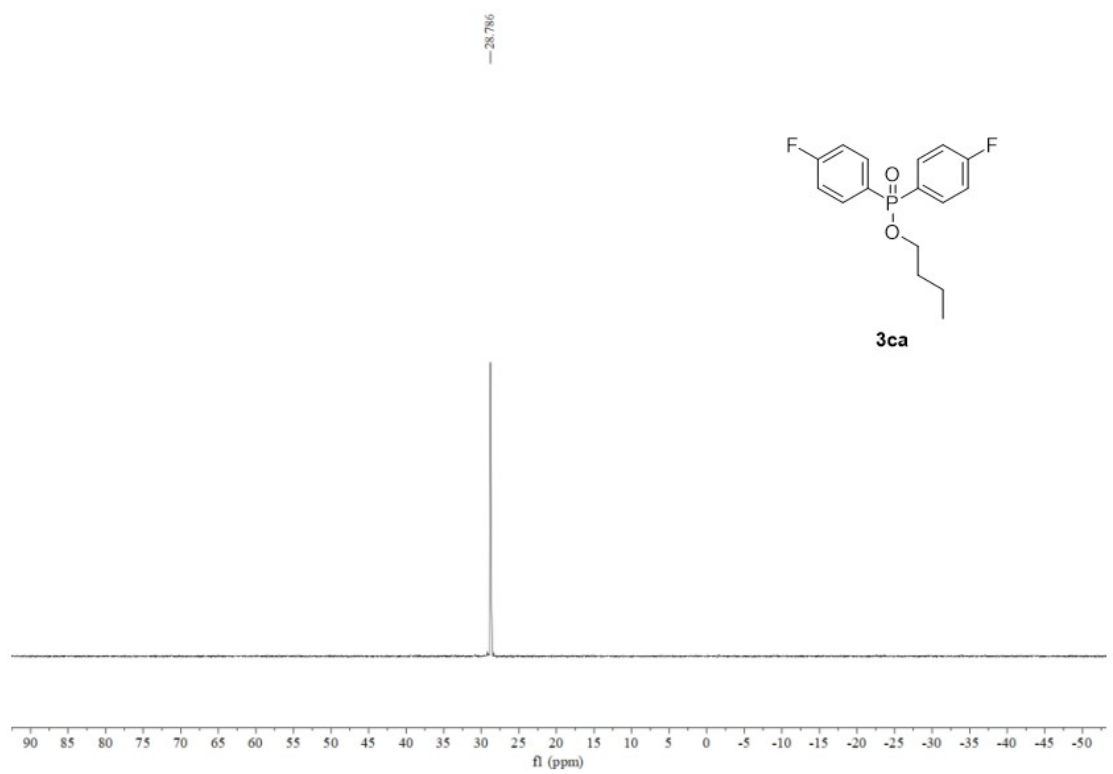
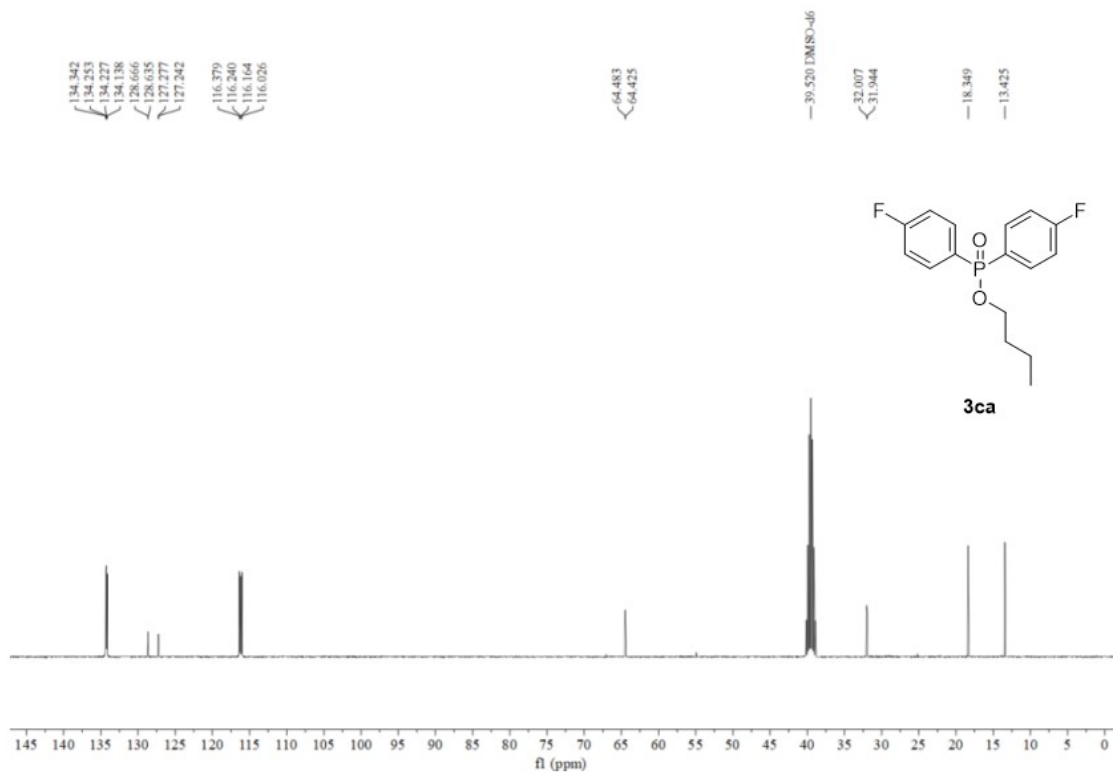


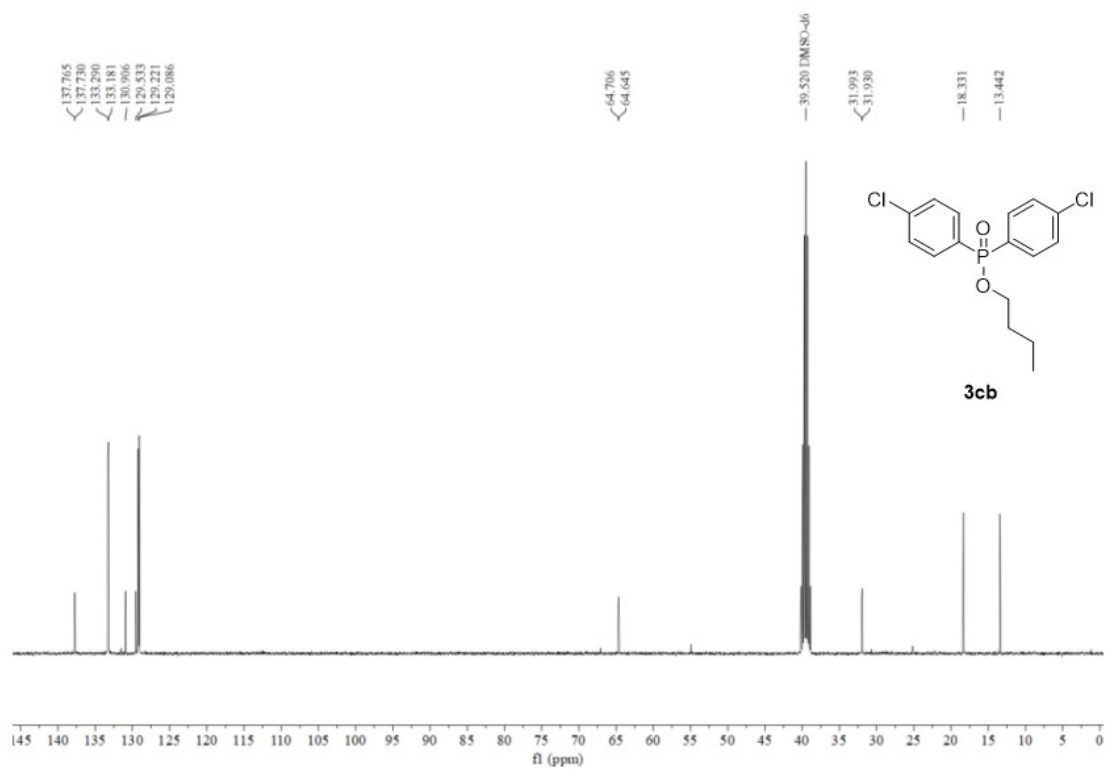
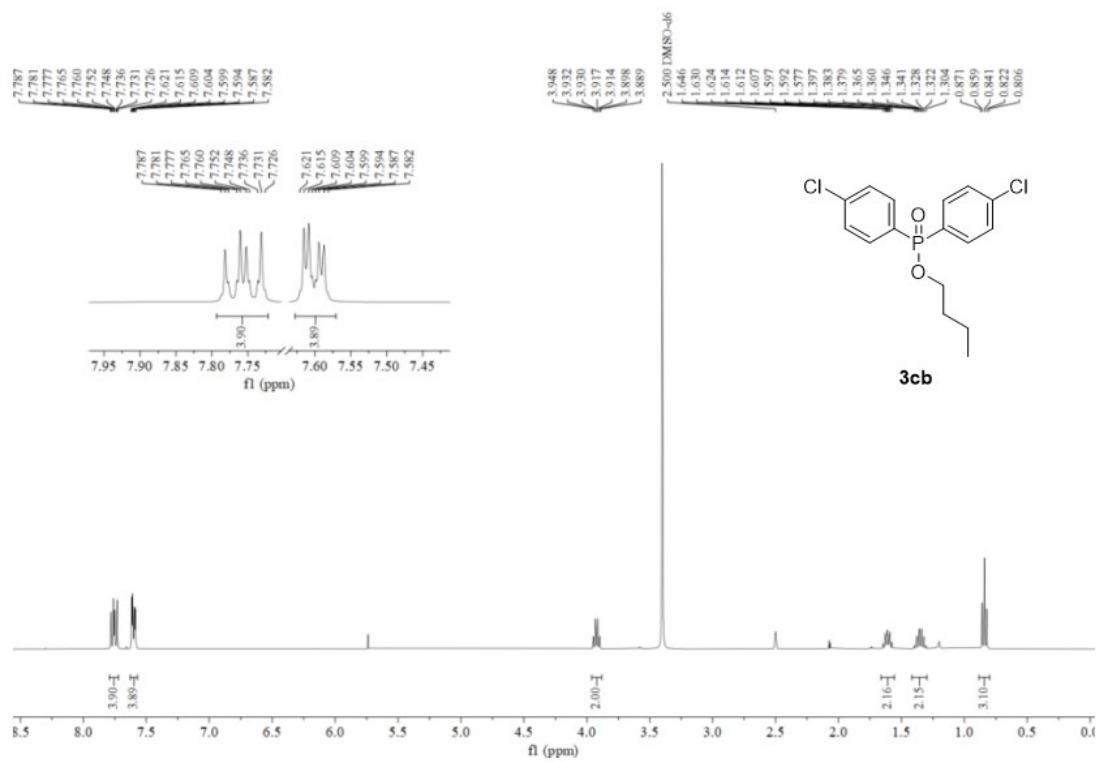


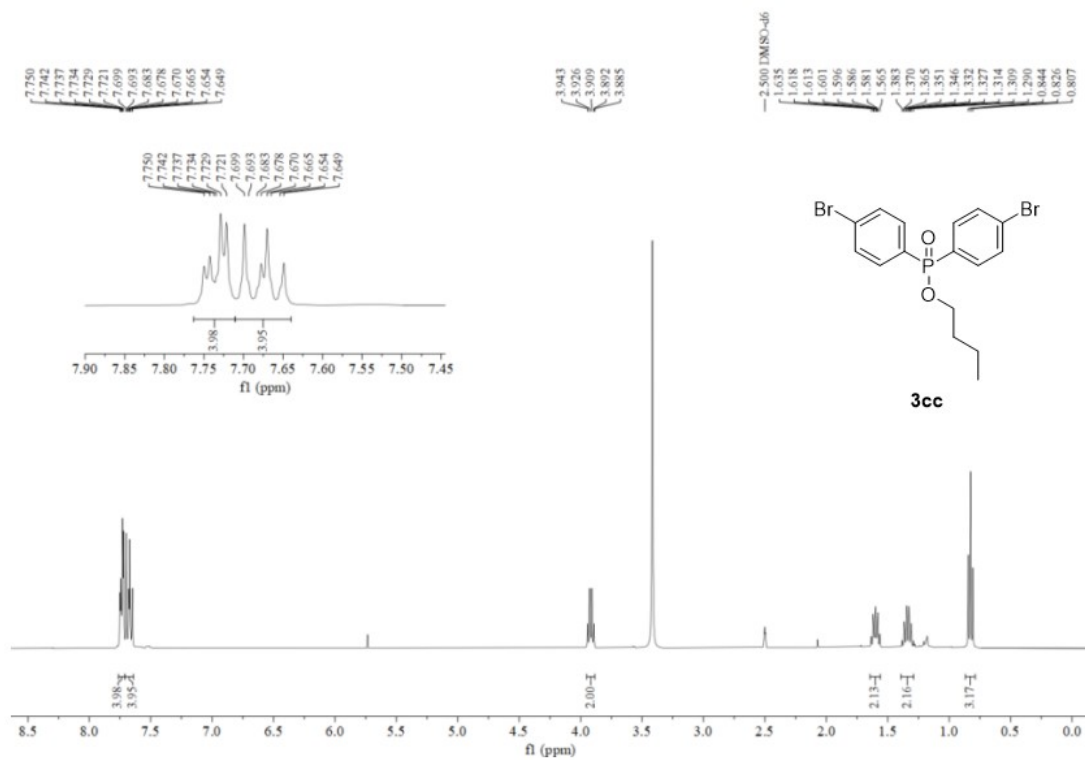
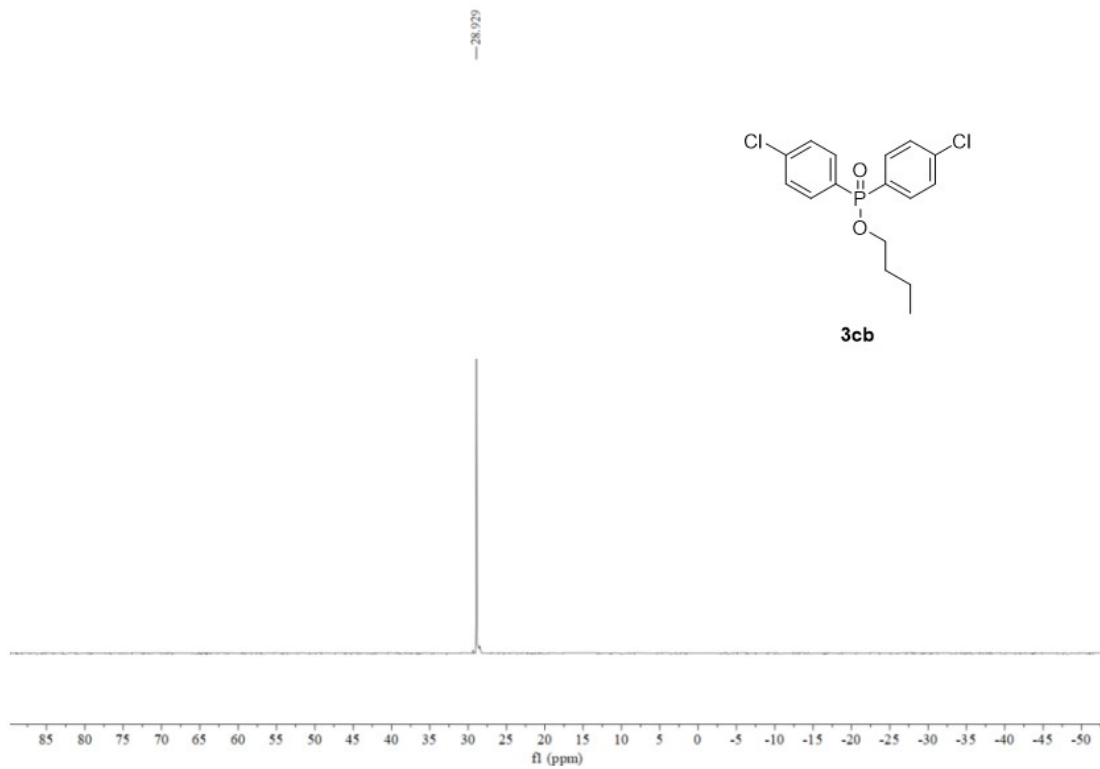


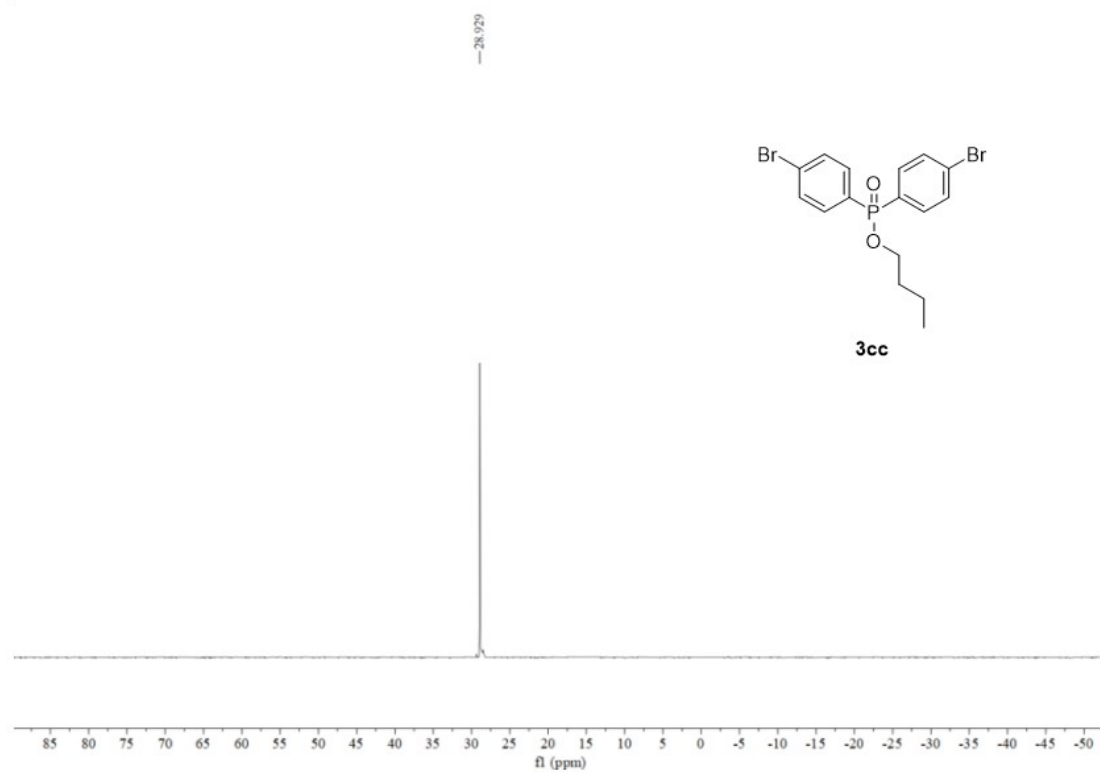
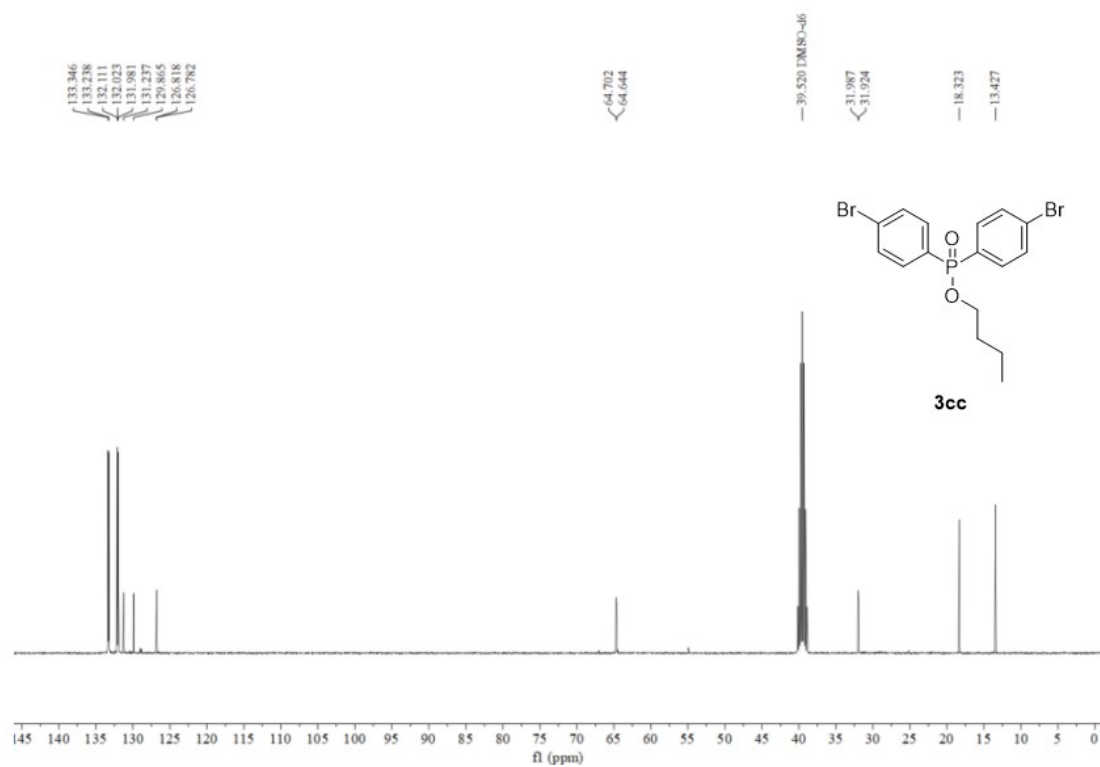


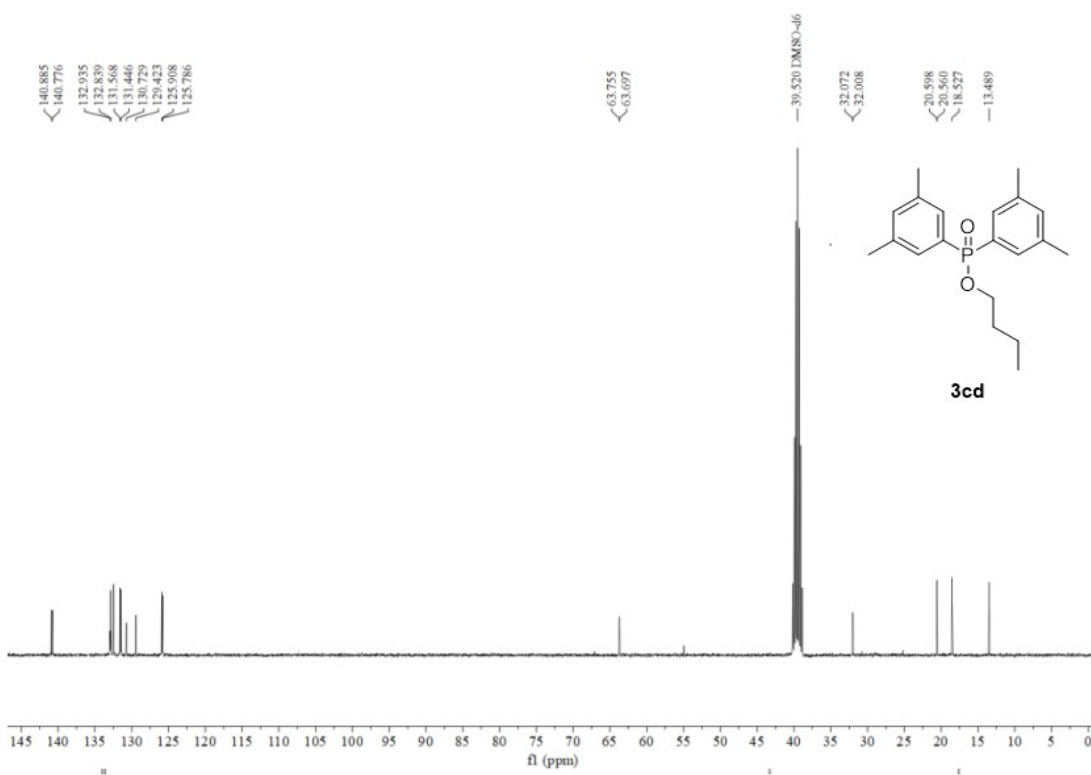
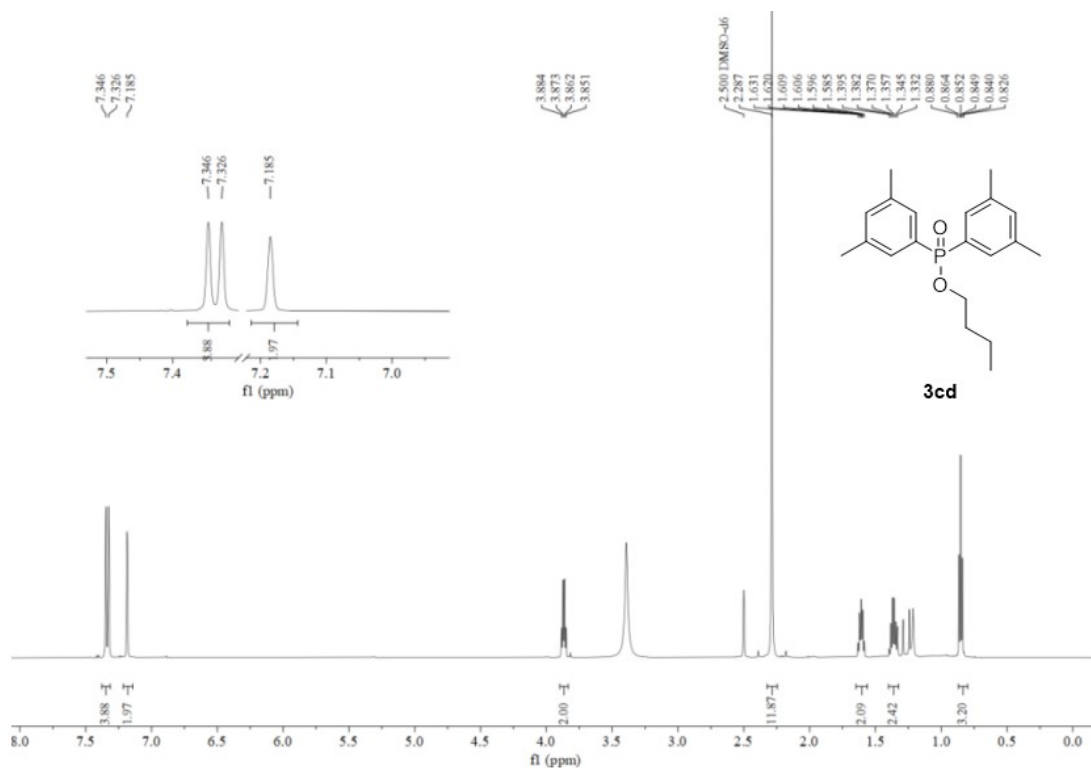


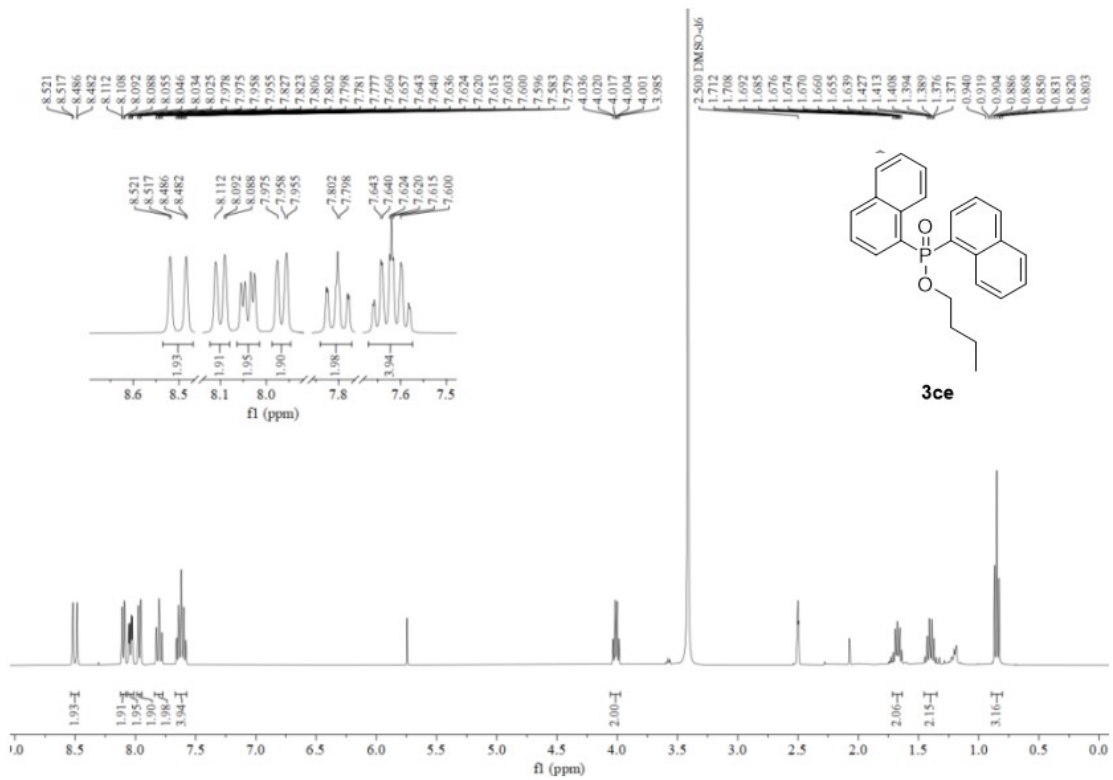
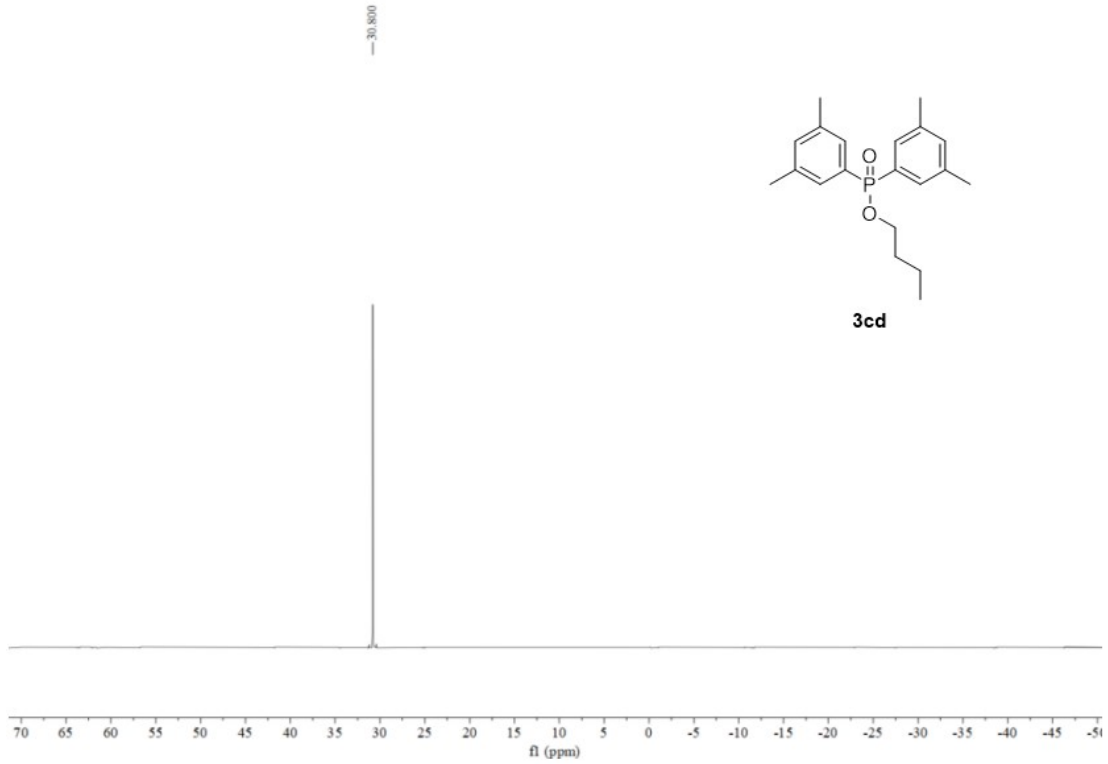


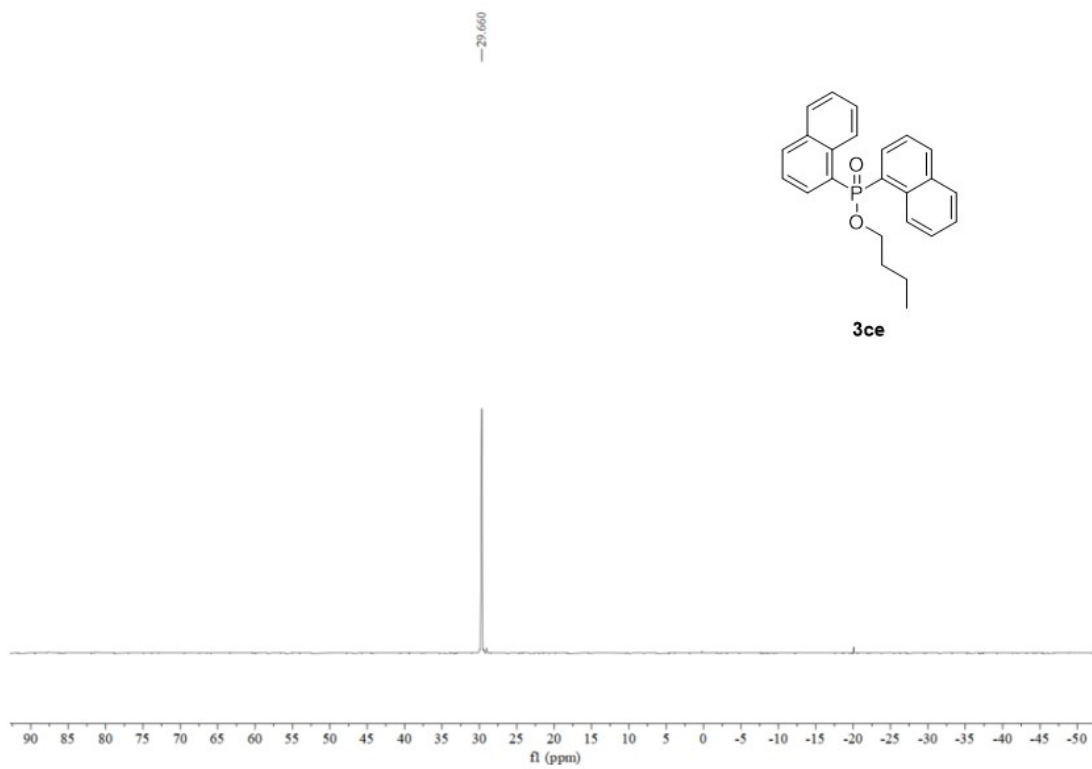
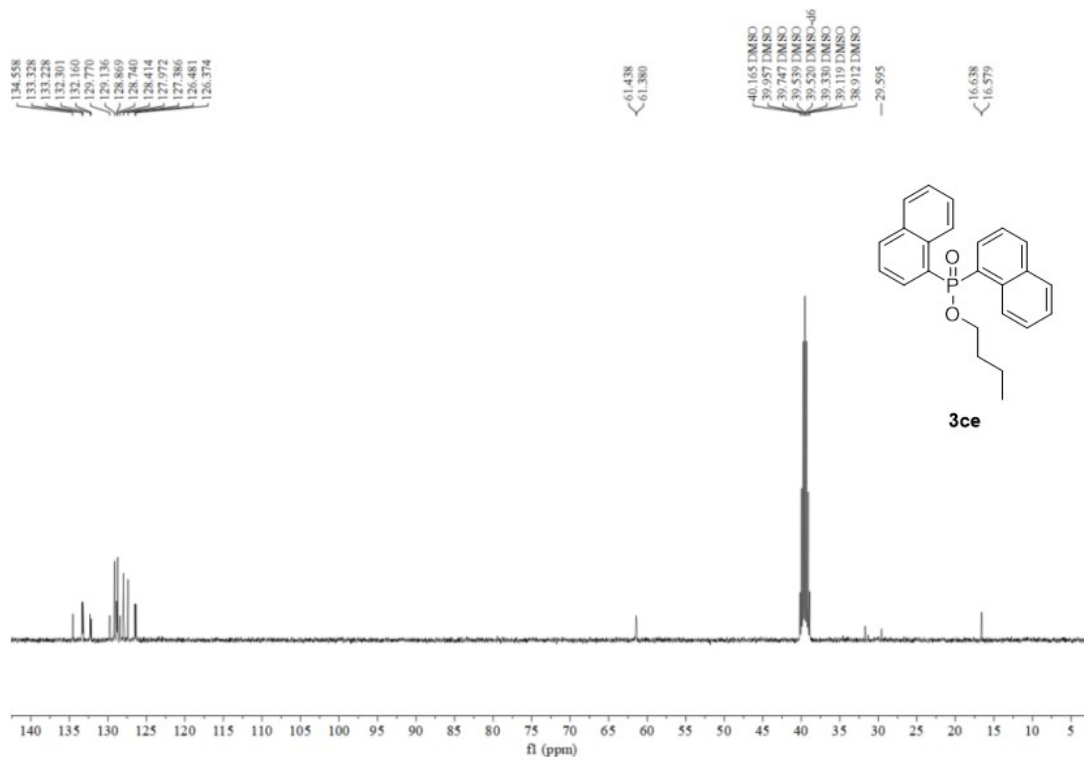


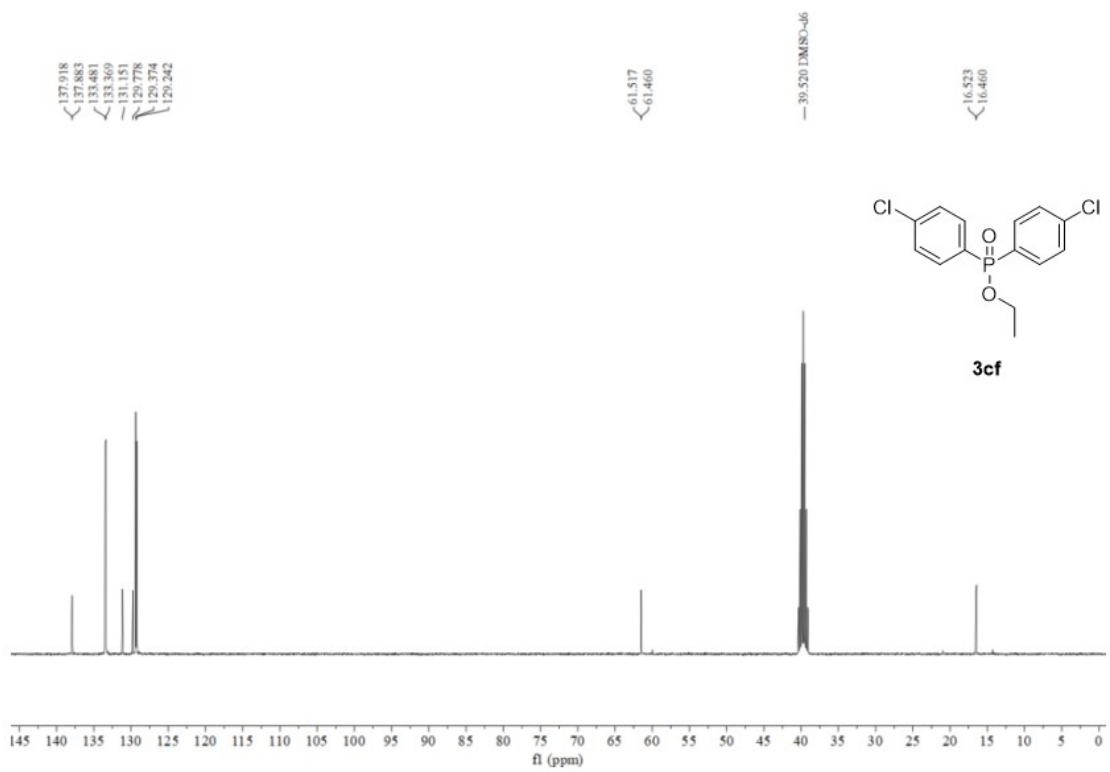
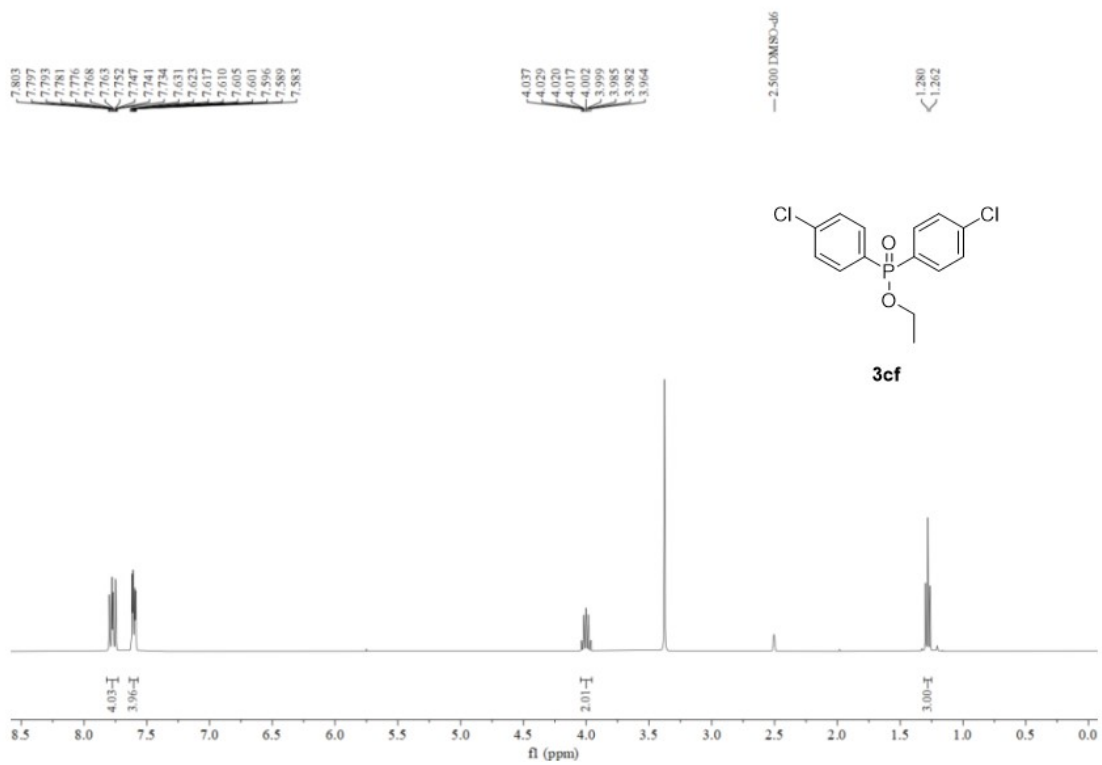




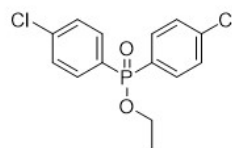




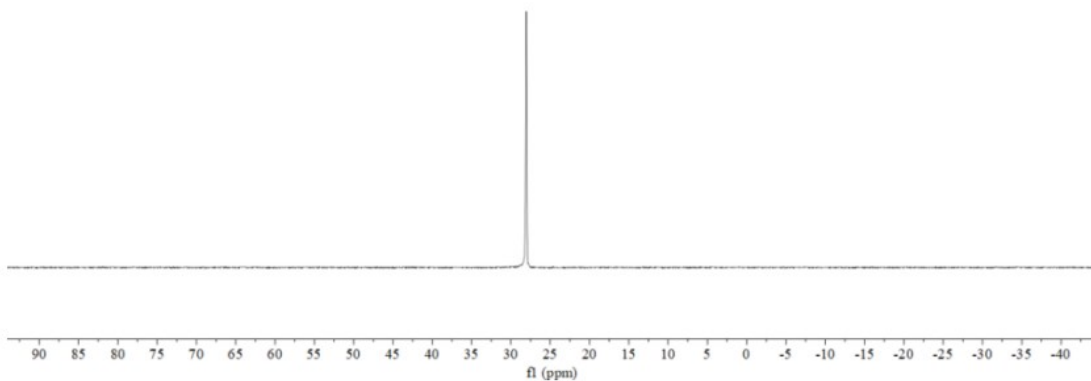




-28.026



3cf

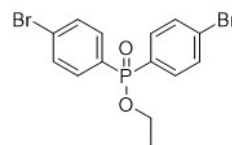


7.772
7.767
7.763
7.760
7.755
7.752
7.746
7.739
7.733
7.730
7.722
7.718
7.712
7.701
7.696
7.689
7.684
7.673
7.668
7.663
7.655

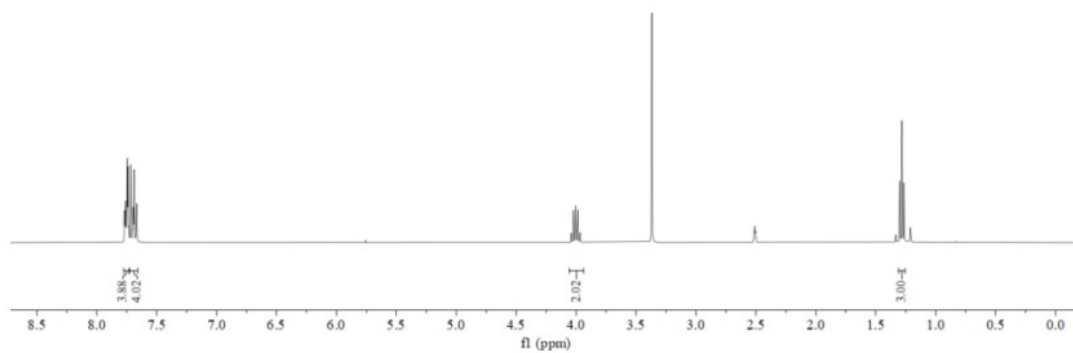
4.041
4.023
4.021
4.006
3.993
3.988
3.986

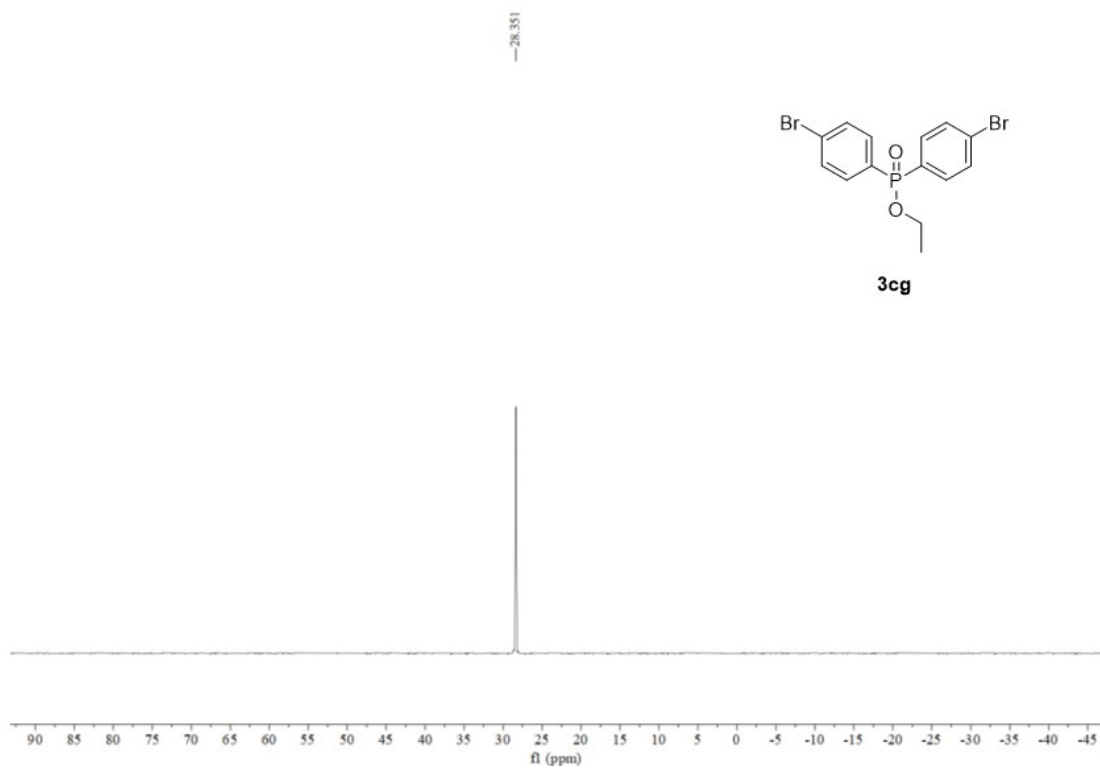
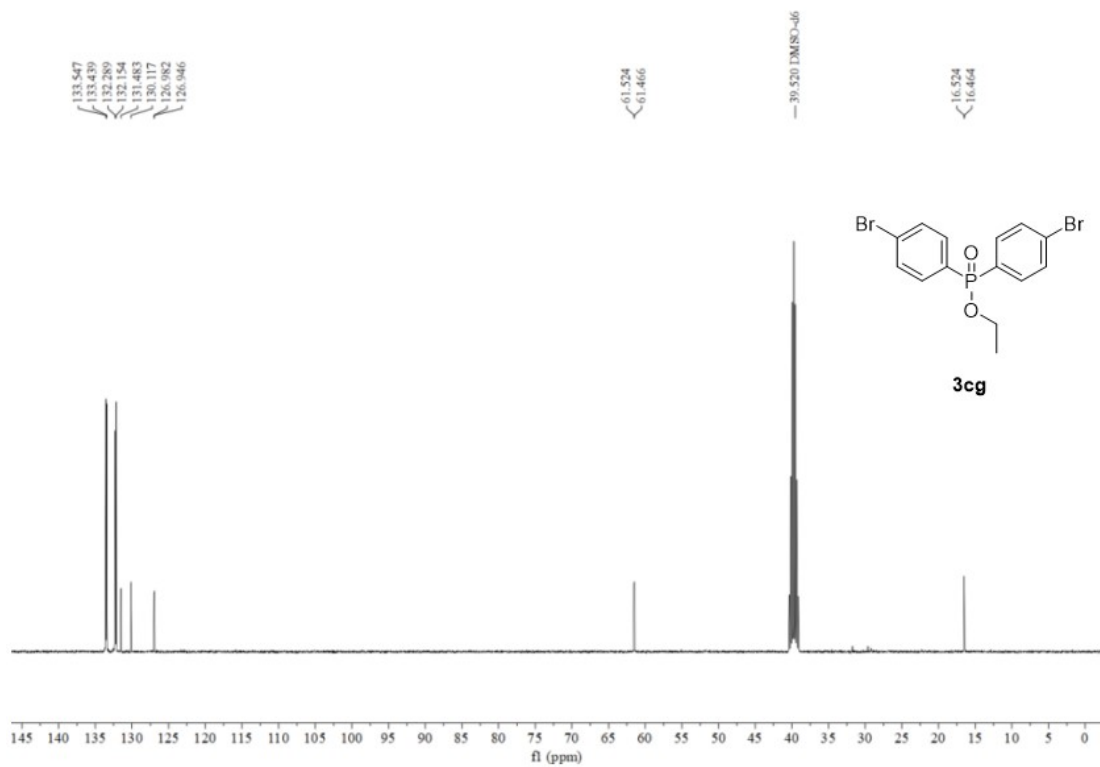
-2.500 (MSO-d6)

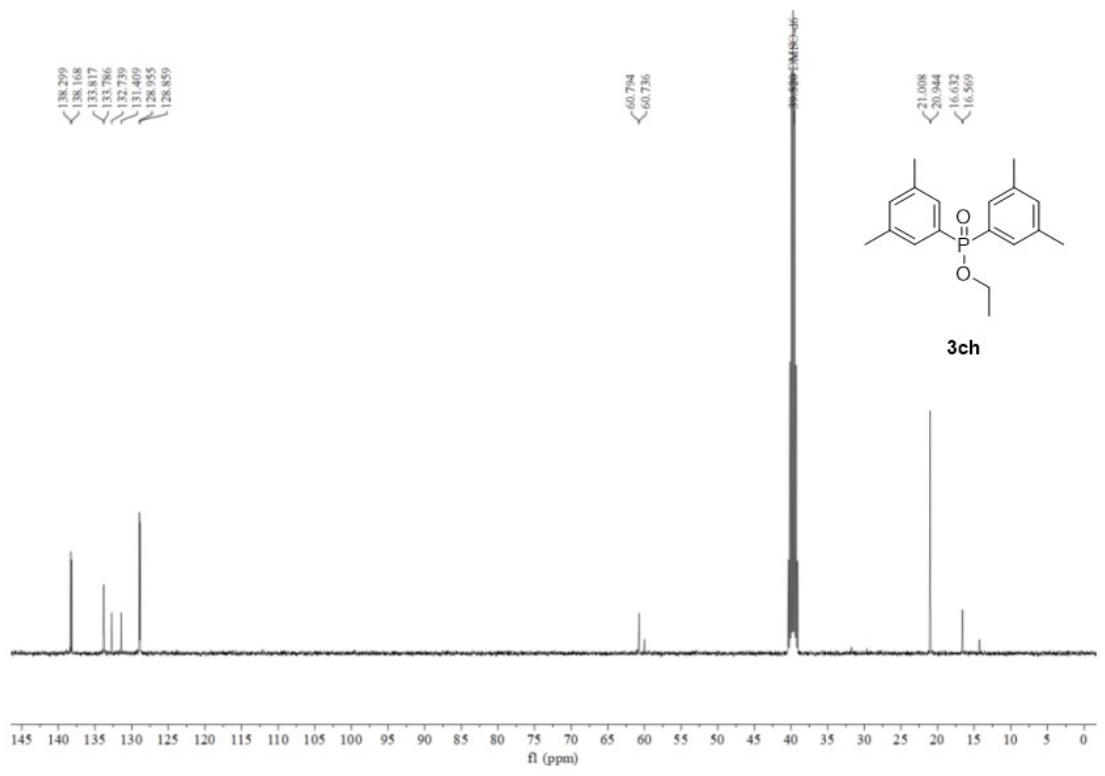
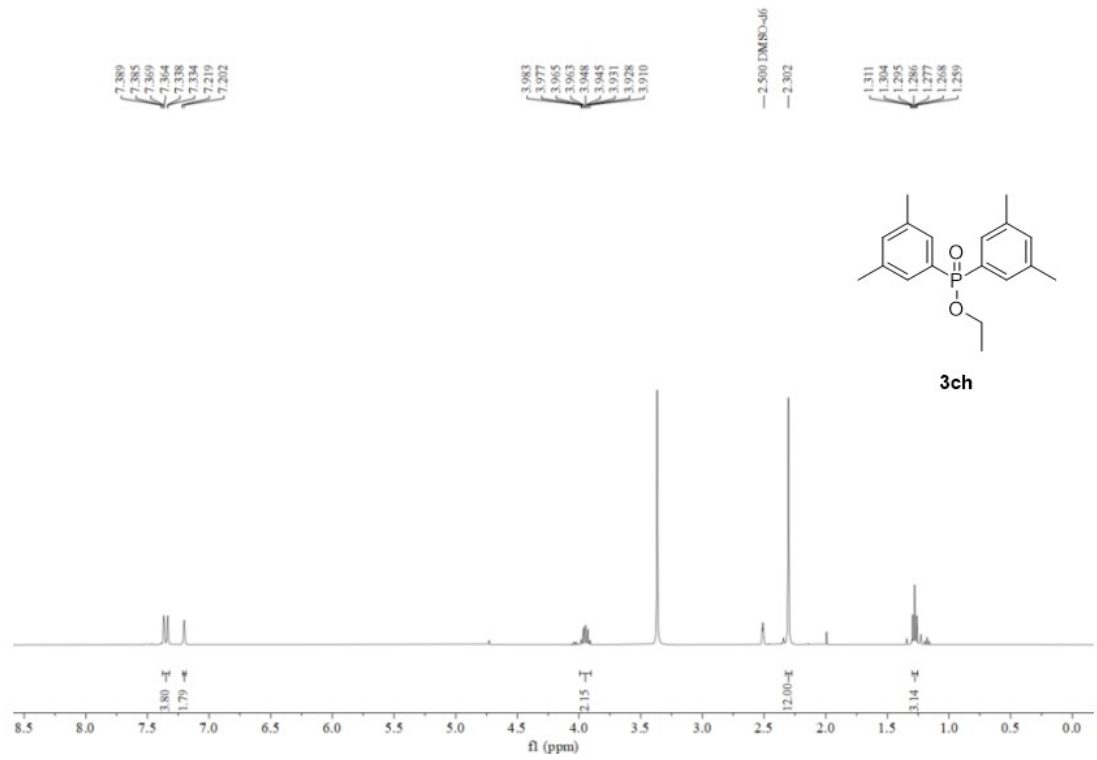
1.300
1.282
1.265

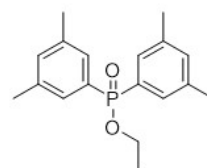
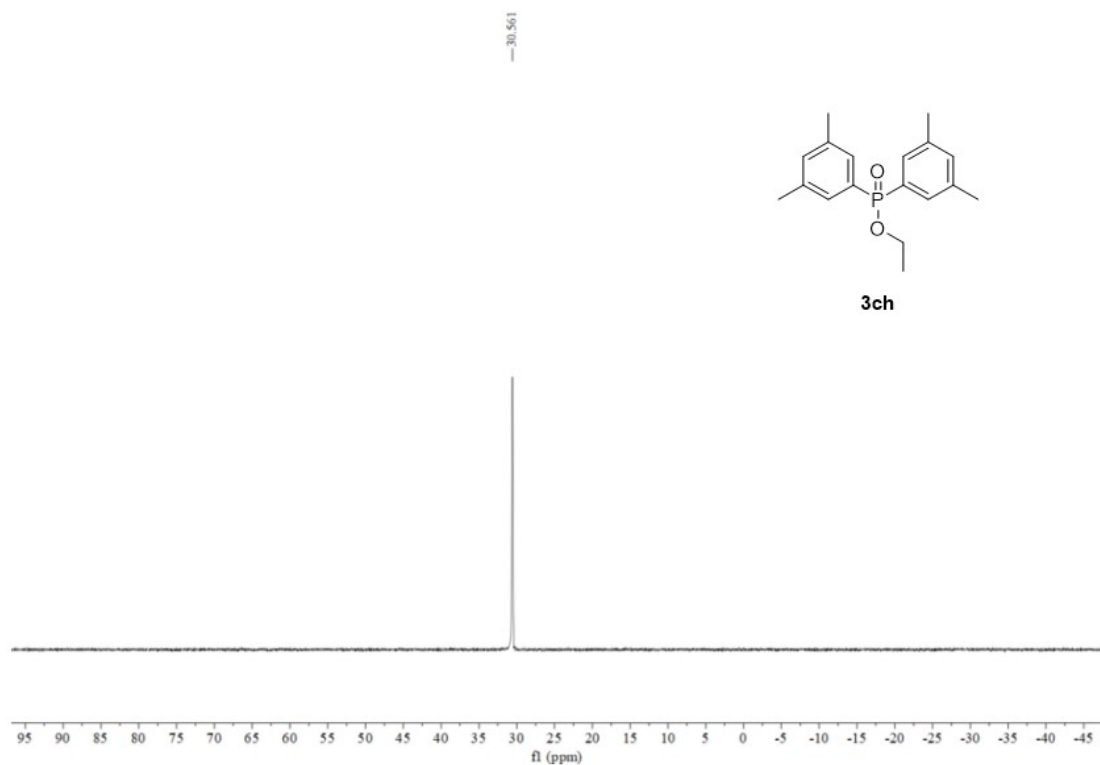


3cg

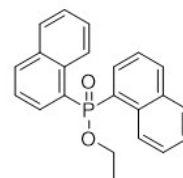
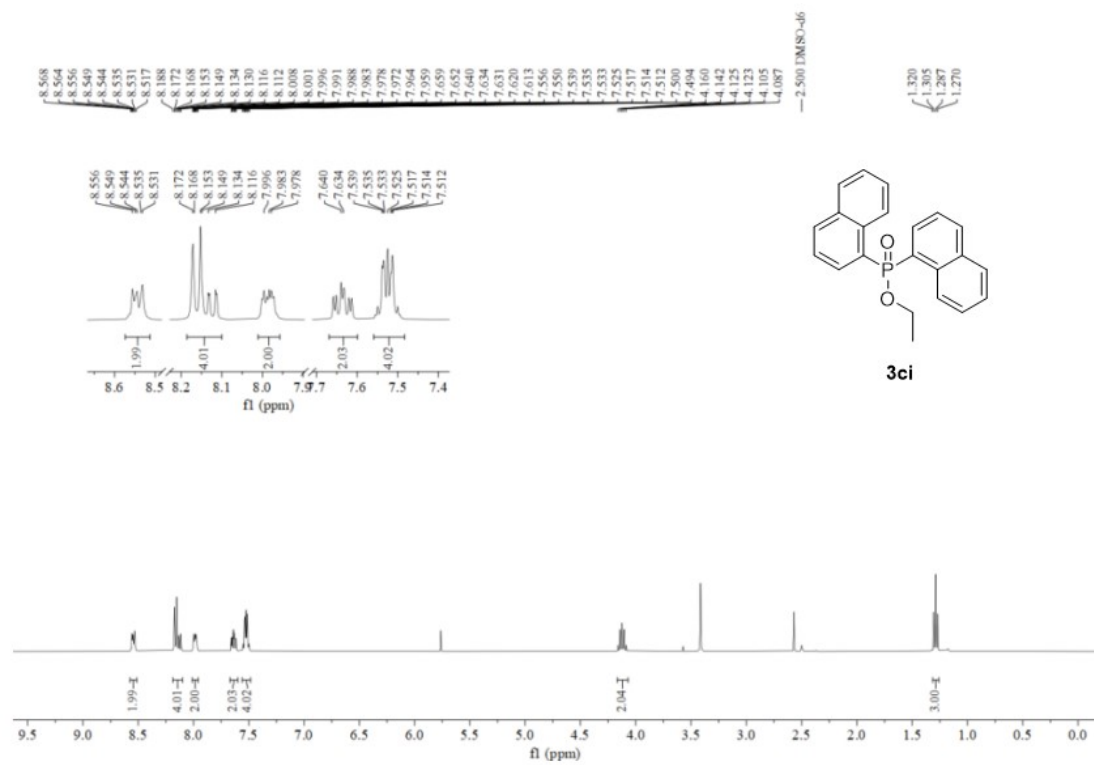








3ch



3ci

