Supporting Information

A Silver-Initiated Free-Radical Intermolecular Hydrophosphinylation of Unactivated Alkenes

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General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. Electron paramagnetic resonance (EPR) data were measured on a Bruker A300 EPR spectrometer (X-band). All products were identified by ^{1}H and ^{13}C NMR, ^{31}P NMR, MS, HRMS, and Element Analysis. The starting materials were purchased from Energy Chemicals, Alfa Aesar, Acros Organics, J&K Chemicals, Adamas, or Aldrich and used without further purification.

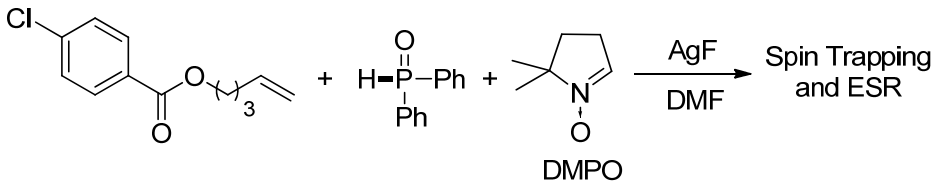
Typical procedure

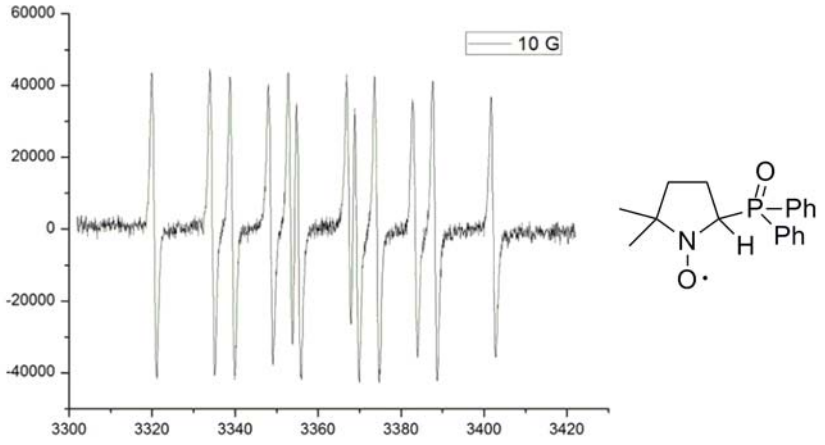
Reaction of H-P(O) with alkenes: A mixture of alkenes (1 equiv., 0.25 mmol), H-P(O) compounds (4 equiv., 1.00 mmol), AgF (20 mol%, 0.05 mmol), and DMF (2 mL) was heated at 110 ^{o}C (the measured temperature of the oil bath) for 24 h in a sealed tube (5 mL). After the reaction finished, the mixture was extracted and evaporated under vacuum and purified by column chromatography to afford the desired product.

ESR studies

Electron spin resonance (ESR) or Electron paramagnetic resonance (EPR) data were measured on a Bruker A300 EPR spectrometer (X-band). The calculated hyperfine splittings g values are obtained by using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as a standard.

General procedure: A mixture of pent-4-en-1-yl 4-chlorobenzoate (0.1 mmol), diphenylphosphine oxide (0.4 mmol), AgF (0.02 mmol), 5,5-dimethyl-1-pyrroline N-oxide (DMPO) (0.12 mmol) in DMF (2 mL) was heated in a sealed tube at 110 ^{o}C. The examples for ESR detection were collected once per hour during the reaction.





ESR studies. ESR spectrum of a solution of pent-4-en-1-yl 4-chlorobenzoate (5.0×10^{-2} mol/L), diphenylphosphine oxide (0.2 mol/L), AgF (1.0×10^{-2} mol/L), and DMPO (6.0×10^{-2} mol/L) in DMF (2 mL), 110 ^{o}C for 2.5 h.

(g = 2.0060, a_N = 1.411 mT; a_H = 1.888 mT; a_P = 3.475 mT)

Physical data and references for the following products:

All known compounds are determined by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

References:

1. Kong, W.; Merino, E.; Nevado, C. *Angew. Chem. Int. Ed.* **2014**, *53*, 5078.

2. Zhang, B.; Daniliuc, C.; Studer, A. *Org. Lett.*, **2014**, *16*, 250.

3. Kagayama, T.; Nakano, A.; Sakaguchi, S.; Ishii, Y. *Org. Lett.*, **Vol. 8**, No. 3, 2006.

4. Xiang, C.; Bian, Y.; Mao, X.; Huang, Z. *J. Org. Chem.,* **2012**, *77*, 7706.

5. Ghebreab, M.; Bange, C.; Waterman, R. *J. Am. Chem. Soc.,* **2014**, *136*, 9240.

6. Crimmin, M.; Barrett, A.; Hill, M.; Hitchcock, P. *Organometallics*, **2007**, *26*, 2953.

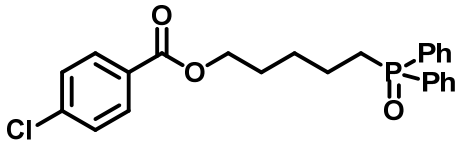
7. Lu, W.; Xi, C. *Organometallics*, **2008**, *27*, 3834.

8. Zhang, C. Li, Z. Zhu, L.; Yu, L. Wang, Z.; Li, C. *J. Am. Chem. Soc.,* **2013**, *135*, 14082.

Physical data for the following products:

0. 5-(diphenylphosphoryl)pentyl 4-chlorobenzoate (m. p. 93 – 95 ^{o}C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.70 (m, 4H), 7.53 – 7.44 (m, 6H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 2.32 – 2.25 (m, 2H), 1.78 – 1.65 (m, 4H), 1.58 – 1.51 (m, 2H).

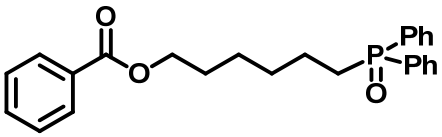
^{13}C NMR (151 MHz, $cdcl_3$): δ 165.7, 139.3, 133.4, 132.7, 131.7, 131.6, 130.9, 130.8, 130.7, 128.7, 128.6, 128.5, 64.9, 29.7(d, *J* = 72.0 Hz), 28.3, 27.5(d, *J* = 14.5 Hz), 21.3(d, *J* = 3.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.06 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{24}H_{25}ClO_3P$ $(M+H)^+$ 427.1224, found 427.1219.

1. 6-(diphenylphosphoryl)hexyl benzoate (m. p. 79 – 81 ^{o}C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 8.00 (m, 2H), 7.75 – 7.68 (m, 4H), 7.55 – 7.42 (m, 9H), 4.27 (t, *J* = 6.4 Hz, 2H), 2.30 – 2.23 (m, 2H), 1.75 – 1.61 (m, 4H), 1.51 – 1.39 (m, 4H).

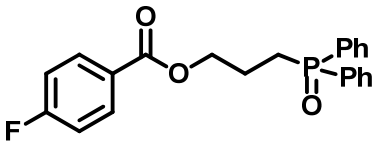
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 133.5, 132.8, 132.6, 131.7, 131.6, 130.8, 130.7, 130.4, 129.5, 128.7, 128.6, 128.3, 64.8, 30.6(d, *J* = 14.4 Hz), 29.6(d, *J* = 71.6 Hz), 28.4, 25.6, 21.4(d, *J* = 3.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.43 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{25}H_{28}O_3P$ $(M+H)^+$ 407.1771, found 407.1766.

2. 3-(diphenylphosphoryl)propyl 4-fluorobenzoate (m. p. 140 – 142 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 8.00 (m, 2H), 7.77 – 7.72 (m, 4H), 7.53 – 7.45 (m, 6H), 7.13 – 7.08 (m, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 2.44 – 2.37 (m, 2H), 2.15 – 2.06 (m, 2H).

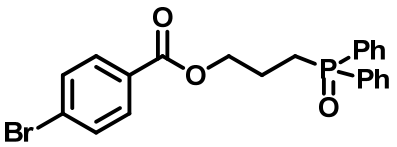
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 133.1, 132.2, 132.1, 131.9, 131.8, 130.8, 130.7, 128.8, 128.7, 126.3, 115.6, 115.4, 64.9(d, *J* = 15.4 Hz), 26.5(d, *J* = 72.2 Hz), 21.4(d, *J* = 3.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 31.83 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{22}H_{21}FO_3P$ $(M+H)^+$ 383.1207, found 383.1203.

3. 3-(diphenylphosphoryl)propyl 4-bromobenzoate (m. p. 140 – 143 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.72 (m, 4H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.45 (m, 6H), 4.36 (t, *J* = 6.4 Hz, 2H), 2.43 – 2.36 (m, 2H), 2.15 – 2.04 (m, 2H).

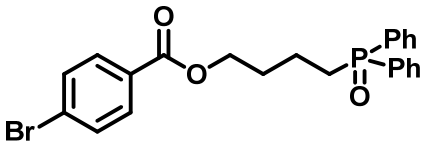
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 133.1, 132.1, 131.9, 131.9, 131.7, 131.1, 130.8, 130.7, 128.9, 128.8, 128.7, 128.2, 65.0(d, *J* = 15.4 Hz), 26.5(d, *J* = 72.1 Hz), 21.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 31.81 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{22}H_{21}BrO_3P$ $(M+H)^+$ 443.0406, found 443.0409.

4. 4-(diphenylphosphoryl)butyl 4-bromobenzoate (m. p. 150 – 151 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.70 (m, 4H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.43 (m, 6H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.36 – 2.29 (m, 2H), 1.92 – 1.81 (m, 2H), 1.80 – 1.74 (m, 2H).

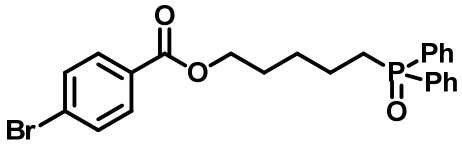
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 133.3, 132.4, 131.8, 131.7, 131.6, 131.1, 130.8, 130.7, 129.1, 128.7, 128.6, 128.0, 64.2, 29.7(d, *J* = 14.6 Hz), 29.3(d, *J* = 72.1 Hz), 18.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.02 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{23}H_{23}BrO_3P$ $(M+H)^+$ 457.0563, found 457.0570.

5. 5-(diphenylphosphoryl)pentyl 4-bromobenzoate (m. p. 112 – 114 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.76 – 7.70 (m, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.43 (m, 6H), 4.26 (t, *J* = 6.4 Hz, 2H), 2.32 – 2.25 (m, 2H), 1.78 – 1.65 (m, 4H), 1.58 – 1.50 (m, 2H).

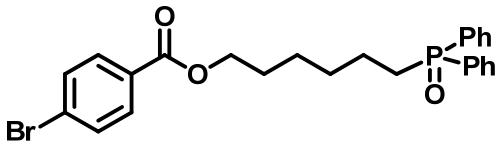
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 133.4, 132.5, 131.6, 131.0, 130.8, 130.7, 129.2, 128.7, 128.6, 127.9, 64.9, 29.7(d, *J* = 71.3 Hz), 28.3, 27.5(d, *J* = 14.6 Hz), 21.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.27 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{24}H_{25}BrO_3P$ $(M+H)^+$ 471.0719, found 471.0713.

6. 6-(diphenylphosphoryl)hexyl 4-bromobenzoate (m. p. 103 – 105 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.70 (m, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.44 (m, 6H), 4.26 (t, *J* = 6.4 Hz, 2H), 2.30 – 2.23 (m, 2H), 1.74 – 1.60 (m, 4H), 1.51 – 1.38 (m, 4H).

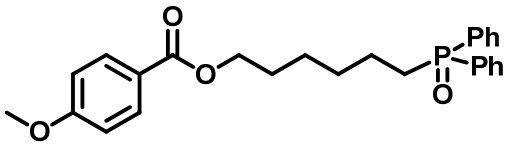
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 133.5, 132.6, 131.7, 131.0, 130.8, 130.7, 129.3, 128.7, 128.6, 127.9, 65.1, 30.5(d, *J* = 14.2 Hz), 29.6(d, *J* = 71.6 Hz), 28.4, 25.5, 21.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.44 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{25}H_{27}BrO_3P$ $(M+H)^+$ 485.0876, found 485.0871.

7. 6-(diphenylphosphoryl)hexyl 4-methoxybenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.75 – 7.70 (m, 4H), 7.52 – 7.44 (m, 6H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.23 (t, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 2.29 – 2.22 (m, 2H), 1.73 – 1.60 (m, 4H), 1.50 – 1.40 (m, 4H).

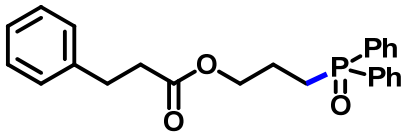
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 163.2, 133.6, 132.6, 131.6, 131.6, 131.5, 130.8, 130.7, 128.7, 128.5, 122.8, 113.5, 64.5, 55.4, 30.6(d, *J* = 14.4 Hz), 29.6(d, *J* = 71.5 Hz), 28.5, 25.6, 21.4(d, *J* = 3.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.39 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{26}H_{30}O_4P$ $(M+H)^+$ 437.1876, found 437.1872.

8. 3-(diphenylphosphoryl)propyl 3-phenylpropanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 4H), 7.55 – 7.45 (m, 6H), 7.27 – 7.23 (m, 2H), 7.16 (dd, *J* = 14.8, 7.2 Hz, 3H), 4.10 (t, *J* = 6.4 Hz, 2H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.27 – 2.20 (m, 2H), 1.97 – 1.88 (m, 2H).

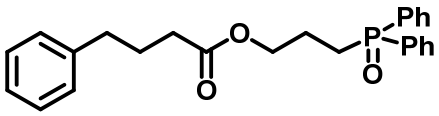
^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 140.4, 133.2, 132.2, 131.9, 131.8, 130.8, 130.7, 128.8, 128.6, 128.5, 128.2, 126.3, 64.3(d, *J* = 15.5 Hz), 35.7, 30.9, 26.4(d, *J* = 72.2 Hz), 21.2(d, *J* = 3.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 31.92 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{24}H_{26}O_3P$ $(M+H)^+$ 393.1614, found 393.1617.

9. 3-(diphenylphosphoryl)propyl 4-phenylbutanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.70 (m, 4H), 7.54 – 7.44 (m, 6H), 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 4.11 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.35 – 2.28 (m, 4H), 2.00 – 1.90 (m, 4H).

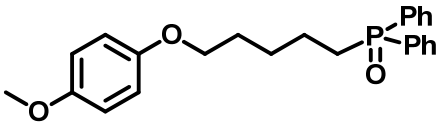
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 141.2, 133.1, 132.1, 131.9, 131.8, 130.8, 130.7, 128.8, 128.6, 128.4, 128.3, 126.0, 64.2(d, *J* = 15.6 Hz), 35.1, 33.5, 26.5(d, *J* = 72.3 Hz), 26.4, 21.2(d, *J* = 3.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 31.89 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{25}H_{28}O_3P$ $(M+H)^+$ 407.1771, found 407.1768.

10. (5-(4-methoxyphenoxy)pentyl)diphenylphosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.71 (m, 4H), 7.50 – 7.45 (m, 6H), 6.82 – 6.76 (m, 4H), 3.85 (t, *J* = 6.4 Hz, 2H), 3.75 (s, 3H), 2.32 – 2.25 (m, 2H), 1.77 – 1.65 (m, 4H), 1.61 – 1.54 (m, 2H).

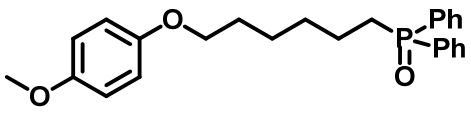
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 153.1, 133.6, 132.6, 131.7, 131.6, 130.8, 130.7, 128.7, 128.6, 115.4, 114.6, 68.2, 55.7, 29.7(d, *J* = 71.5 Hz), 28.9, 27.5(d, *J* = 14.7 Hz), 21.3(d, *J* = 3.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.30 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{24}H_{28}O_3P$ $(M+H)^+$ 395.1771, found 395.1767.

11. (6-(4-methoxyphenoxy)hexyl)diphenylphosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.71 (m, 4H), 7.50 – 7.44 (m, 6H), 6.83 – 6.78 (m, 4H), 3.85 (t, *J* = 6.4 Hz, 2H), 3.76 (s, 3H), 2.30 – 2.23 (m, 2H), 1.77 – 1.60 (m, 4H), 1.50 – 1.43 (m, 4H).

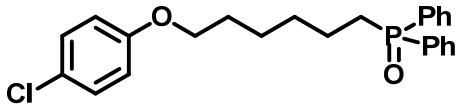
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 153.2, 133.6, 132.7, 131.6, 131.6, 130.8, 130.7, 128.7, 128.6, 115.4, 114.6, 68.4, 55.7, 30.7(d, *J* = 14.3 Hz), 29.7(d, *J* = 71.5 Hz), 29.1, 25.6, 21.4(d, *J* = 3.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.44 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{25}H_{30}O_3P$ $(M+H)^+$ 409.1927, found 409.1925.

12. (6-(4-chlorophenoxy)hexyl)diphenylphosphine oxide (m. p. 79 – 81 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.70 (m, 4H), 7.53 – 7.44 (m, 6H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.87 (t, *J* = 6.4 Hz, 2H), 2.30 – 2.23 (m, 2H), 1.73 – 1.61 (m, 4H), 1.50 – 1.44 (m, 4H).

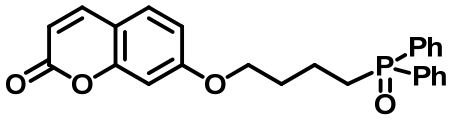
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 133.6, 132.7, 131.7, 131.6, 130.8, 130.7, 129.2, 128.7, 128.6, 125.3, 115.7, 68.0, 30.6(d, *J* = 14.3 Hz), 29.7(d, *J* = 71.5 Hz), 28.9, 25.5, 21.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.41 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{24}H_{27}ClO_2P$ $(M+H)^+$ 413.1432, found 413.1430.

13. 7-(4-(diphenylphosphoryl)butoxy)-2H-chromen-2-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.72 (m, 4H), 7.61 (d, *J* = 10.4 Hz, 1H), 7.55 – 7.45 (m, 6H), 7.34 (d, *J* = 8.8 Hz, 1H), 6.78 – 6.73 (m, 2H), 6.23 (d, *J* = 9.2 Hz, 1H), 3.99 (t, *J* = 6.0 Hz, 2H), 2.38 – 2.31 (m, 2H), 1.97 – 1.89 (m, 2H), 1.86 – 1.81 (m, 2H).

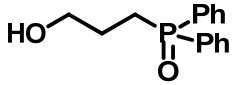
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 161.2, 155.8, 143.4, 133.4, 132.4, 131.8, 131.7, 130.8, 130.7, 128.8, 128.7, 128.6, 113.1, 112.8, 112.5, 101.4, 67.7, 30.0(d, *J* = 13.9 Hz), 29.4(d, *J* = 71.5 Hz), 18.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.14 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{25}H_{24}O_4P$ $(M+H)^+$ 419.1407, found 419.1406.

14. (3-hydroxypropyl)diphenylphosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/2)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.71 (m, 4H), 7.54 – 7.44 (m, 6H), 3.91 (s, 1H), 3.70 (t, *J* = 5.2 Hz, 2H), 2.44 – 2.38 (m, 2H), 1.93 – 1.83 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 132.9, 131.9, 131.8, 130.8, 130.7, 128.8, 128.7, 62.5(d, *J* = 9.2 Hz), 27.6(d, *J* = 71.2 Hz), 25.4(d, *J* = 4.1 Hz).

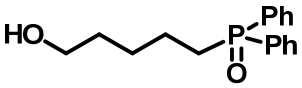
^{31}P NMR (162 MHz, $CDCl_3$): δ 34.64 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{15}H_{18}O_2P$ $(M+H)^+$ 261.1039, found 261.1042.

15. (5-hydroxypentyl)diphenylphosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl

acetate = 1/2)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.70 (m, 4H), 7.54 – 7.44 (m, 6H), 3.60 (t, *J* = 6.0 Hz, 2H), 2.31 – 2.24 (m, 2H), 1.69 (s, 1H), 1.69 – 1.61 (m, 2H), 1.59 – 1.46 (m, 4H).

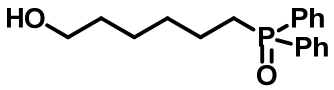
^{13}C NMR (151 MHz, $cdcl_3$): δ 133.4, 132.8, 131.7, 131.6, 130.8, 130.7, 128.7, 128.6, 62.4, 32.1, 29.6(d, *J* = 71.9 Hz), 27.0(d, *J* = 14.2 Hz), 21.2(d, *J* = 4.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.58 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{17}H_{22}O_2P$ $(M+H)^+$ 289.1352, found 289.1349.

16. (6-hydroxyhexyl)diphenylphosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/2)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.69 (m, 4H), 7.52 – 7.43 (m, 6H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.28 – 2.21 (m, 2H), 2.12 (s, 1H), 1.67 – 1.57 (m, 2H), 1.53 – 1.45 (m, 2H), 1.44 – 1.30 (m, 4H).

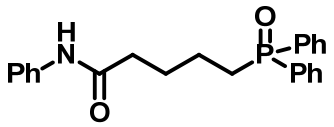
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.5, 132.5, 131.6, 131.6, 130.8, 130.7, 128.6, 128.5, 62.4, 32.3, 30.5(d, *J* = 14.0 Hz), 29.5(d, *J* = 71.6 Hz), 25.1, 21.4(d, *J* = 3.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.78 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{18}H_{24}O_2P$ $(M+H)^+$ 303.1508, found 303.1506.

17. 5-(diphenylphosphoryl)-N-phenylpentanamide (m. p. 163 – 165 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 7.73 – 7.68 (m, 4H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.47 – 7.42 (m, 4H), 7.28 – 7.24 (m, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.37 – 2.30 (m, 2H), 1.90 – 1.83 (m, 2H), 1.76 – 1.66 (m, 2H).

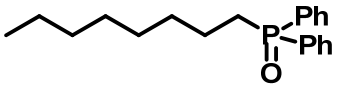
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 138.7, 133.1, 132.1, 131.9, 130.7, 130.6, 128.8, 128.7, 128.7, 123.7, 119.8, 36.7, 29.0(d, *J* = 71.5 Hz), 26.8(d, *J* = 12.4 Hz), 21.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ 33.53 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{23}H_{25}NO_2P$ $(M+H)^+$ 378.1617, found 378.1613.

18. octyldiphenylphosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.71 (m, 4H), 7.52 – 7.43 (m, 6H), 2.28 – 2.21 (m, 2H), 1.66 – 1.56 (m, 2H), 1.41 – 1.34 (m, 2H), 1.22 – 1.16 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H).

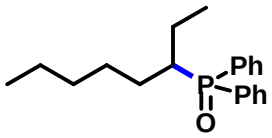
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.7, 132.8, 131.6, 131.5, 130.8, 130.7, 128.6, 128.5, 31.7, 31.0(d, *J* = 14.5 Hz), 29.7(d, *J* = 71.6 Hz), 29.0, 22.6, 21.4(d, *J* = 4.0 Hz), 14.0.

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.43 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{20}H_{28}OP$ $(M+H)^+$ 315.1872, found 315.1875.

19. (R)-octan-3-yldiphenylphosphine oxide (m. p. 89 – 92 ^{o}C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.77 (m, 4H), 7.51 – 7.42 (m, 6H), 2.20 – 2.12 (m, 1H), 1.81 – 1.40 (m, 5H), 1.23 – 1.09 (m, 5H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H).

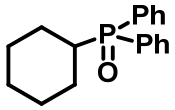
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.6, 132.7, 131.3, 131.2, 130.9, 130.8, 128.5, 128.4, 38.5(d, *J* = 70.4 Hz), 31.8, 27.6(d, *J* = 9.4 Hz), 26.8, 22.3, 20.6, 13.9, 12.6(d, *J* = 9.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 36.45 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{20}H_{27}OP$ $(M+H)^+$ 315.1872, found 315.1875.

20. cyclohexyldiphenylphosphine oxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ7.80 – 7.75 (m, 4H), 7.51 – 7.43 (m, 6H), 2.28 – 2.18 (m, 1H), 1.91 – 1.65 (m, 6H), 1.55 – 1.49 (m, 1H), 1.31 – 1.18 (m, 3H).

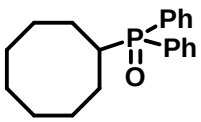
^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6, 131.6, 131.4, 131.3, 131.1, 131.0, 128.6, 128.4, 37.2(d, *J* = 72.6 Hz), 26.4(d, *J* = 13.3 Hz), 25.8, 24.8(d, *J* = 2.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 34.38 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{18}H_{22}OP$ $(M+H)^+$ 285.1403, found 285.1400.

21. cyclooctyldiphenylphosphine oxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.76 (m, 4H), 7.50 – 7.42 (m, 6H), 2.49 – 2.40 (m, 1H), 1.87 – 1.77 (m, 2H), 1.73 – 1.64 (m, 4H), 1.63 – 1.53 (m, 6H), 1.42 – 1.40 (m, 2H).

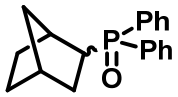
^{13}C NMR (100 MHz, $CDCl_3$): δ 133.2, 132.2, 131.3, 131.2, 131.0, 130.9, 128.5, 128.4, 35.6(d, *J* = 70.0 Hz), 26.9, 26.3(d, *J* = 12.6 Hz), 25.9, 25.8(d, *J* = 1.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 38.66 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{20}H_{26}OP$ $(M+H)^+$ 313.1716, found 313.1720.

22. bicyclo[2.2.1]heptan-2-yldiphenylphosphine oxide

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.70 (m, 4H), 7.52 – 7.39 (m, 6H), 2.49 (d, *J* = 8.8 Hz, 1H), 2.35 (s, 1H), 2.30 – 2.26 (m, 1H), 1.86 – 1.83 (m, 2H), 1.62 – 1.57 (m, 2H), 1.46 – 1.38 (m, 1H), 1.33 – 1.23 (m, 2H), 1.17 (d, *J* = 10.0 Hz, 1H).

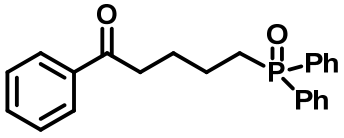
^{13}C NMR (100 MHz, $CDCl_3$): δ 134.2, 133.0, 131.4, 131.3, 131.2, 131.0, 130.9, 130.9, 130.8, 128.6, 128.5, 128.4, 40.0(d, *J* = 72.5 Hz), 38.2, 37.3, 36.4(d, *J* = 2.9 Hz), 32.1(d, *J* = 14.8 Hz), 31.4(d, *J* = 4.3 Hz), 28.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ 33.88 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{19}H_{22}OP$ $(M+H)^+$ 297.1403, found 297.1400.

23. 5-(diphenylphosphoryl)-1-phenylpentan-1-one (m. p. 140 – 143 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.88 (m, 2H), 7.76 – 7.71 (m, 4H), 7.54 – 7.42 (m, 9H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.36 – 2.29 (m, 2H), 1.90 – 1.82 (m, 2H), 1.80 – 1.67 (m, 2H).

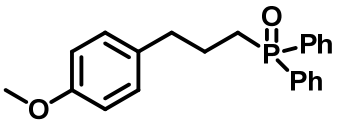
^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 136.8, 133.5, 133.0, 132.5, 131.7, 131.6, 130.8, 130.7, 128.7, 128.6, 128.5, 128.0, 38.0, 29.7(d, *J* = 71.5 Hz), 25.4(d, *J* = 15.1 Hz), 21.3(d, *J* = 3.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.17 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{23}H_{24}O_2P$ $(M+H)^+$ 363.1508, found 363.1504.

24. (3-(4-methoxyphenyl)propyl)diphenylphosphine oxide (m. p. 130 – 132 °C)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.65 (m, 4H), 7.50 – 7.42 (m, 6H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.26 – 2.20 (m, 2H), 2.04 – 1.87 (m, 2H).

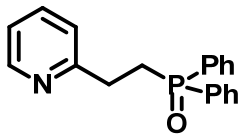
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 133.5, 132.9, 132.6, 131.6, 131.5, 130.8, 130.7, 129.4, 128.6, 128.5, 113.8, 55.2, 35.7(d, *J* = 14.8 Hz), 28.9(d, *J* = 71.6 Hz), 23.2(d, *J* = 3.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.46 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{22}H_{24}O_2P$ $(M+H)^+$ 351.1508, found 351.1513.

25. diphenyl(2-(pyridin-2-yl)ethyl)phosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 4.4 Hz, 1H), 7.82 – 7.75 (m, 4H), 7.54 – 7.42 (m, 7H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.14 – 3.08 (m, 2H), 2.82 – 2.75 (m, 2H).

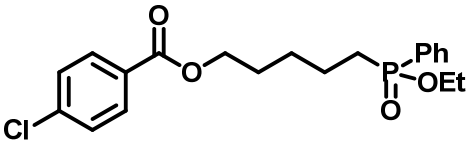
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 149.2, 136.4, 133.3, 132.3, 131.7, 131.6, 130.8, 130.7, 128.7, 128.6, 123.0, 121.4, 29.7(d, *J* = 2.7 Hz), 29.2(d, *J* = 71.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.17 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{19}H_{19}NOP$ $(M+H)^+$ 308.1199, found 308.1198.

26. 5-(ethoxy(phenyl)phosphoryl)pentyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.79 – 7.74 (m, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 4.12 – 4.02 (m, 1H), 3.88 – 3.79 (m, 1H), 2.01 – 1.81 (m, 2H), 1.77 – 1.56 (m, 4H), 1.53 – 1.44 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 139.3, 132.2, 131.6, 131.5, 130.9, 128.8, 128.7, 128.5, 64.9, 60.5(d, *J* = 6.0 Hz), 29.7(d, *J* = 100.6 Hz), 28.3, 27.2(d, *J* = 15.6 Hz), 21.5, 16.5(d, *J* = 6.3 Hz).

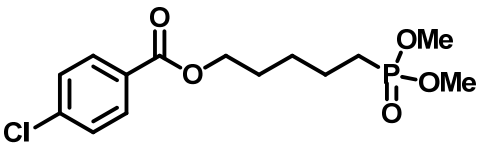
^{31}P NMR (162 MHz, $CDCl_3$): δ 44.24 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{20}H_{25}ClO_4P$ $(M+H)^+$ 395.1173, found 395.1178.

27. 5-(dimethoxyphosphoryl)pentyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl

acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 1.82 – 1.69 (m, 2H), 1.67 – 1.62 (m, 4H), 1.57 – 1.50 (m, 2H).

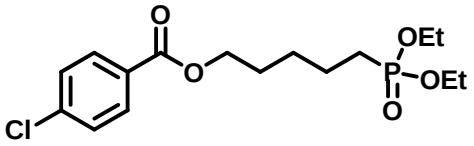
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 139.3, 130.9, 128.8, 128.7, 64.9, 52.3(d, *J* = 6.6 Hz), 28.3, 27.0(d, *J* = 16.6 Hz), 25.3, 23.9, 22.1(d, *J* = 5.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 34.53 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{14}H_{21}ClO_5P$ $(M+H)^+$ 335.0810, found 335.0814.

28. 5-(diethoxyphosphoryl)pentyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 4.16 – 4.02 (m, 4H), 1.82 – 1.75 (m, 2H), 1.72 – 1.62 (m, 4H), 1.57 – 1.47 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 139.3, 130.9, 128.8, 128.7, 64.9, 61.5(d, *J* = 6.6 Hz), 28.3, 27.1(d, *J* = 16.7 Hz), 26.4, 25.0, 22.2(d, *J* = 5.1 Hz), 16.5(d, *J* = 5.9 Hz).

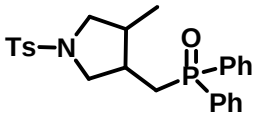
^{31}P NMR (162 MHz, $CDCl_3$): δ 31.99 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{16}H_{25}ClO_5P$ $(M+H)^+$ 363.1123, found 363.1127.

29. ((4-methyl-1-tosylpyrrolidin-3-yl)methyl)diphenylphosphine oxide

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl

acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.66 (m, 5H), 7.62 (t, *J* = 8.8 Hz, 2H), 7.57 – 7.43 (m, 7H), 3.30 – 3.23 (m, 2H), 3.03 – 2.99 (m, 2H), 2.40 (s, 3H), 2.27 – 2.18 (m, 2H), 2.07 – 1.97 (m, 2H), 0.77 (d, *J* = 6.8 Hz, 3H).

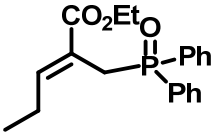
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 134.0, 132.0, 131.9, 130.7, 130.6, 129.6, 128.9, 128.8, 128.7, 128.7, 127.4, 54.1, 51.5(d, *J* = 6.1 Hz), 36.2(d, *J* = 9.3 Hz), 35.8, 28.2(d, *J* = 71.3 Hz), 21.5, 13.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ 30.21 (s, 1P).

HRMS (ESI, m/z): Calculated for $C_{25}H_{29}NO_3PS(M+H)^+$ 454.1600, found 454.1595.

30. (*E*)-ethyl 2-((diphenylphosphoryl)methyl)pent-2-enoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.76 (m, 4H), 7.52 – 7.42 (m, 6H), 6.94 (dd, *J* = 12.8, 7.6 Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 2H), 3.51 (d, *J* = 14.4 Hz, 2H), 2.36 – 2.26 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.6 Hz, 3H).

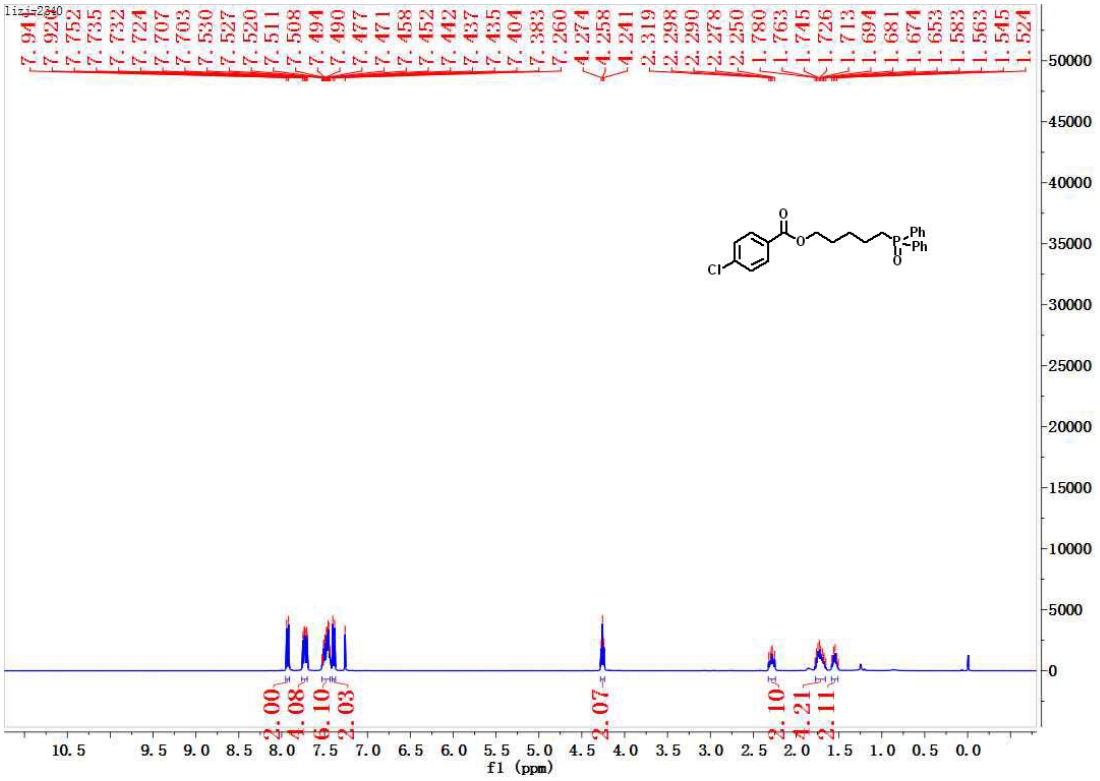
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 149.0(d, *J* = 6.1 Hz), 133.1, 132.1, 131.7, 131.6, 131.2, 131.1, 128.4, 128.3, 122.0(d, *J* = 9.2 Hz), 60.7, 29.6(d, *J* = 67.6 Hz), 23.1, 14.0, 12.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ 29.06 (s, 1P).

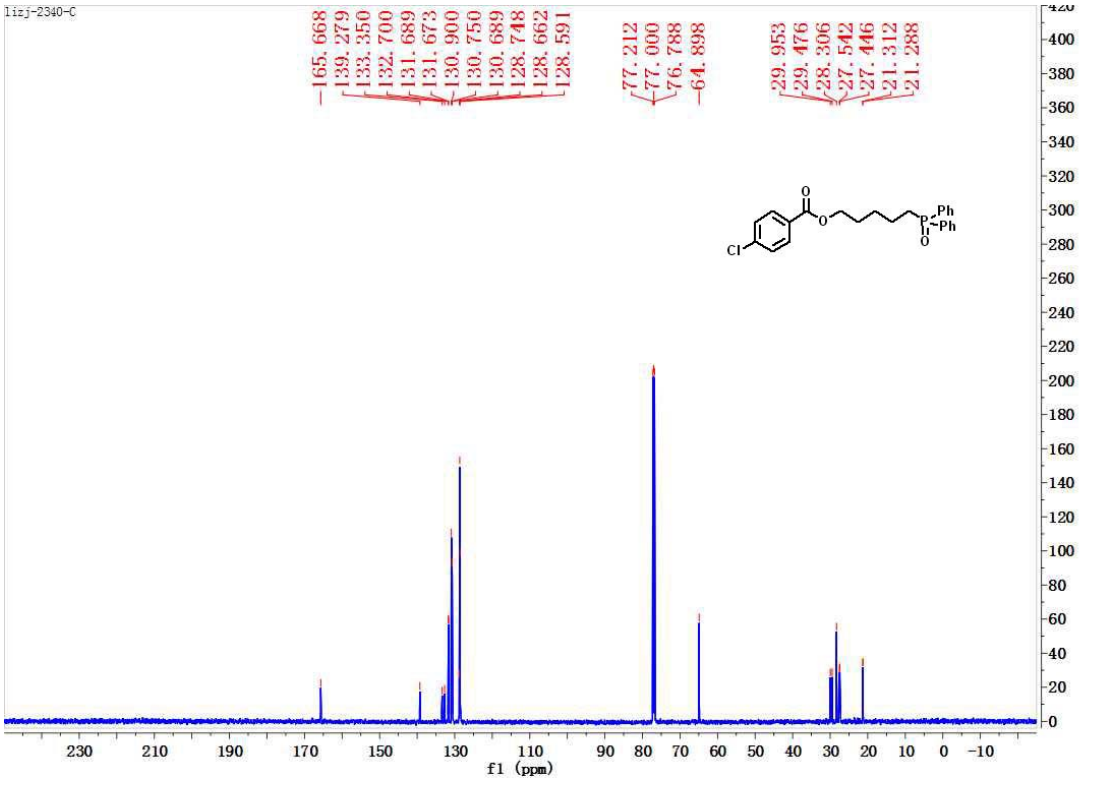
HRMS (ESI, m/z): Calculated for $C_{20}H_{24}O_3P$ $(M+H)^+$ 365.1277, found 365.1273.

Copies of the ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, NOE

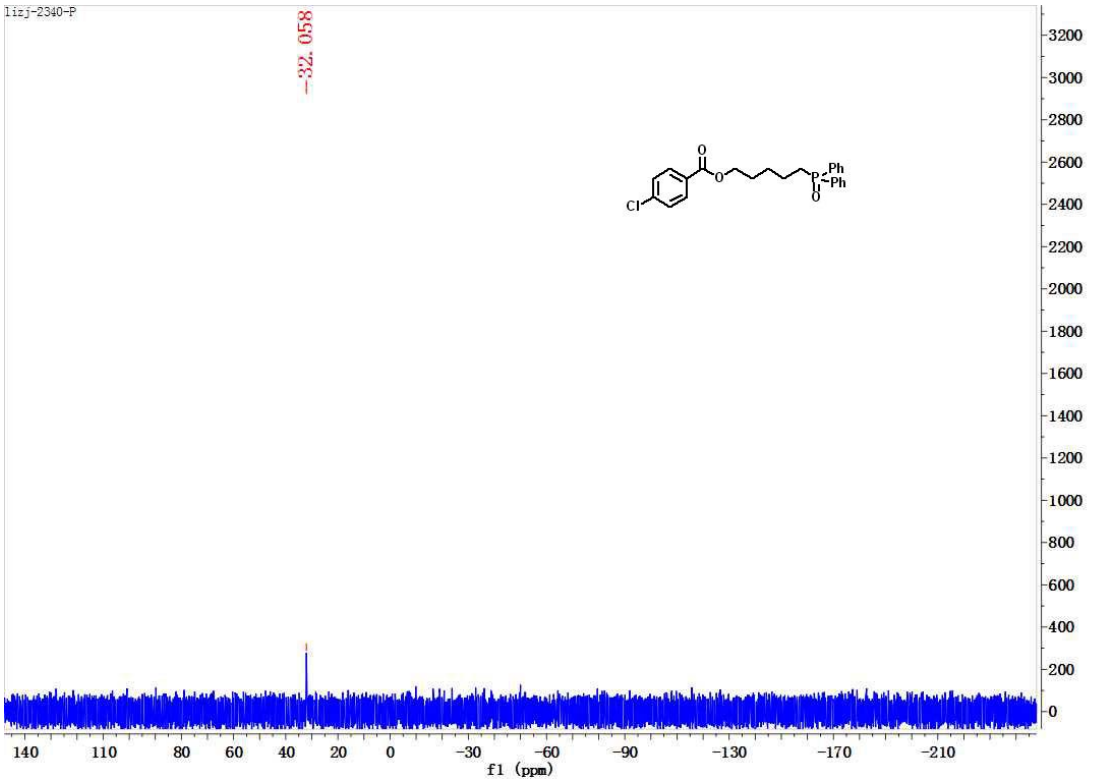
0-^{1}H NMR



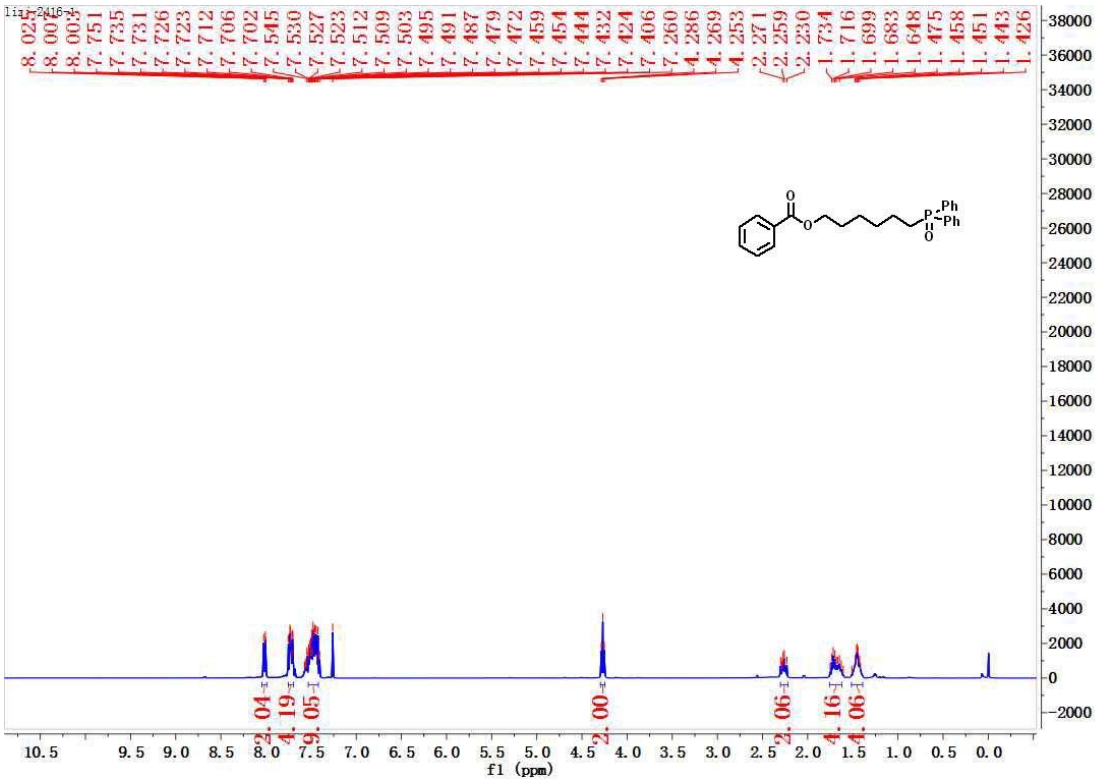
0-^{13}C NMR



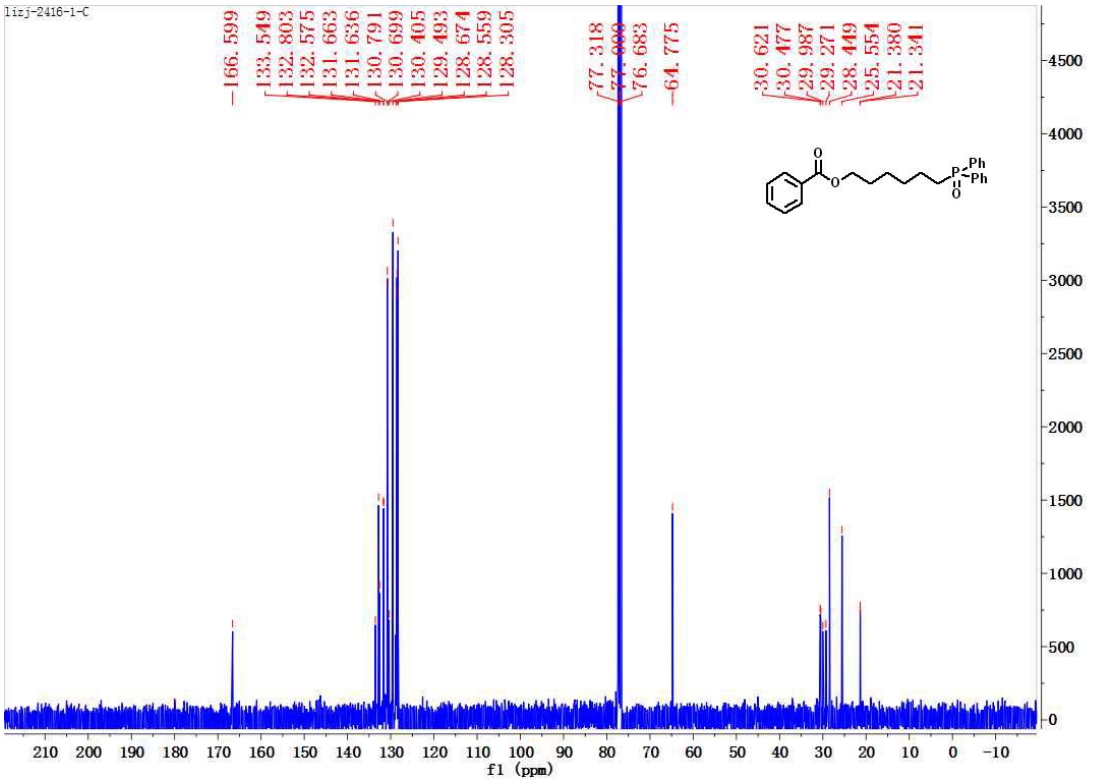
0-^{31}P NMR



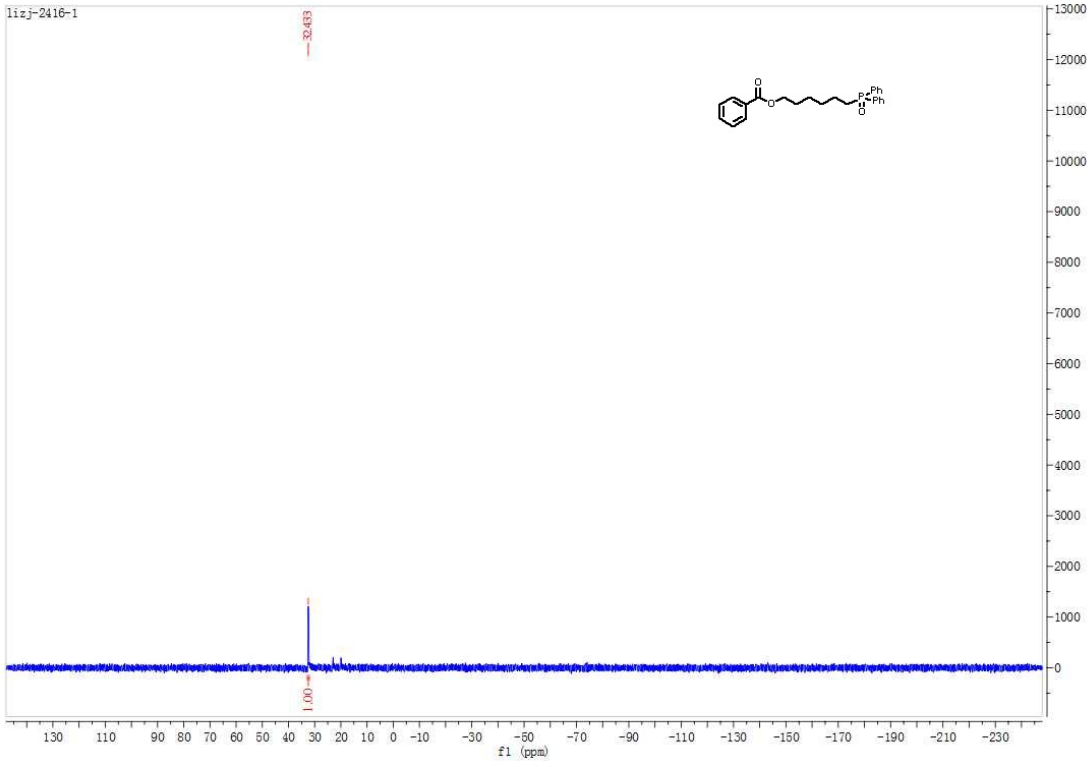
1-^{1}H NMR



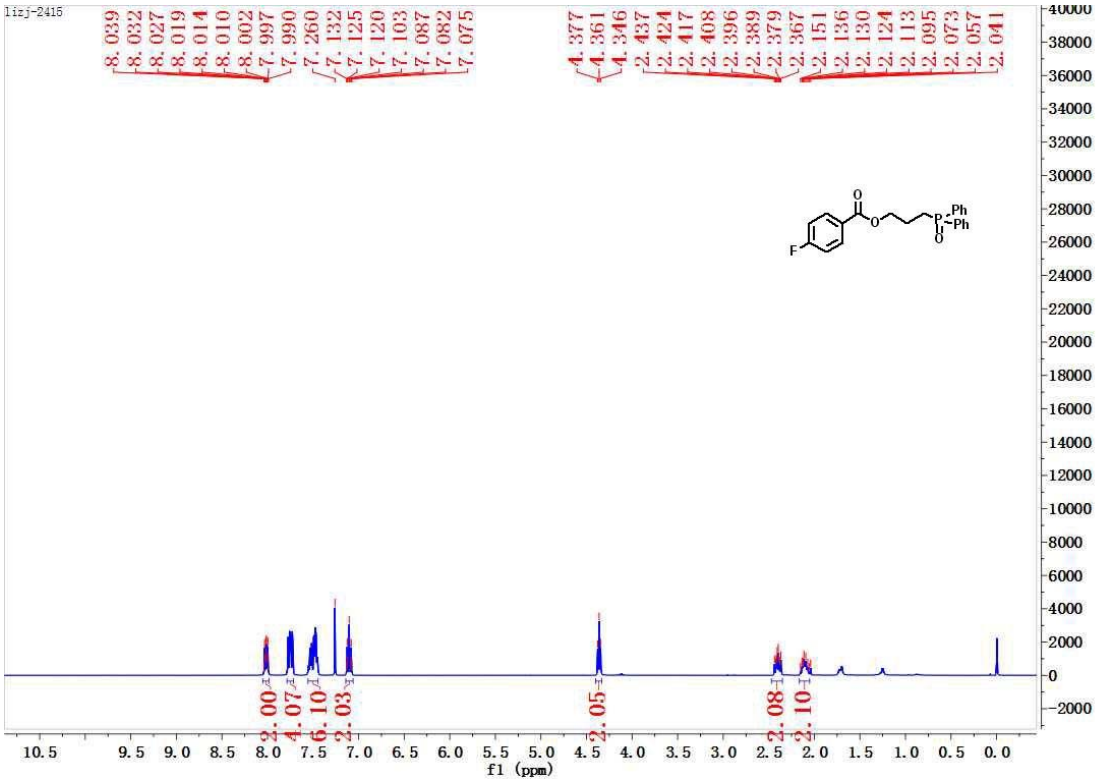
1-^{13}C NMR



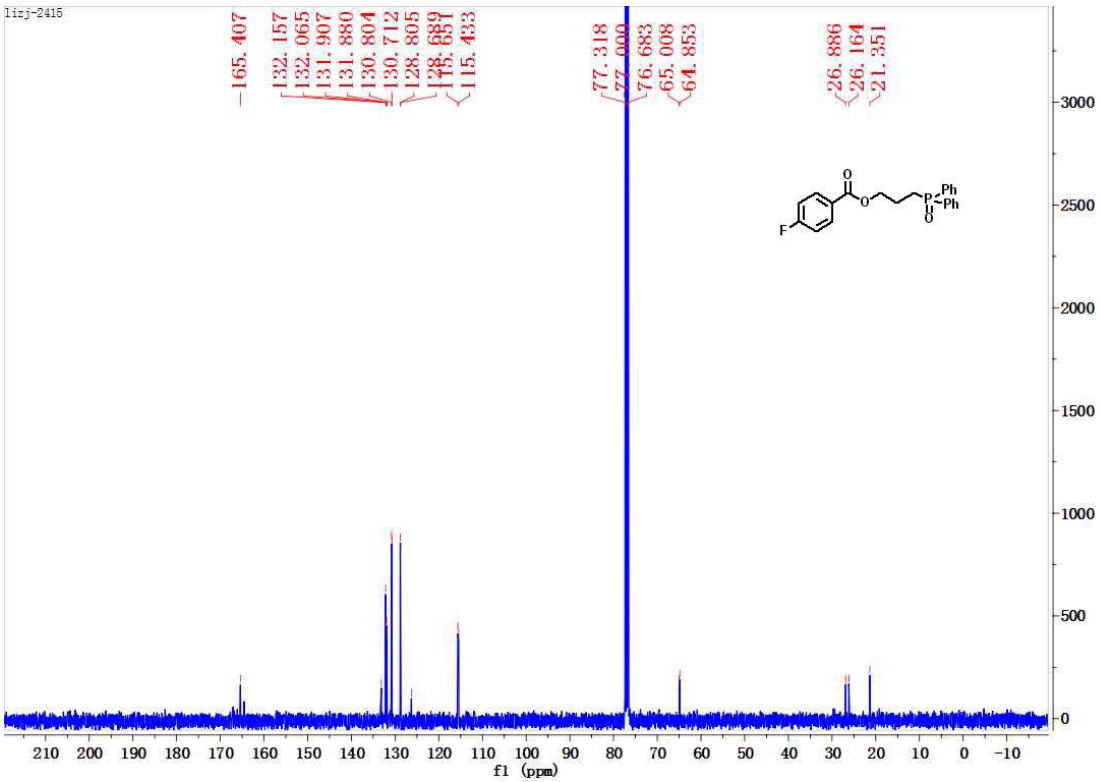
1-^{31}P NMR



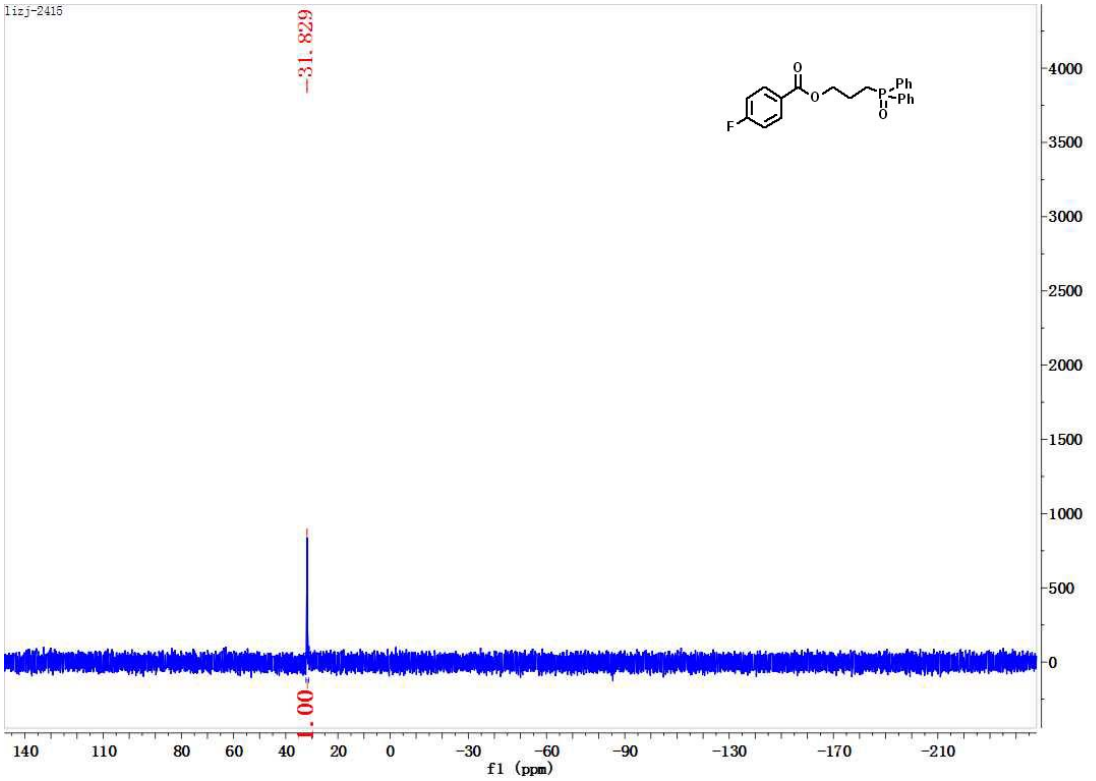
2-^{1}H NMR



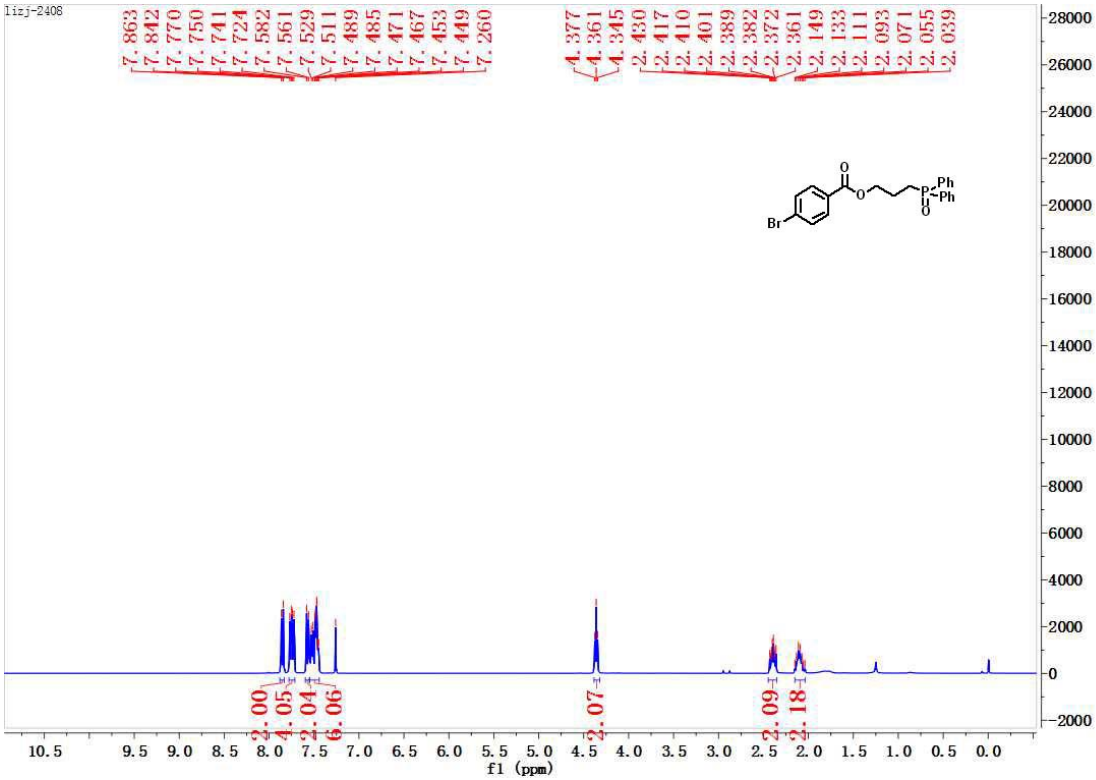
2-^{13}C NMR



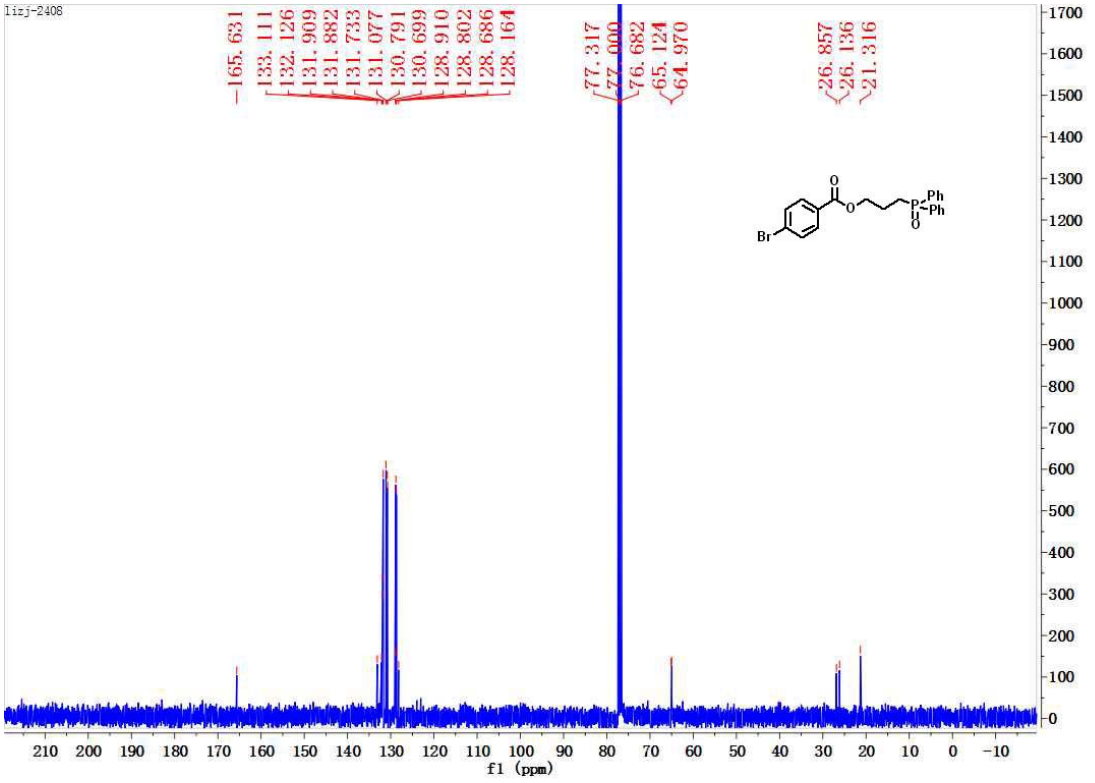
2-^{31}P NMR



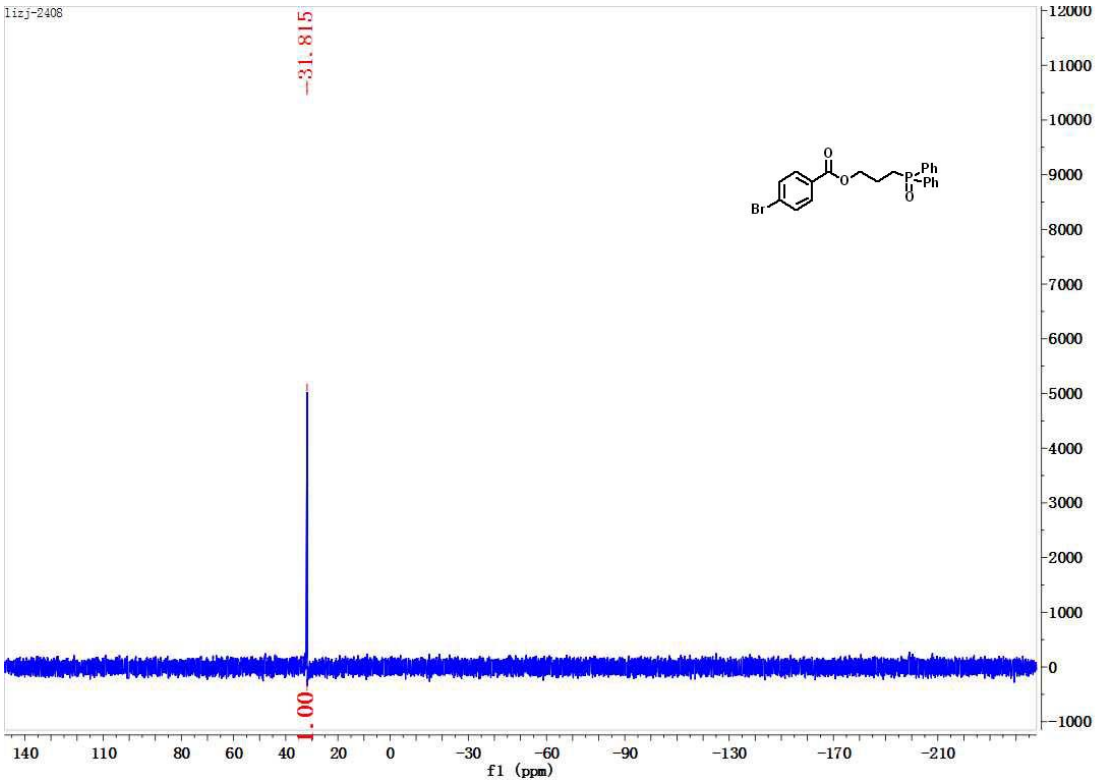
3-^{1}H NMR



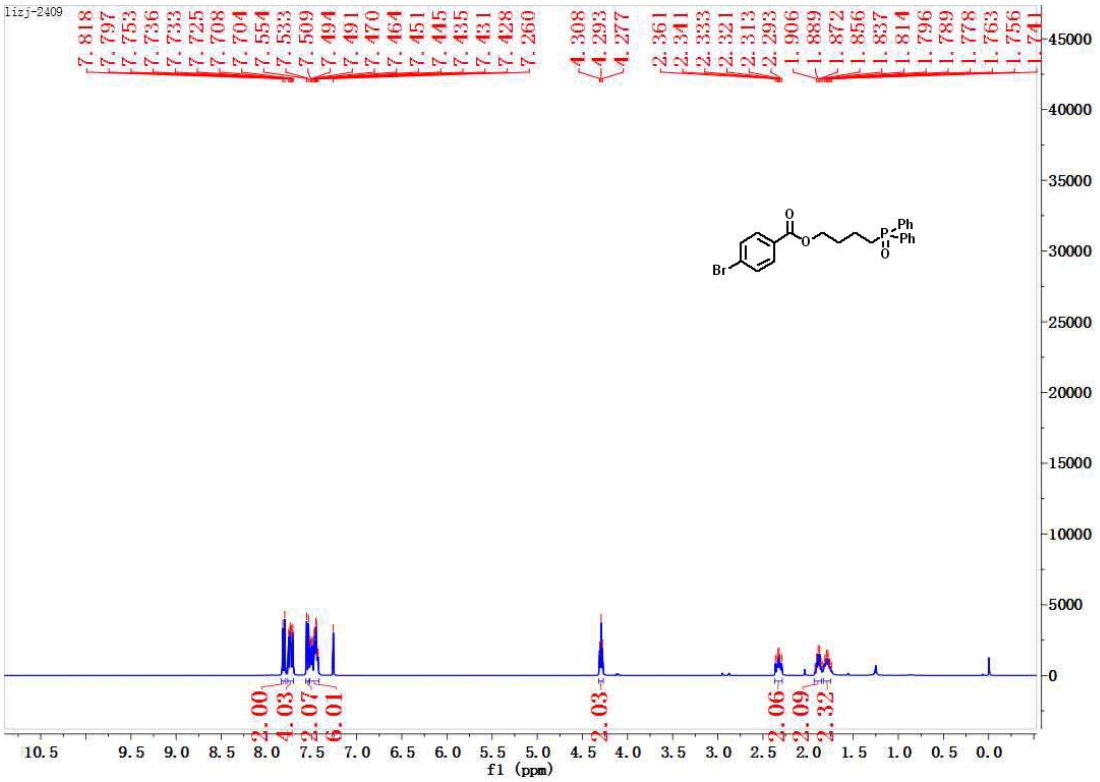
3-^{13}C NMR



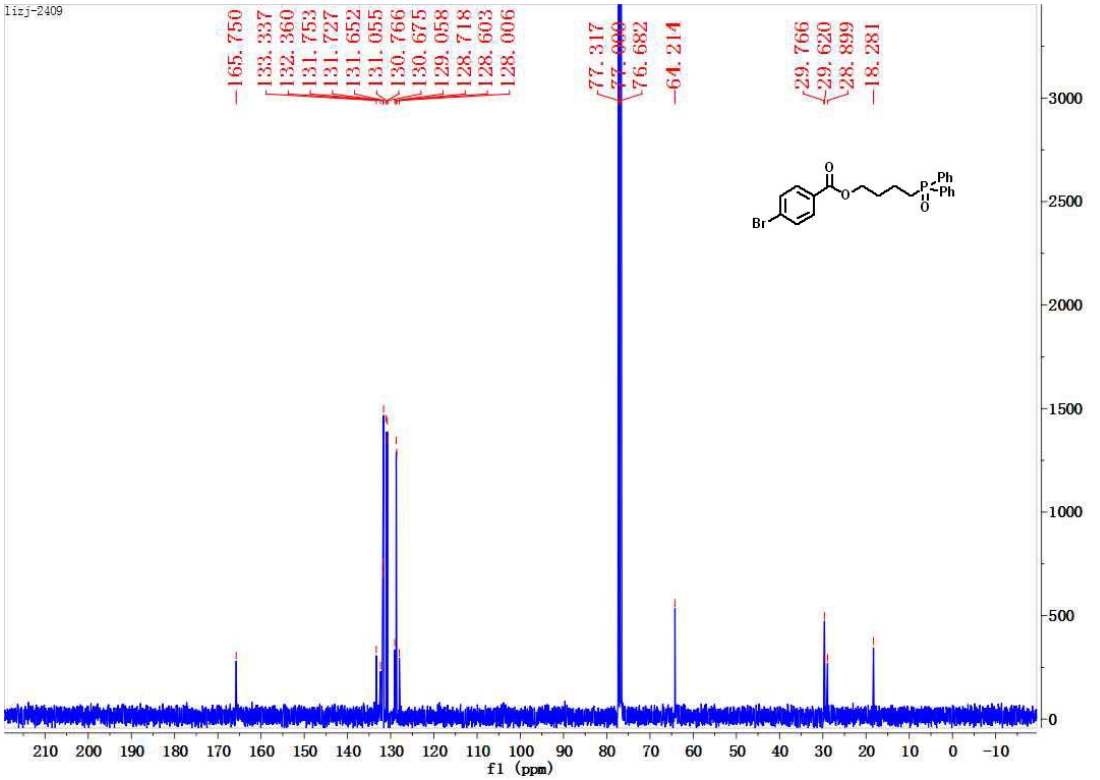
3-^{31}P NMR



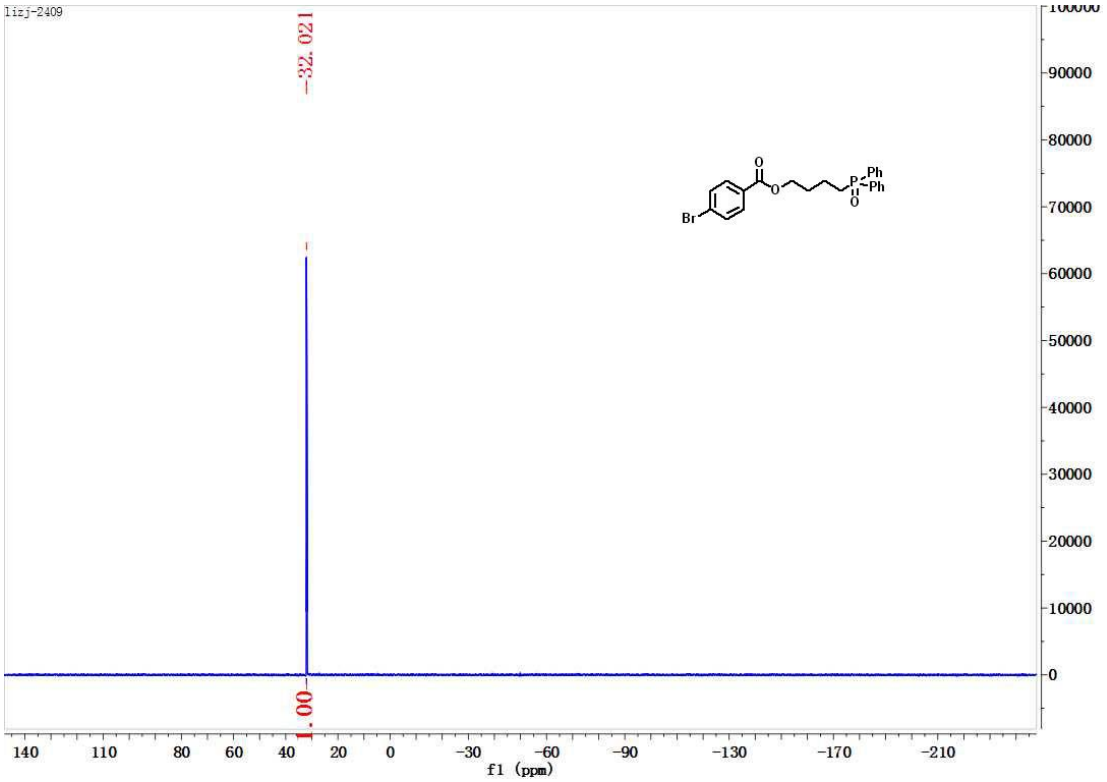
4-^{1}H NMR



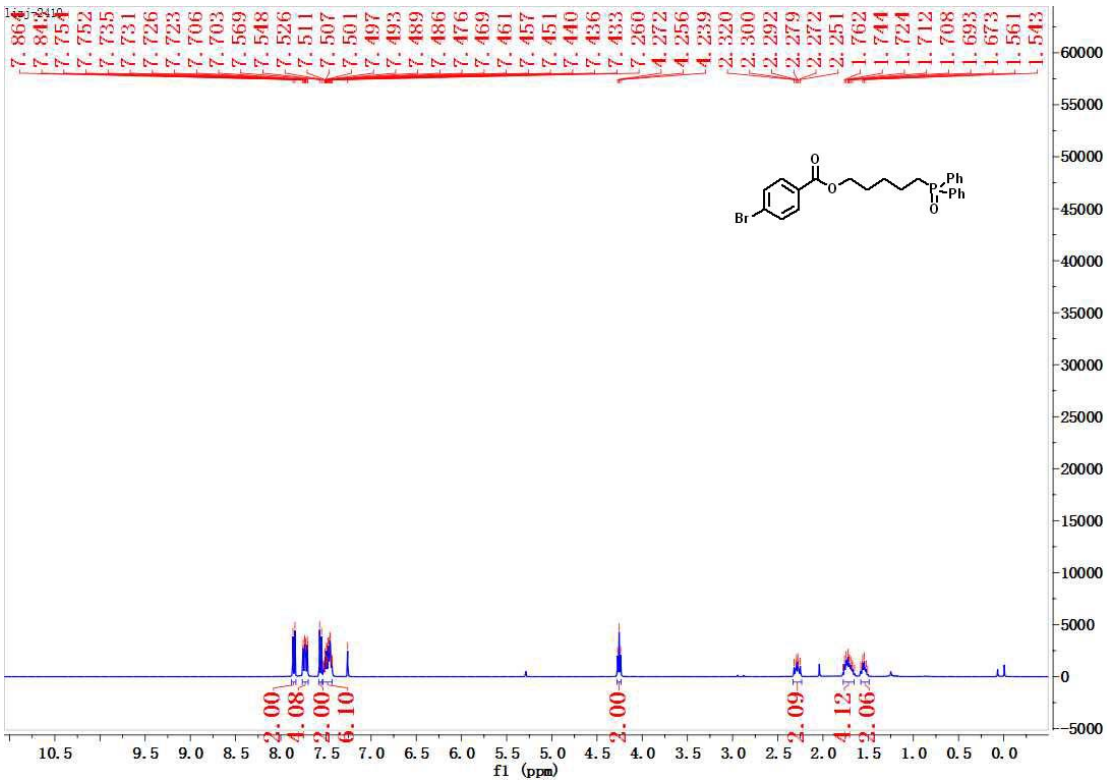
4-^{13}C NMR



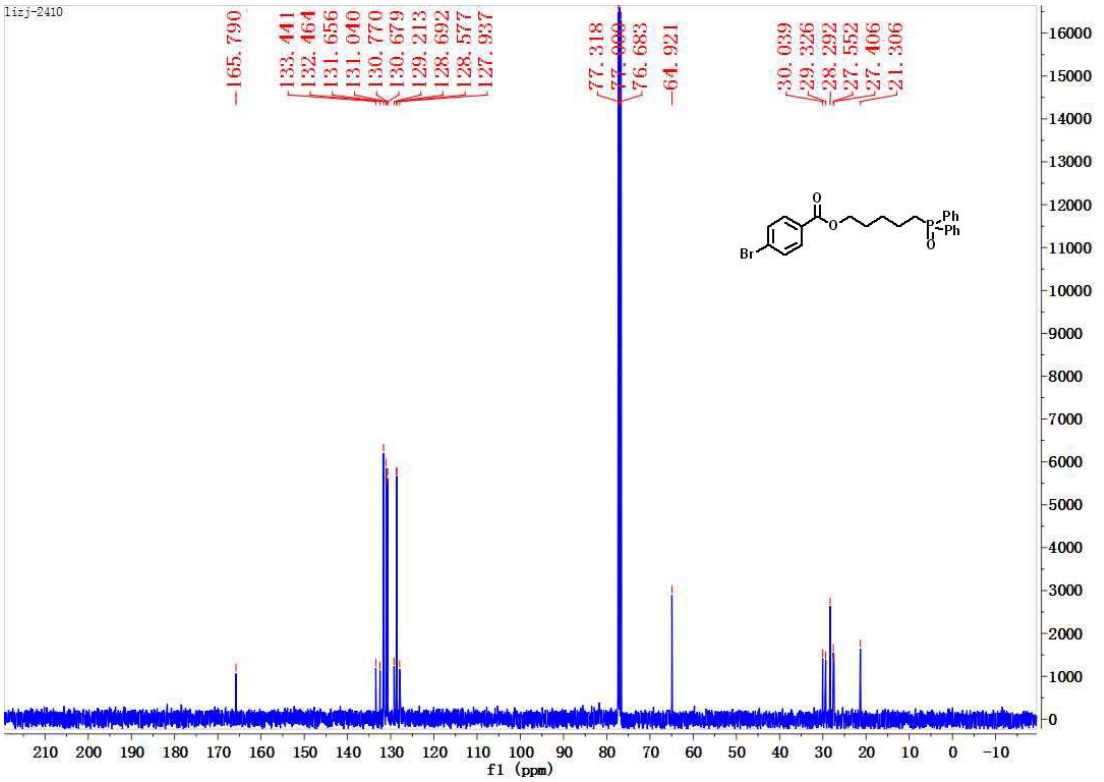
4-^{31}P NMR



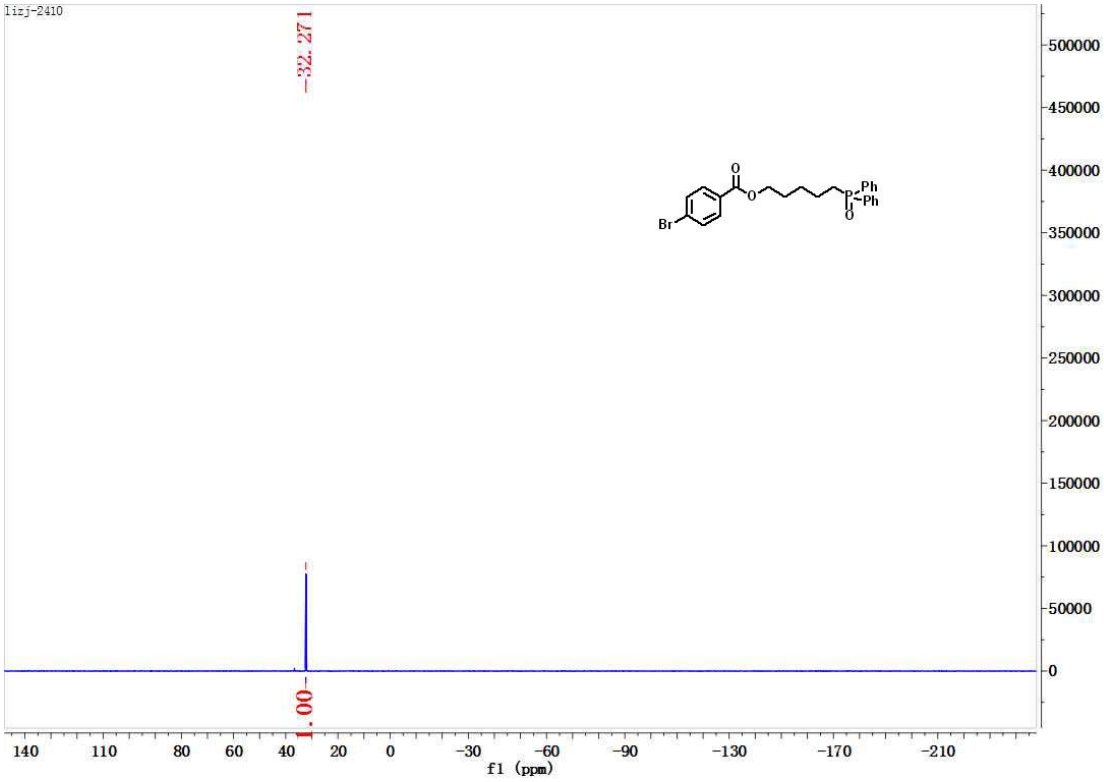
5-^{1}H NMR



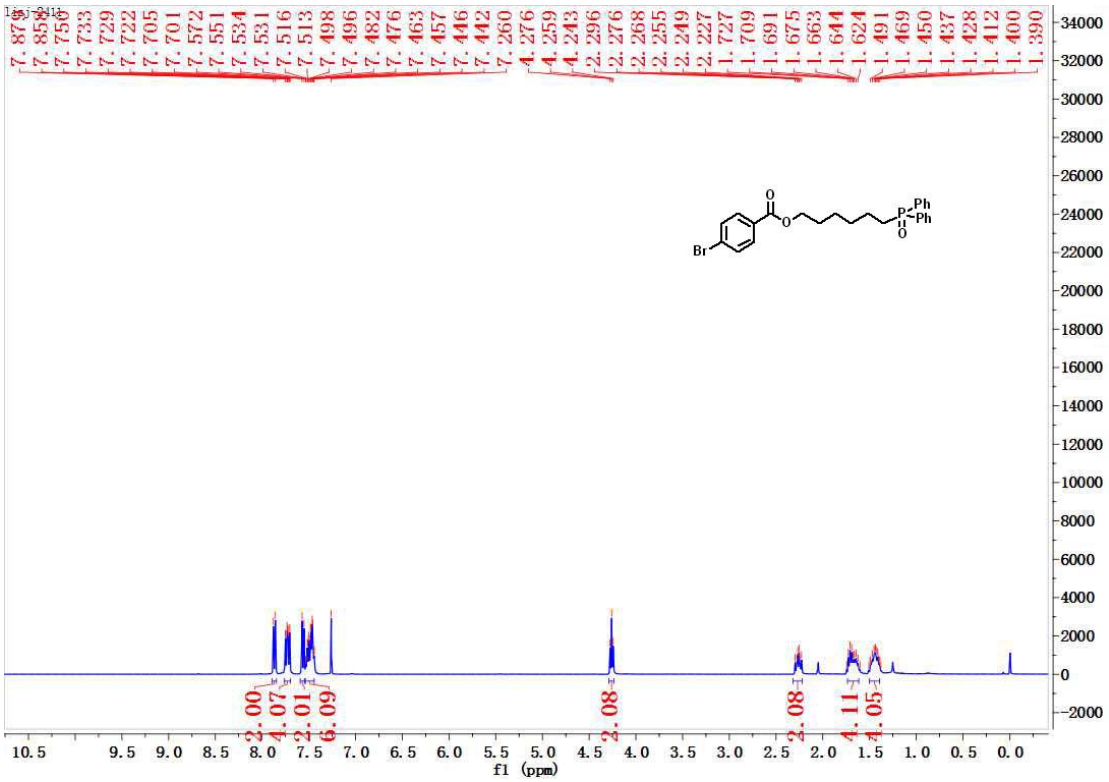
5-^{13}C NMR



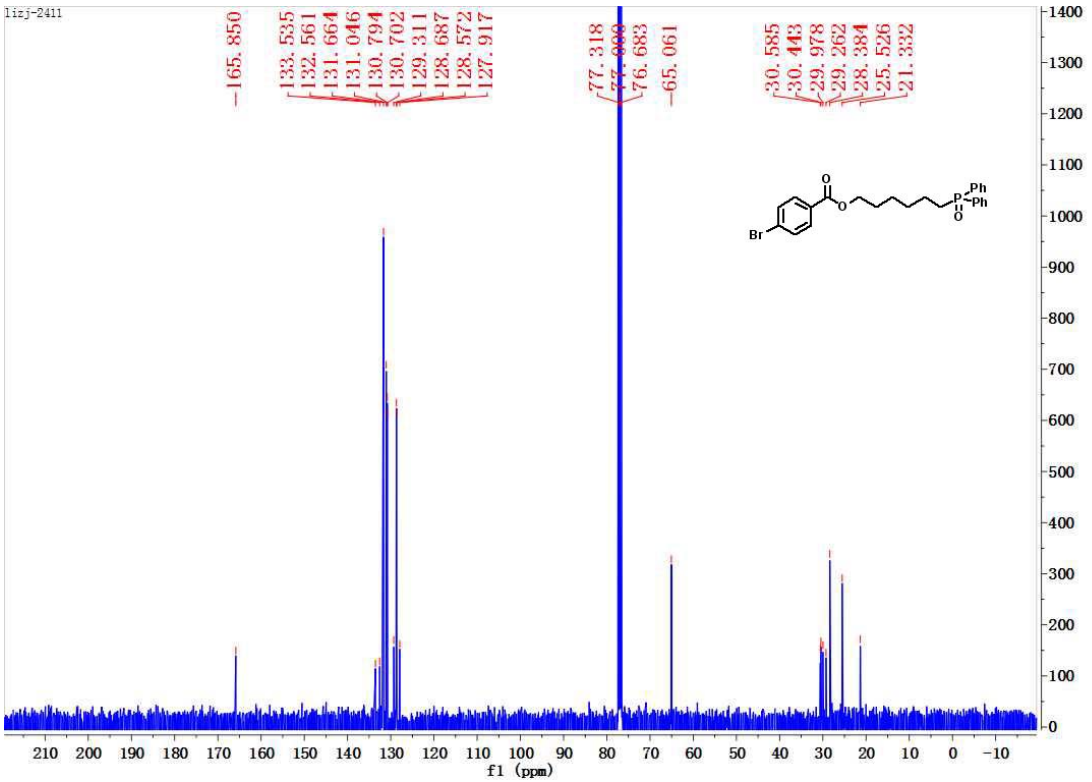
5-^{31}P NMR



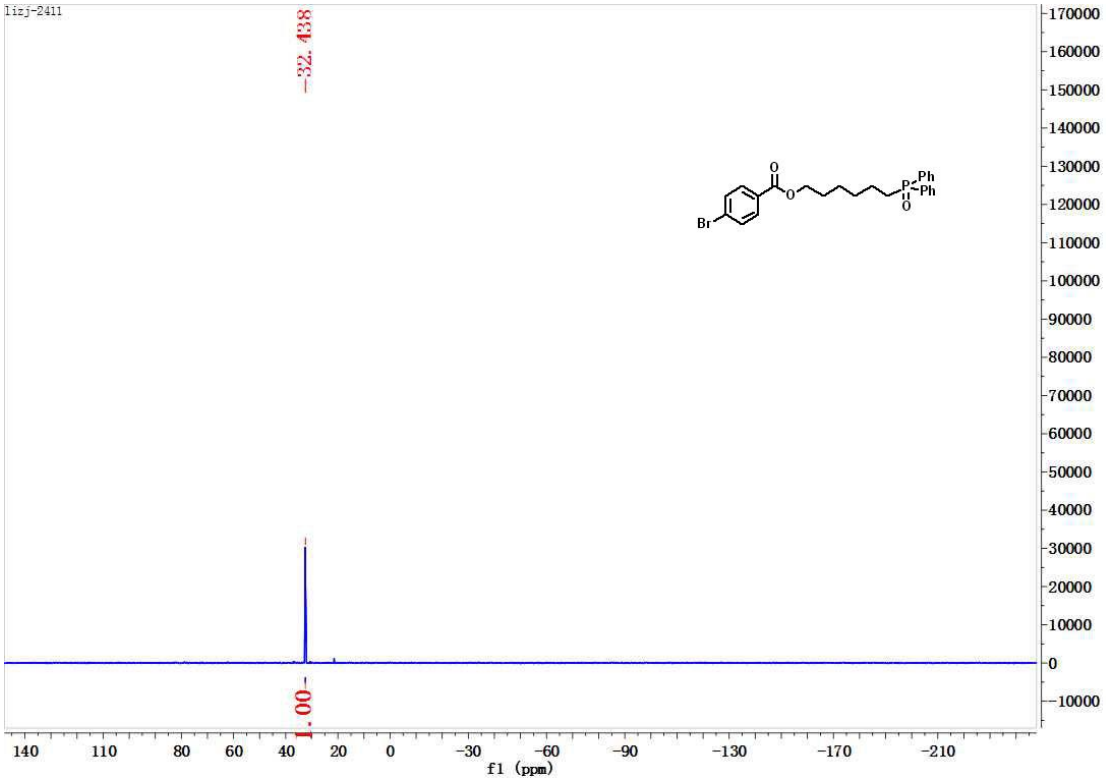
6-^{1}H NMR



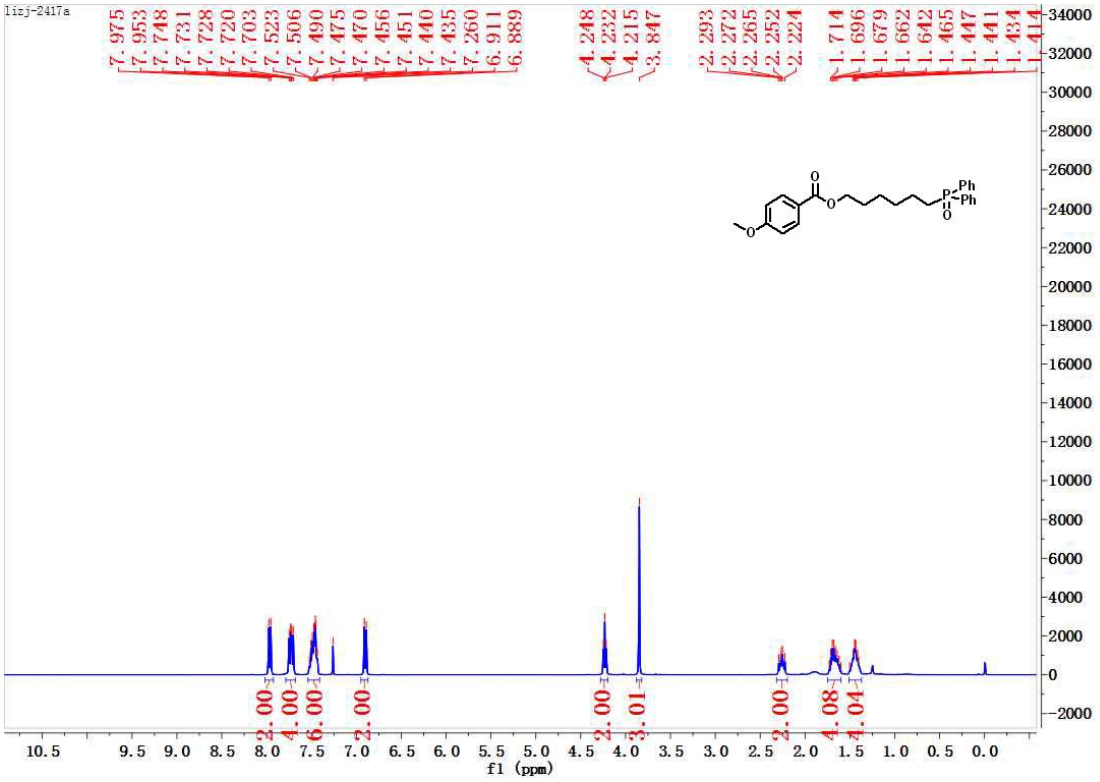
6-^{13}C NMR



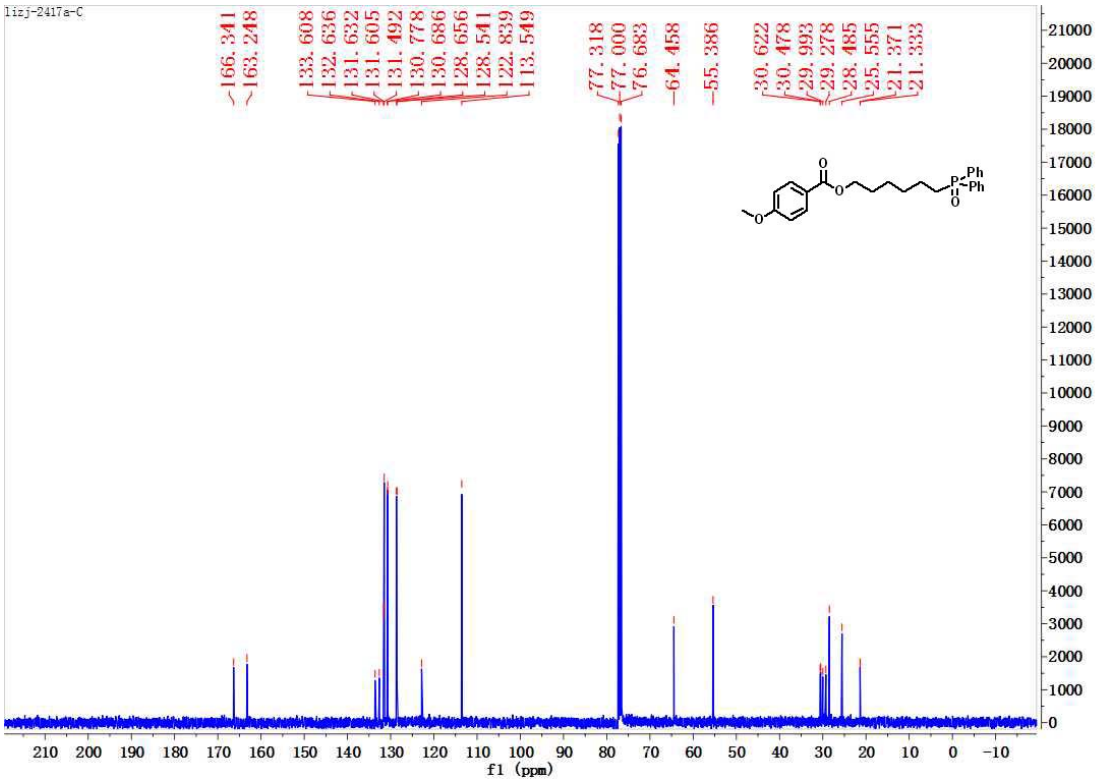
6-^{31}P NMR



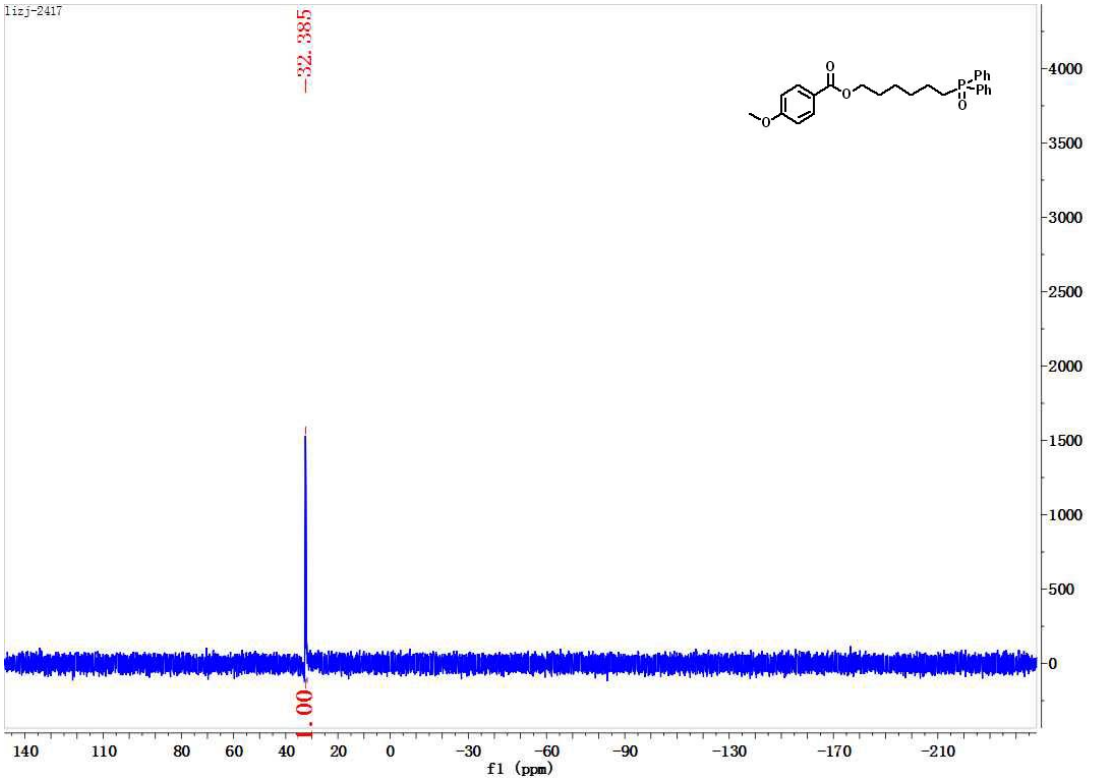
7-^{1}H NMR



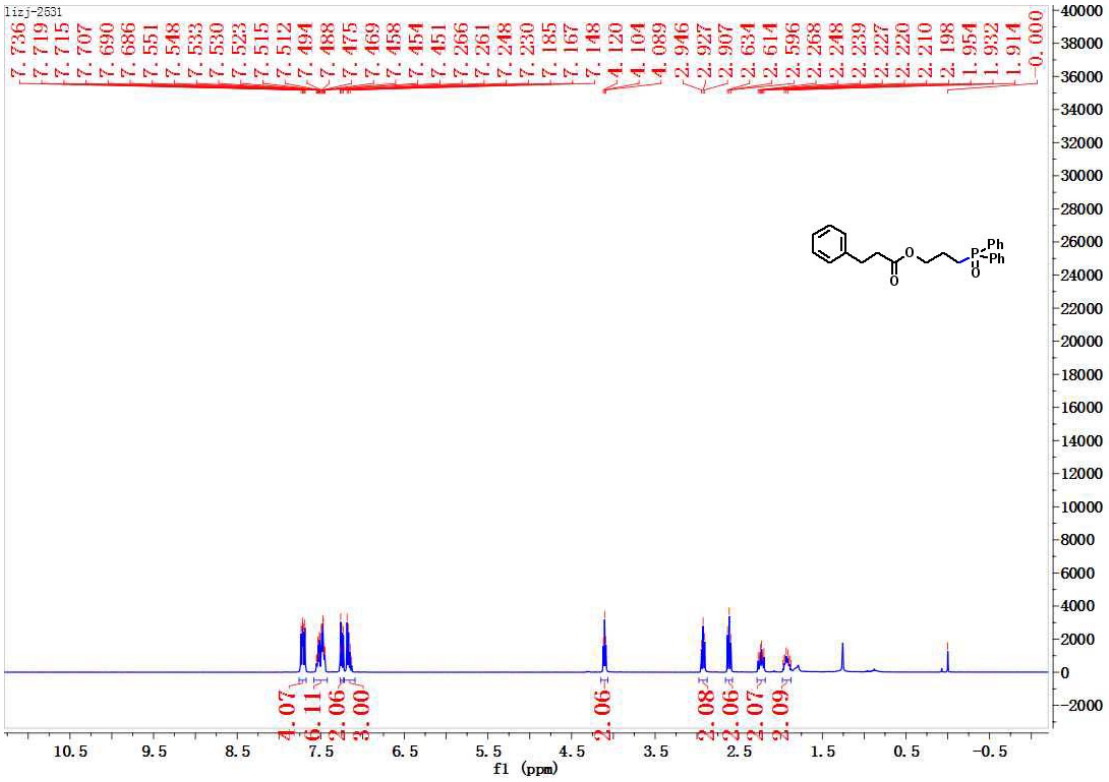
7-^{13}C NMR



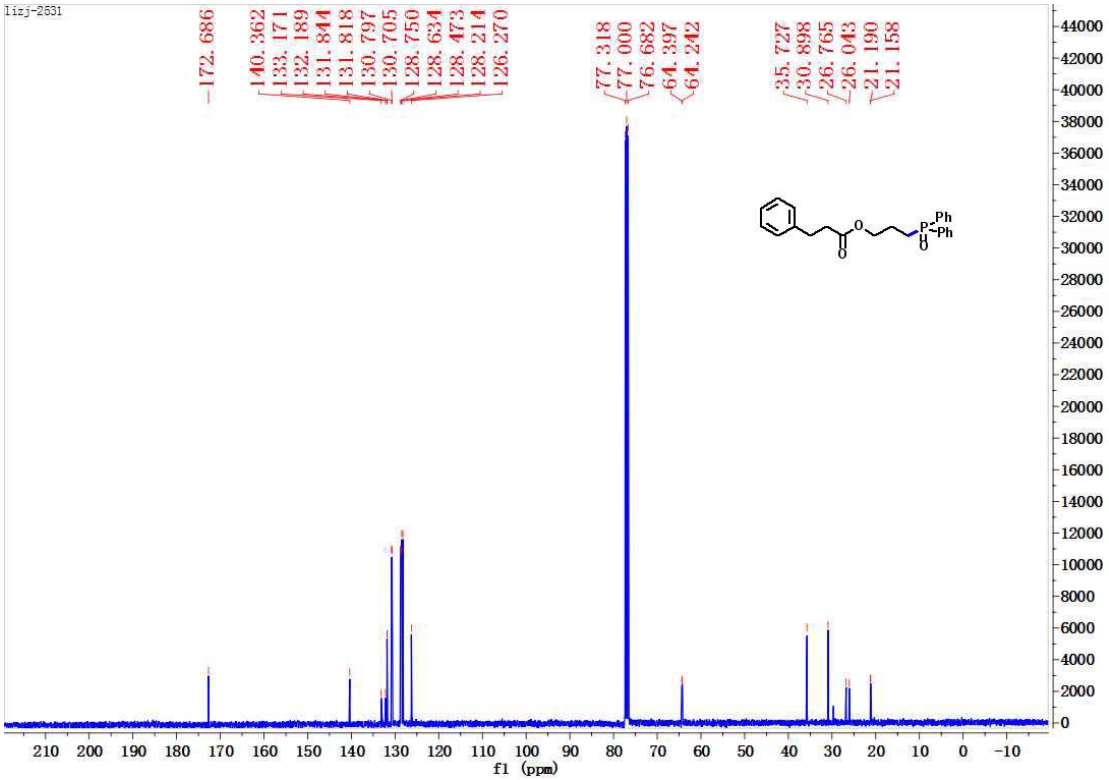
7-^{31}P NMR



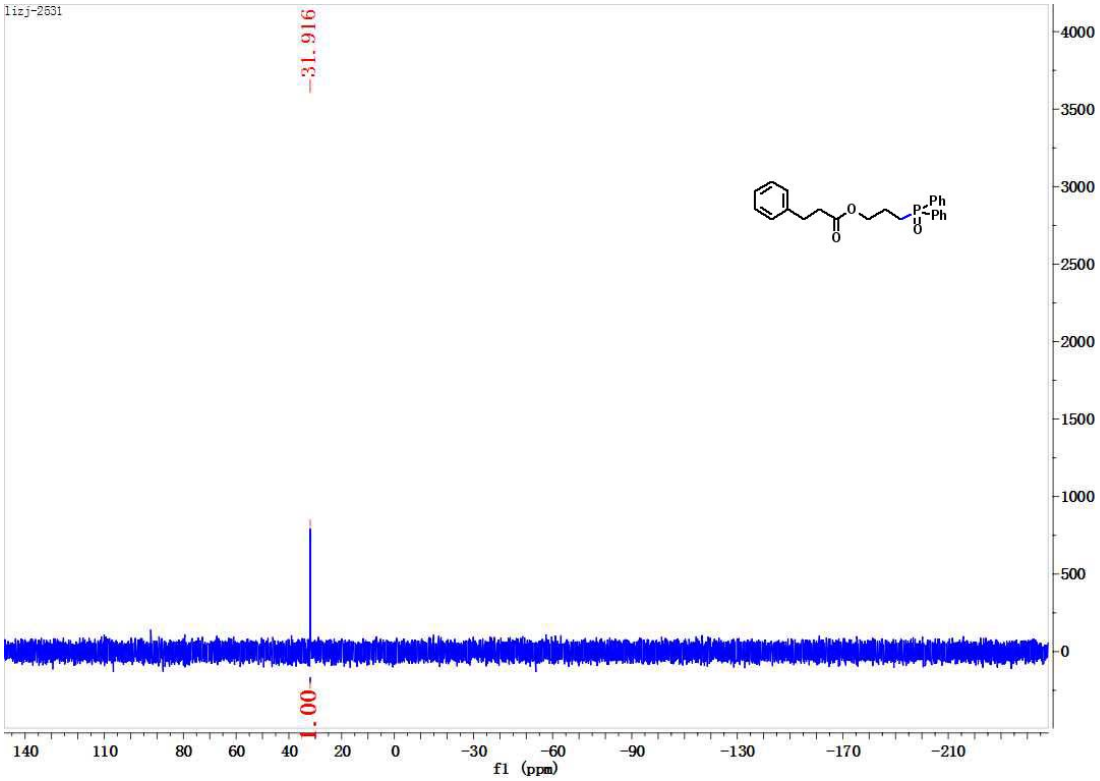
8-^{1}H NMR



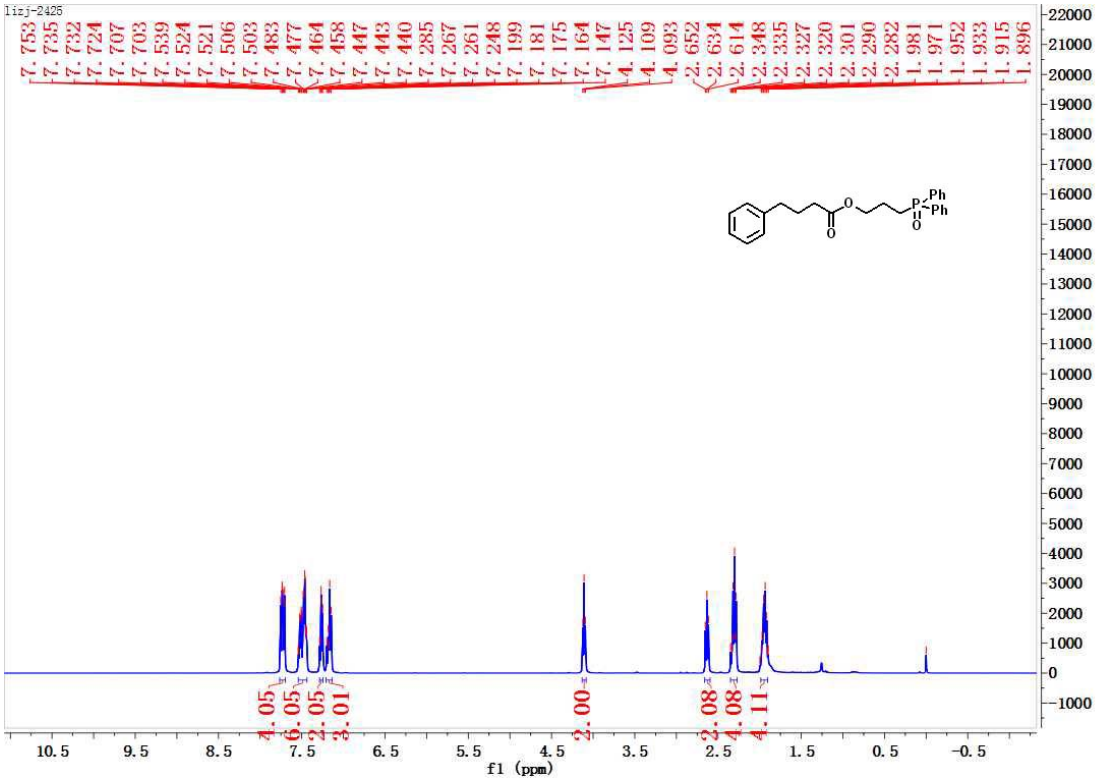
8-^{13}C NMR



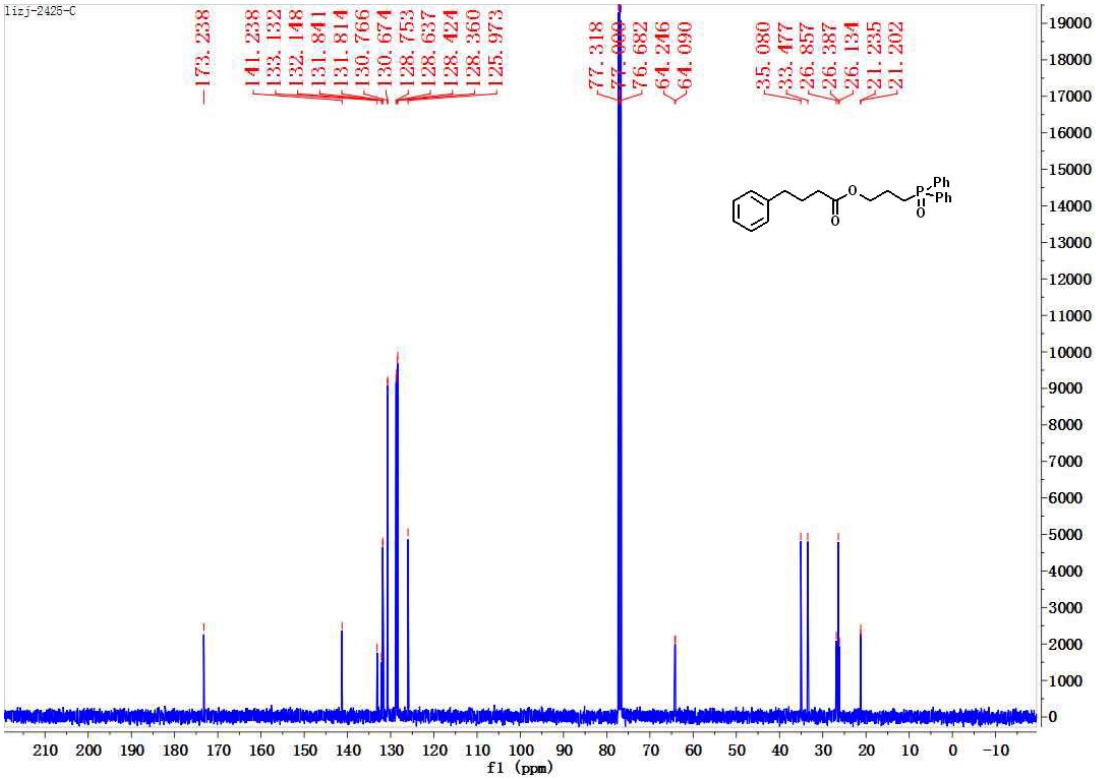
8-^{31}P NMR



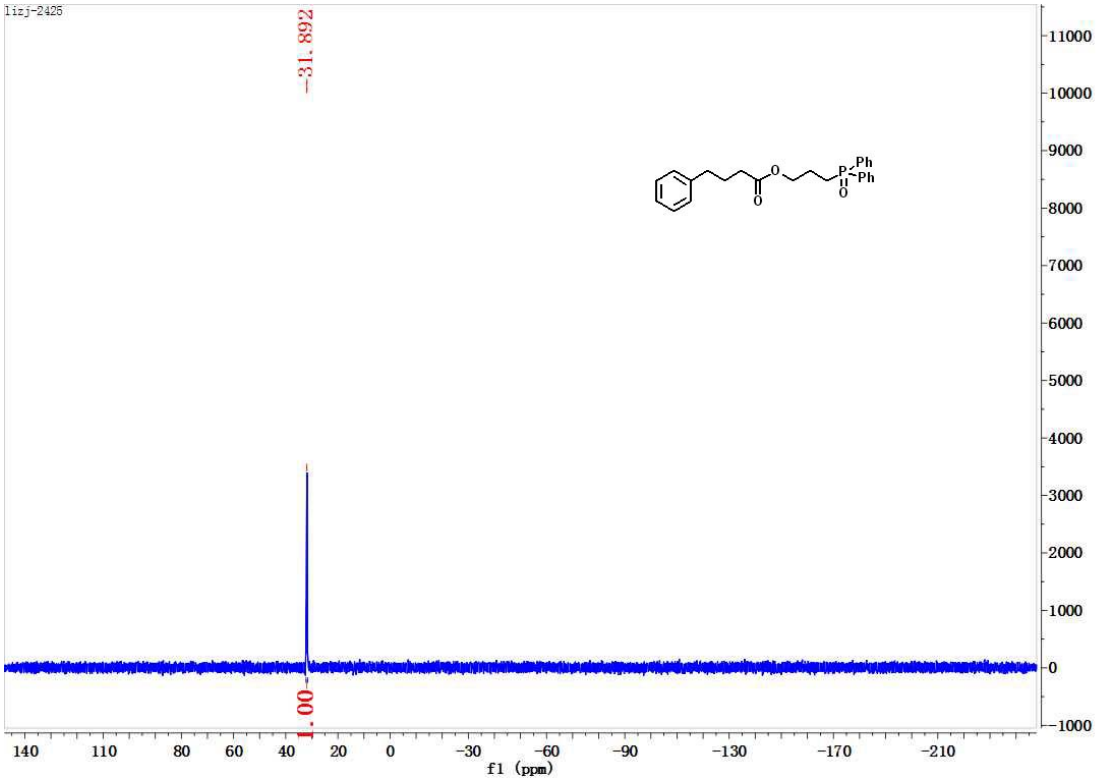
9-^{1}H NMR



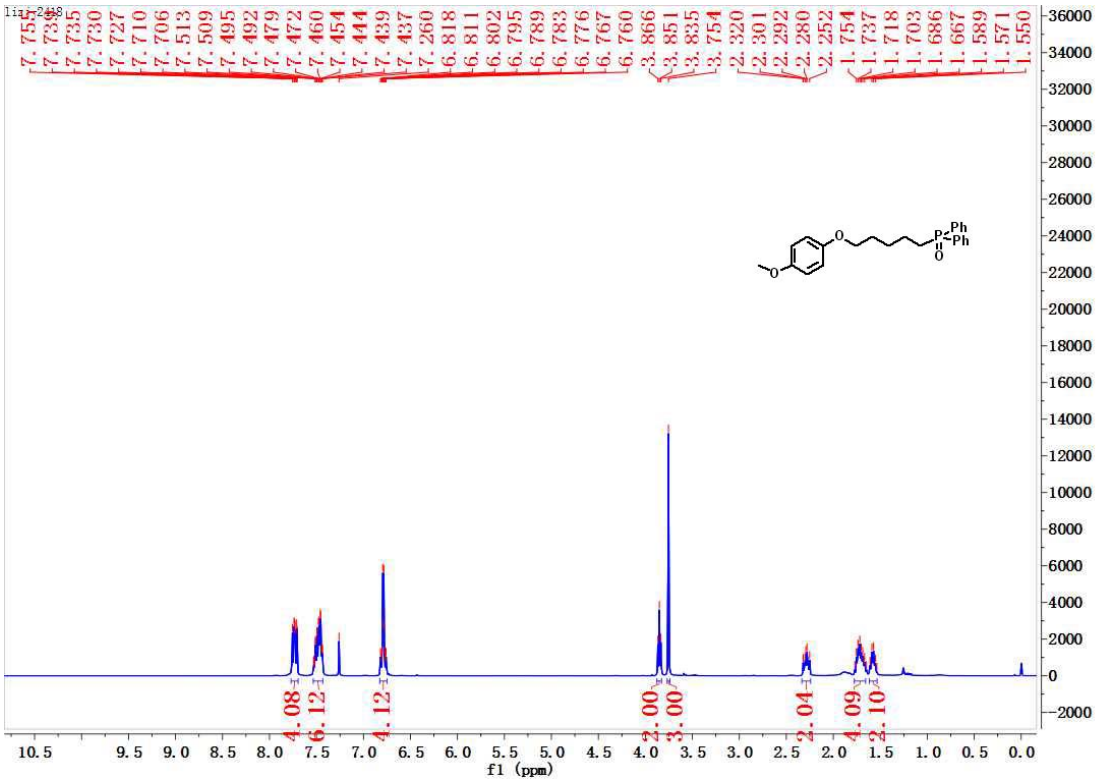
9-^{13}C NMR



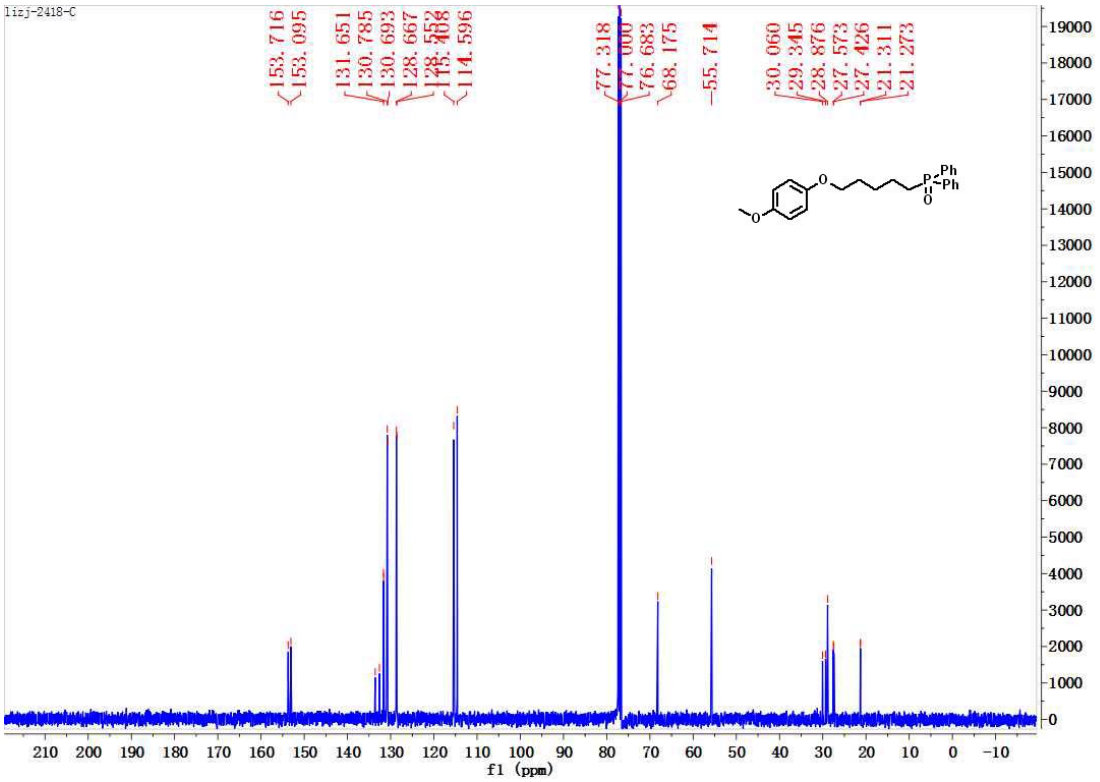
9-^{31}P NMR



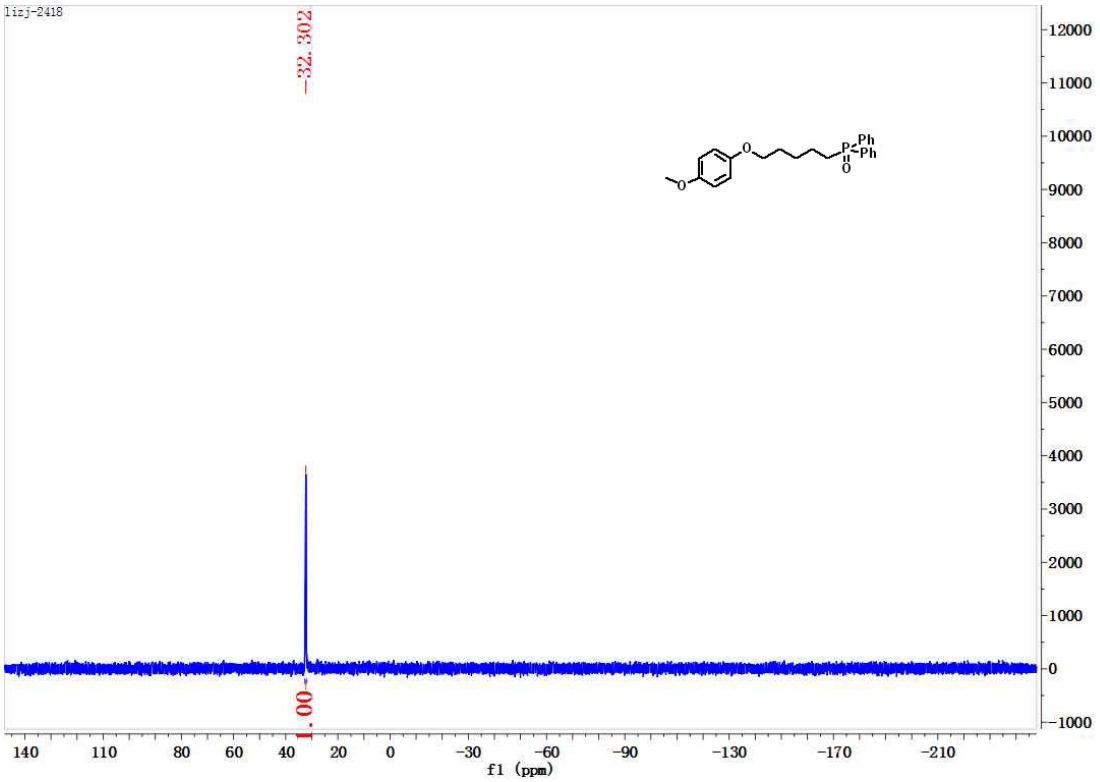
10-^{1}H NMR



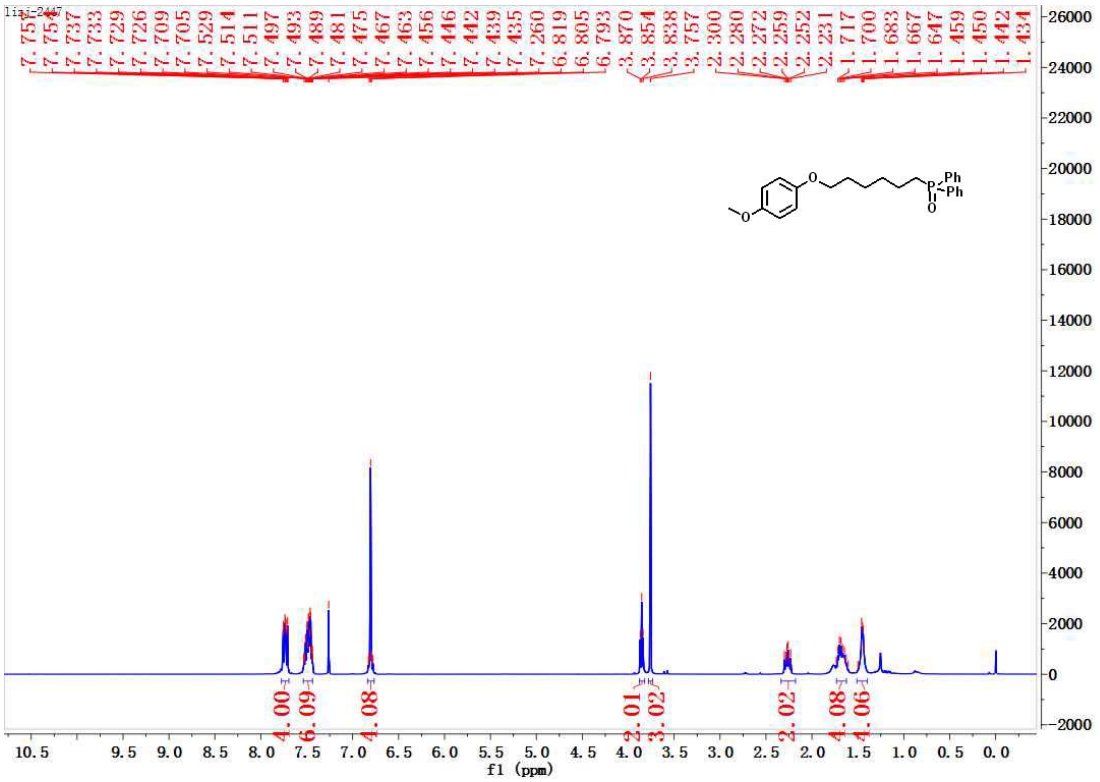
10-^{13}C NMR



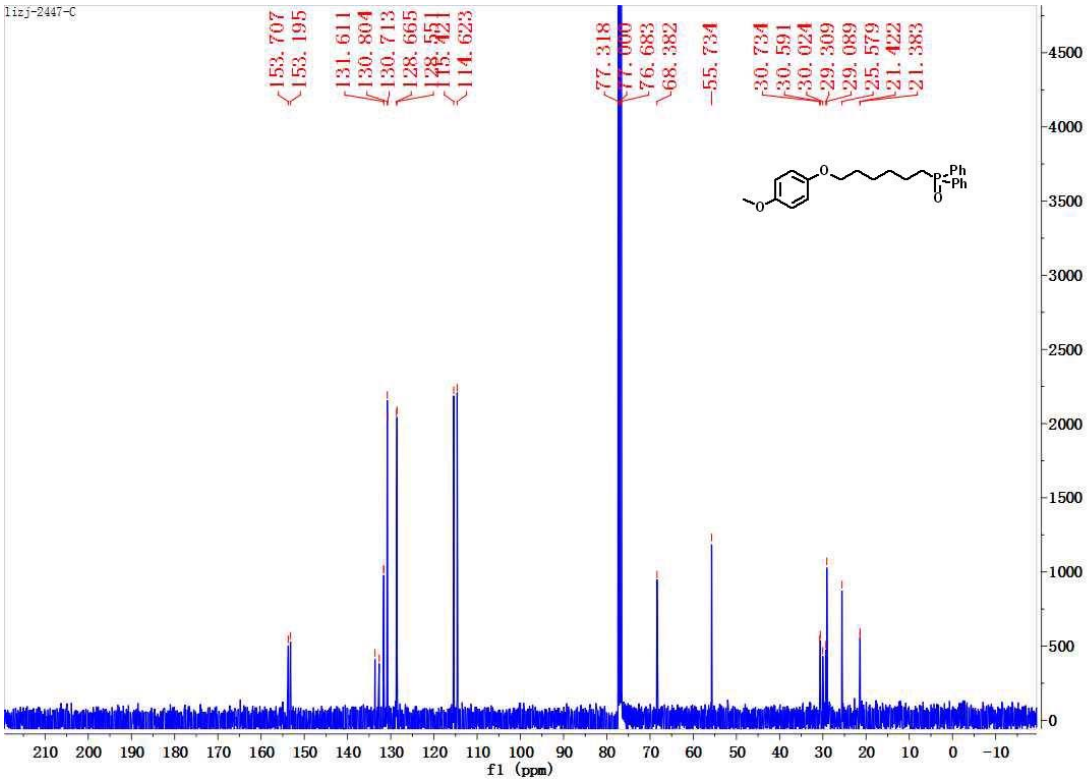
10-^{31}P NMR



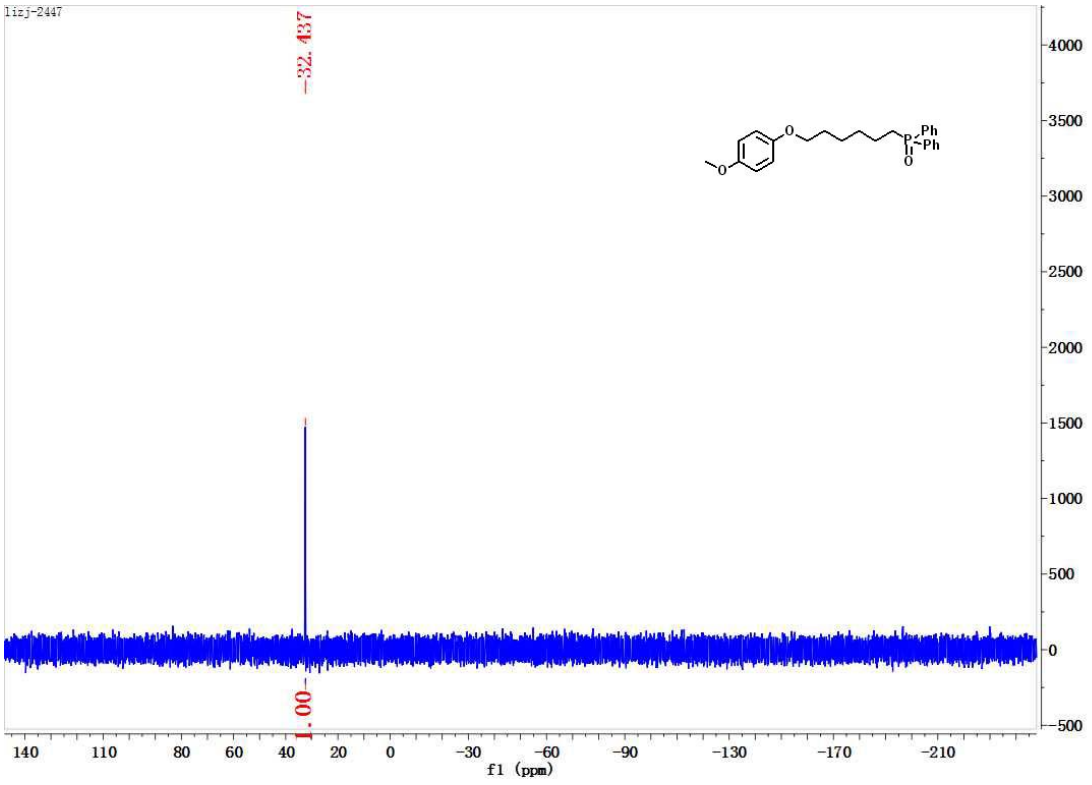
11-^{1}H NMR



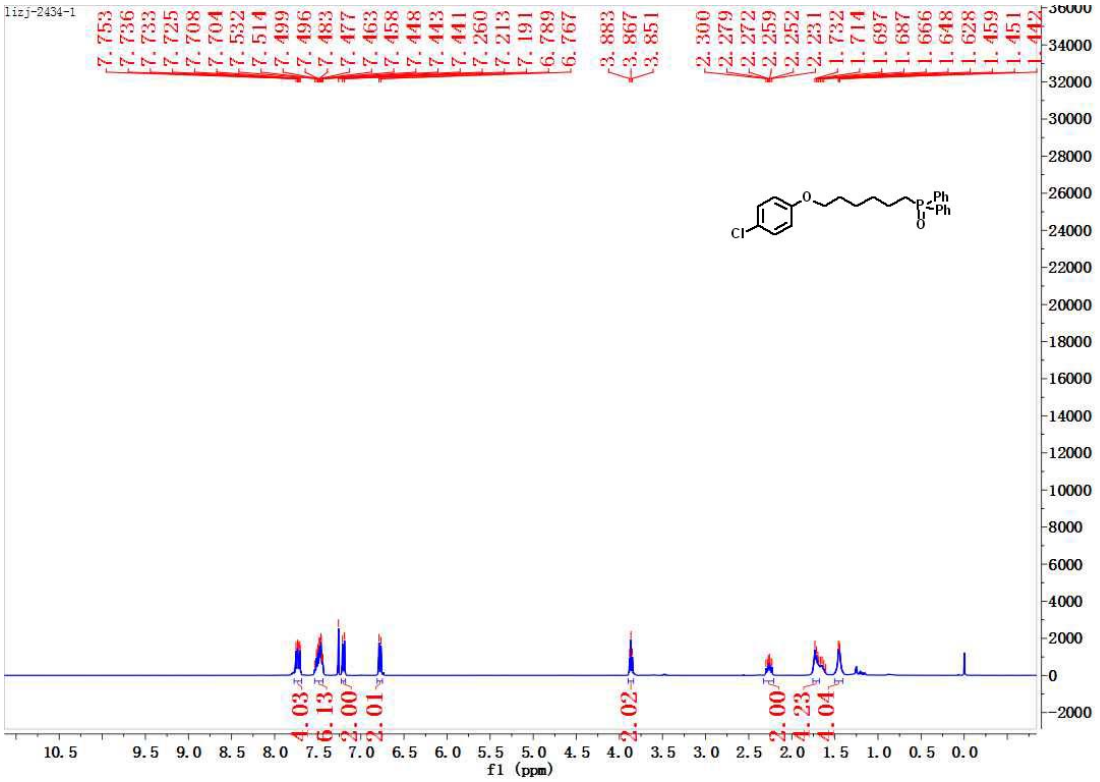
11-^{13}C NMR



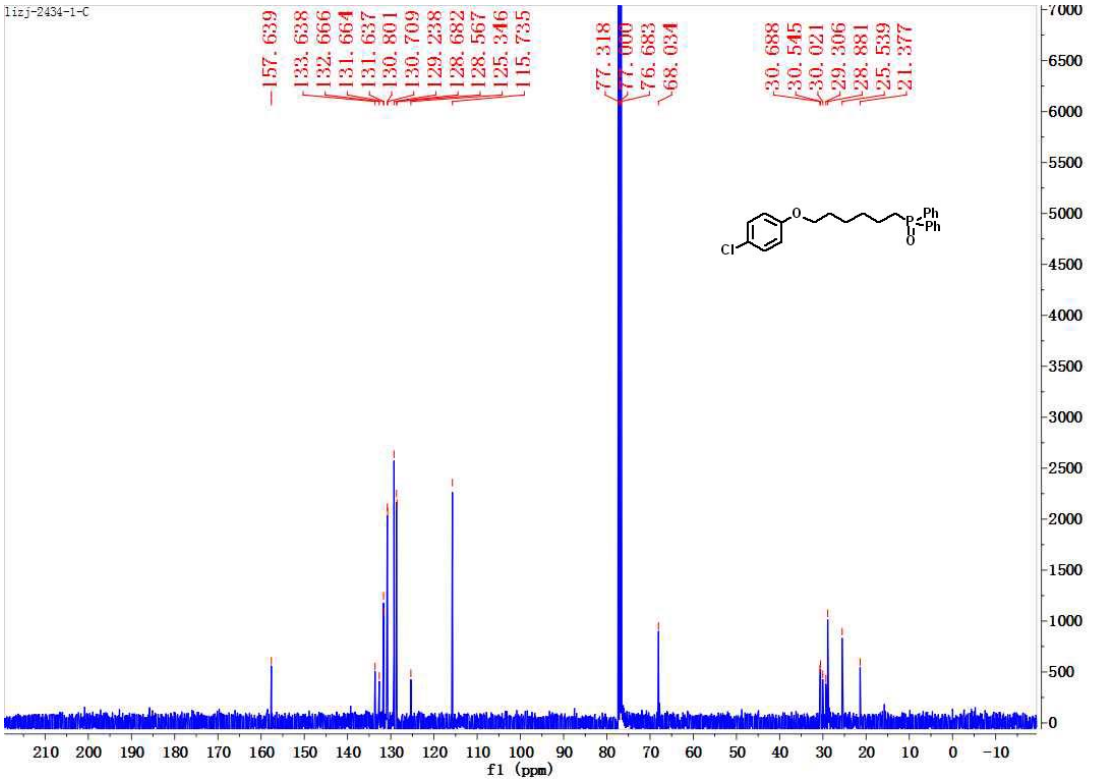
11-^{31}P NMR



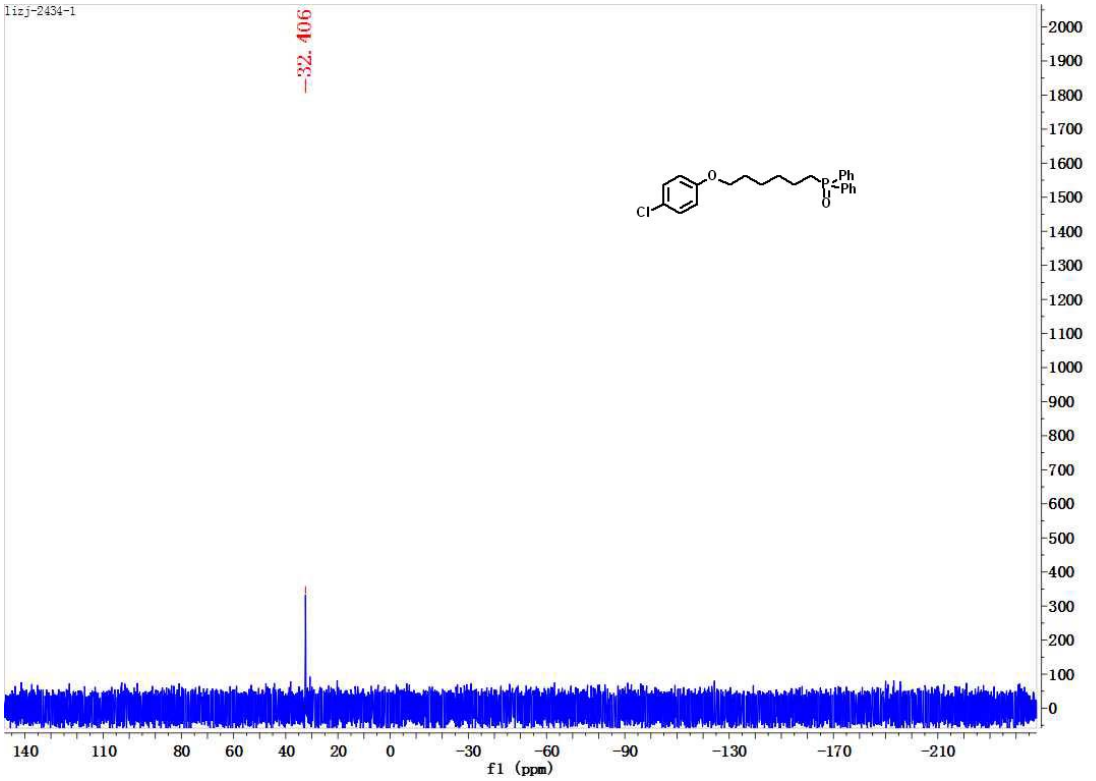
12-^{1}H NMR



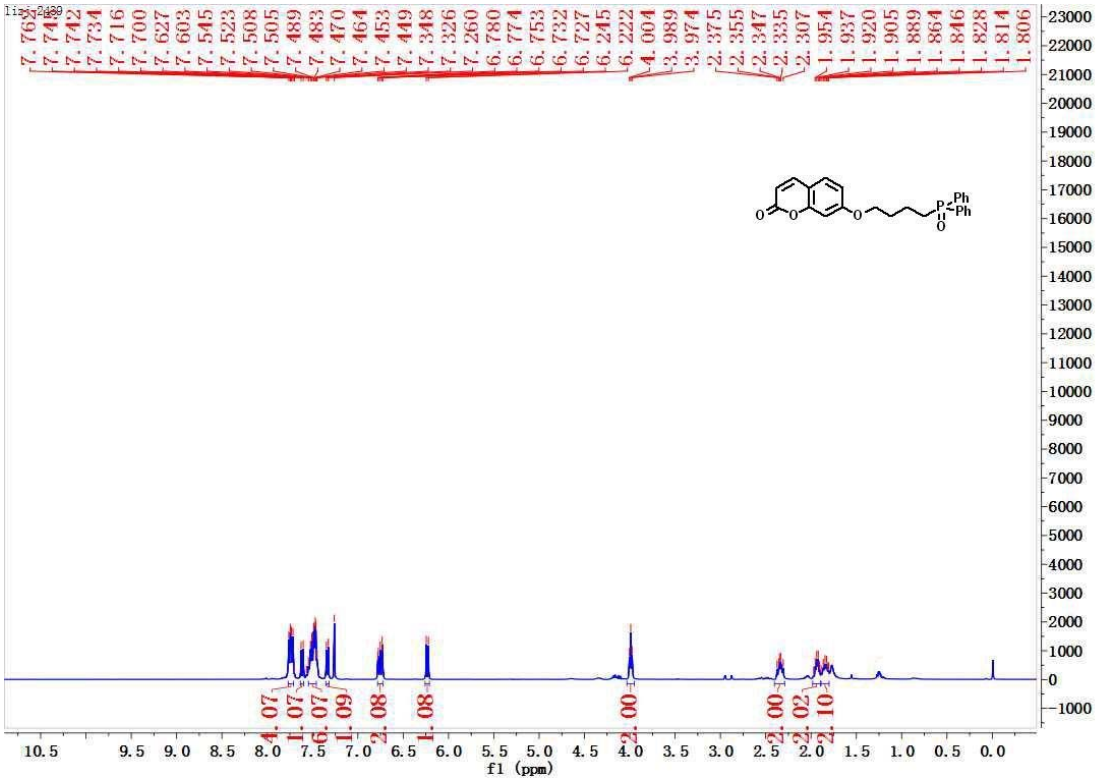
12-^{13}C NMR



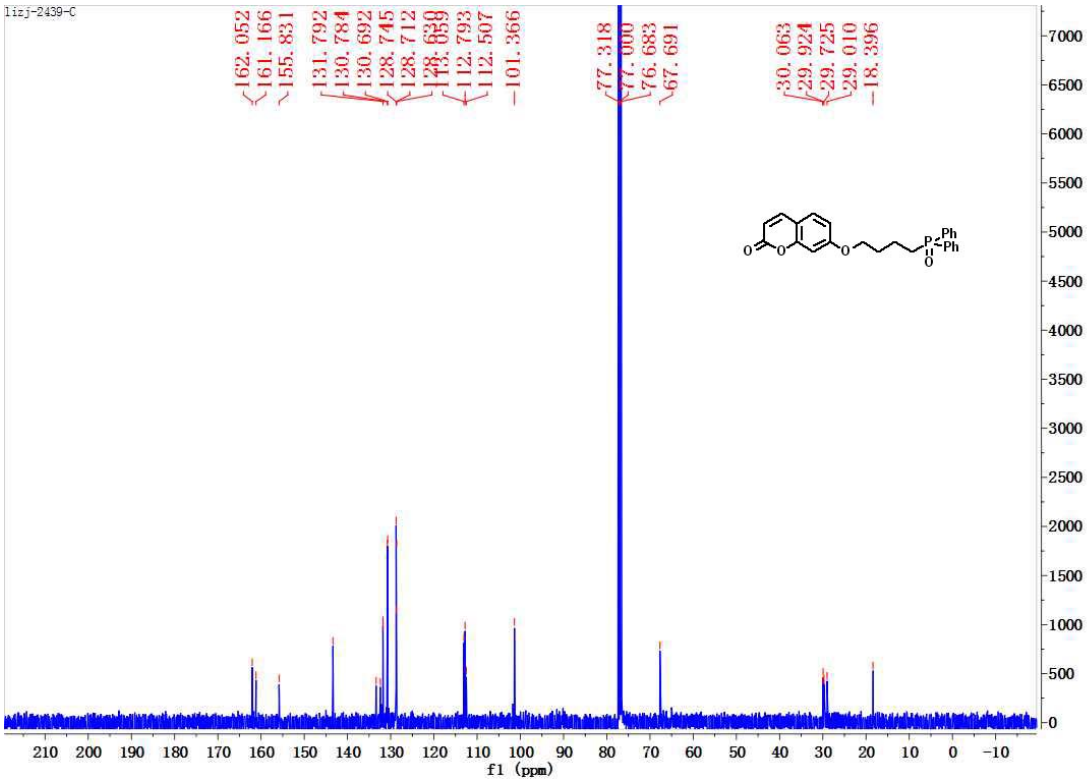
12-^{31}P NMR



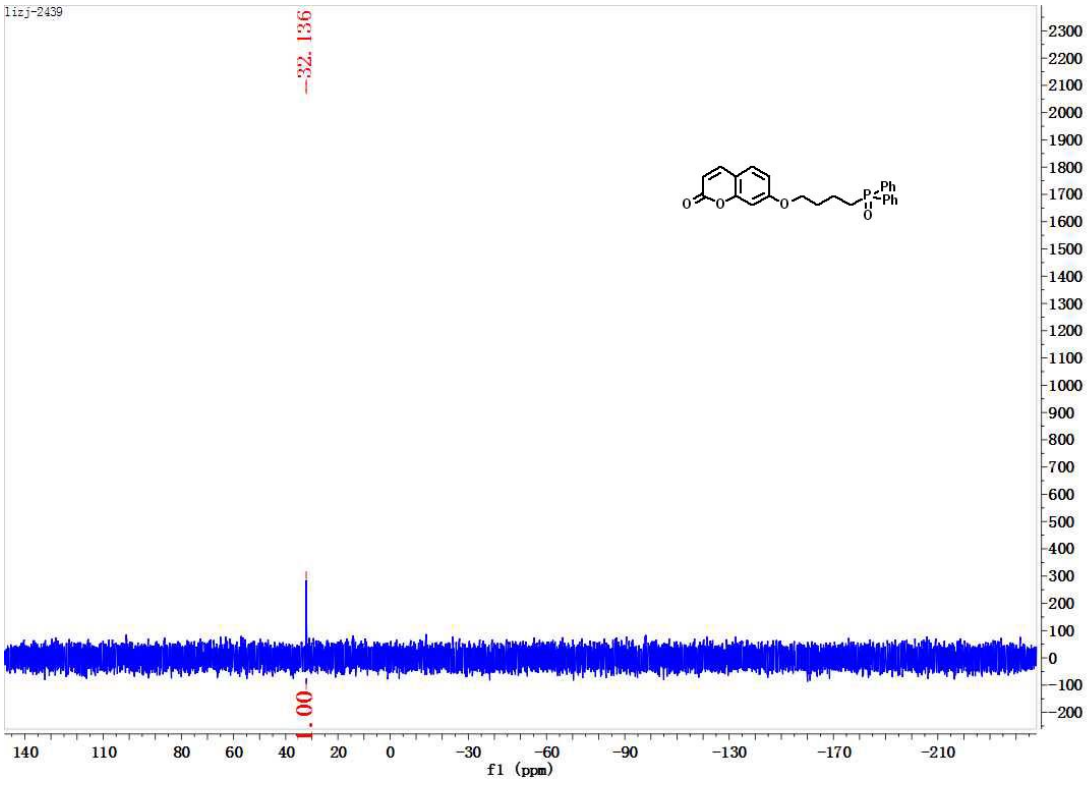
13-^{1}H NMR



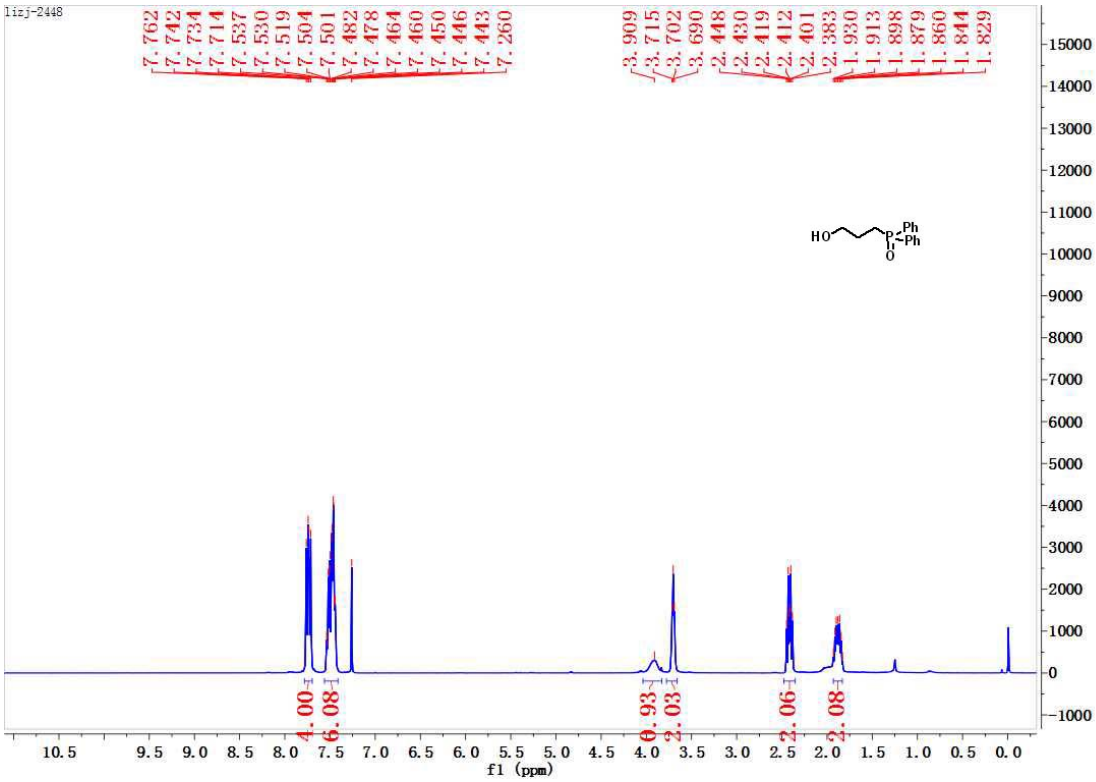
13-^{13}C NMR



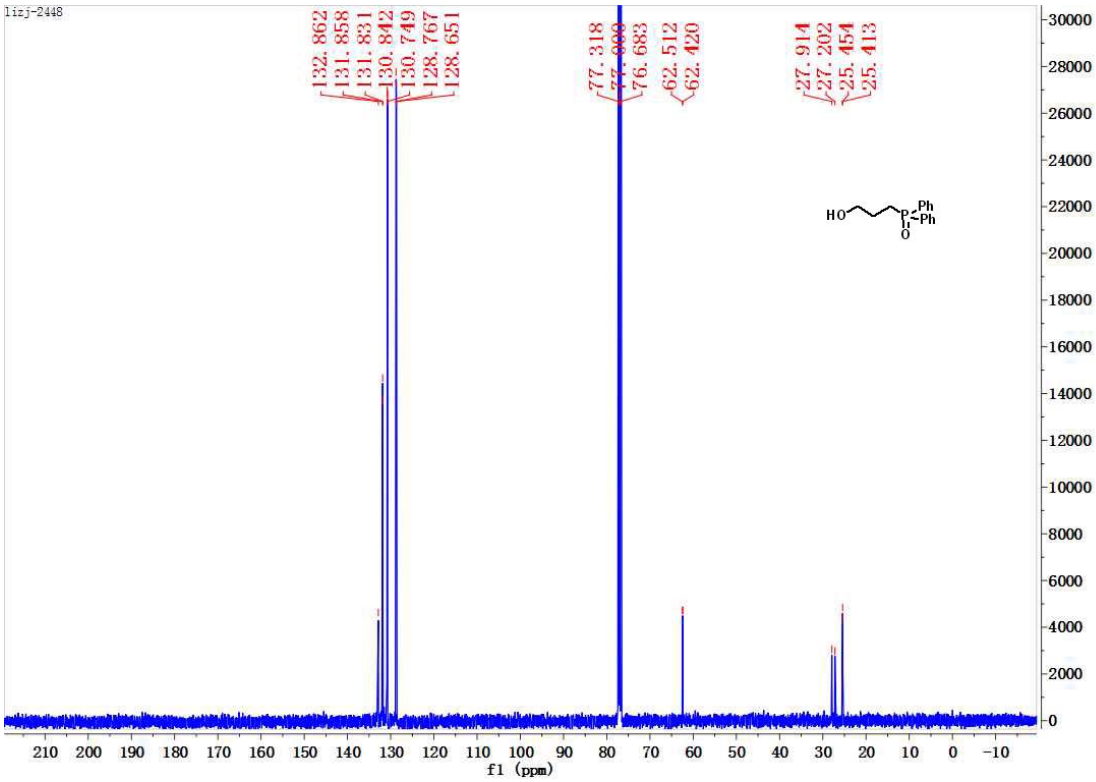
13-^{31}P NMR



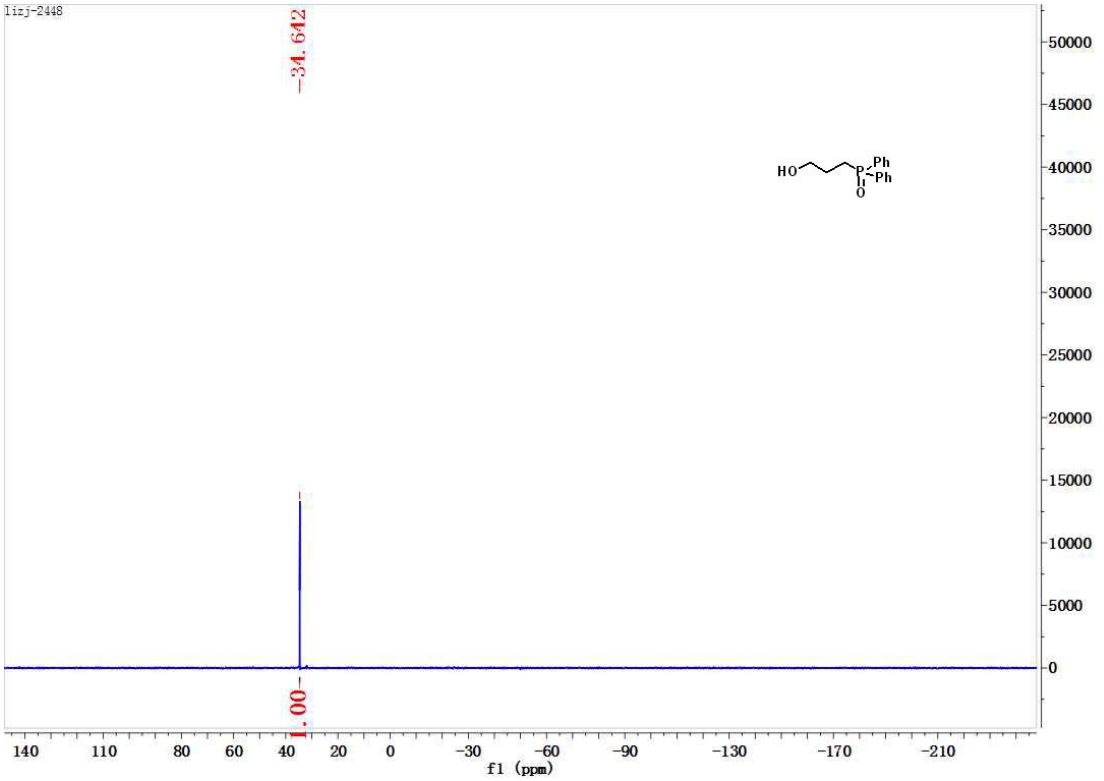
14-^{1}H NMR



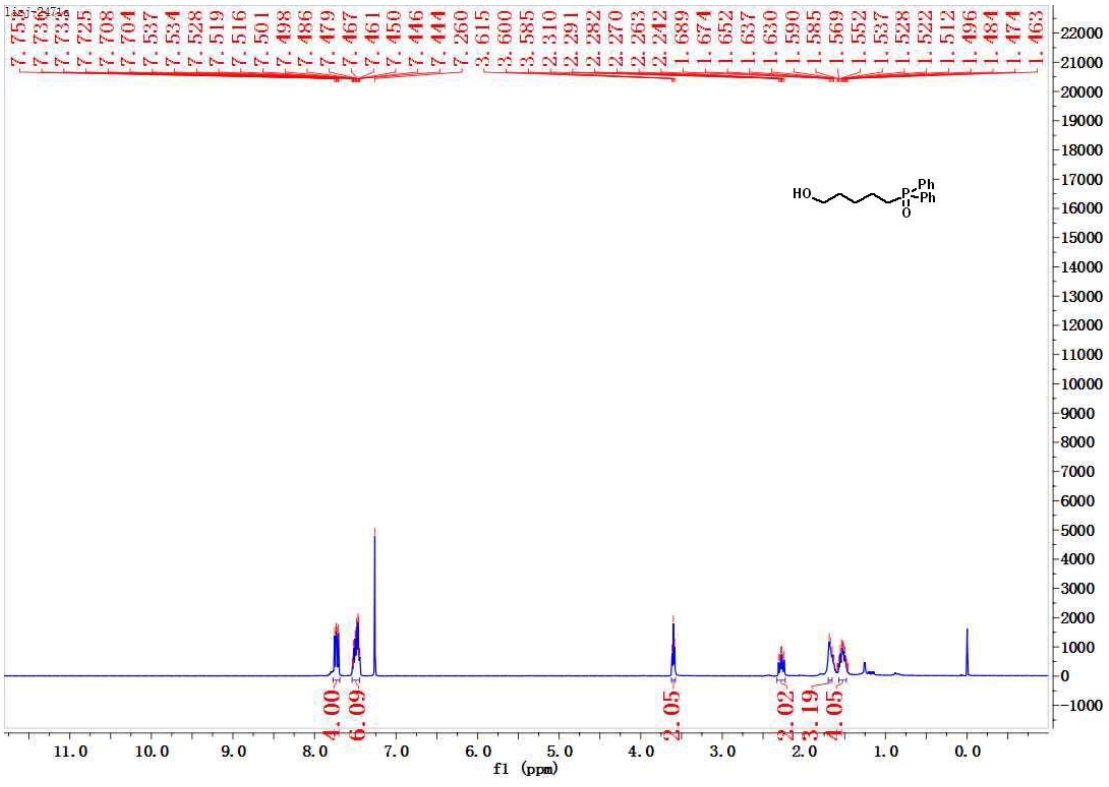
14-^{13}C NMR



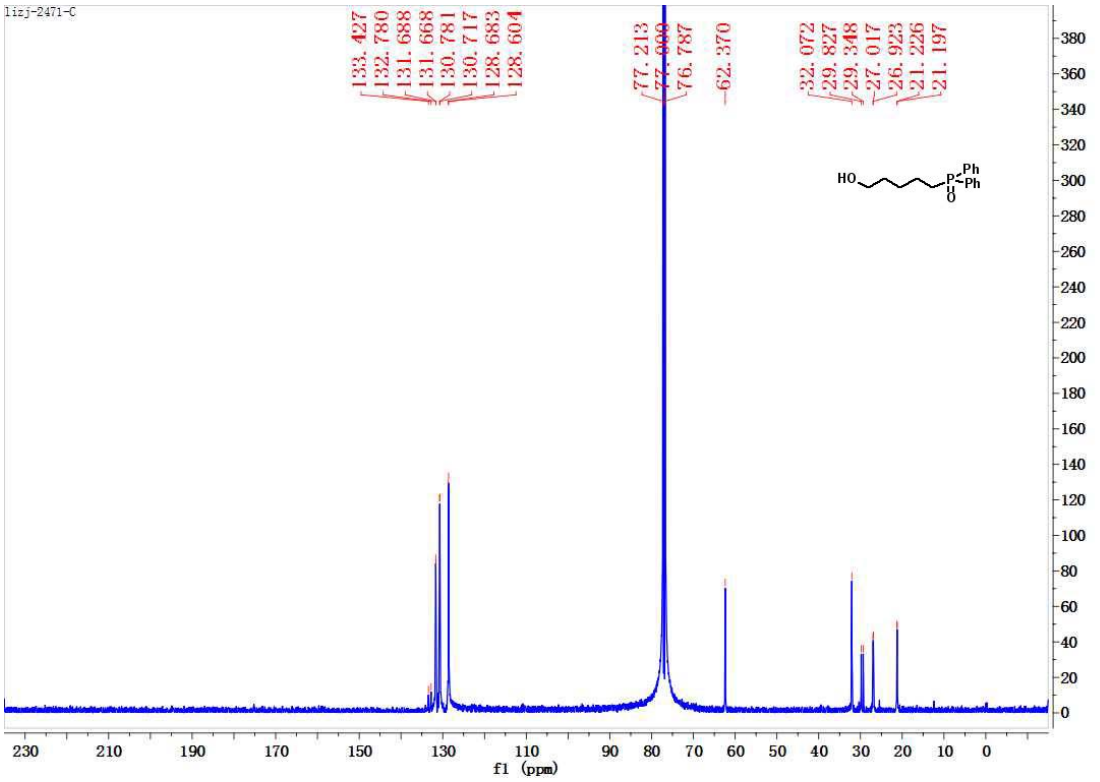
14-^{31}P NMR



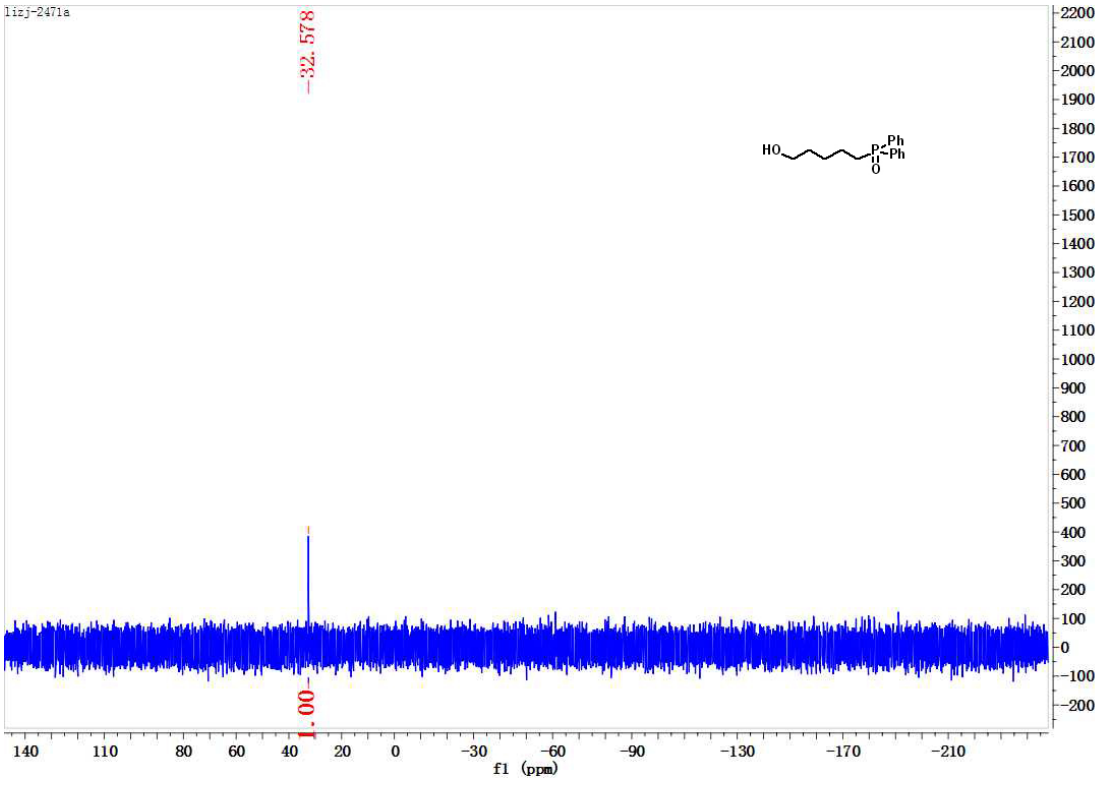
15-^{1}H NMR



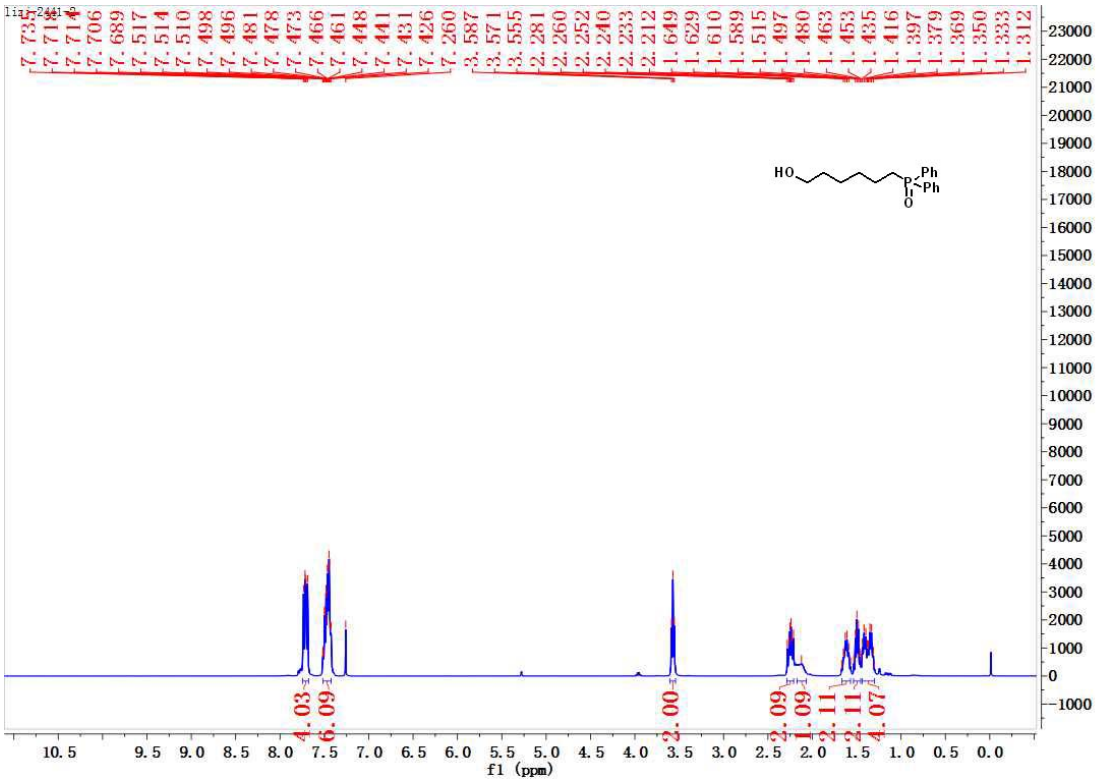
15-^{13}C NMR



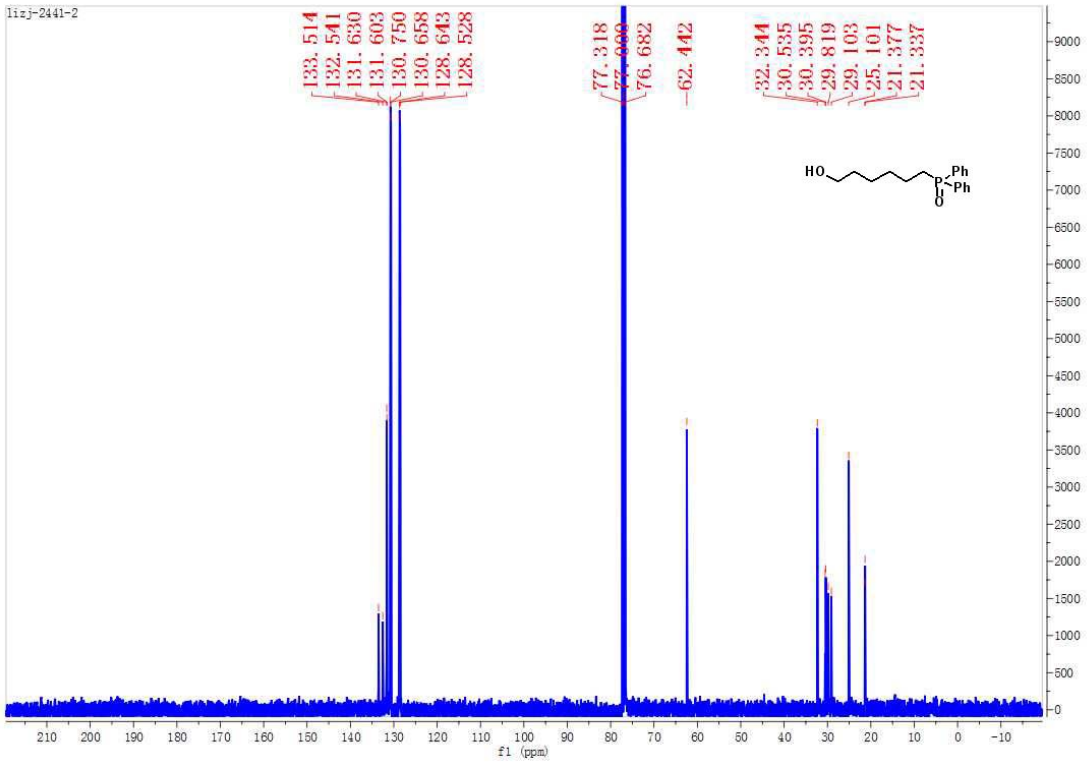
15-^{31}P NMR



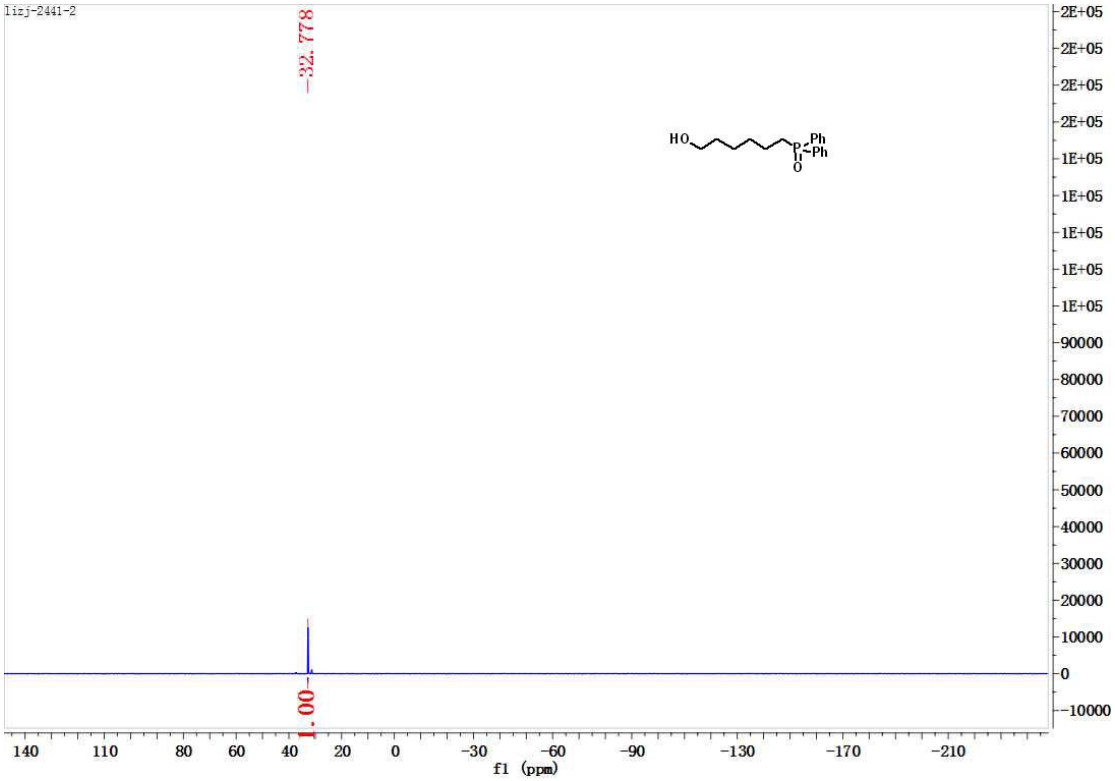
16-^{1}H NMR



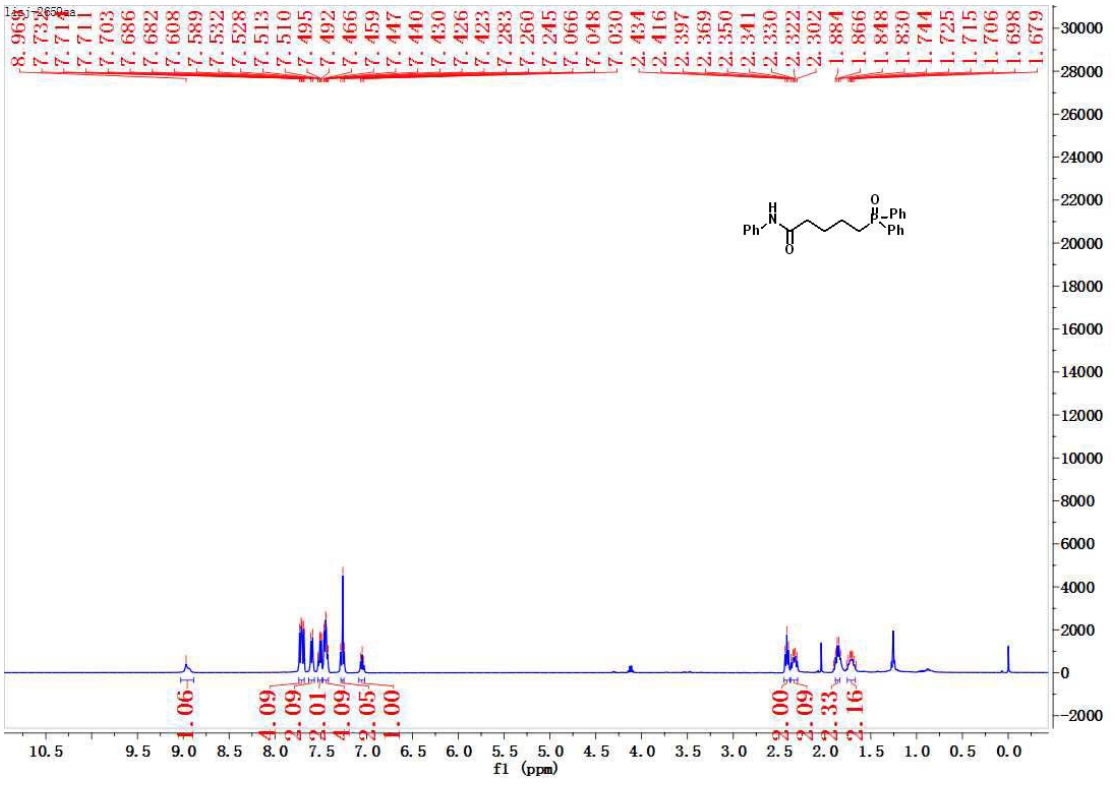
16-^{13}C NMR



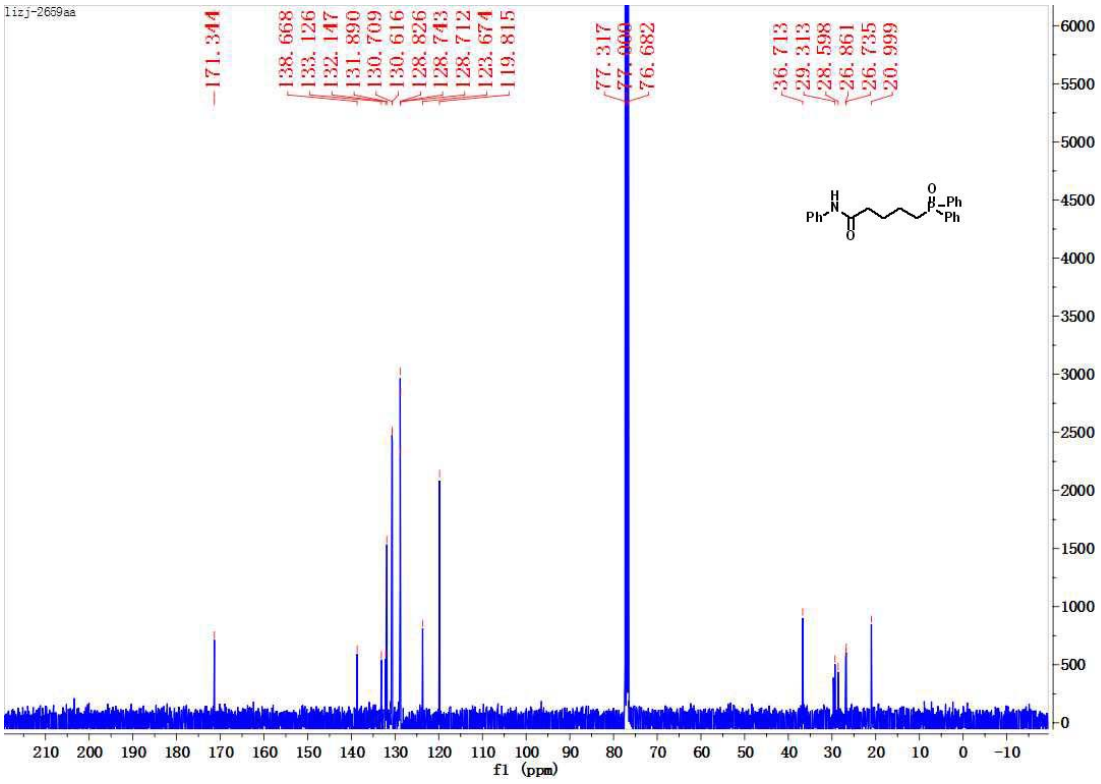
16-^{31}P NMR



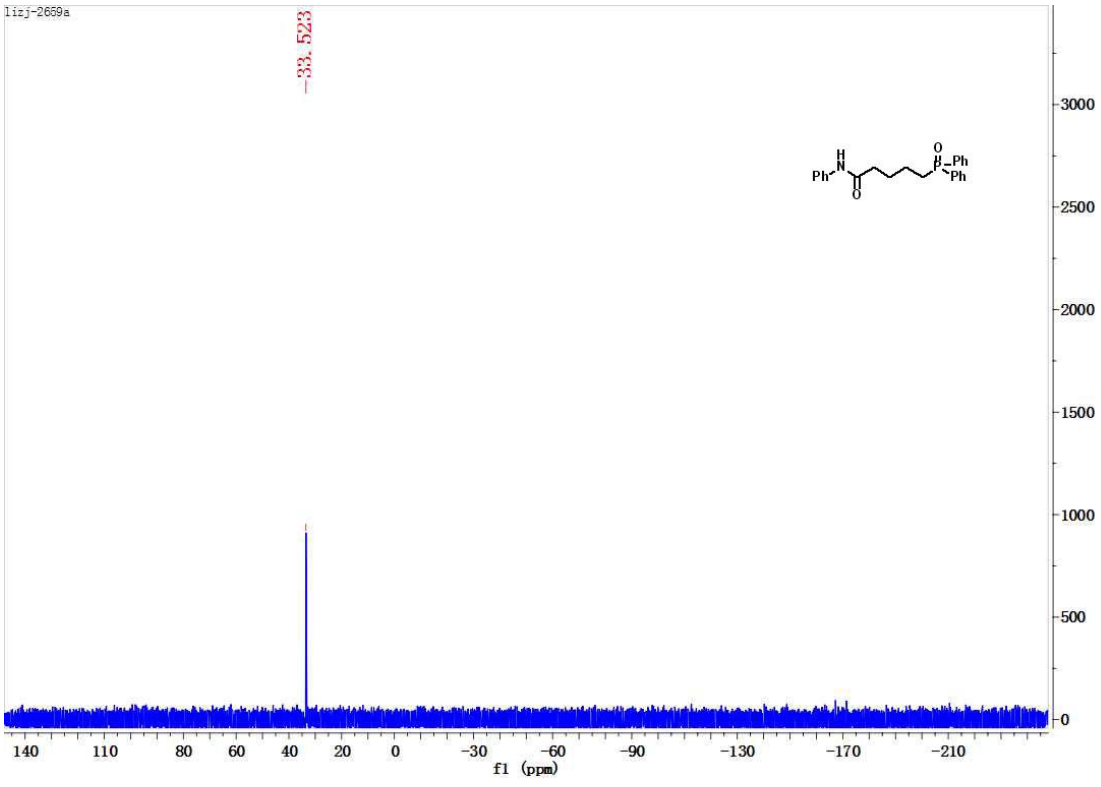
17-^{1}H NMR



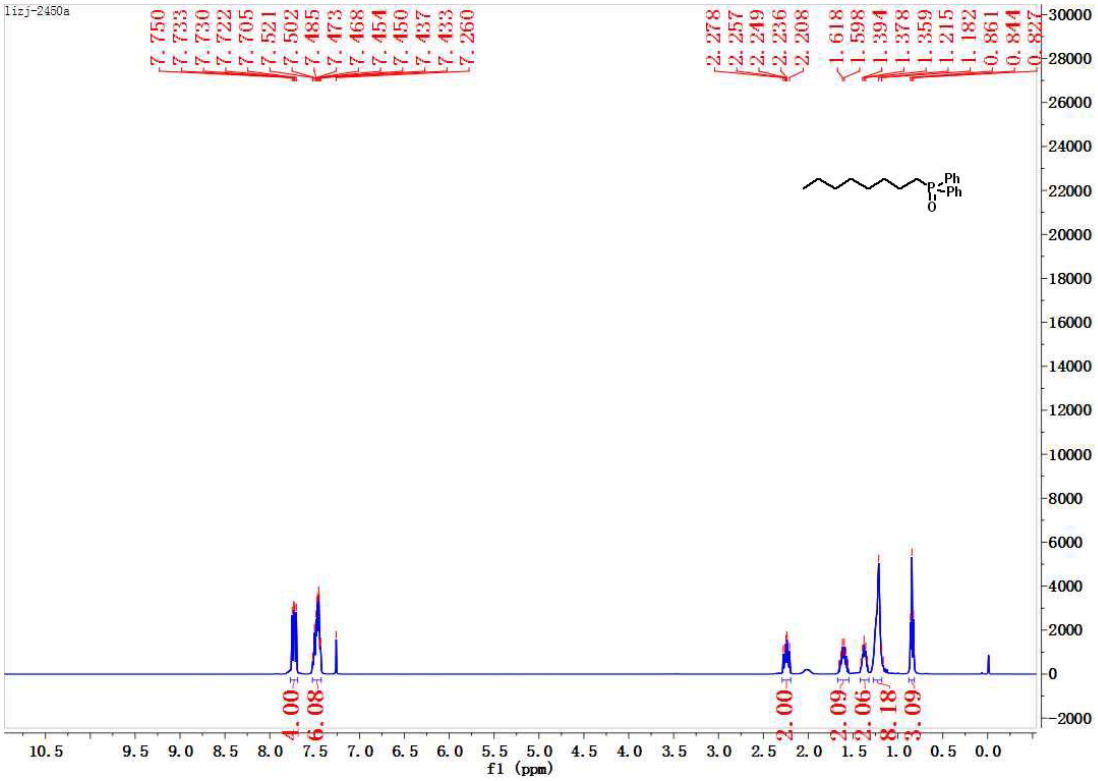
17-^{13}C NMR



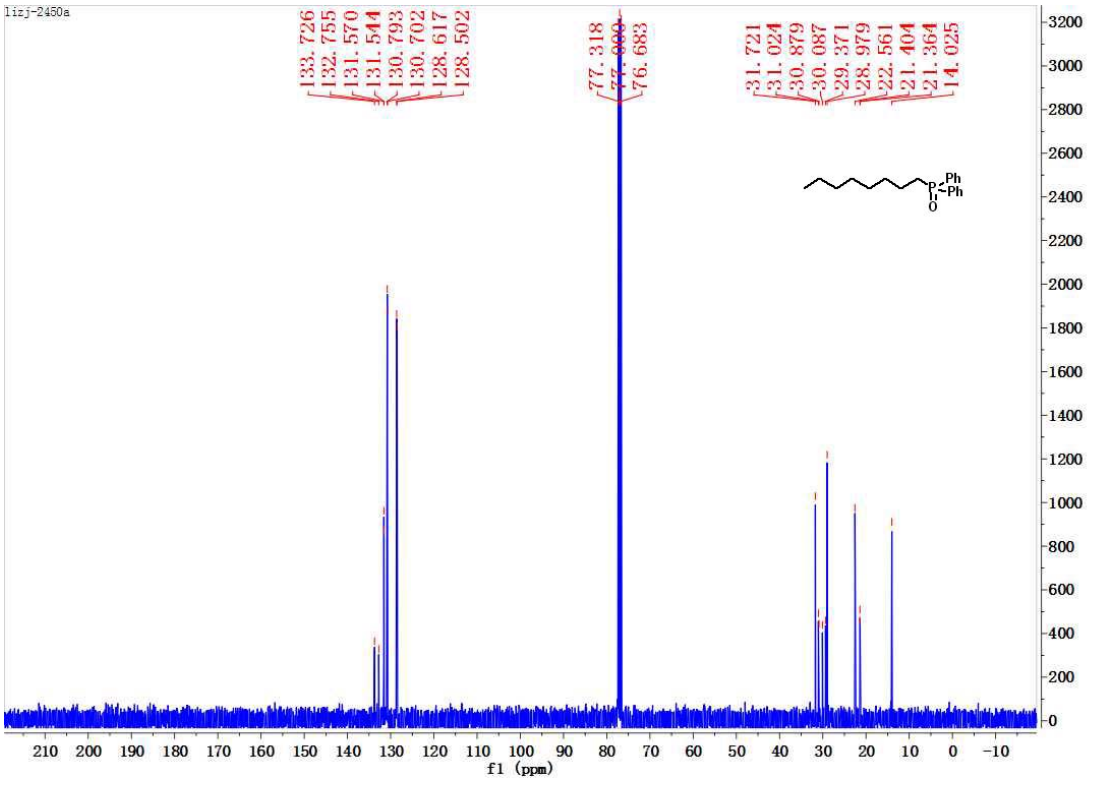
17-^{31}P NMR



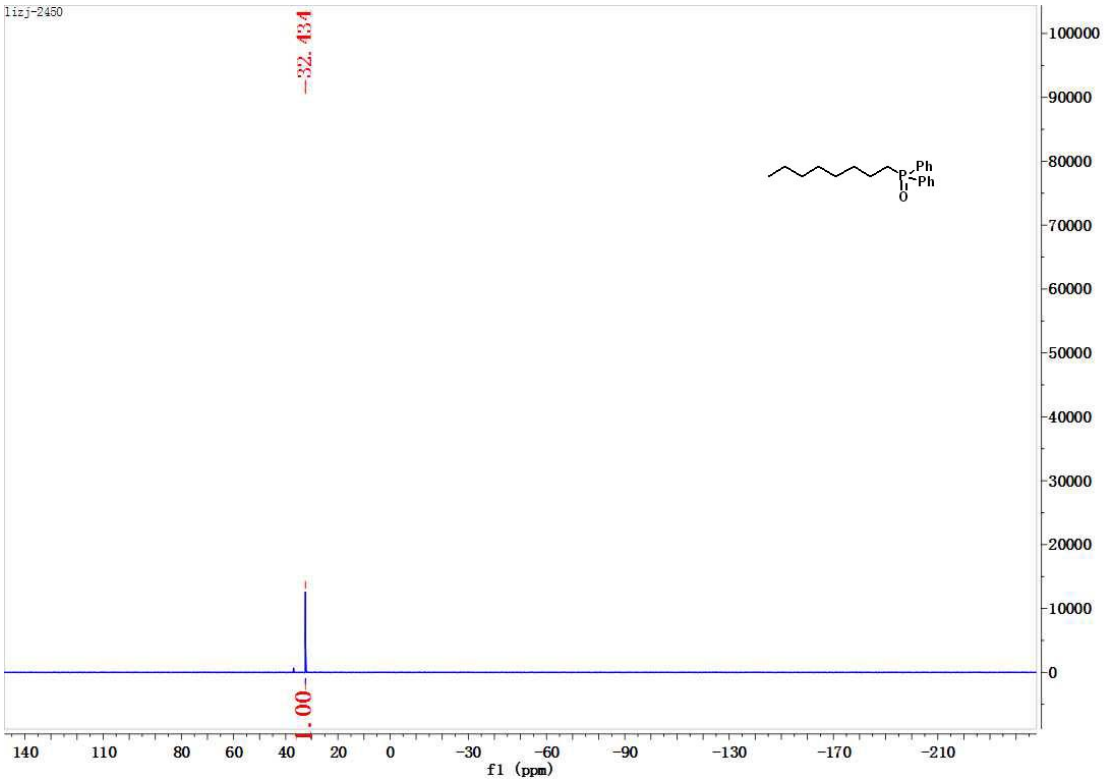
18-^{1}H NMR



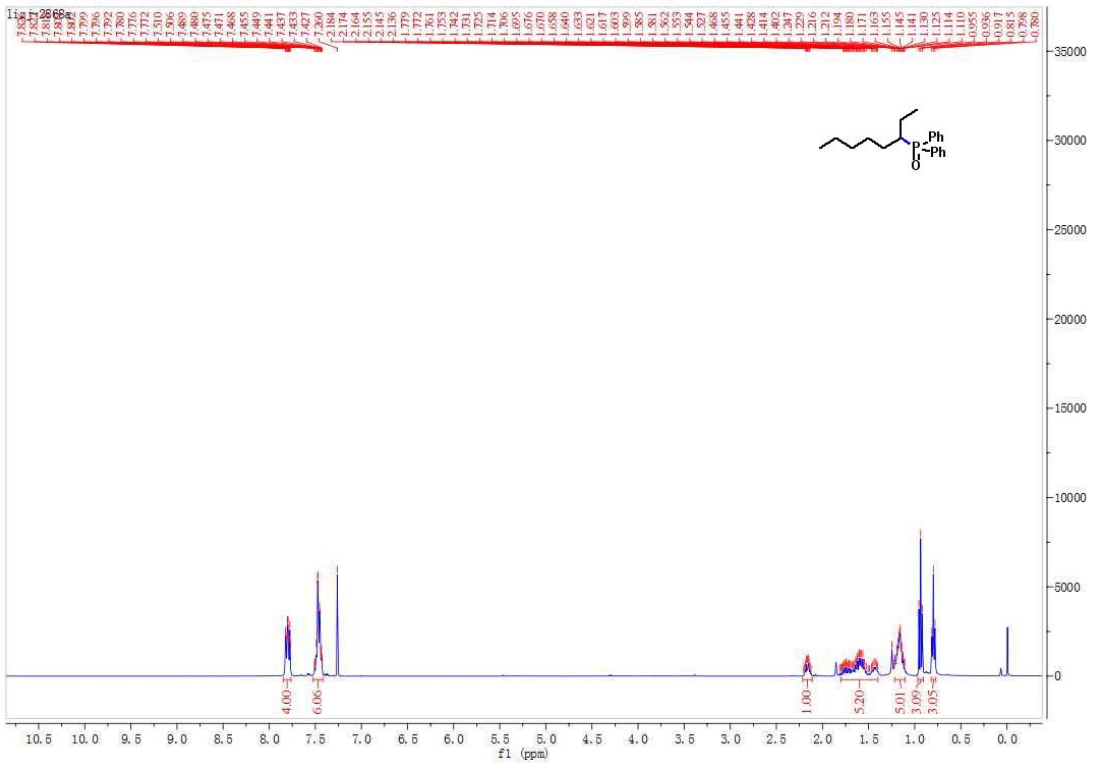
18-^{13}C NMR



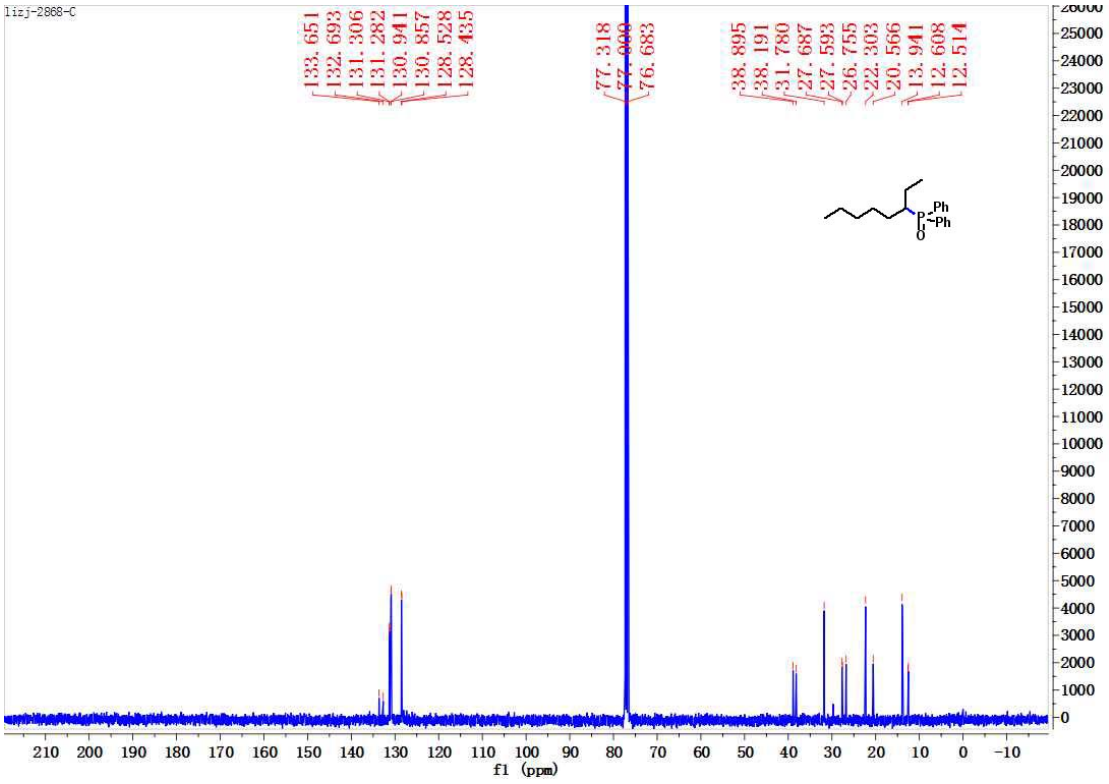
18-^{31}P NMR



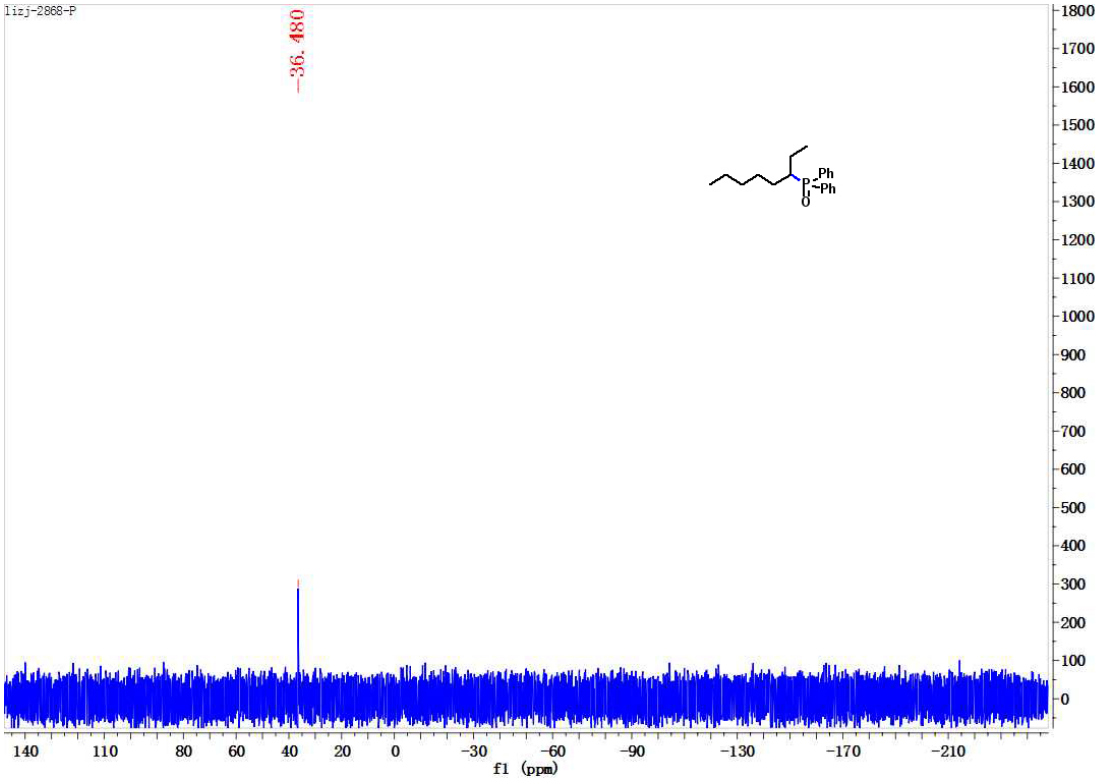
19-^{1}H NMR



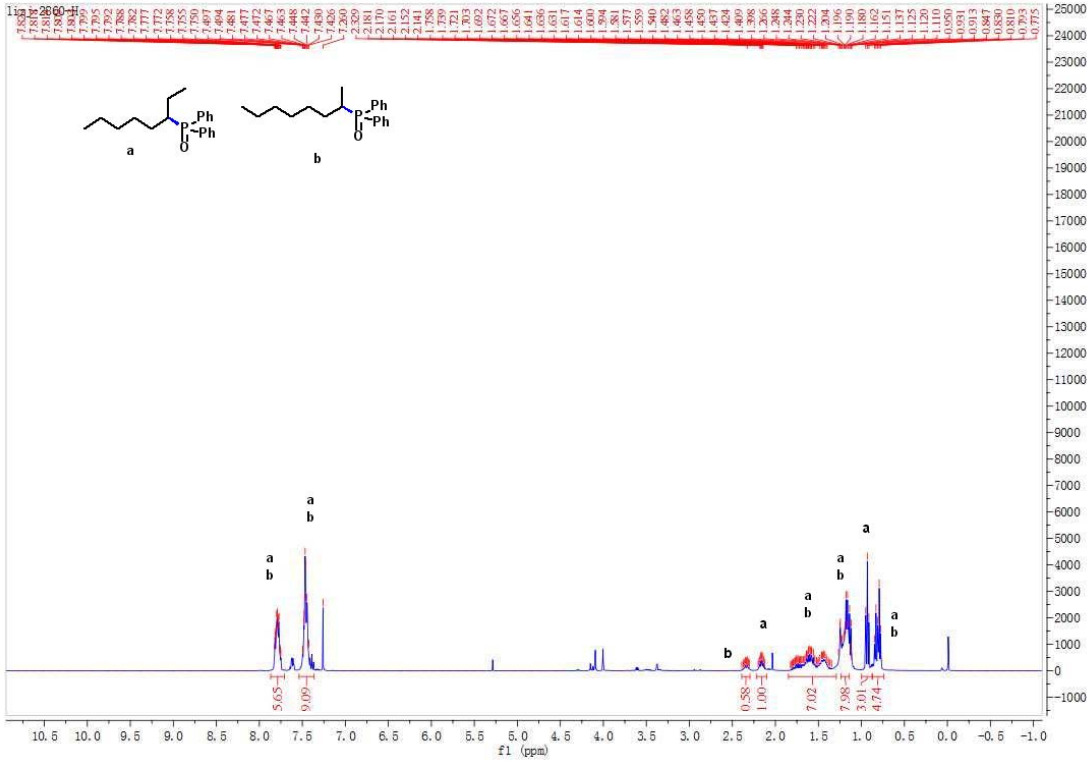
19-^{13}C NMR



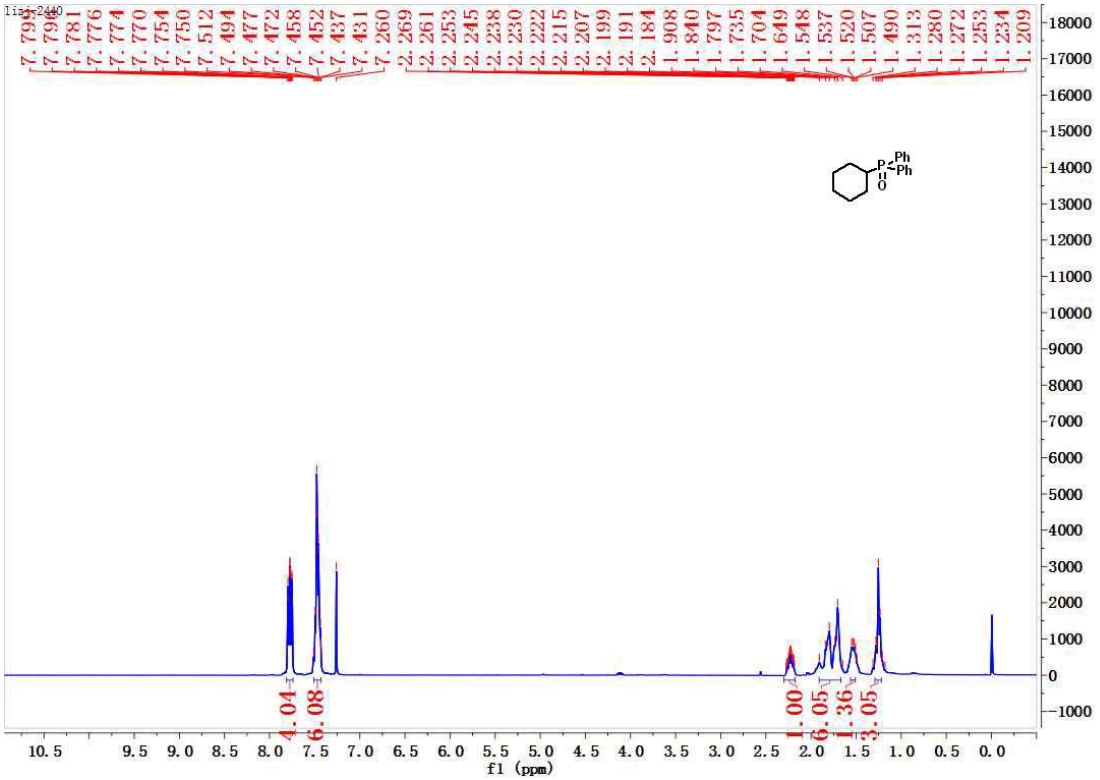
19-^{31}P NMR



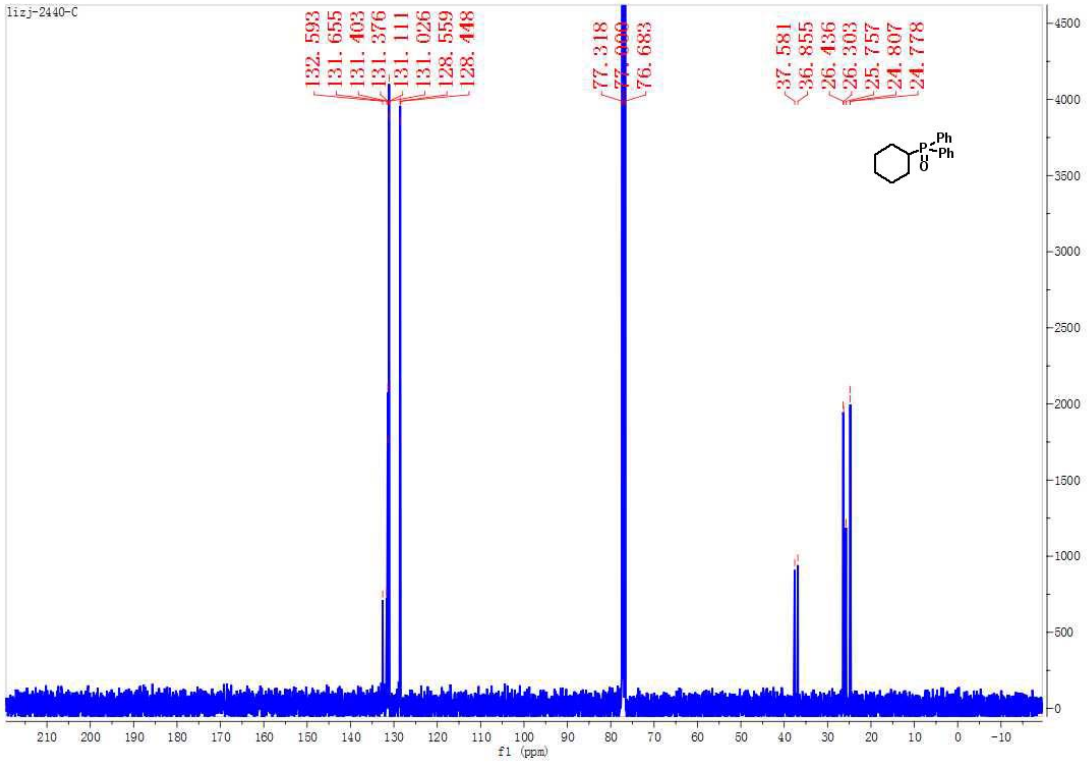
19a and b-^{1}H NMR



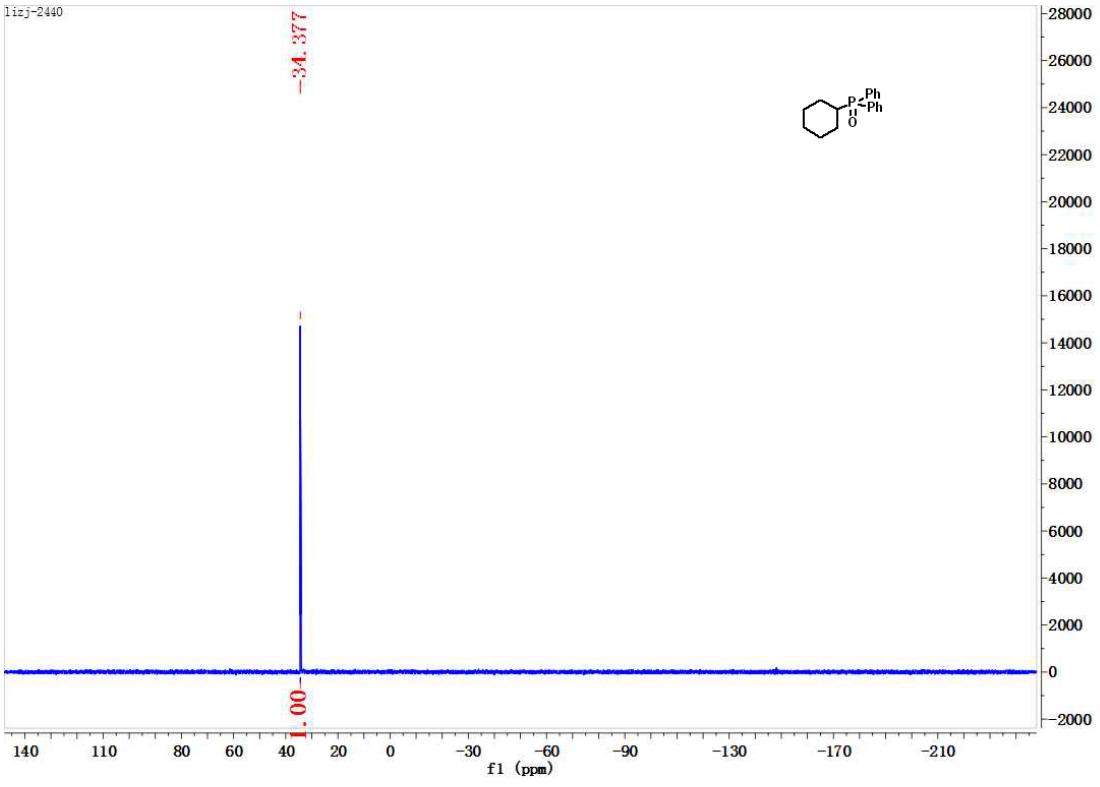
20-^{1}H NMR



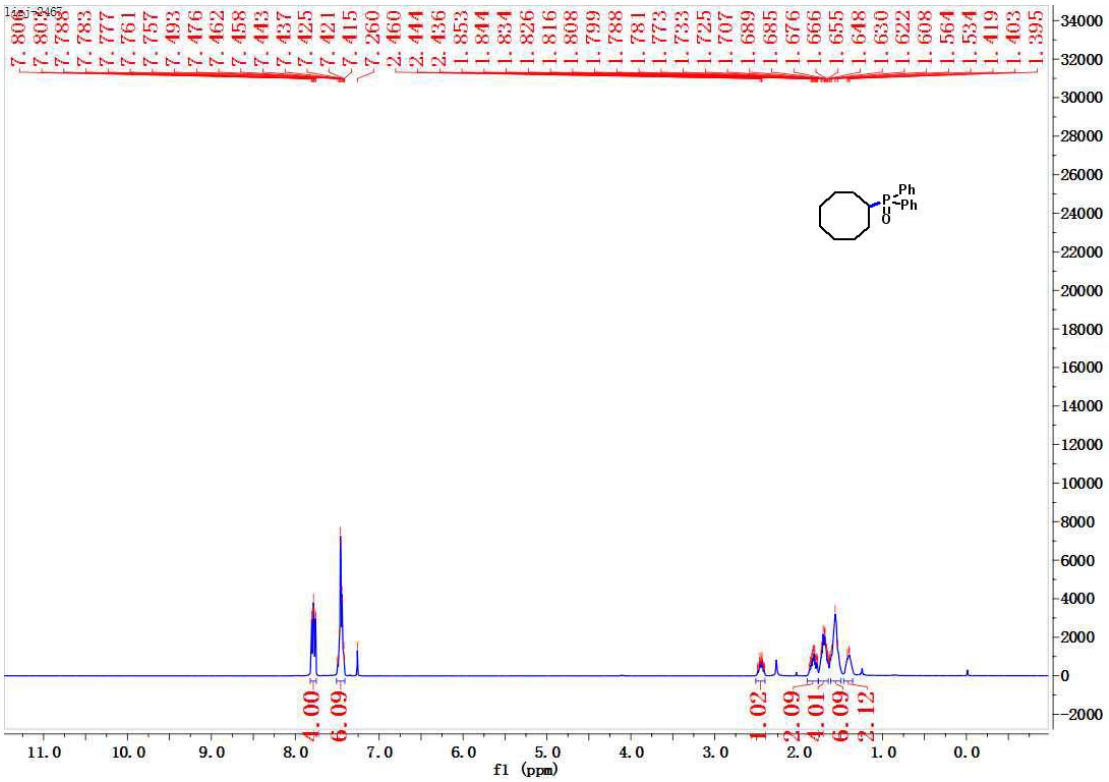
20-^{13}C NMR



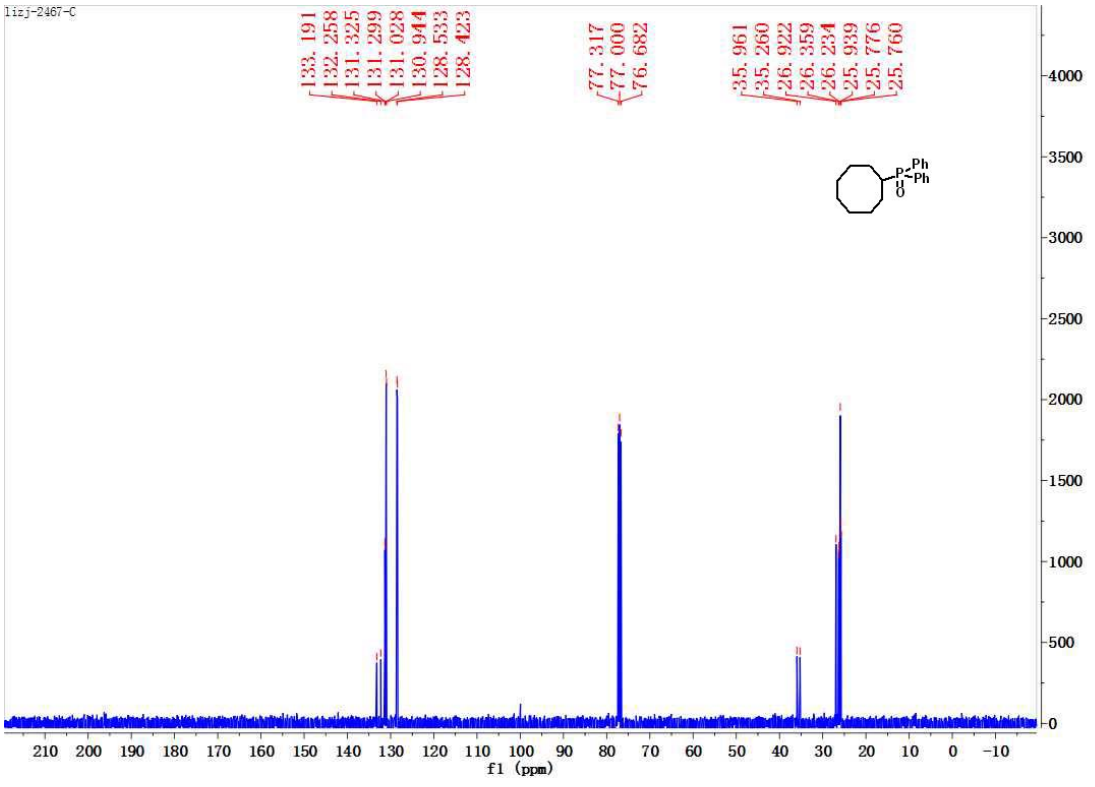
20-^{31}P NMR



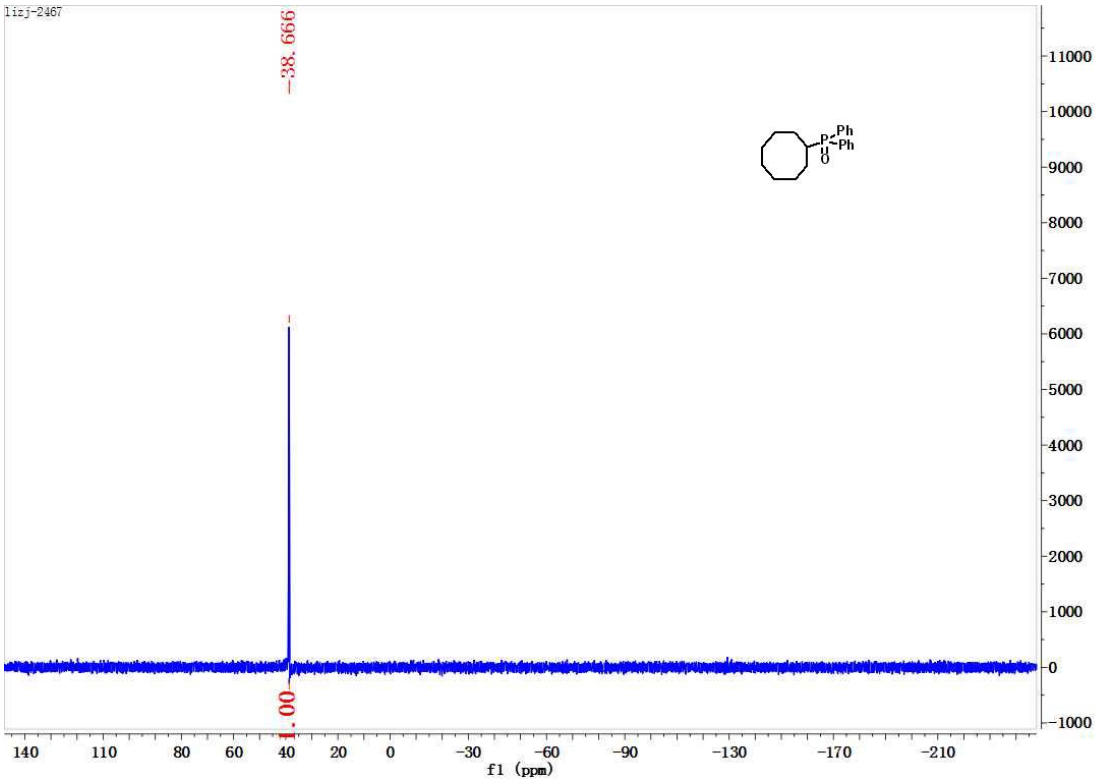
21-^{1}H NMR



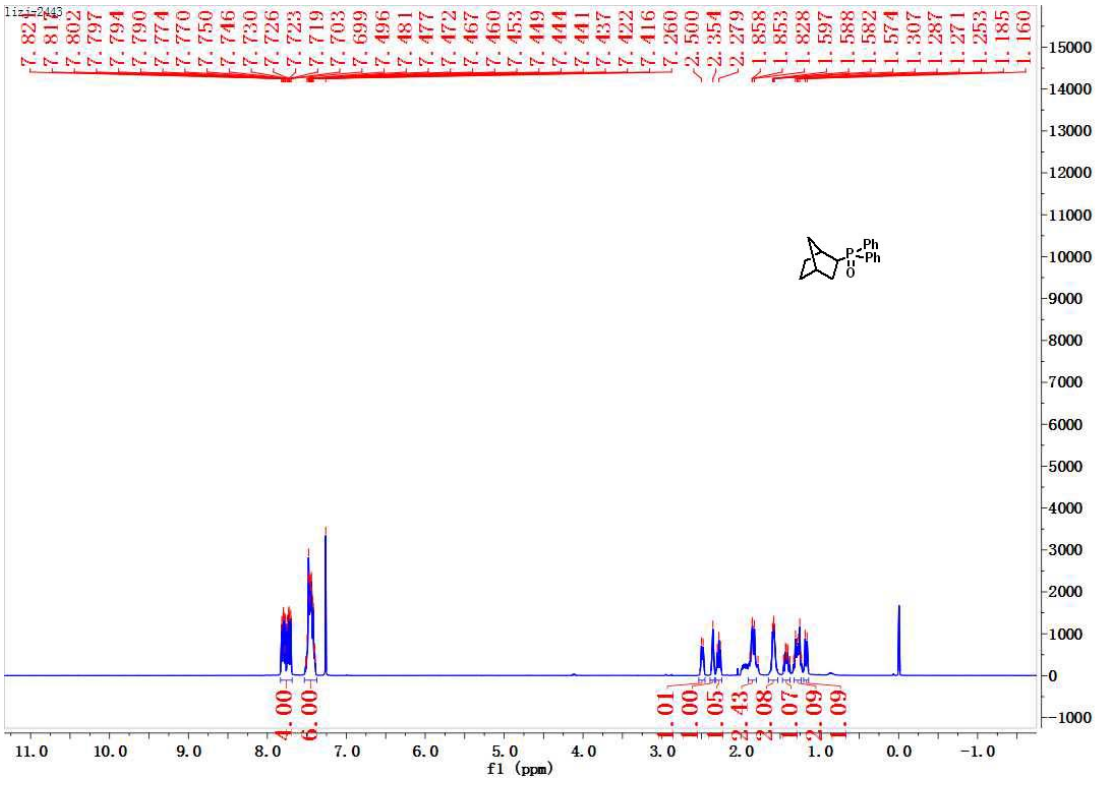
21-^{13}C NMR



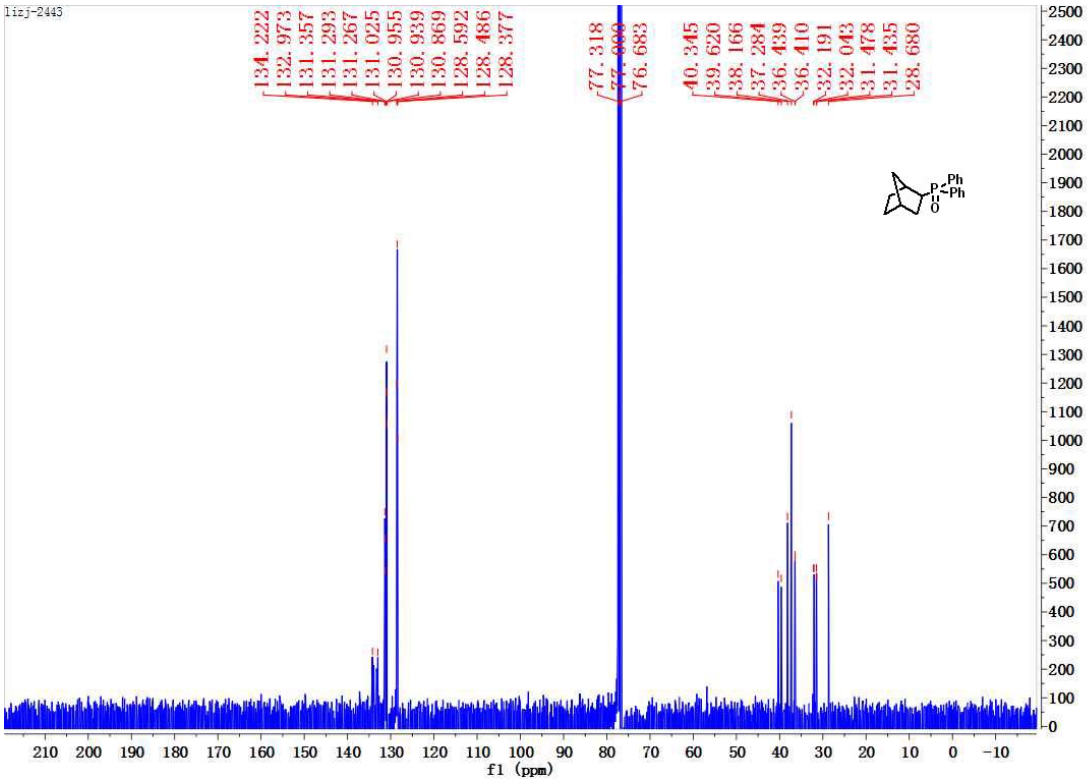
21-^{31}P NMR



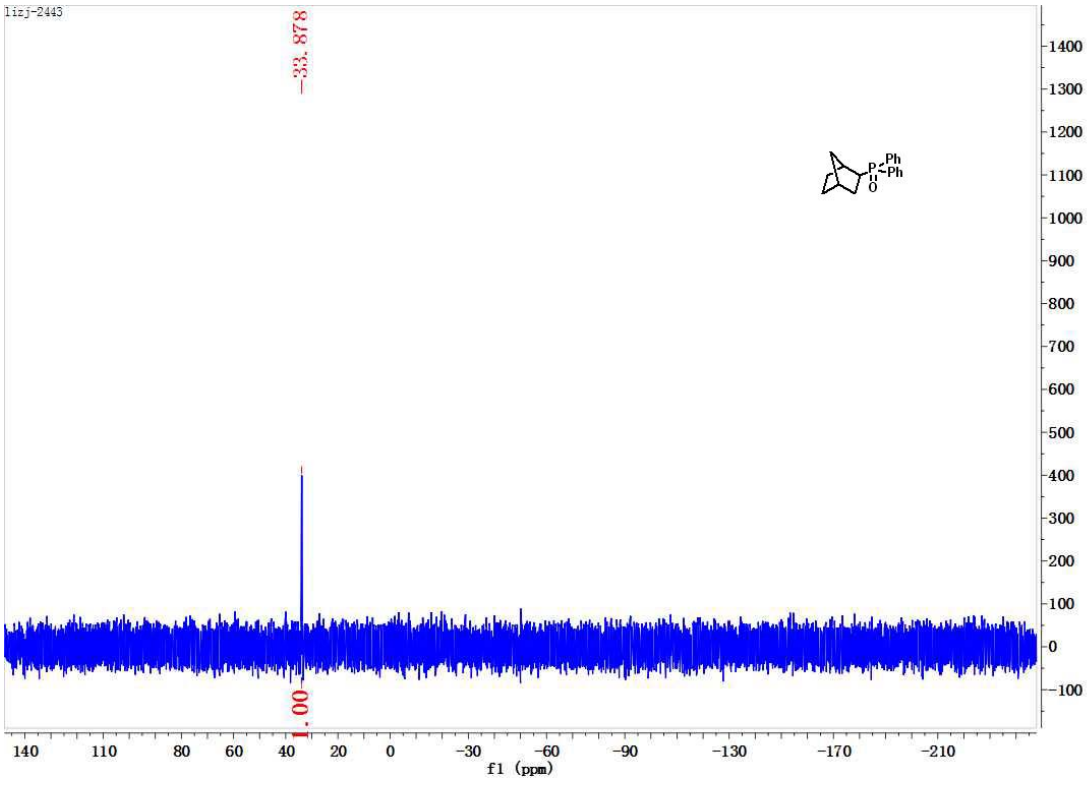
22-^{1}H NMR



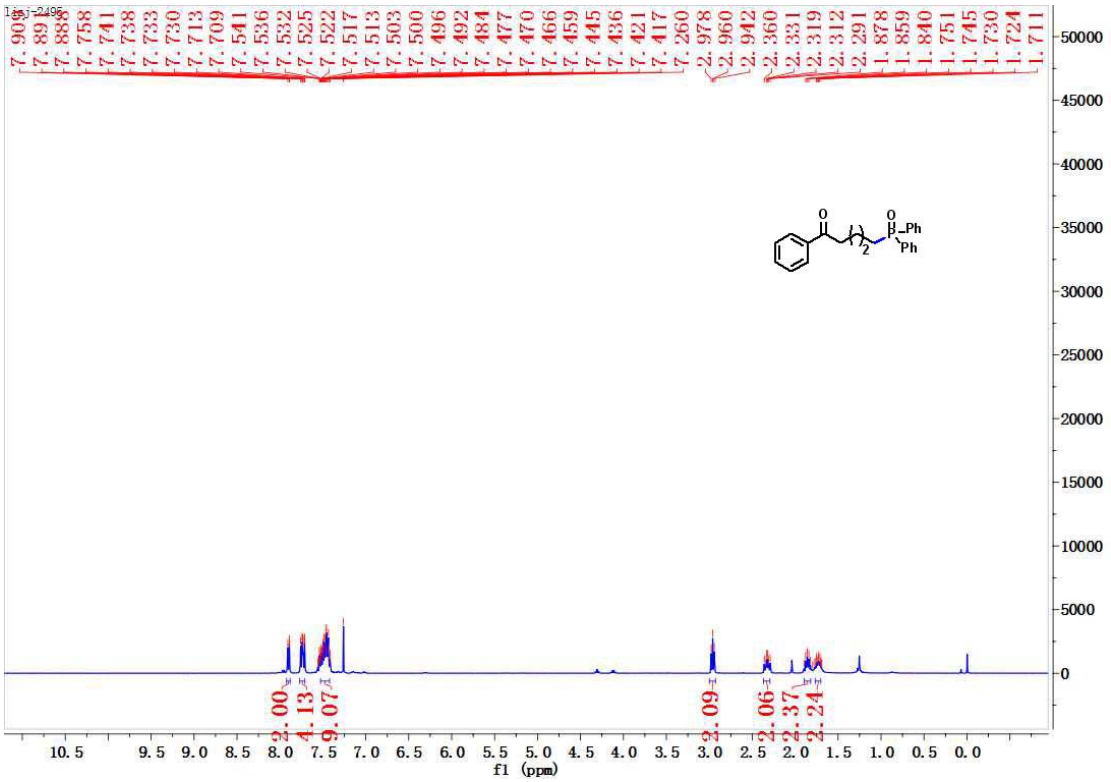
22-^{13}C NMR



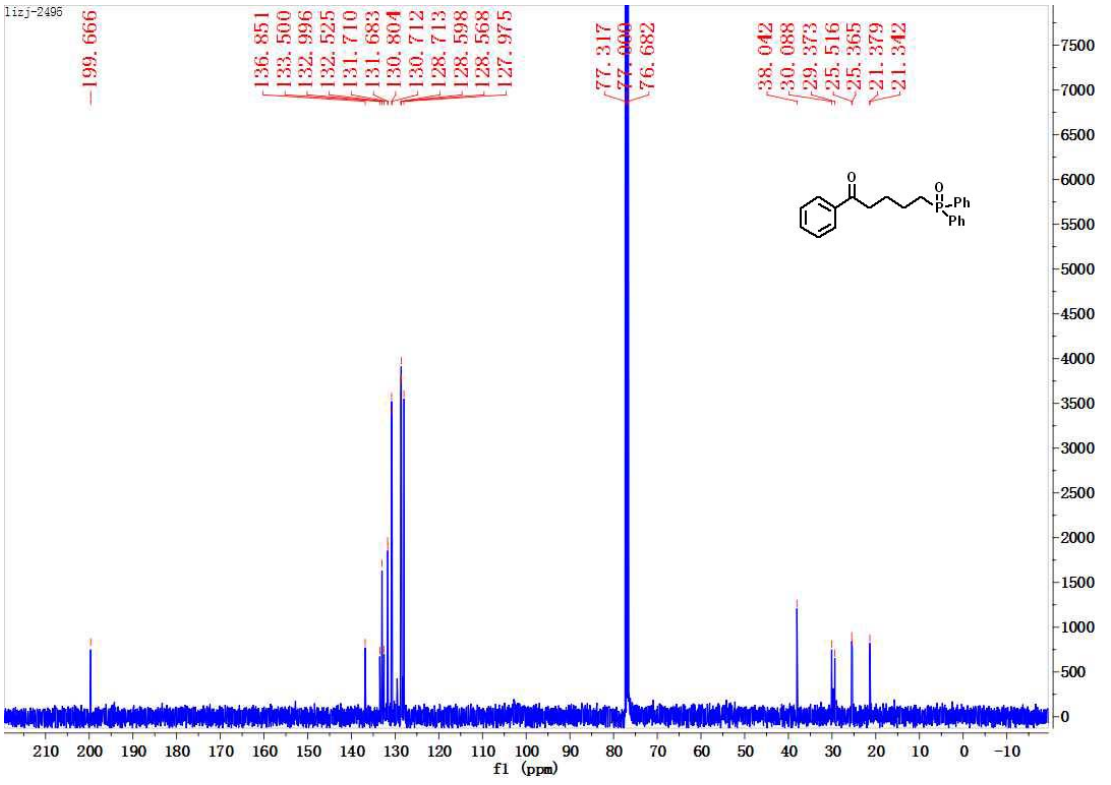
22-^{31}P NMR



23-^{1}H NMR



23-^{13}C NMR



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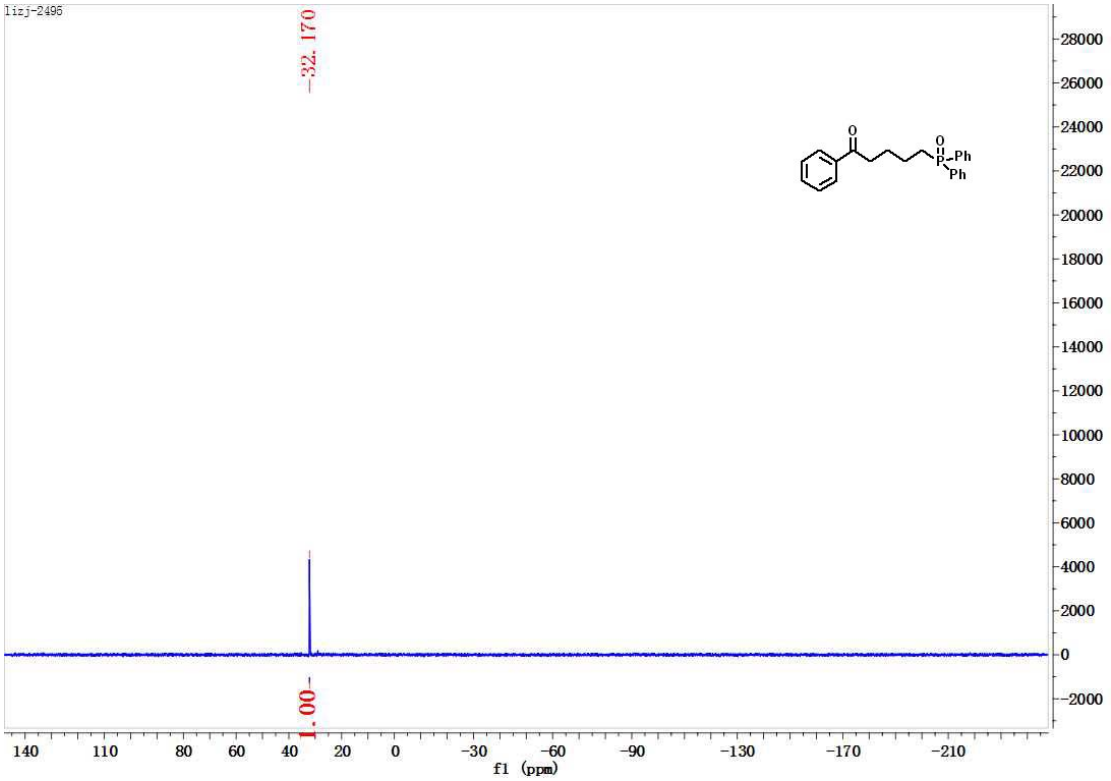
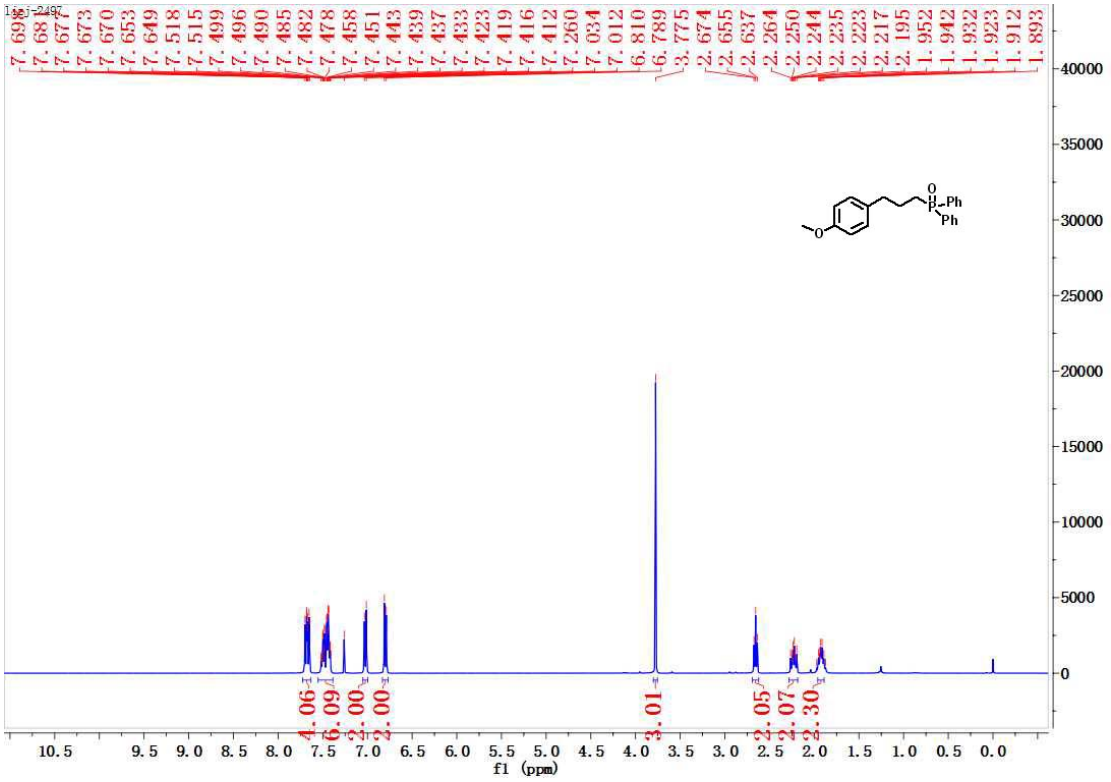


24-^{1}H NMR



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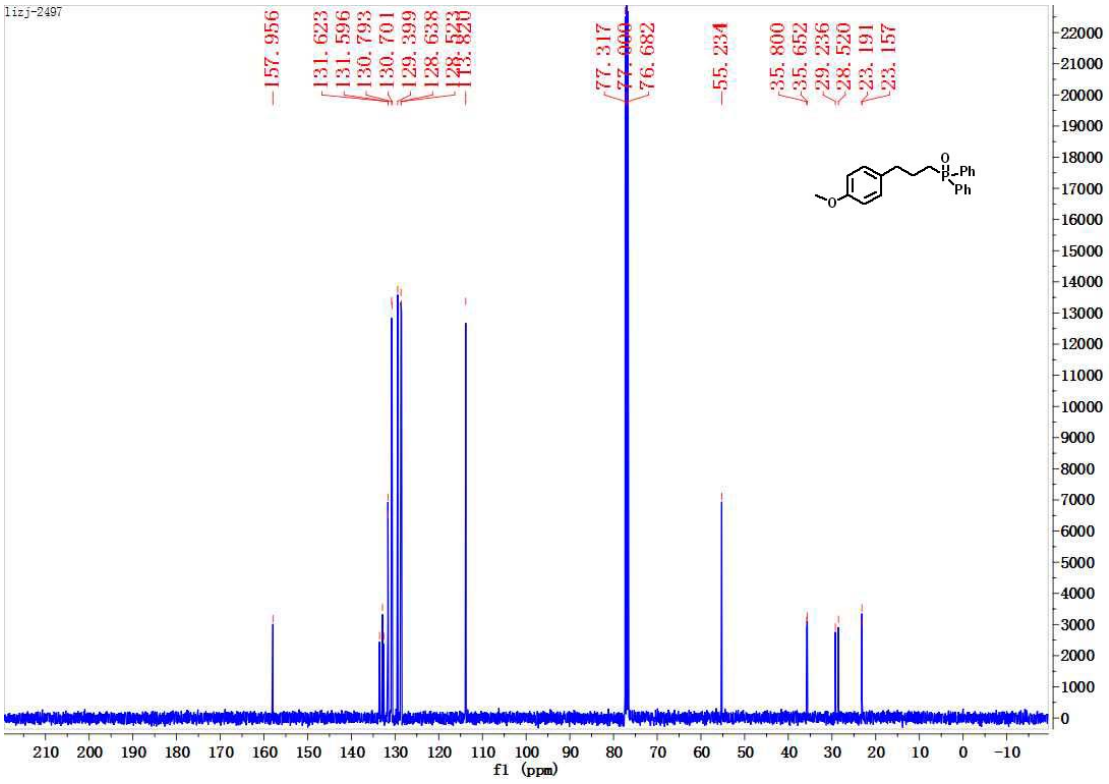

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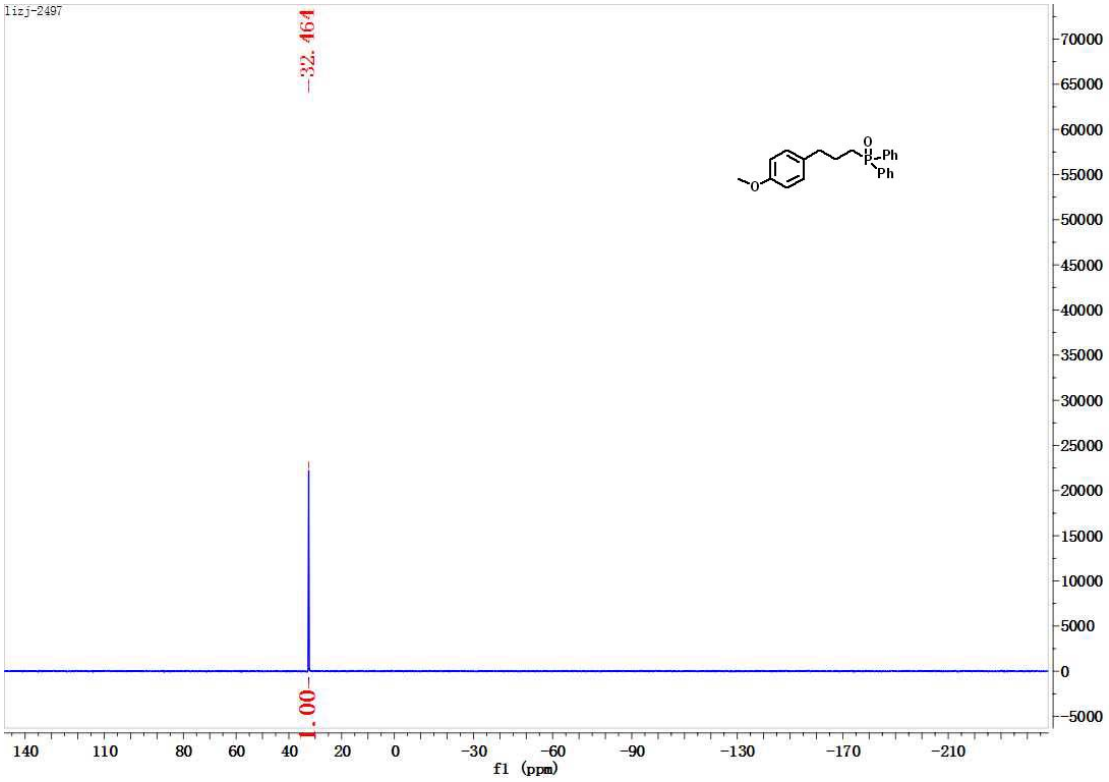
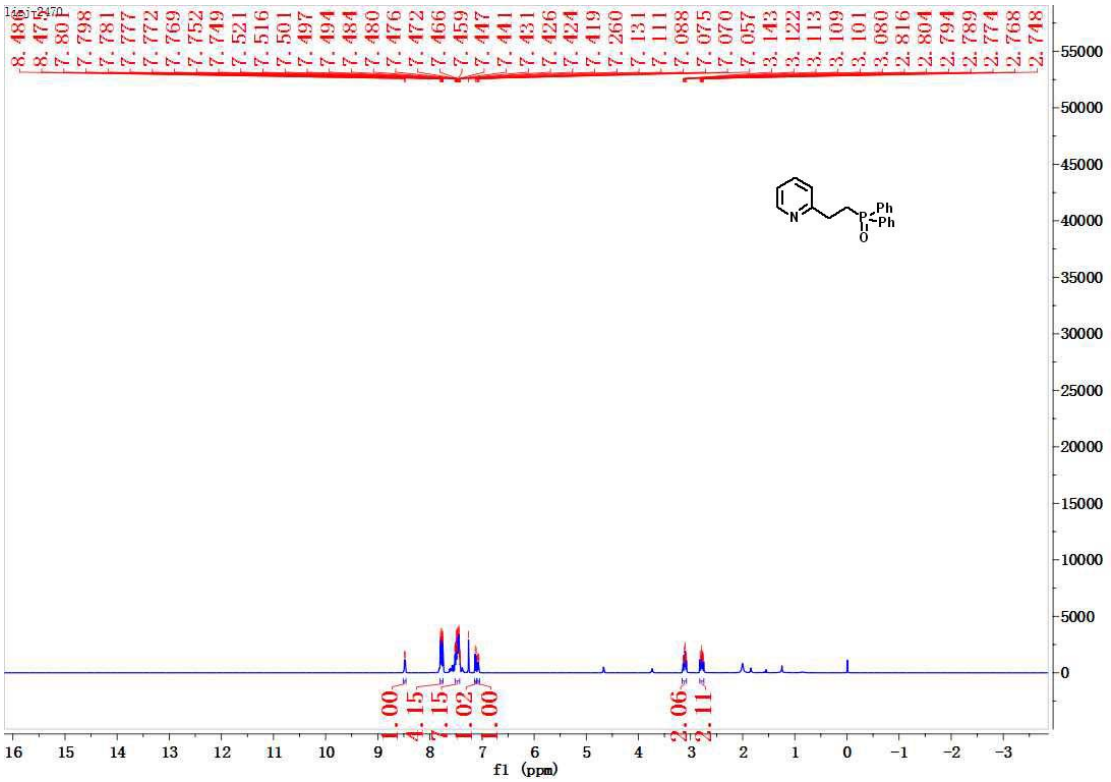
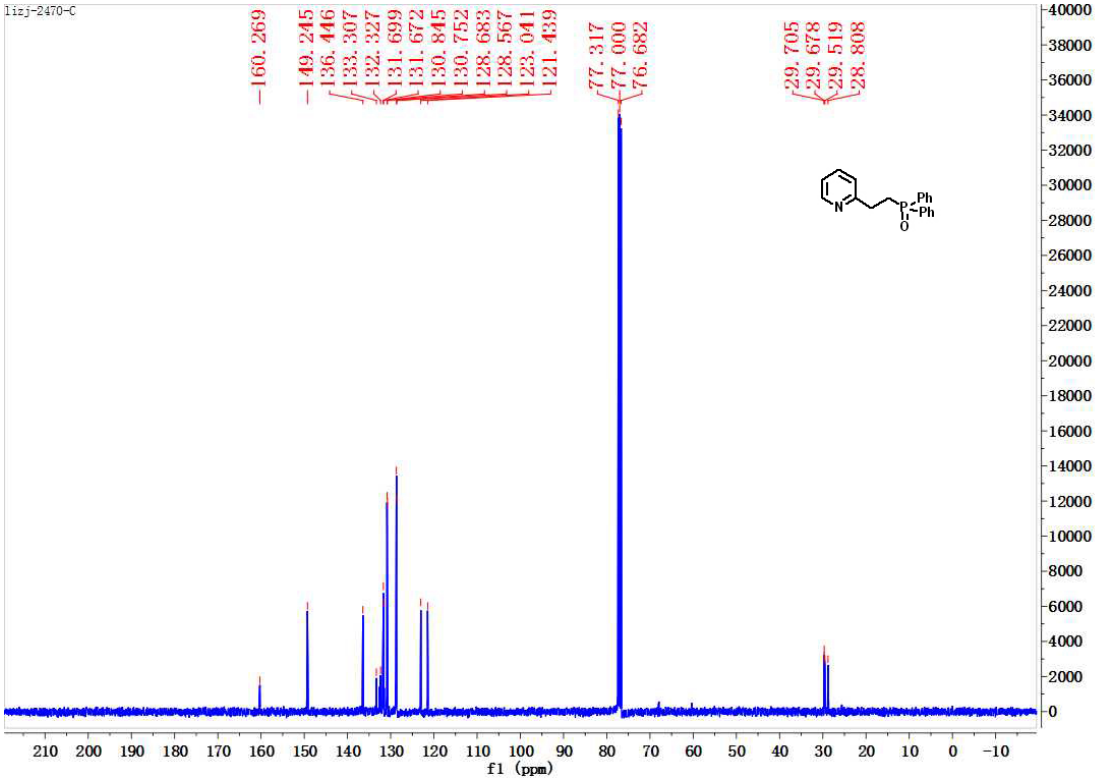


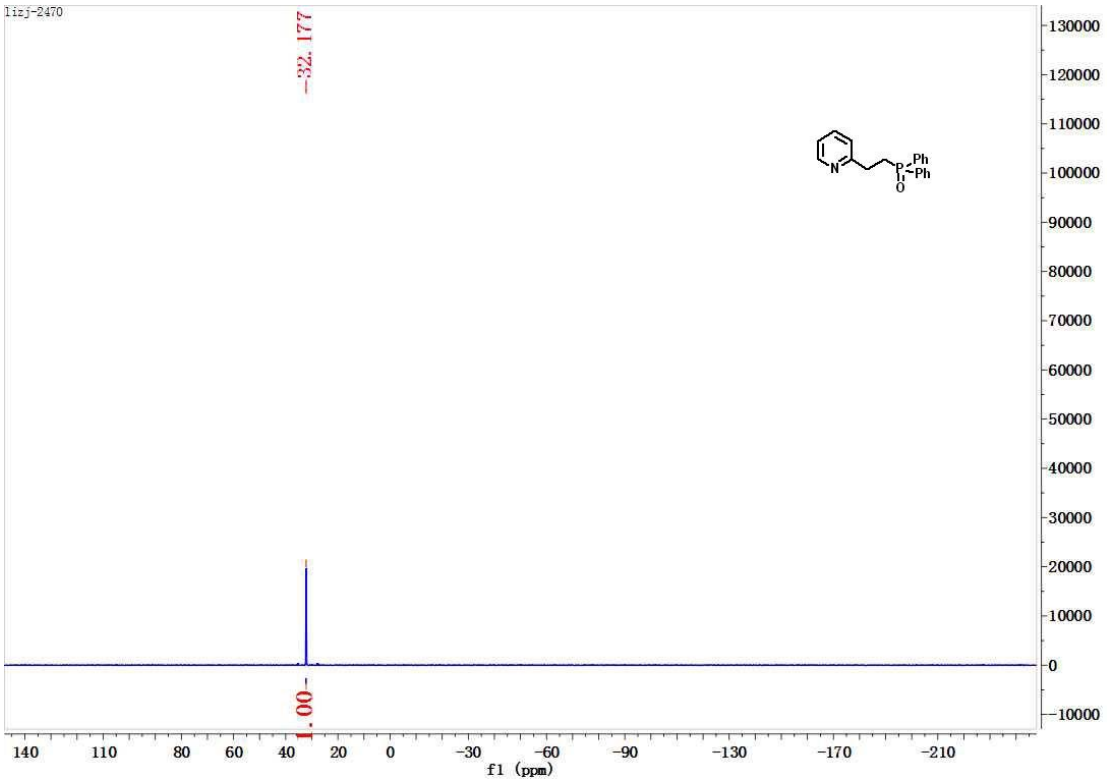
25-^{1}H NMR



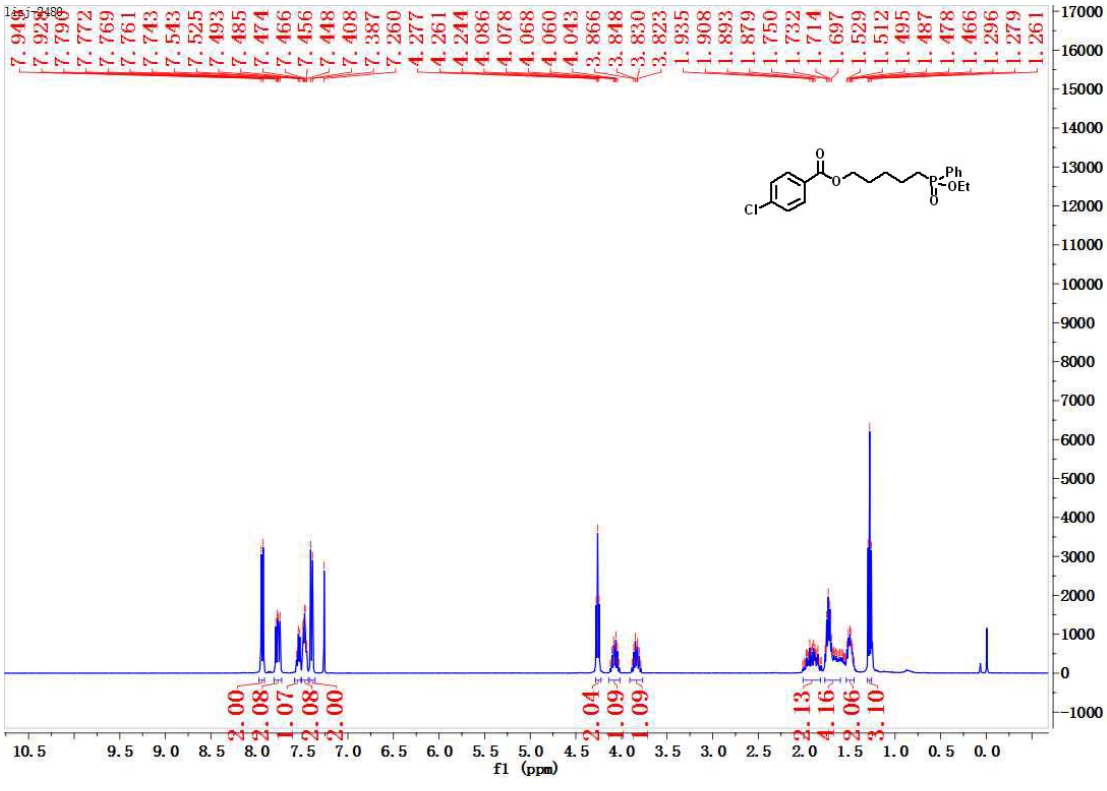
25-^{13}C NMR



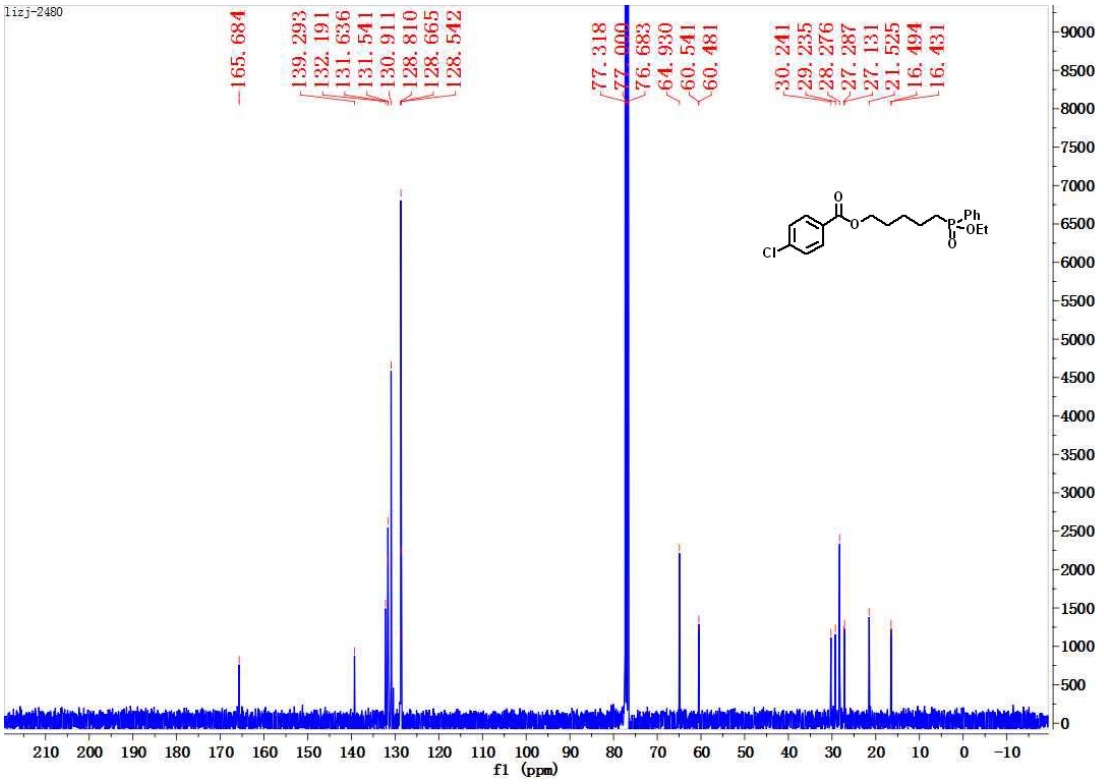
25-^{31}P NMR



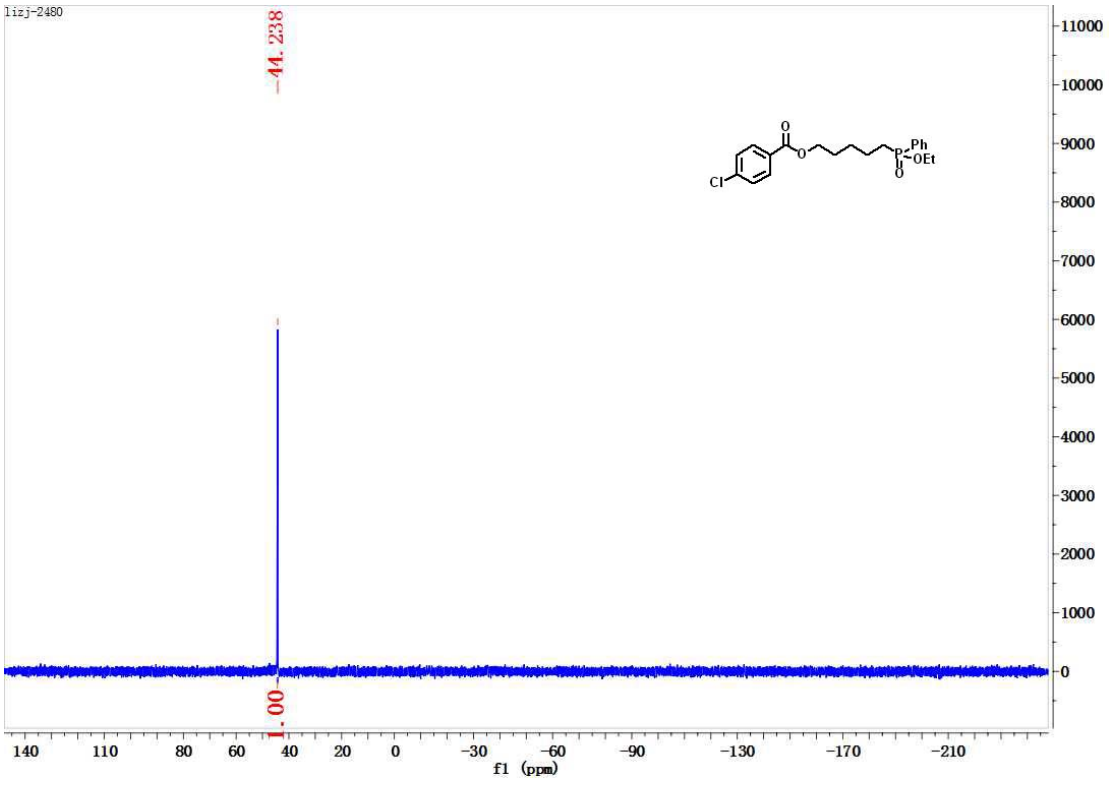
26-^{1}H NMR



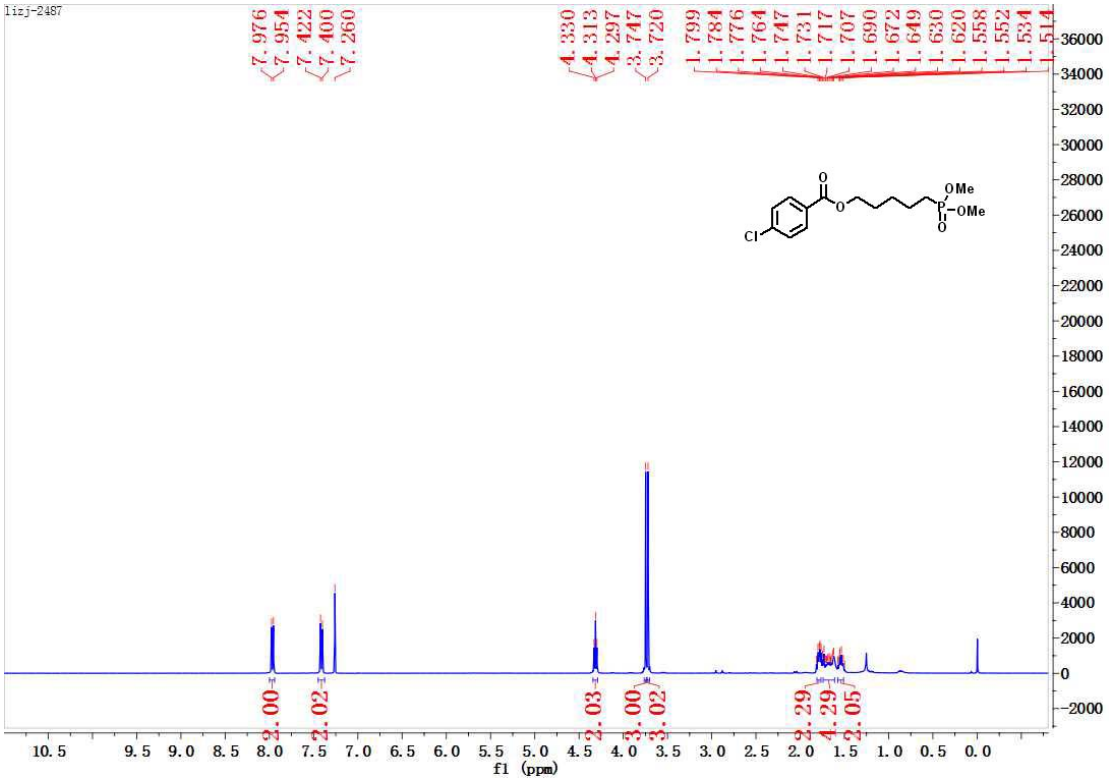
26-^{13}C NMR



26-^{31}P NMR



27-^{1}H NMR



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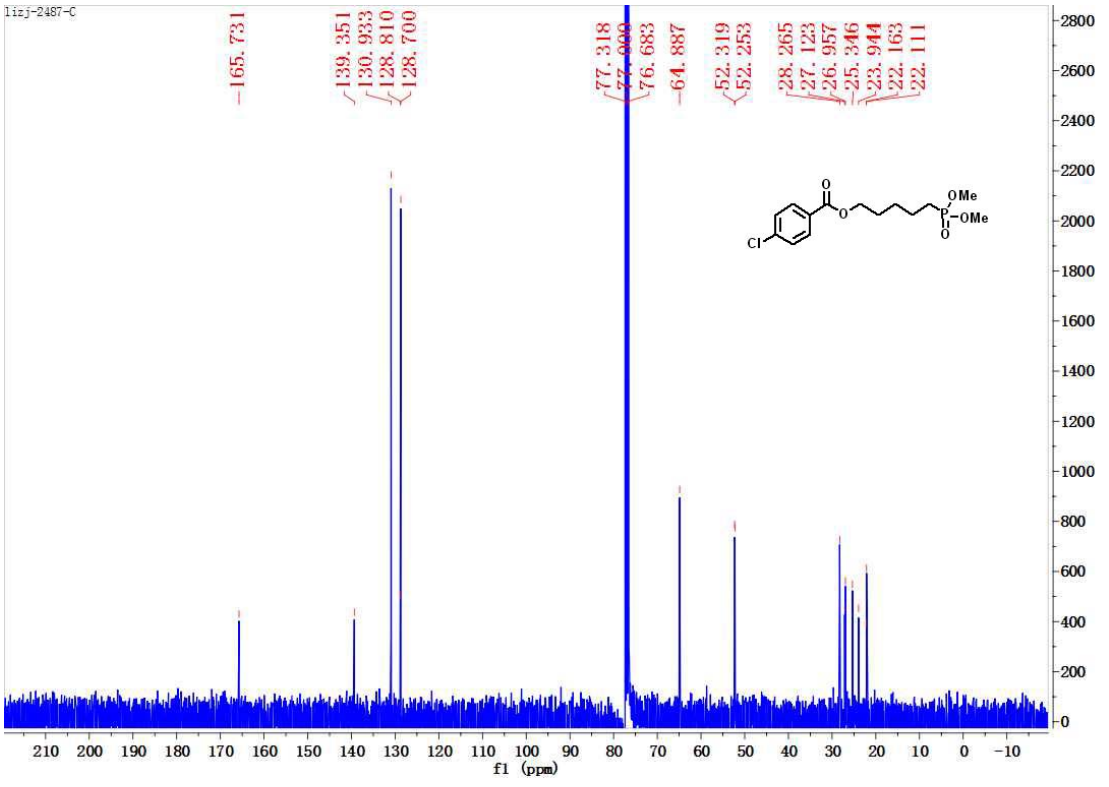

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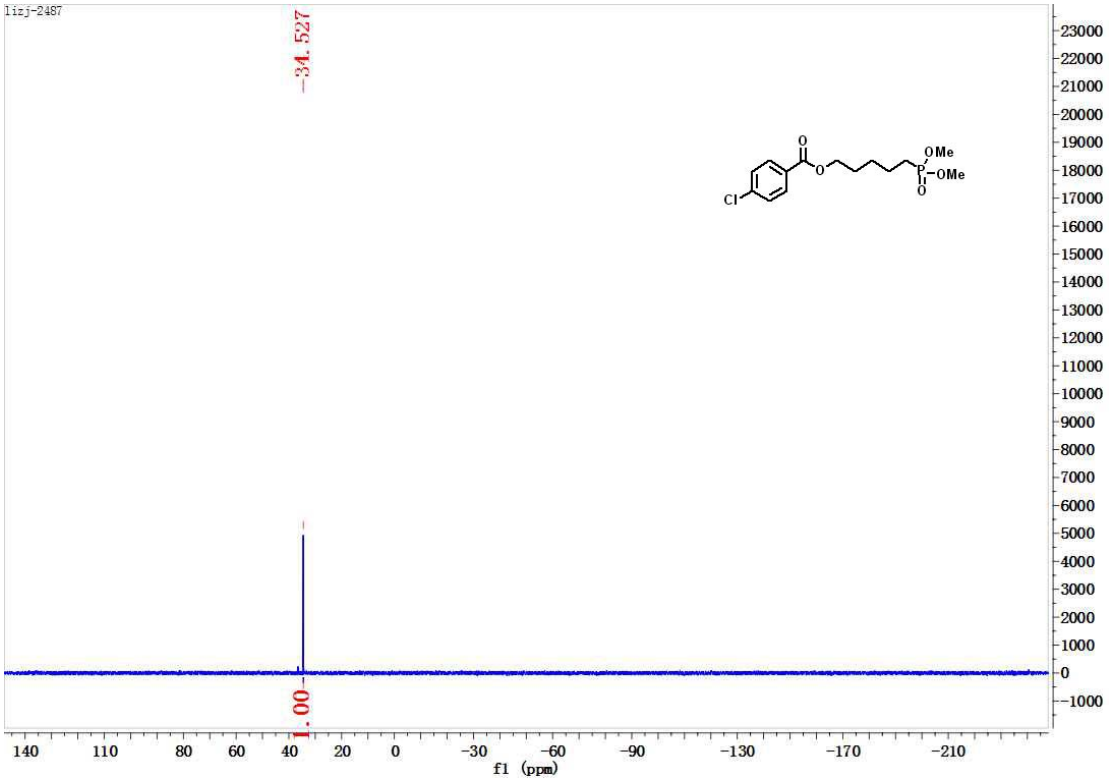
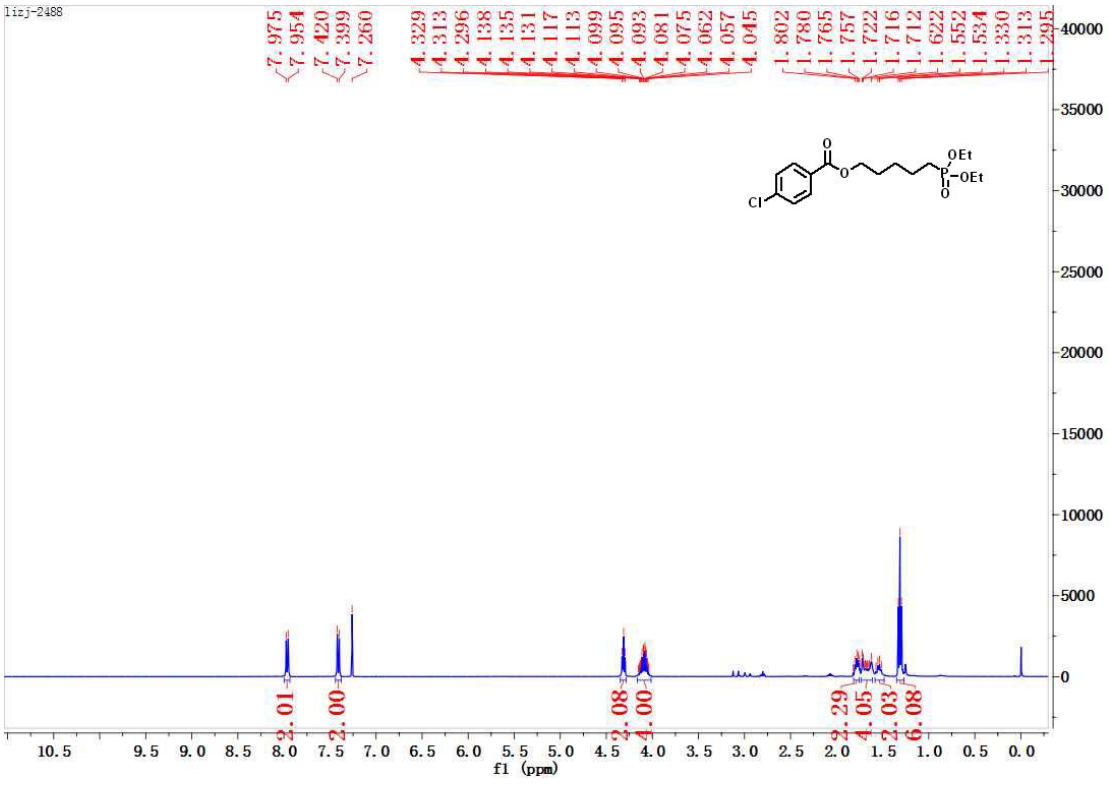
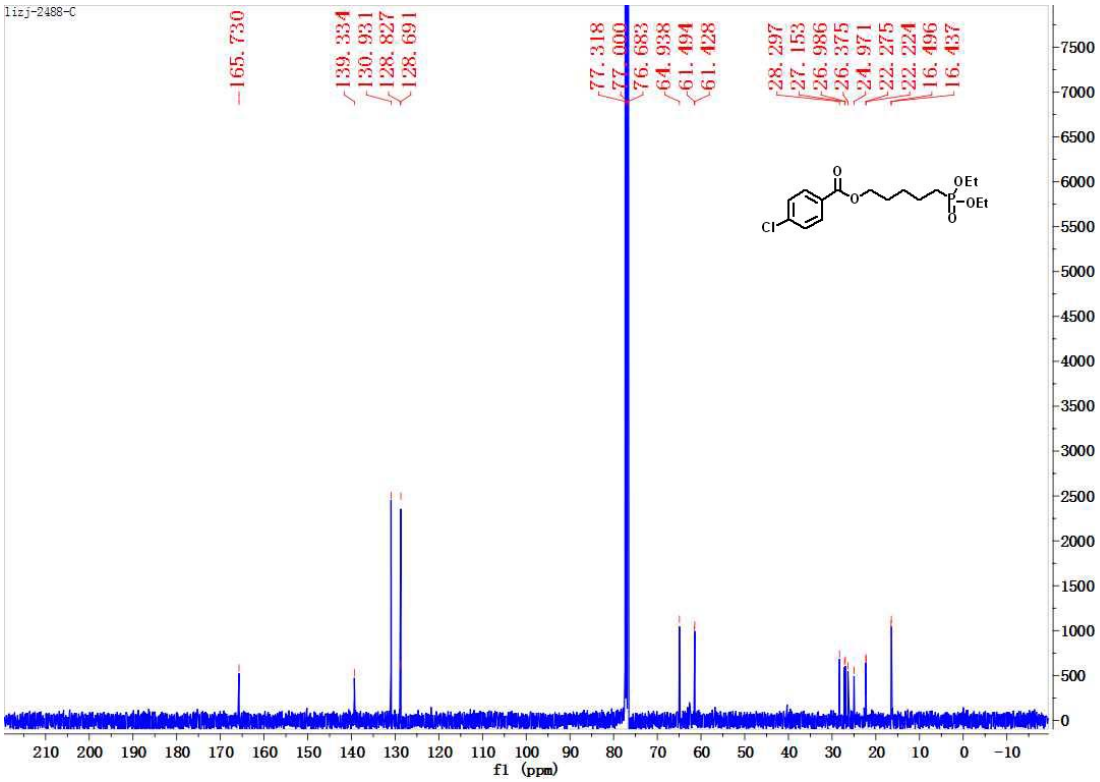


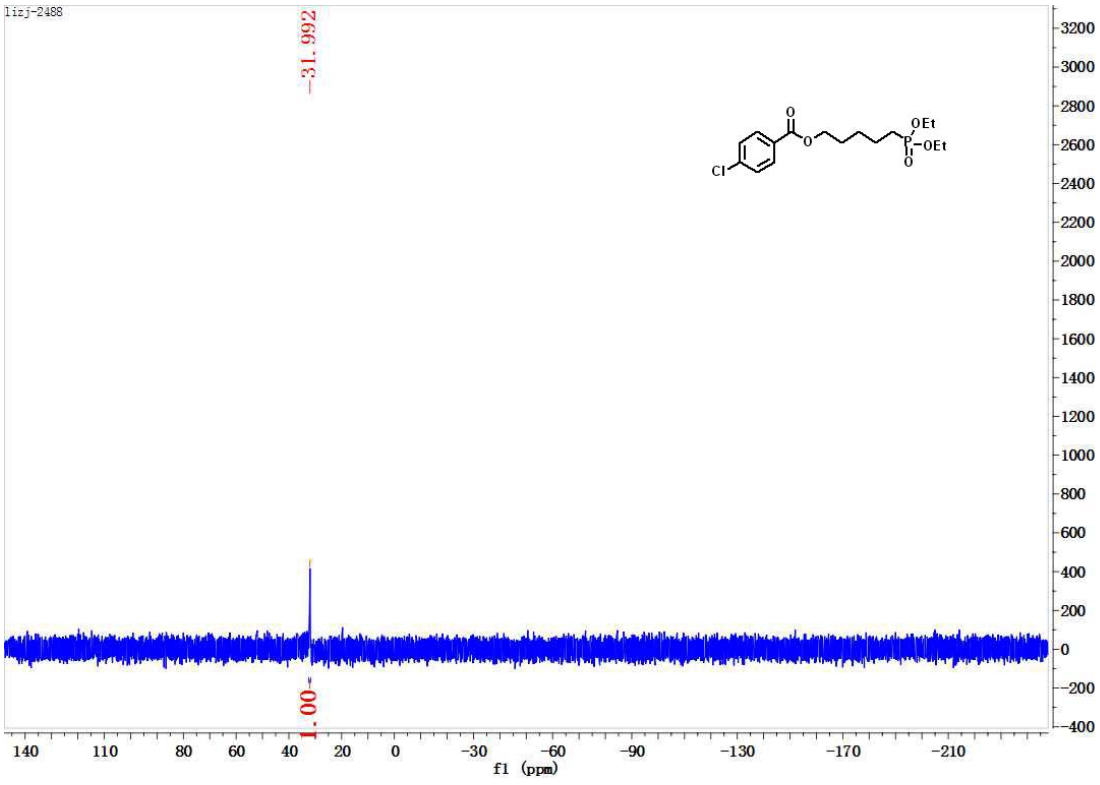
28-^{1}H NMR



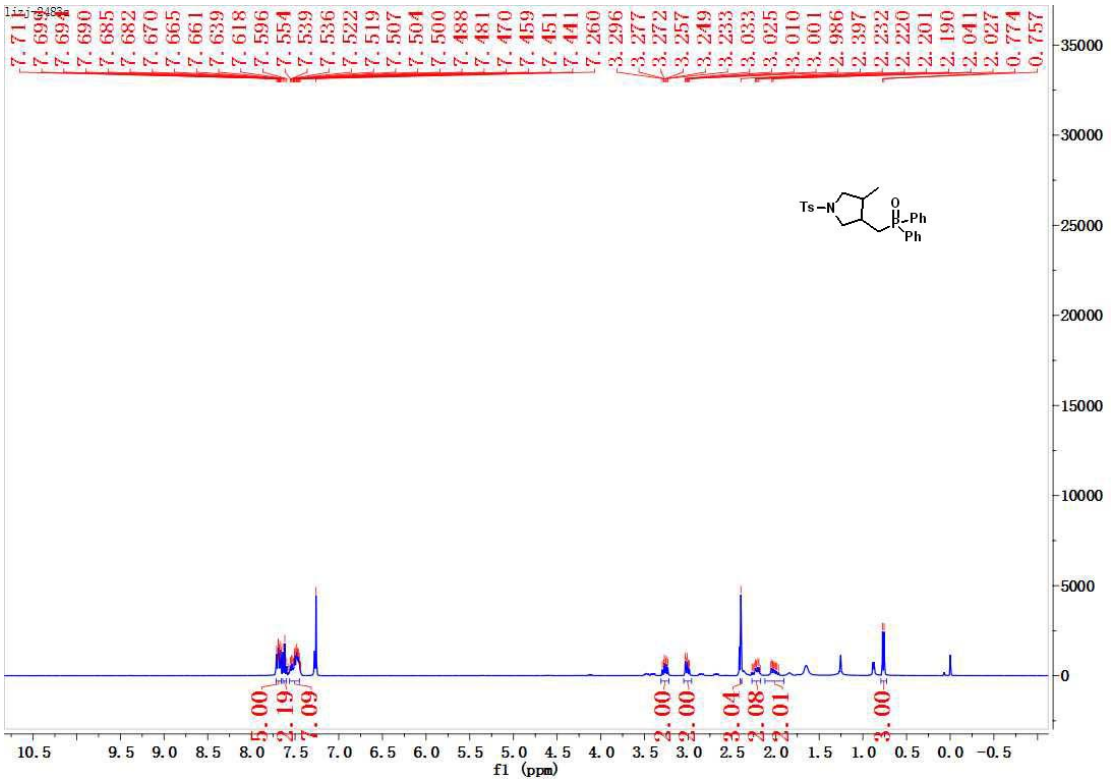
28-^{13}C NMR



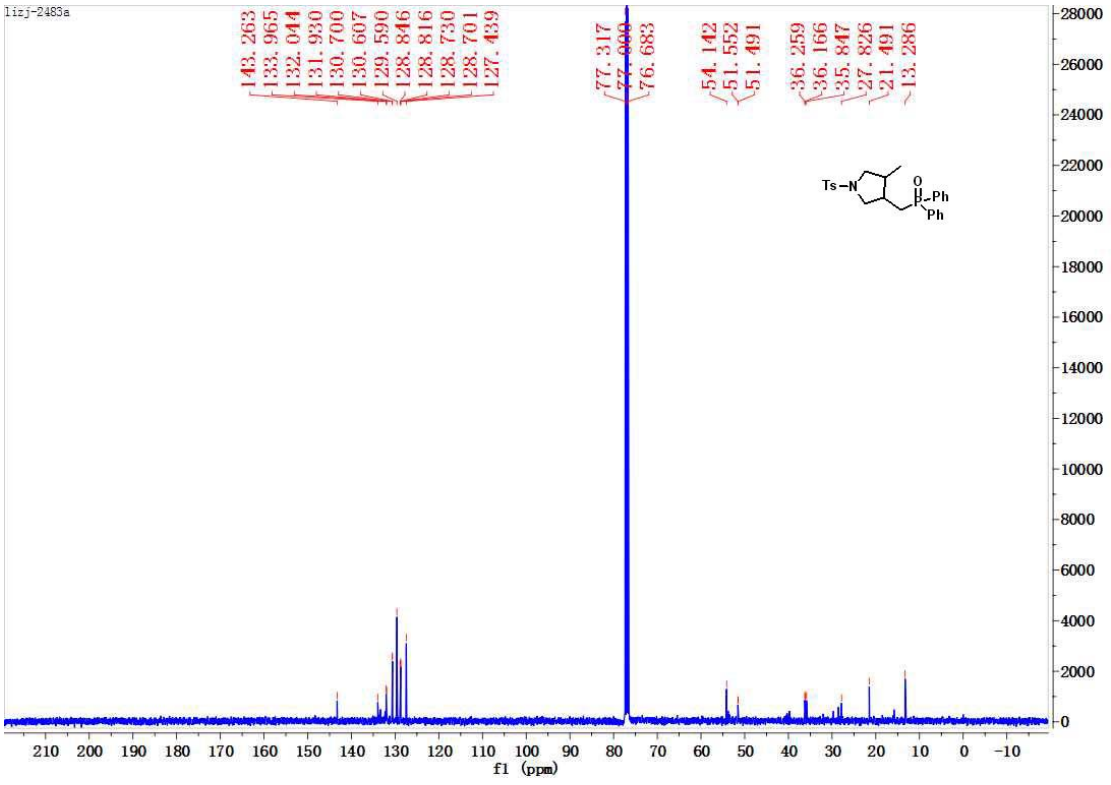
28-^{31}P NMR



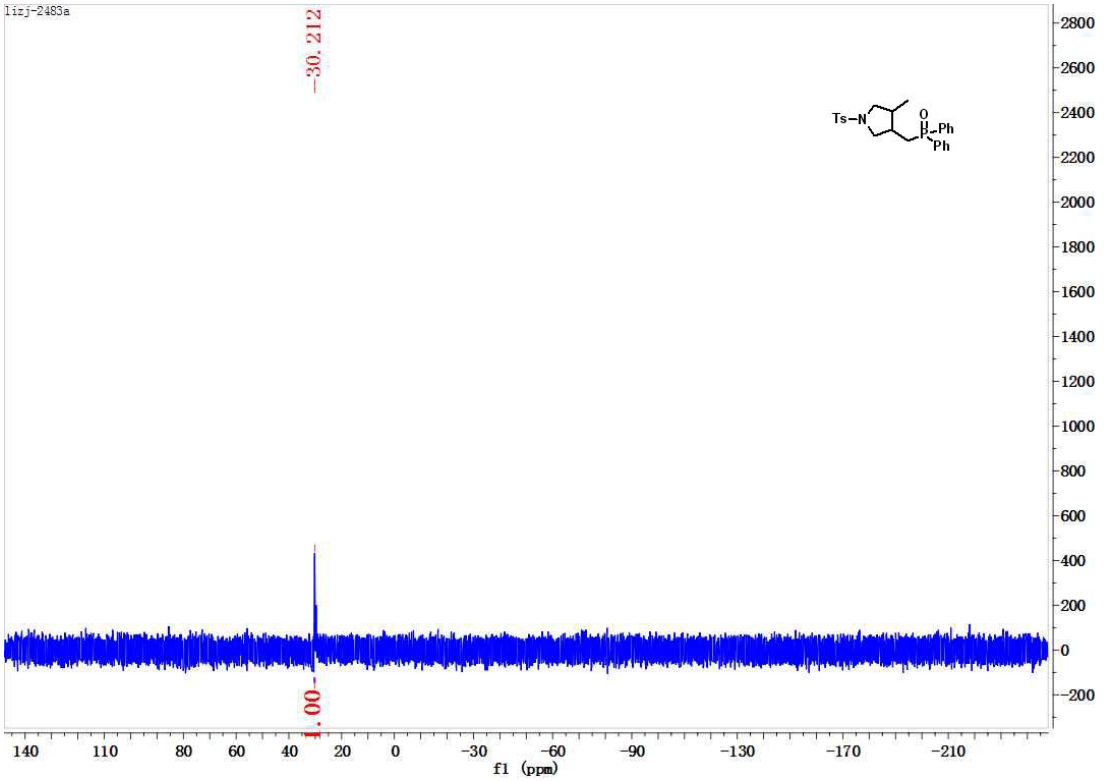
29-^{1}H NMR



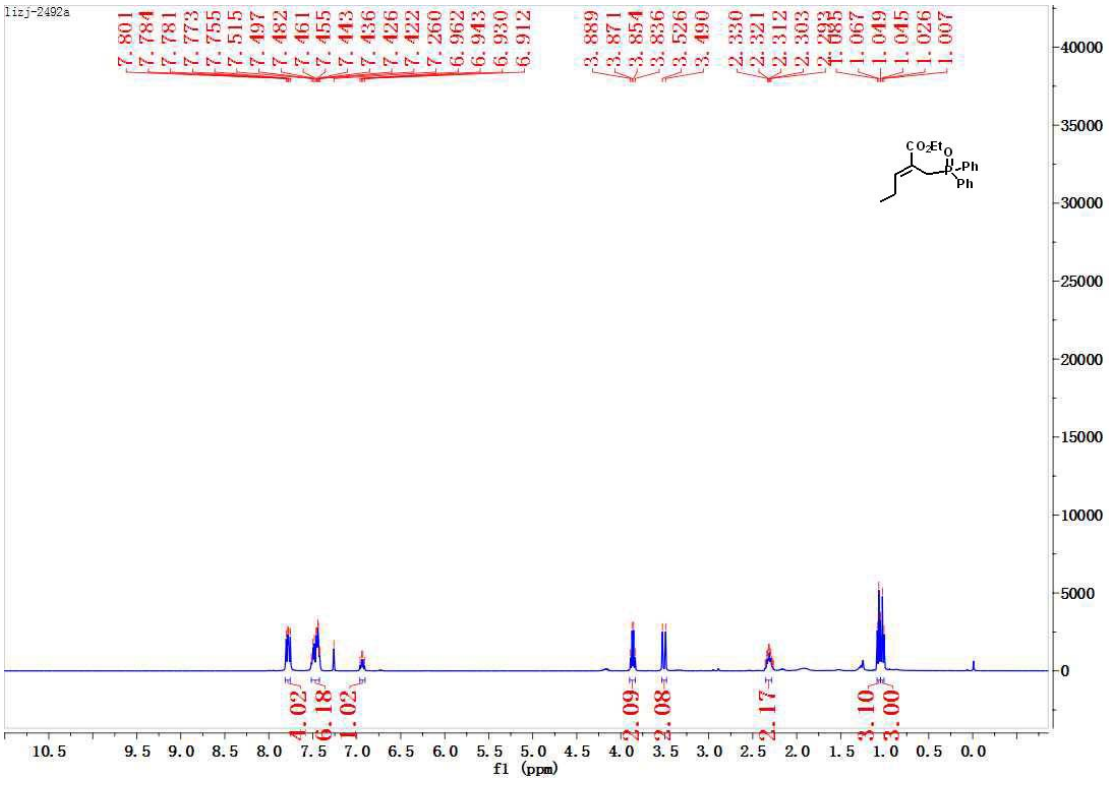
29-^{13}C NMR



29-^{31}P NMR



30-^{1}H NMR



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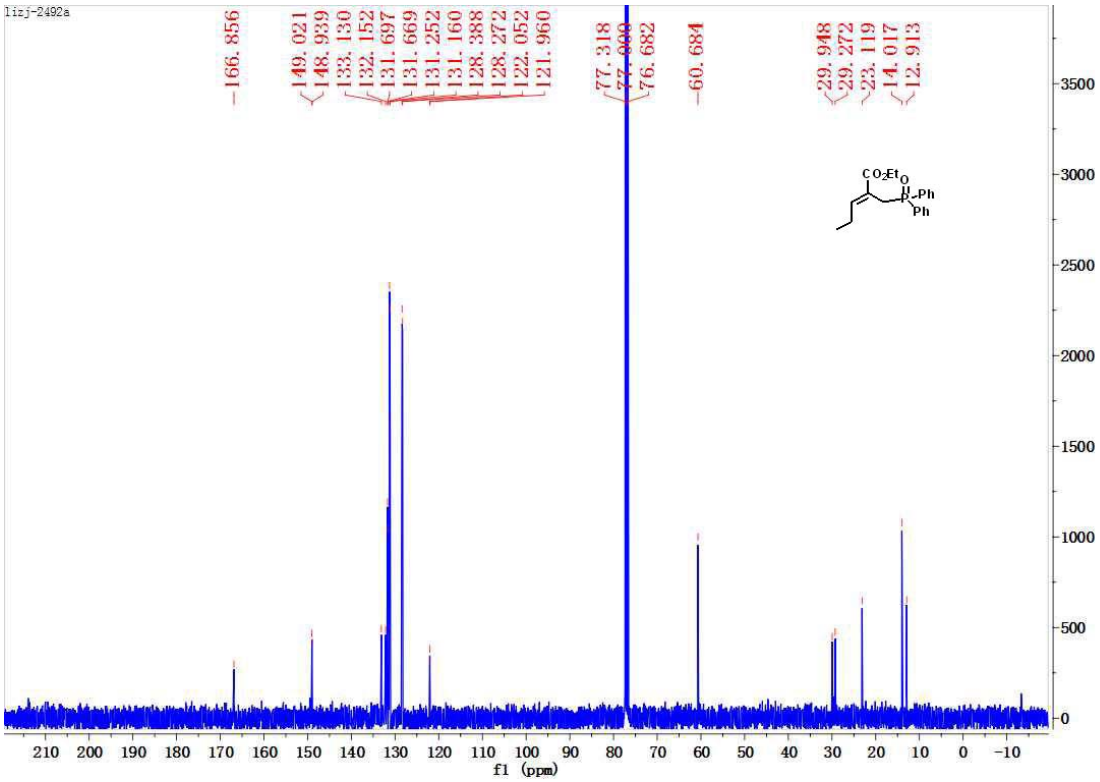
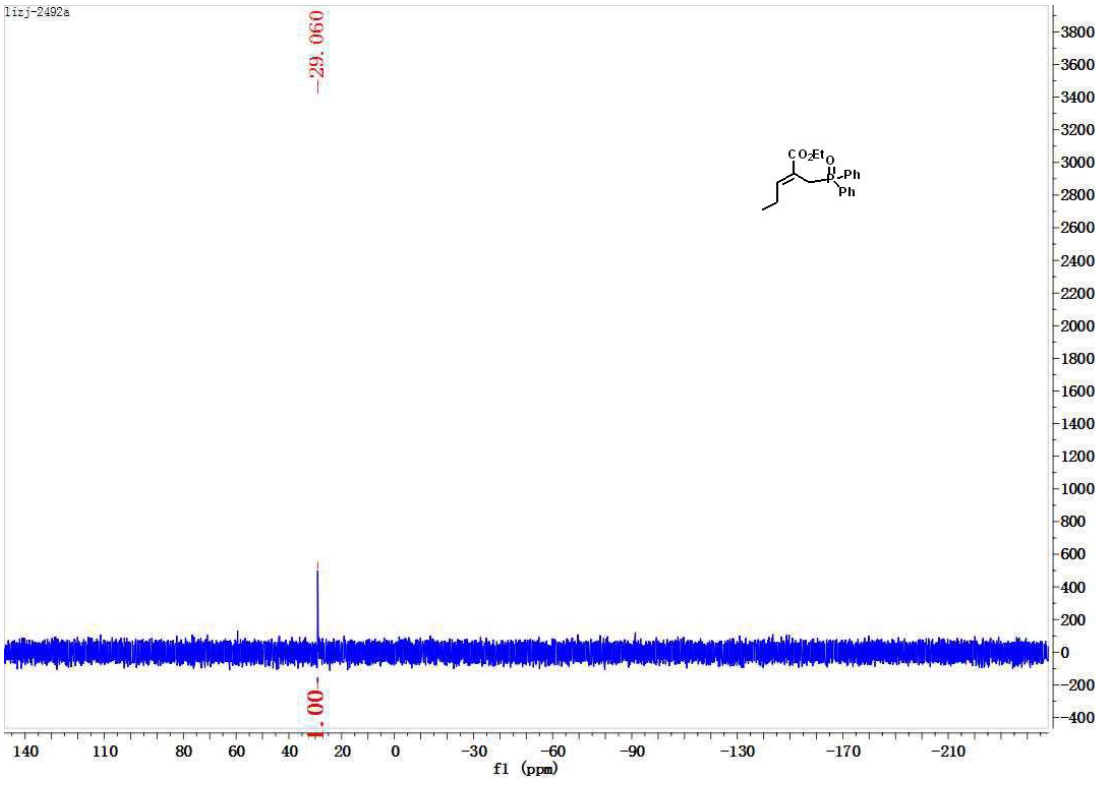
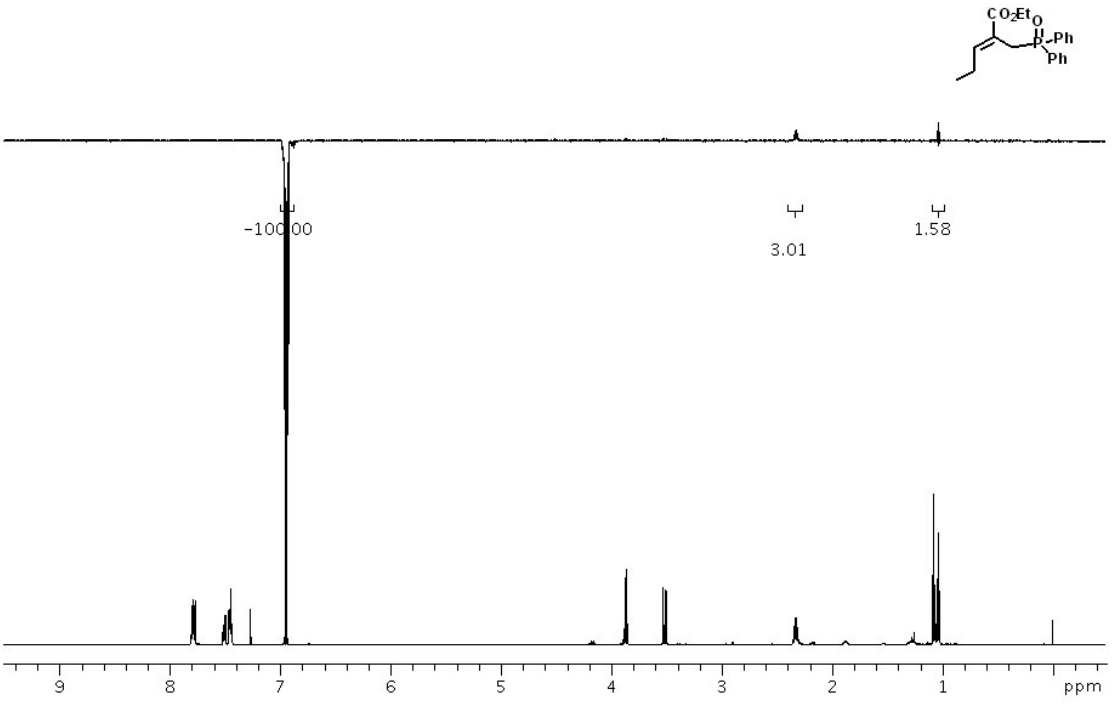


30-^{31}P NMR



30-NOE-1



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