Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Exogenous-oxidant-free electrochemical oxidative C-H phosphonylation with hydrogen evolution

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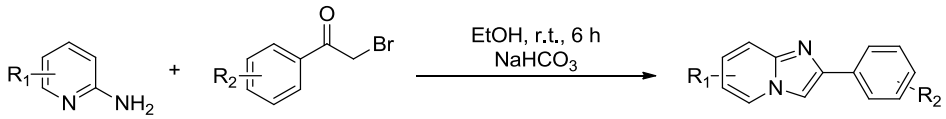
Table of Contents

General Information

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is 60-90 ^{o}C). The acetonitrile used in all reactions was dried with 4 Å molecular sieves. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 162 MHz (^{31}P NMR). Tetramethylsilane was used as the internal standard. All ^{1}H, ^{13}C and ^{31}P NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants were reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument, the mass of molecular ion ($[M+H]^{+}$) was accurately reported. GC-Ms spectra were recorded on a Shimadzu GC-Ms QP2010 Ultra. Hydrogen gas content was analyzed by gas chromatography (7890-II, Tianmei, China, TCD, nitrogen as a carrier gas and 5 Å molecular sieve column, a thermal conductivity detector).

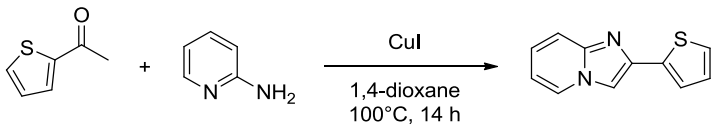
Experimental procedure

1. General procedure for the preparation of imidazo[1,2-a]pyridines:[1]



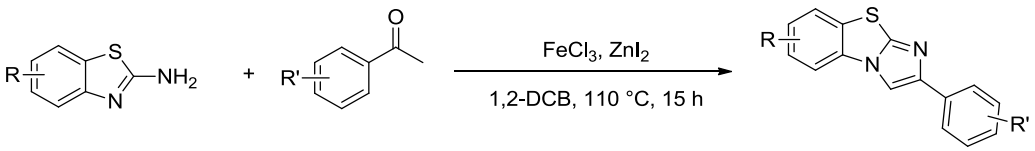
$NaHCO_3$ (15.6 mmol) was added to an ethanol solution containing 2-bromoacetophenones (10.0 mmol) and 2-aminopyridines (12.5 mmol). The reaction mixture was stirred at room temperature for 6 hours. After completion of the reaction, the resulting mixture was diluted with water (30 mL) and then extracted with ether (3 × 20 mL). The combined organic layer was washed with brine (25 mL), dried with anhydrous Na_2SO_4, and concentrated under vacuum to obtain the crude product, which was purified by silica gel column with petroleum ether/ethyl acetate as the eluent to give the analytical pure imidazopyridines.

2. Procedure for the preparation of 2-(thiophen-2-yl)imidazo[1,2-a]pyridine:[2]



An oven-dried flask was charged with 2-aminopyridine (12.0 mmol), 1-(thiophen-2-yl)ethanone (10.0 mmol), CuI (2.0 mmol), and dioxane (30 mL). The mixture was stirred at 100 ^{o}C under air for 14 h. After the completion of the reaction (monitored by TLC), the reaction solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3/1) as eluent to afford pure product.

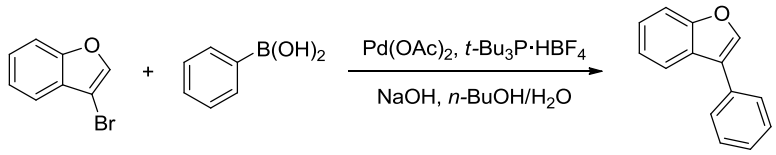
3. General procedure for the preparation of benzo[d]-imidazo[2,1-b]thiazole:[3]



A mixture of benzo[d]thiazol-2-amine (12.0 mmol), acetophenone (10.0 mmol), iron(III) chloride (2.0 mmol) and zinc(II) iodide (1.0 mmol) was stirred in 1,2-dichlorobenzene (1,2-DCB) under 110 ^{o}C for 15 h. After completion (TLC), the reaction mixture was cooled to room temperature and extracted with dichloromethane (10 mL) then washed with brine (5 mL) and dried over

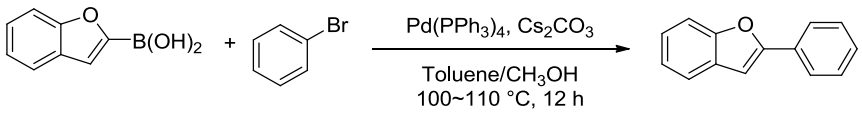
Na_2SO_4. After evaporation of solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (9/1) as eluent.

4. Procedure for the preparation of 3-aryl-benzofuran:[4]



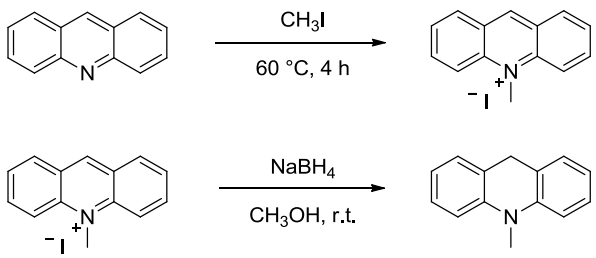
There were $Pd(OAc)_2$ (0.0025 mmol), *t*-Bu_3P•HBF_4 (0.003 mmol), phenylboronic acid (0.60 mmol) and 3-bromobenzofuran (0.50 mmol) and 2.80 mL of *n*-butanol in a nitrogen-filled Schlenk tube. The mixture was pre-stirred at room temperature for 15 min, and then a solution of NaOH (0.85 mmol) in 0.68 mL of degassed H_2O was added to initiate the Suzuki reaction. The reaction mixture was stirred vigorously at room temperature until the 3-bromobenzofuran was fully consumed. At the end of the reaction, the organic phase was separated and the aqueous phase was further extracted with Et_2O (3 mL × 3). The combined organic extracts were concentrated on a rotary evaporator. The resulting residue was purified by silica gel flash chromatography to obtain the desired coupling product. The title compound was isolated as colorless oil, which was separated by flash chromatography with hexane as eluent.

5. Procedure for the preparation of 2-phenylbenzofuran:[5]



A round bottom flask was charged with bromobenzene (2 mmol), benzofuran-2-ylbor-onic acid (3.0 mmol), $Pd(PPh_3)_4$ (0.2 mmol), and Cs_2CO_3 (2.8 mmol), which toluene (16 mL) and CH_3OH (4 mL) were subsequently added into. Then, the reaction mixture was heated in an oil bath at 100–110 ^oC until a TLC analysis of an aliquot indicated a complete conversion of the starting materials (12 h). The reaction mixture was then cooled to 23 ^oC and quenched with saturated NH_4Cl solution. Aqueous phase was extracted with ethyl acetate (10 mL × 3), and the combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, filtrated and concentrated under reduced pressure to afford the crude furan or benzofuran derivatives. Concentration in vacuum followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product.

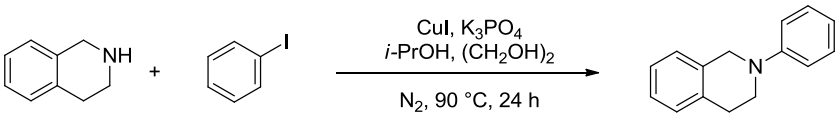
6. Procedure for the preparation of *N*-methyl-acridane 1-H:[6]



Acridine (7.8 mmol) was dissolved in a sealed tube containing excess iodomethane (6 mL). The reaction vessel was heated at 60 ^{o}C for 4 hours and then iodomethane was removed under vacuum, leaving a red solid. The latter was washed with hexane affording *N*-methyl-acridinium iodide as a red solid.

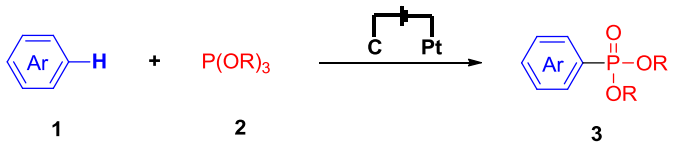
N-methyl-acridinium iodide (2.2 mmol) was dissolved in CH_3OH (10 mL), obtaining a dark red solution. While stirring, $NaBH_4$ (6.5 mmol) was added at room temperature. After a minute, the solution became pale yellow with a whitish precipitate. And then added an excess of water (10 mL). The solid was separated from the solution by filtration and left drying under vacuum at 40 ^{o}C overnight, obtaining *N*-methyl-acridane 1-H was obtained as a grey solid.

7. General procedure for the preparation of *N*-aryl-1,2,3,4-tetrahydroisoquinolines:[7]



Copper(I) iodide (1.0 mmol) and potassium phosphate (20.0 mmol) were put into a 50 mL three-neck flask. The three-neck flask was evacuated and backfilled with argon. 2-Propanol (10.0 mL), ethylene glycol (30.0 mmol), 1,2,3,4-tetrahydro-isoquinoline (10.0 mmol) and aryl iodide (10.0 mmol) were added successively by syringes at room temperature. The reaction mixture was heated at 90 ^{o}C for 24 h and then allowed to cool to room temperature. DCM (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with DCM (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1), and the fraction with R_f = 0.5 was collected to give the desired products.

8. General procedure for the electrochemical oxidative C(sp^2)–H phosphonylation:

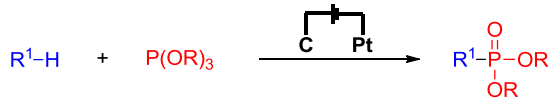


1 2 3

1 (0.3 mmol), **2** (0.6 mmol), $^{n}Bu_4NPF_6$ (0.1 mmol) were combined and added into an oven-dried undivided three-necked bottle which was equipped with a stir bar. The bottle was equipped with graphite rod (ϕ 6 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (10.0 mL) was injected into the tube via syringe. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at 50 ^{o}C for 6 h. When the reaction was finished, the pure product was obtained by flash column chromatography on silica gel.

Figure S1. The experimental setup for electrolysis.

9. General procedure for the electrochemical oxidative C(sp^3)–H phosphonylation:



4 2 5

4 (0.3 mmol), **2** (0.6 mmol), $^{n}Bu_4NPF_6$ (0.1 mmol) were combined and added into an oven-dried undivided three-necked bottle which was equipped with a stir bar. The bottle was equipped with graphite rod (ϕ 6 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (10.0 mL) was injected into the tube via syringe. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at 70 ^{o}C for 6 h. When the reaction was finished, the pure product was obtained by flash column chromatography on silica gel.

10. Procedure for cyclic voltammetry (CV):

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 10.0 mL of acetonitrile containing $^{n}Bu_4NPF_6$ (0.1 mmol) was poured into the electrochemical cell in all experiments. The scan rate was 0.1 V/s, ranging from 0 V to 2.5 V.

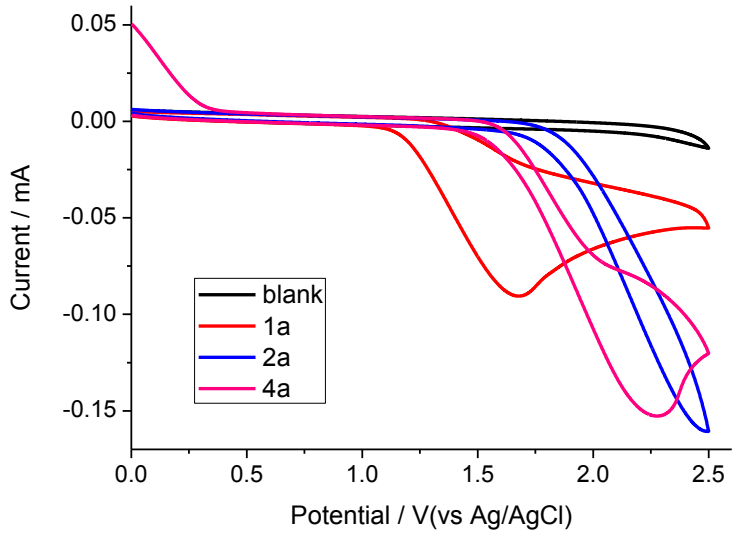
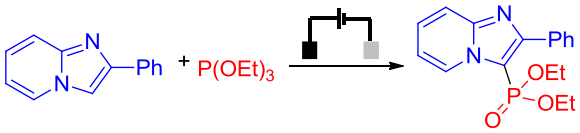


Figure S2. Cyclic voltammograms of **1a** (0.1 mmol), **2a** (0.1 mmol), and **4a** (0.1 mmol).

11. Conditions screening:

Table S1. Screening of electric current and time [a]

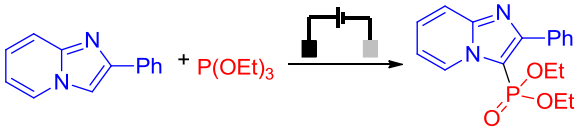


1a **2a** **3a**

Entry	I (mA)	time (h)	Yield (%) [b]
1	2	12	49
2	3	8	57
3	**4**	**6**	**70**
4	5	4.8	64
5	6	4	58
6	8	3	57

[a] Reaction conditions: carbon rod anode, platinum plate cathode, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), $^{n}Bu_4NBF_4$ (0.1 mmol), CH_3CN (10 mL), 50 °C. [b] Yields were determined by ^{31}P NMR using PPh_3 as the internal standard.

Table S2. Screening of electrolyte dosage [a]

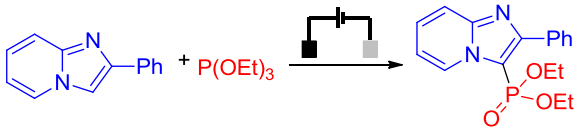


1a **2a** **3a**

Entry	$^{n}Bu_4NPF_6$ (mmol)	Yield (%) [b]
1	0.05	58
2	**0.10**	**77**
3	0.15	68

[a] Reaction conditions: carbon rod anode, platinum plate cathode, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), CH_3CN (10 mL), 50 °C, 4 mA, 6 h. [b] Yields were determined by ^{31}P NMR using PPh_3 as the internal standard.

Table S3. Screening of temperature [a]



1a **2a** **3a**

Entry	Temperature (°C)	Yield (%) [b]
1	45	60
2	**50**	**77**
3	55	74

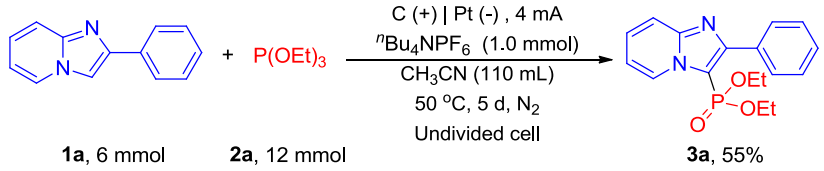
[a] Reaction conditions: carbon rod anode, platinum plate cathode, undivided cell, **1a** (0.3 mmol), **2a** (0.6 mmol), $^{n}Bu_4NPF_6$ (0.1 mmol), CH_3CN (10 mL), 4 mA, 6 h. [b] Yields were determined by ^{31}P NMR using PPh_3 as the internal standard.

12. Procedure for gram-scale reaction:

12.1 The electrochemical oxidative C(sp^2)–H phosphonylation:

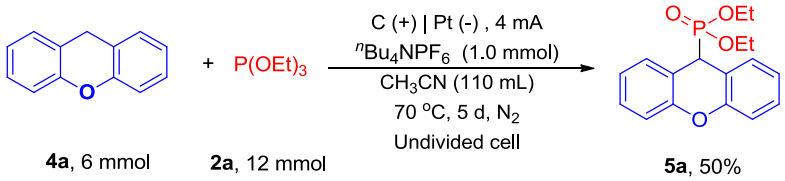
In an oven-dried three-necked flask equipped with a stir bar, **1a** (6.0 mmol), **2a** (12.0 mmol), $^{n}Bu_4NPF_6$ (1.0 mmol) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (110 mL) was injected into the tube via syringe. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at 50 °C

for 5 d. When the reaction was finished, the pure product was obtained by flash column chromatography on silica gel.

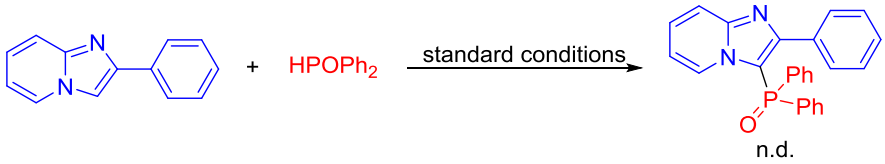


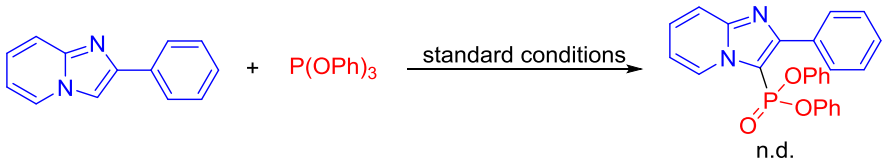
12.2 The electrochemical oxidative C(sp^3)–H phosphonylation:

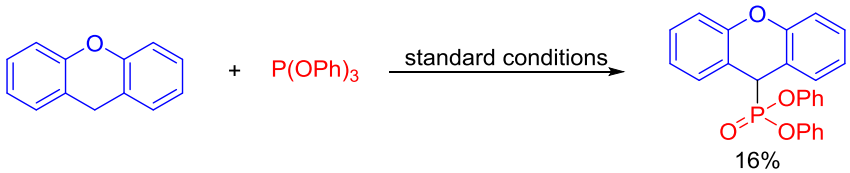
In an oven-dried three-necked flask equipped with a stir bar, **4a** (6.0 mmol), **2a** (12.0 mmol), $^{n}Bu_4NPF_6$ (1.0 mmol) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, CH_3CN (110 mL) was injected into the tube via syringe. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at 70 °C for 5 d. When the reaction was finished, the pure product was obtained by flash column chromatography on silica gel.

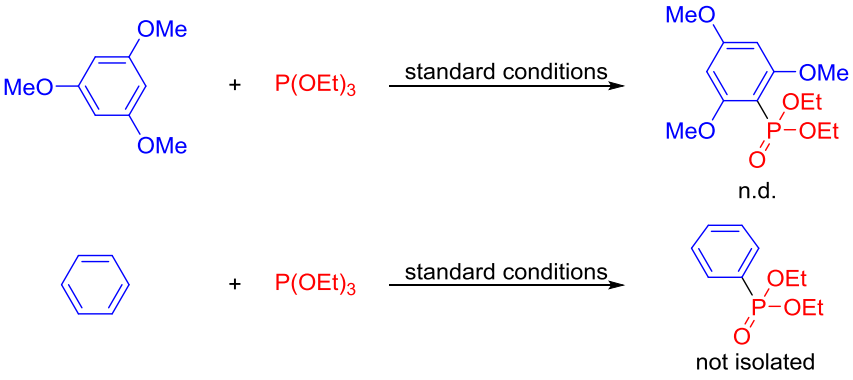


13. Unsuccessful substrates:

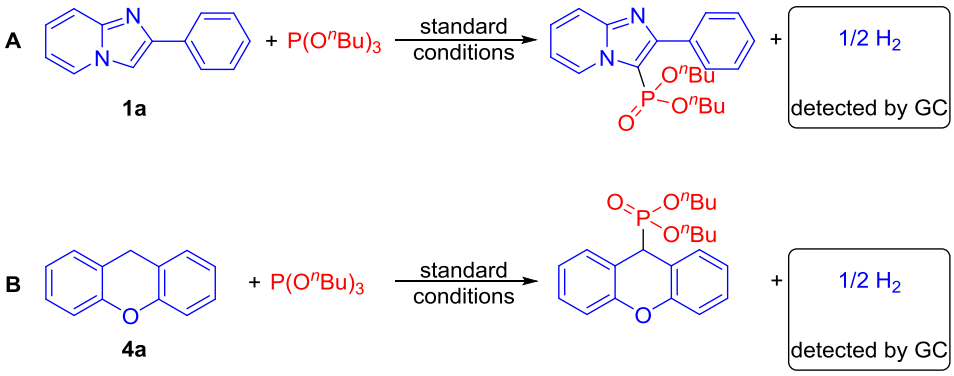








14. Monitoring the atmosphere by GC



When reaction was finished, the gas mixture was analyzed by GC and H_2 could be detected.

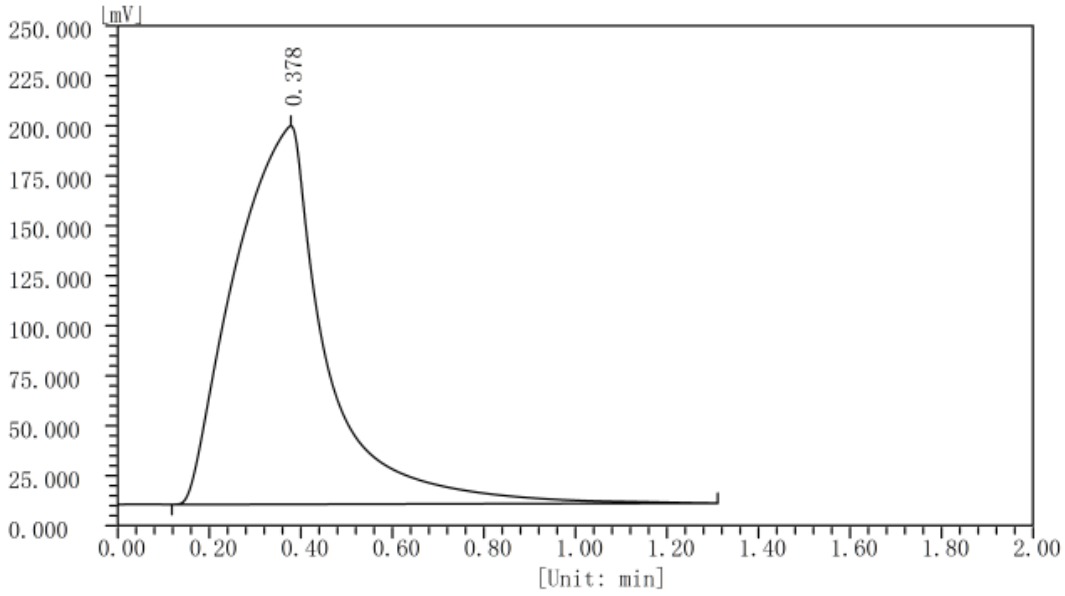


Figure S3. Monitoring the atmosphere by GC (Reaction A)

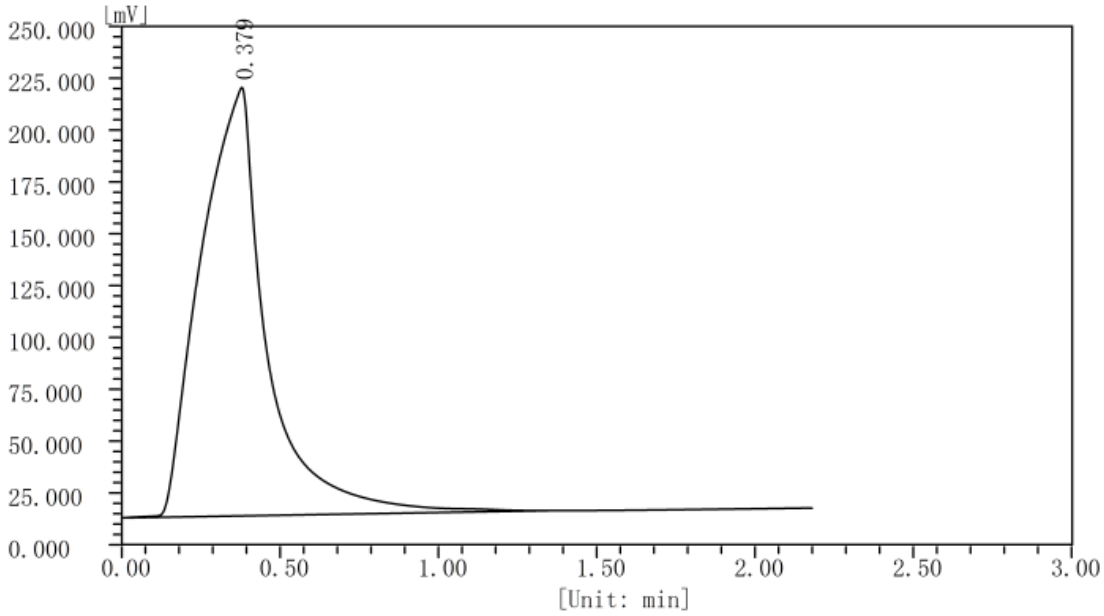
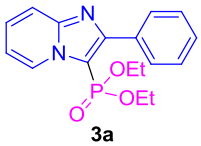


Figure S4. Monitoring the atmosphere by GC (Reaction B)

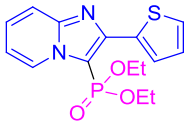
Detail descriptions for products



3a

Diethyl (2-phenylimidazo[1,2-*a*]pyridin-3-yl)phosphonate (3a)[8]

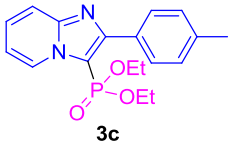
Colorless oil was obtained in 70% isolated yield, 68.9 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 7.0 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.36 (m, 4H), 6.96 (t, *J* = 6.9 Hz, 1H), 4.18 – 4.05 (m, 2H), 3.98 – 3.86 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.86 (d, J_{C-P} = 17.6 Hz), 148.07 (d, J_{C-P} = 14.4 Hz), 133.53, 129.66, 128.76, 128.35, 127.81, 127.46, 117.28, 113.42, 107.27 (d, J_{C-P} = 227.0 Hz), 62.36 (d, J_{C-P} = 5.0 Hz), 15.81 (d, J_{C-P} = 7.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.09.



3b

Diethyl (2-(thiophen-2-yl)imidazo[1,2-*a*]pyridin-3-yl)phosphonate (3b)

White solid was obtained in 61% isolated yield, 61.1 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 7.0 Hz, 1H), 7.91 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.44 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.94 (td, *J* = 6.9, 1.0 Hz, 1H), 4.24 – 4.15 (m, 2H), 4.07 – 3.97 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.45 (d, J_{C-P} = 17.0 Hz), 147.88 (d, J_{C-P} = 14.3 Hz), 135.93, 128.59, 128.40, 127.83, 127.78, 127.61, 117.03, 113.54, 105.37 (d, J_{C-P} = 225.2 Hz), 62.52 (d, J_{C-P} = 4.6 Hz), 16.00 (d, J_{C-P} = 7.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.86; **HRMS (ESI)**: Calculated for $C_{15}H_{18}N_2O_3PS$ $[M+H]^+$: 337.0770; Found: 337.0765.

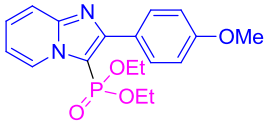


3c

Diethyl (2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)phosphonate (3c)

White solid was obtained in 66% isolated yield, 70.4 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 7.0 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 2H), 6.94 (t, *J* = 6.5 Hz, 1H), 4.17 – 4.06 (m, 2H), 3.97 – 3.87 (m, 2H), 2.41 (s, 3H),

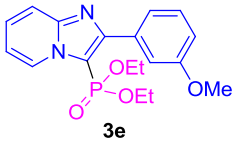
1.16 (t, J = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ154.94 (d, $J_{C\text{-}P}$ = 17.6 Hz), 147.93 (d, $J_{C\text{-}P}$ = 14.4 Hz), 138.47, 130.50, 129.38, 128.38, 128.16, 127.20, 117.04, 113.12, 106.74 (d, $J_{C\text{-}P}$ = 226.9 Hz), 62.15 (d, $J_{C\text{-}P}$ = 4.9 Hz), 21.12, 15.69 (d, $J_{C\text{-}P}$ = 7.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.33; **HRMS (ESI)**: Calculated for $C_{18}H_{22}N_2O_3P$ $[M+H]^+$: 345.1363; Found: 345.1372.



3d

Diethyl (2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)phosphonate (3d)

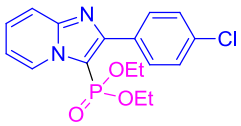
White solid was obtained in 55% isolated yield, 59.2 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.19 (d, J = 7.0 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.73 (d, J = 8.9 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.01 – 6.92 (m, 3H), 4.17 – 4.08 (m, 2H), 3.99 – 3.89 (m, 2H), 3.87 (s, 3H), 1.17 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.22, 154.60 (d, $J_{C\text{-}P}$ = 17.8 Hz), 147.97 (d, $J_{C\text{-}P}$ = 14.3 Hz), 131.03, 128.38, 127.56, 125.79, 117.06, 113.37, 113.33, 106.52 (d, $J_{C\text{-}P}$ = 226.8 Hz), 62.37 (d, $J_{C\text{-}P}$ = 4.9 Hz), 55.25, 15.92 (d, $J_{C\text{-}P}$ = 7.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.42; **HRMS (ESI)**: Calculated for $C_{18}H_{22}N_2O_4P$ $[M+H]^+$: 361.1312; Found: 361.1302.



3e

Diethyl (2-(3-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)phosphonate (3e)

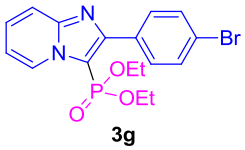
Colorless oil was obtained in 65% isolated yield, 67.4 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.22 (d, J = 7.0 Hz, 1H), 7.73 (dd, J = 9.0, 0.6 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.42 – 7.33 (m, 2H), 7.01 – 6.93 (m, 2H), 4.19 – 4.09 (m, 2H), 4.01 – 3.91 (m, 2H), 3.88 (s, 3H), 1.17 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.95, 154.56 (d, $J_{C\text{-}P}$ = 17.5 Hz), 147.88 (d, $J_{C\text{-}P}$ = 14.4 Hz), 134.64, 128.70, 128.21, 127.36, 122.02, 117.13, 114.97, 114.52, 113.31, 107.12 (d, $J_{C\text{-}P}$ = 226.9 Hz), 62.26 (d, $J_{C\text{-}P}$ = 5.0 Hz), 55.10, 15.70 (d, $J_{C\text{-}P}$ = 7.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.06; **HRMS (ESI)**: Calculated for $C_{18}H_{22}N_2O_4P$ $[M+H]^+$: 361.1312; Found: 361.1316.



3f

Diethyl (2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)phosphonate (3f)

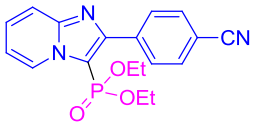
White solid was obtained in 63% isolated yield, 68.5 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 7.0 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.45 – 7.38 (m, 3H), 6.97 (t, *J* = 6.9 Hz, 1H), 4.23 – 4.09 (m, 2H), 4.00 – 3.89 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ153.52 (d, J_{C-P} = 17.6 Hz), 148.03 (d, J_{C-P} = 14.3 Hz), 134.99, 131.96, 131.03, 128.41, 128.13, 127.78, 117.32, 113.68, 107.48 (d, J_{C-P} = 226.7 Hz), 62.51 (d, J_{C-P} = 5.0 Hz), 15.96 (d, J_{C-P} = 6.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.79; **HRMS (ESI)**: Calculated for $C_{17}H_{19}ClN_2O_3P$ $[M+H]^+$: 365.0816; Found: 365.0822.



3g

Diethyl (2-(4-bromophenyl)imidazo[1,2-*a*]pyridin-3-yl)phosphonate (3g)

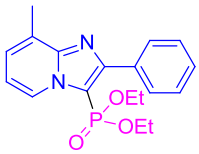
White solid was obtained in 67% isolated yield, 81.6 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 6.7 Hz, 1H), 7.83 – 7.70 (m, 3H), 7.59 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.37 (m, 1H), 6.98 (t, *J* = 6.7 Hz, 1H), 4.21 – 4.07 (m, 2H), 4.01 – 3.88 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ153.61 (d, J_{C-P} = 17.6 Hz), 148.07 (d, J_{C-P} = 14.3 Hz), 132.46, 131.25, 131.03, 128.34, 127.70, 123.26, 117.31, 113.62, 107.37 (d, J_{C-P} = 226.6 Hz), 62.47 (d, J_{C-P} = 5.0 Hz), 15.93 (d, J_{C-P} = 7.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.77; **HRMS (ESI)**: Calculated for $C_{17}H_{19}BrN_2O_3P$ $[M+H]^+$: 409.0311; Found: 409.0314.



3h

Diethyl (2-(4-cyanophenyl)imidazo[1,2-*a*]pyridin-3-yl)phosphonate (3h)

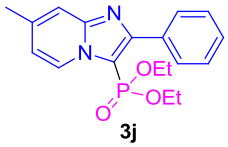
White solid was obtained in 46% isolated yield, 48.8 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 7.0 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.81 – 7.72 (m, 3H), 7.50 – 7.44 (m, 1H), 7.03 (t, *J* = 6.9 Hz, 1H), 4.25 – 4.12 (m, 2H), 4.04 – 3.91 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.26 (d, J_{C-P} = 17.4 Hz), 147.96 (d, J_{C-P} = 14.1 Hz), 137.88, 131.68, 130.44, 128.42, 128.27, 118.76, 117.49, 114.19, 112.41, 108.52 (d, J_{C-P} = 226.2 Hz), 62.74 (d, J_{C-P} = 5.1 Hz), 15.99 (d, J_{C-P} = 6.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.00; **HRMS (ESI)**: Calculated for $C_{18}H_{19}N_3O_3P$ $[M+H]^+$: 356.1159; Found: 356.1146.



3i

Diethyl (8-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)phosphonate (3i)

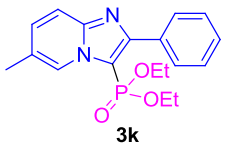
White solid was obtained in 67% isolated yield, 69.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 6.9 Hz, 1H), 7.85 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.17 (d, *J* = 6.9 Hz, 1H), 6.86 (t, *J* = 6.9 Hz, 1H), 4.15 – 4.04 (m, 2H), 3.96 – 3.85 (m, 2H), 2.68 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.39 (d, J_{C-P} = 17.6 Hz), 148.36 (d, J_{C-P} = 14.2 Hz), 133.83, 129.68, 128.49, 127.69, 127.22, 126.07, 125.89, 113.29, 107.52 (d, J_{C-P} = 226.6 Hz), 62.17 (d, J_{C-P} = 5.0 Hz),17.09, 15.72 (d, J_{C-P} = 7.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.34; **HRMS (ESI)**: Calculated for $C_{18}H_{22}N_2O_3P$ $[M+H]^+$: 345.1363; Found: 345.1372.



3j

Diethyl (7-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)phosphonate (3j)

Colorless oil was obtained in 58% isolated yield, 60.1 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 7.1 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.49 (s, 1H), 7.47 – 7.40 (m, 3H), 6.79 (dd, *J* = 7.1, 1.7 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.96 – 3.85 (m, 2H), 2.45 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.93 (d, J_{C-P} = 17.7 Hz), 148.54 (d, J_{C-P} = 14.3 Hz), 138.75, 133.67, 129.60, 128.66, 127.77, 127.42, 115.97, 115.78, 106.47 (d, J_{C-P} = 227.9 Hz), 62.27 (d, J_{C-P} = 5.0 Hz), 21.24, 15.80 (d, J_{C-P} = 7.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.41; **HRMS (ESI)**: Calculated for $C_{18}H_{22}N_2O_3P$ $[M+H]^+$: 345.1363; Found: 345.1372.

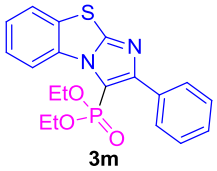


3k

Diethyl (6-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)phosphonate (3k)[8]

White solid was obtained in 62% isolated yield, 62.7 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.85 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.48 – 7.37 (m, 3H), 7.24 (dd, *J* = 9.1, 1.2 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.97 – 3.85 (m, 2H), 2.40 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.61 (d, J_{C-P} = 17.7 Hz), 147.10 (d, J_{C-P} = 14.4 Hz), 133.69, 130.54,

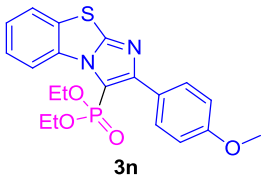
129.62, 128.66, 127.78, 126.06, 123.32, 116.54, 106.81 (d, $J_{C\text{-}P}$ = 227.2 Hz), 62.31 (d, $J_{C\text{-}P}$ = 5.0 Hz), 18.36, 15.81 (d, $J_{C\text{-}P}$ = 7.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.42.



3m

Diethyl (2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazol-3-yl)phosphonate (3m)[9]

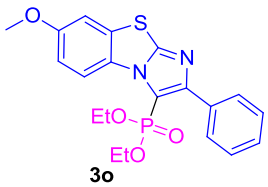
White solid was obtained in 85% isolated yield, 98.5 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.69 (m, 3H), 7.54 – 7.48 (m, 1H), 7.45 – 7.35 (m, 4H), 4.22 – 4.10 (m, 2H), 3.98 – 3.88 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.66 (d, $J_{C\text{-}P}$ = 18.7 Hz), 152.66 (d, $J_{C\text{-}P}$ = 14.8 Hz), 133.66, 133.39, 129.85, 128.66, 127.63, 126.41, 125.15, 123.79, 116.64, 111.21 (d, $J_{C\text{-}P}$ = 228.8 Hz), 62.60 (d, $J_{C\text{-}P}$ = 5.4 Hz), 15.80 (d, $J_{C\text{-}P}$ = 7.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.43.



3n

Diethyl (2-(4-methoxyphenyl)benzo[*d*]imidazo[2,1-*b*]thiazol-3-yl)phosphonate (3n)

White solid was obtained in 58% isolated yield, 71.4 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 3H), 7.53 – 7.46 (m, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.21 – 4.10 (m, 2H), 4.01 – 3.90 (m, 2H), 3.86 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.08, 157.70 (d, $J_{C\text{-}P}$ = 18.9 Hz), 152.64 (d, $J_{C\text{-}P}$ = 14.9 Hz), 133.50, 131.19, 129.80, 126.39, 126.11, 125.06, 123.79, 116.62, 113.11, 110.50 (d, $J_{C\text{-}P}$ = 228.8 Hz), 62.55 (d, $J_{C\text{-}P}$ = 5.3 Hz), 55.24, 15.92 (d, $J_{C\text{-}P}$ = 7.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.76; **HRMS (ESI)**: Calculated for $C_{20}H_{22}N_2O_4PS$ $[M+H]^+$: 417.1032; Found: 417.1035.

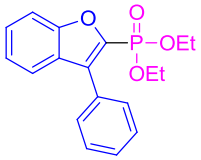


3o

Diethyl (7-methoxy-2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazol-3-yl)phosphonate (3o)

White solid was obtained in 79% isolated yield, 98.1 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 9.2 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.05

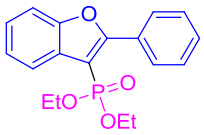
(dd, J = 9.2, 2.5 Hz, 1H), 4.19 – 4.09 (m, 2H), 3.99 – 3.90 (m, 2H), 3.85 (s, 3H), 1.15 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.09, 156.94 (d, J_{C-P} = 18.8 Hz), 151.85 (d, J_{C-P} = 15.0 Hz), 133.60, 131.10, 129.70, 128.46, 127.52, 127.43, 117.23, 113.49, 110.80 (d, J_{C-P} = 228.7 Hz), 107.76, 62.46 (d, J_{C-P} = 5.4 Hz), 55.63 (d, J_{C-P} = 4.7 Hz), 15.72 (d, J_{C-P} = 6.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 7.56; **HRMS (ESI)**: Calculated for $C_{20}H_{22}N_2O_4PS$ $[M+H]^+$: 417.1032; Found: 417.1043.



3p

Diethyl (3-phenylbenzofuran-2-yl)phosphonate (3p)[10]

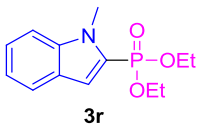
Colorless oil was obtained in 51% isolated yield, 50.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 4H), 7.52 – 7.41 (m, 4H), 7.33 – 7.26 (m, 1H), 4.22 – 4.11 (m, 2H), 4.11 – 4.00 (m, 2H), 1.21 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.27 (d, J_{C-P} = 11.8 Hz), 141.22 (d, J_{C-P} = 236.2 Hz), 132.08 (d, J_{C-P} = 23.2 Hz), 130.26, 129.77 (d, J_{C-P} = 1.0 Hz), 128.38, 128.29, 127.43 (d, J_{C-P} = 12.1 Hz), 127.08, 123.51 (d, J_{C-P} = 1.0 Hz), 121.55, 112.12 (d, J_{C-P} = 1.2 Hz), 62.98 (d, J_{C-P} = 5.4 Hz), 15.97 (d, J_{C-P} = 6.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.31.



3q

Diethyl (2-phenylbenzofuran-3-yl)phosphonate (3q)[10]

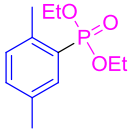
Colorless oil was obtained in 33% isolated yield, 32.1 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 – 7.97 (m, 3H), 7.58 – 7.52 (m, 1H), 7.51 – 7.44 (m, 3H), 7.40 – 7.30 (m, 2H), 4.22 – 4.11 (m, 2H), 4.11 – 4.00 (m, 2H), 1.24 (t, J = 7.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.63 (d, J_{C-P} = 25.9 Hz), 154.05 (d, J_{C-P} = 15.1 Hz), 130.17, 129.54 (d, J_{C-P} = 11.6 Hz), 129.42, 129.13 (d, J_{C-P} = 0.6 Hz), 128.19, 125.18, 123.79, 122.44, 111.01, 102.77 (d, J_{C-P} = 211.3 Hz), 62.12 (d, J_{C-P} = 5.2 Hz), 16.10 (d, J_{C-P} = 6.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 13.46.



3r

Diethyl (1-methyl-1*H*-indol-2-yl)phosphonate (3r)[8]

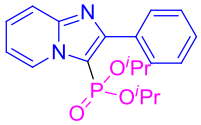
Colorless oil was obtained in 37% isolated yield, 28.6 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.19 – 7.14 (m, 2H), 4.25 – 4.17 (m, 2H), 4.17 – 4.09 (m, 2H), 3.95 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.01 (d, $J_{C\text{-}P}$ = 12.3 Hz), 126.45 (d, $J_{C\text{-}P}$ = 15.6 Hz), 126.15 (d, $J_{C\text{-}P}$ = 217.6 Hz), 124.47, 122.09 (d, $J_{C\text{-}P}$ = 1.3 Hz), 120.21 (d, $J_{C\text{-}P}$ = 0.9 Hz), 114.03 (d, $J_{C\text{-}P}$ = 17.4 Hz), 109.91 (d, $J_{C\text{-}P}$ = 2.2 Hz), 62.58 (d, $J_{C\text{-}P}$ = 5.3 Hz), 31.75, 16.25 (d, $J_{C\text{-}P}$ = 6.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 10.05.



3s

Diethyl (2,5-dimethylphenyl)phosphonate (3s)[11]

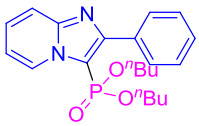
Colorless oil was obtained in 38% isolated yield, 27.6 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 14.8, 2.0 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 7.7, 5.8 Hz, 1H), 4.21 – 4.01 (m, 4H), 2.51 (s, 3H), 2.34 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.49 (d, $J_{C\text{-}P}$ = 9.9 Hz), 134.90 (d, $J_{C\text{-}P}$ = 14.8 Hz), 134.53 (d, $J_{C\text{-}P}$ = 10.5 Hz), 133.15 (d, $J_{C\text{-}P}$ = 3.2 Hz), 131.12 (d, $J_{C\text{-}P}$ = 15.8 Hz), 126.25 (d, $J_{C\text{-}P}$ = 182.6 Hz), 61.76 (d, $J_{C\text{-}P}$ = 5.4 Hz), 20.74, 20.63 (d, $J_{C\text{-}P}$ = 3.5 Hz), 16.28 (d, $J_{C\text{-}P}$ = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.07.



3t

Diisopropyl (2-phenylimidazo[1,2-*a*]pyridin-3-yl)phosphonate (3t)[8]

White solid was obtained in 75% isolated yield, 80.9 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 7.0 Hz, 1H), 7.94 (d, *J* = 6.6 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.47 – 7.34 (m, 4H), 6.94 (t, *J* = 6.9 Hz, 1H), 4.70 – 4.56 (m, 2H), 1.33 (d, *J* = 6.2 Hz, 6H), 1.02 (d, *J* = 6.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.41 (d, $J_{C\text{-}P}$ = 17.5 Hz), 147.83 (d, $J_{C\text{-}P}$ = 14.4 Hz), 133.83, 129.81, 128.64, 128.48, 127.77, 127.22, 117.22, 113.23, 108.53 (d, $J_{C\text{-}P}$ = 227.6 Hz), 71.58 (d, $J_{C\text{-}P}$ = 4.8 Hz), 23.91, 23.32; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 5.71.

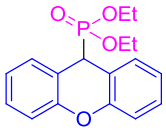


3u

Dibutyl (2-phenylimidazo[1,2-*a*]pyridin-3-yl)phosphonate (3u)

Colorless oil was obtained in 74% isolated yield, 84.7 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.22 (d,

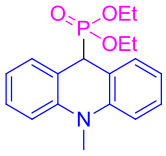
J = 7.0 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.35 (m, 4H), 6.95 (t, *J* = 6.9 Hz, 1H), 4.10 – 4.01 (m, 2H), 3.90 – 3.80 (m, 2H), 1.51 – 1.42 (m, 4H), 1.29 – 1.19 (m, 4H), 0.82 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.75 (d, J_{C-P} = 17.5 Hz), 147.98 (d, J_{C-P} = 14.4 Hz), 133.50, 129.53, 128.62, 128.28, 127.72, 127.32, 117.16, 113.27, 107.15 (d, J_{C-P} = 227.6 Hz), 65.91 (d, J_{C-P} = 5.4 Hz), 31.86 (d, J_{C-P} = 7.2 Hz), 18.41, 13.30; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 8.41; **HRMS (ESI)**: Calculated for $C_{21}H_{28}N_2O_3P$ $[M+H]^+$: 387.1832; Found: 387.1835.



5a

Diethyl 9*H*-xanthen-9-ylphosphonate (5a)[12]

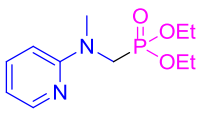
Colorless oil was obtained in 87% isolated yield, 81.7 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.27 – 7.21 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 4H), 4.45 (d, *J* = 24.7 Hz, 1H), 3.90 – 3.80 (m, 4H), 1.14 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.06 (d, J_{C-P} = 5.2 Hz), 129.93 (d, J_{C-P} = 4.3 Hz), 128.49 (d, J_{C-P} = 3.5 Hz), 122.94 (d, J_{C-P} = 3.0 Hz), 116.96 (d, J_{C-P} = 8.2 Hz), 116.31 (d, J_{C-P} = 3.2 Hz), 62.81 (d, J_{C-P} = 7.4 Hz), 40.10 (d, J_{C-P} = 137.7 Hz), 16.04 (d, J_{C-P} = 7.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.88.



5b

Diethyl (10-methyl-9,10-dihydroacridin-9-yl)phosphonate (5b)[13]

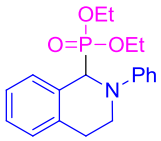
White solid was obtained in 74% isolated yield, 73.8 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 4H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.51 (d, *J* = 25.5 Hz, 1H), 3.88 – 3.77 (m, 4H), 3.36 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.74 (d, J_{C-P} = 4.3 Hz), 129.69 (d, J_{C-P} = 5.6 Hz), 128.06 (d, J_{C-P} = 3.8 Hz), 120.50 (d, J_{C-P} = 3.2 Hz), 118.47 (d, J_{C-P} = 7.2 Hz), 112.26 (d, J_{C-P} = 2.9 Hz), 62.59 (d, J_{C-P} = 7.4 Hz), 44.47 (d, J_{C-P} = 140.3 Hz), 33.05, 16.24 (d, J_{C-P} = 5.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.81.



5c

Diethyl ((methyl(pyridin-3-yl)amino)methyl)phosphonate (5c)

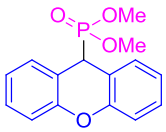
Colorless oil was obtained in 46% isolated yield, 35.6 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 5.5, 1.8 Hz, 1H), 7.51 – 7.45 (m, 1H), 6.60 (dd, *J* = 7.5, 4.3 Hz, 2H), 4.18 (d, *J* = 8.8 Hz, 2H), 4.14 – 4.05 (m, 4H), 3.13 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.77, 147.35, 137.41, 112.40, 105.90, 62.00 (d, $J_{C\text{-}P}$ = 6.6 Hz), 44.94 (d, $J_{C\text{-}P}$ = 156.8 Hz), 37.23, 16.28 (d, $J_{C\text{-}P}$ = 5.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.04; **HRMS (ESI)**: Calculated for $C_{11}H_{20}N_2O_3P$ $[M+H]^+$: 259.1206; Found: 259.1207.



5d

Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (5d)[14]

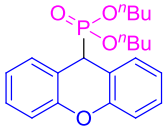
Colorless oil was obtained in 30% isolated yield, 31.3 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 6.6 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 11.8, 5.6 Hz, 3H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 5.18 (d, *J* = 20.0 Hz, 1H), 4.15 – 3.95 (m, 4H), 3.94 – 3.83 (m, 1H), 3.67 – 3.58 (m, 1H), 3.14 – 2.92 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.34 (d, $J_{C\text{-}P}$ = 5.8 Hz), 136.41 (d, $J_{C\text{-}P}$ = 5.6 Hz), 130.58, 129.10, 128.71, 128.08 (d, $J_{C\text{-}P}$ = 4.6 Hz), 127.42, 125.83, 118.41, 114.72, 62.81 (d, $J_{C\text{-}P}$ = 109.1 Hz), 58.76 (d, $J_{C\text{-}P}$ = 162.8 Hz), 43.43, 26.70, 16.39; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 22.17.



5e

Dimethyl 9*H*-xanthen-9-ylphosphonate (5e)[12]

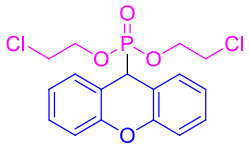
White solid was obtained in 62% isolated yield, 52.4 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.30 – 7.23 (m, 2H), 7.09 (t, *J* = 7.8 Hz, 4H), 4.51 (d, *J* = 24.7 Hz, 1H), 3.54 (d, *J* = 10.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.24 (d, $J_{C\text{-}P}$ = 5.3 Hz), 129.98 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.82 (d, $J_{C\text{-}P}$ = 3.6 Hz), 123.29 (d, $J_{C\text{-}P}$ = 3.2 Hz), 116.86 (d, $J_{C\text{-}P}$ = 8.2 Hz), 116.61 (d, $J_{C\text{-}P}$ = 3.4 Hz), 53.66 (d, $J_{C\text{-}P}$ = 7.4 Hz), 39.90 (d, $J_{C\text{-}P}$ = 141.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 23.32.



5f

Dibutyl 9*H*-xanthen-9-ylphosphonate (5f)[12]

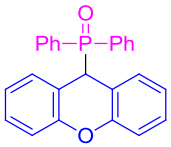
Colorless oil was obtained in 88% isolated yield, 99.1 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.8, 2.3 Hz, 2H), 7.29 – 7.19 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 4H), 4.48 (d, *J* = 24.7 Hz, 1H), 3.85 – 3.73 (m, 4H), 1.54 – 1.41 (m, 4H), 1.31 – 1.19 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.20 (d, $J_{C\text{-}P}$ = 5.3 Hz), 130.07 (d, $J_{C\text{-}P}$ = 4.4 Hz), 128.61 (d, $J_{C\text{-}P}$ = 3.6 Hz), 123.05 (d, $J_{C\text{-}P}$ = 3.2 Hz), 117.14 (d, $J_{C\text{-}P}$ = 8.2 Hz), 116.45 (d, $J_{C\text{-}P}$ = 3.3 Hz), 66.57 (d, $J_{C\text{-}P}$ = 7.7 Hz), 40.17 (d, $J_{C\text{-}P}$ = 141.1 Hz), 32.35 (d, $J_{C\text{-}P}$ = 5.8 Hz), 18.45, 13.48; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 20.90.



5g

Bis(2-chloroethyl) 9*H*-xanthen-9-ylphosphonate (5g)

Colorless oil was obtained in 68% isolated yield, 77.0 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.24 (m, 2H), 7.16 – 7.06 (m, 4H), 4.59 (d, *J* = 24.5 Hz, 1H), 4.12 – 3.97 (m, 4H), 3.52 (t, *J* = 5.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.23 (d, $J_{C\text{-}P}$ = 5.4 Hz), 130.10 (d, $J_{C\text{-}P}$ = 4.6 Hz), 129.08 (d, $J_{C\text{-}P}$ = 3.7 Hz), 123.36 (d, $J_{C\text{-}P}$ = 3.2 Hz), 116.69 (d, $J_{C\text{-}P}$ = 3.4 Hz), 116.19 (d, $J_{C\text{-}P}$ = 8.4 Hz), 66.27 (d, $J_{C\text{-}P}$ = 7.4 Hz), 42.66 (d, $J_{C\text{-}P}$ = 5.9 Hz), 40.89 (d, $J_{C\text{-}P}$ = 1.7 Hz), 39.48 (d, $J_{C\text{-}P}$ = 0.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 21.86; **HRMS (ESI)**: Calculated for $C_{17}H_{17}Cl_2NaO_4P$ $[M+Na]^+$: 409.0134; Found: 409.0126.



5h

Diphenyl(9*H*-xanthen-9-yl)phosphine oxide (5h)[12]

White solid was obtained in 68% isolated yield, 78.1 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.46 (m, 6H), 7.42 – 7.30 (m, 4H), 7.16 (t, *J* = 7.7 Hz, 2H), 6.99 – 6.82 (m, 6H), 4.92 (d, *J* = 17.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.58 (d, $J_{C\text{-}P}$ = 4.0 Hz), 132.17 (d, $J_{C\text{-}P}$ = 8.3 Hz), 132.01 (d, $J_{C\text{-}P}$ = 2.2 Hz), 130.11 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.38 (d, $J_{C\text{-}P}$ = 95.7 Hz), 128.62 (d, $J_{C\text{-}P}$ = 2.6 Hz), 128.09 (d, $J_{C\text{-}P}$ = 11.2 Hz), 122.85 (d, $J_{C\text{-}P}$ = 2.3 Hz), 116.96 (d, $J_{C\text{-}P}$ = 4.4 Hz), 116.34 (d, $J_{C\text{-}P}$ = 2.2 Hz), 45.37 (d, $J_{C\text{-}P}$ = 64.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.02.

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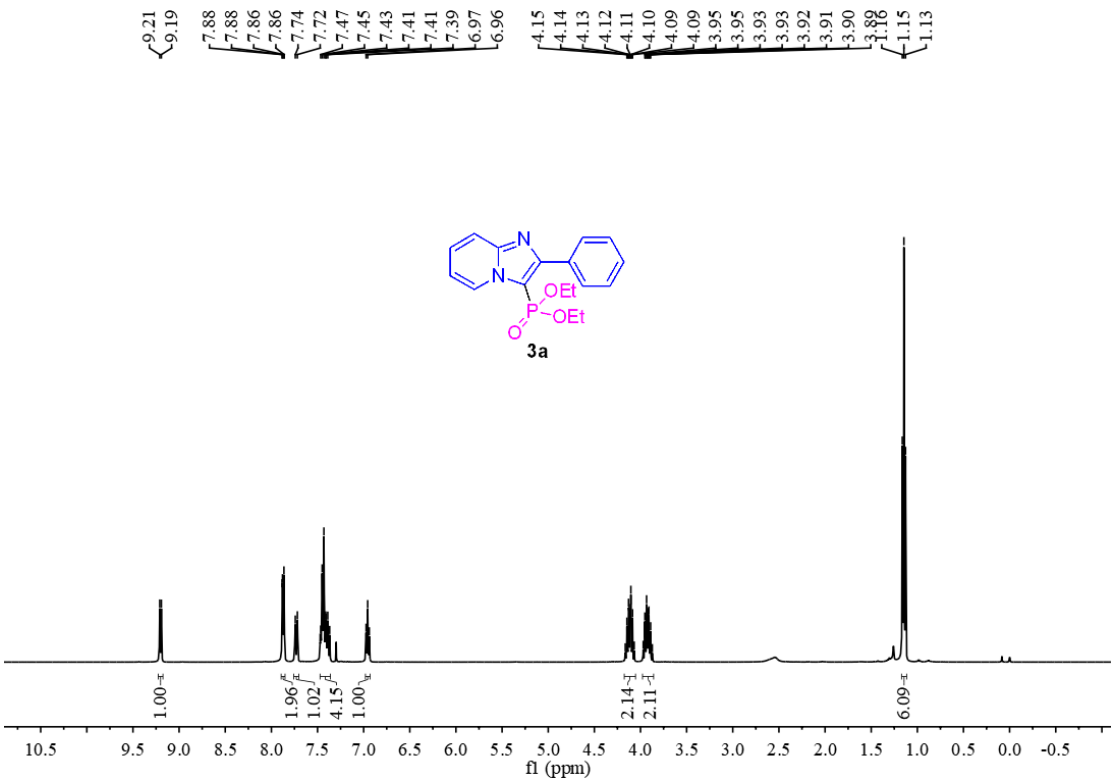
Copies of ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR Spectra

^{1}H NMR



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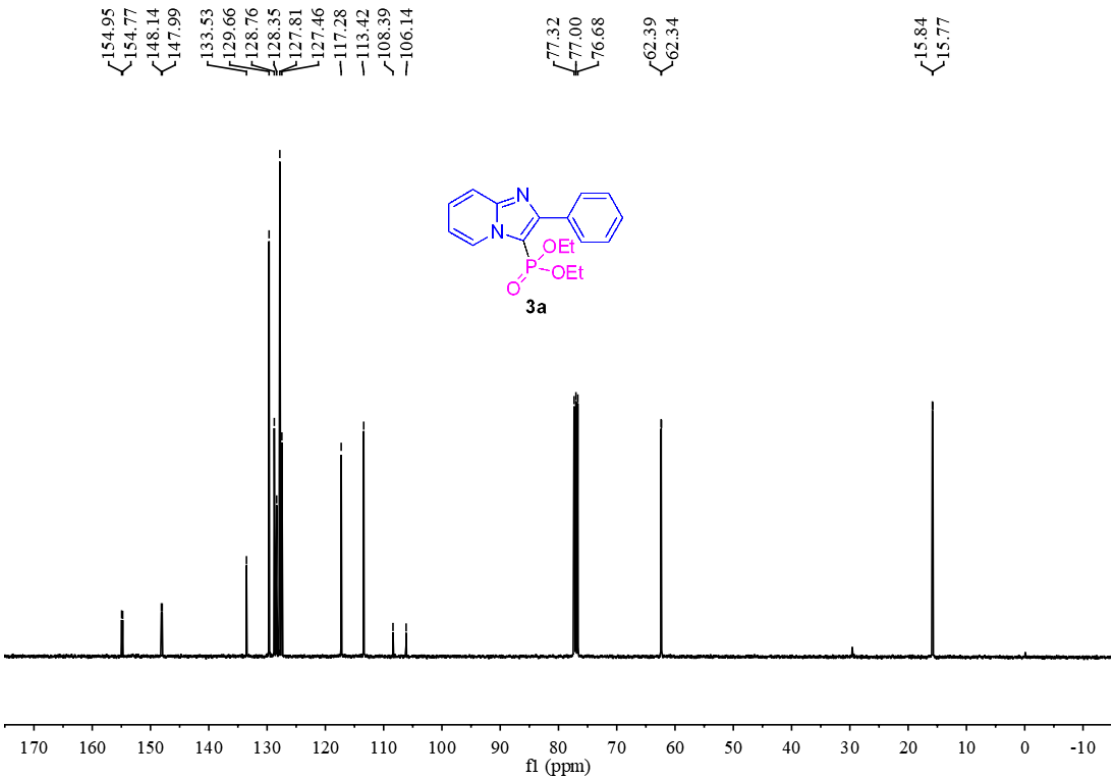

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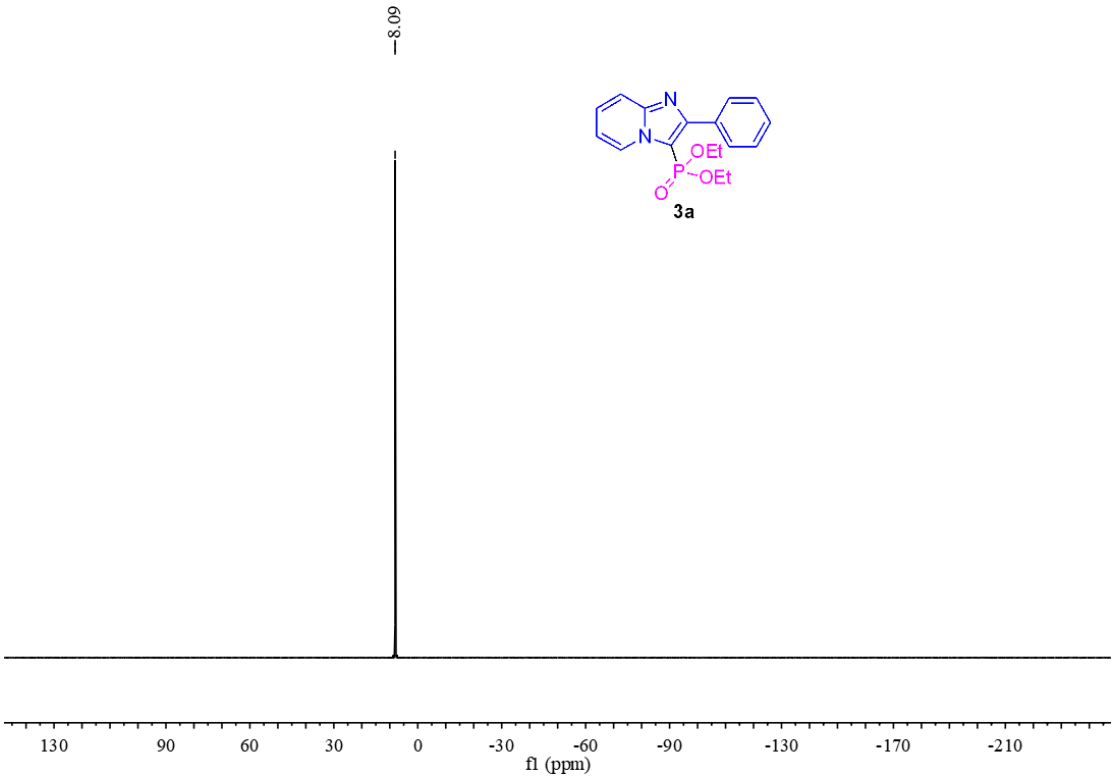

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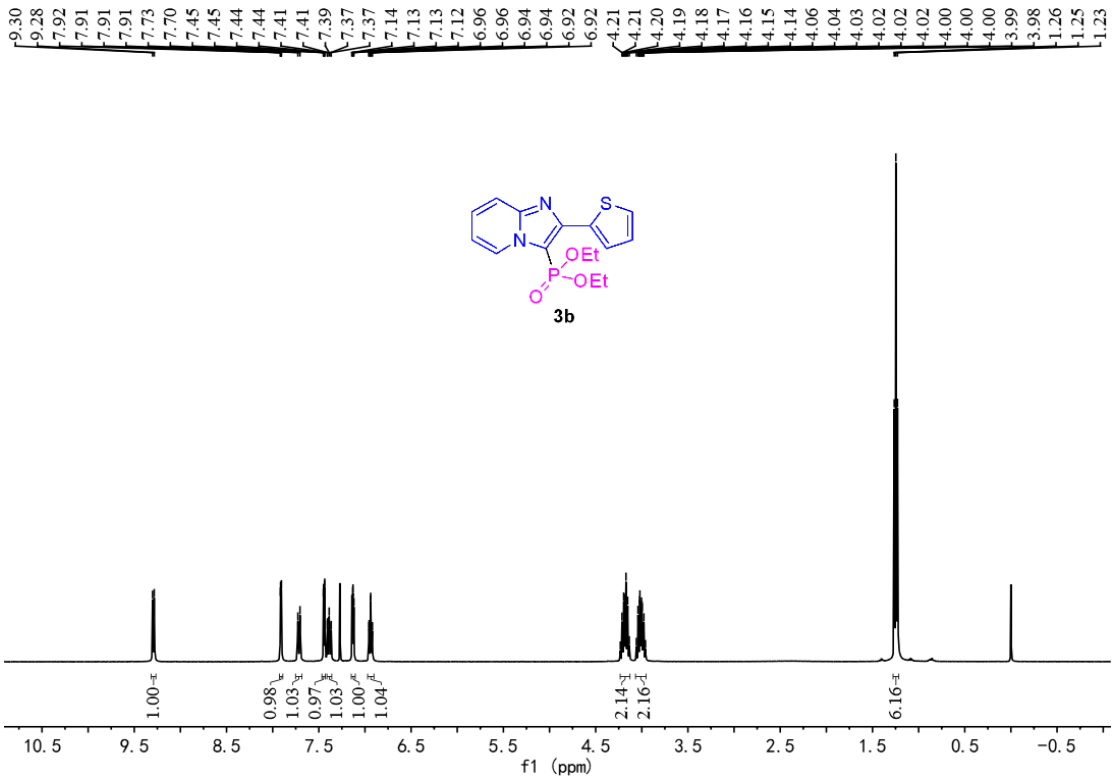

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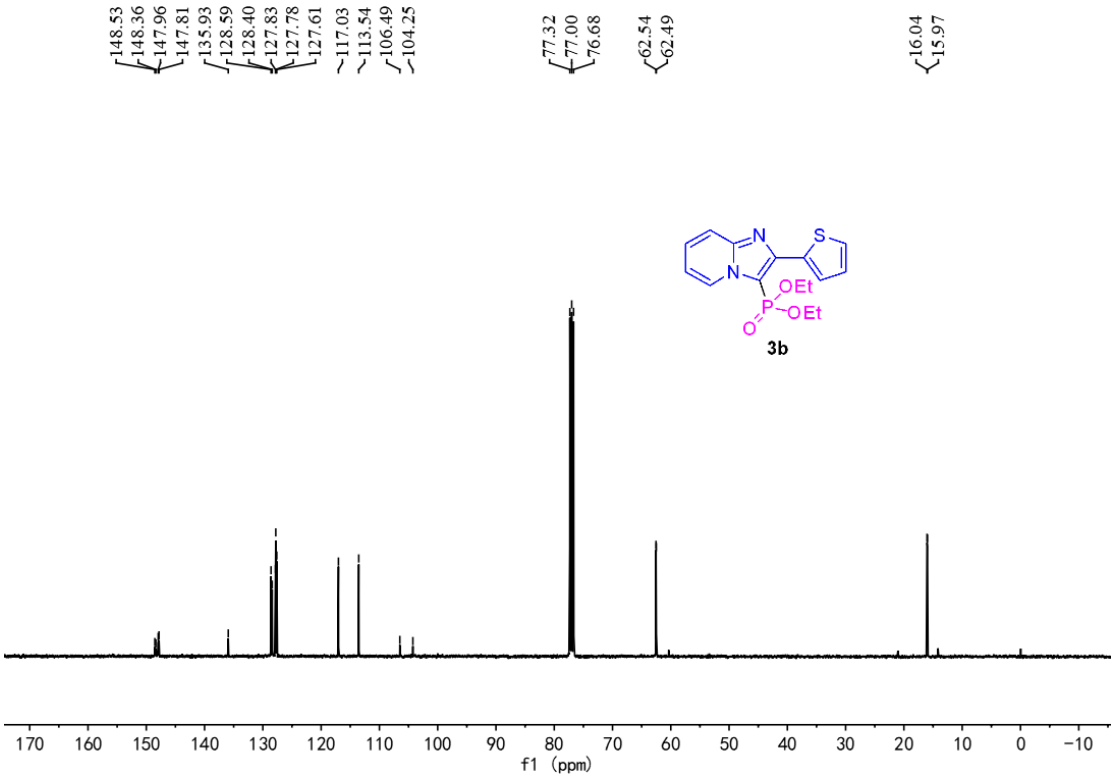

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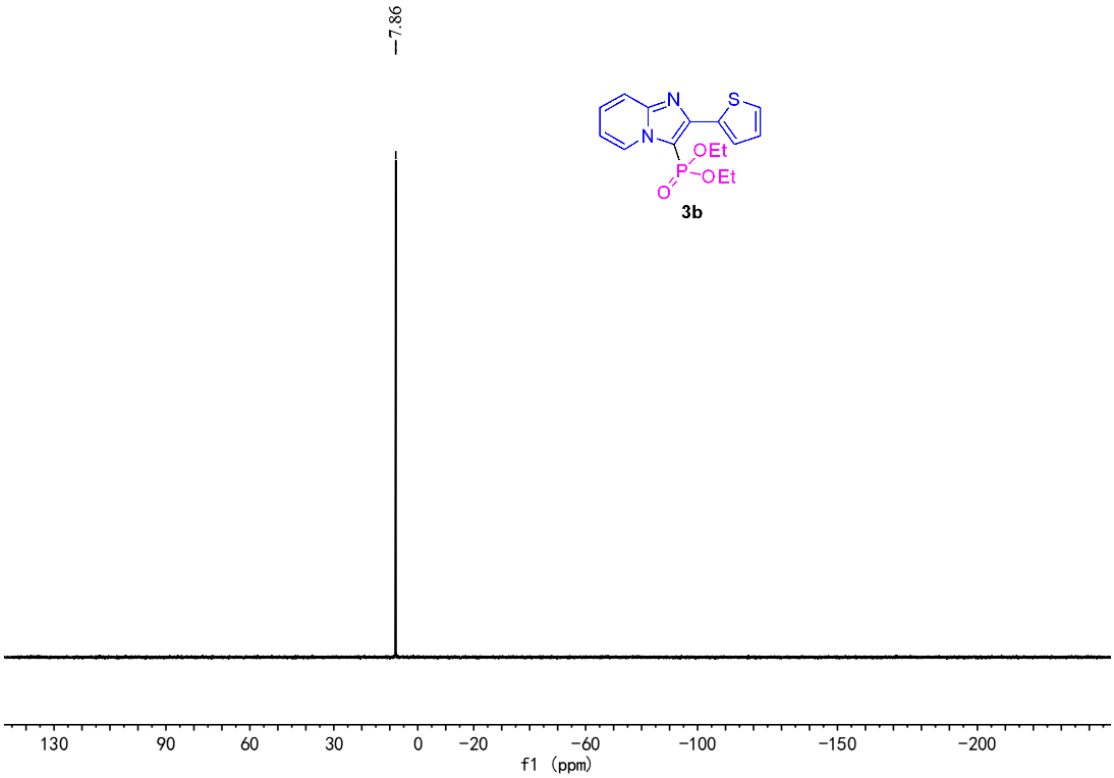

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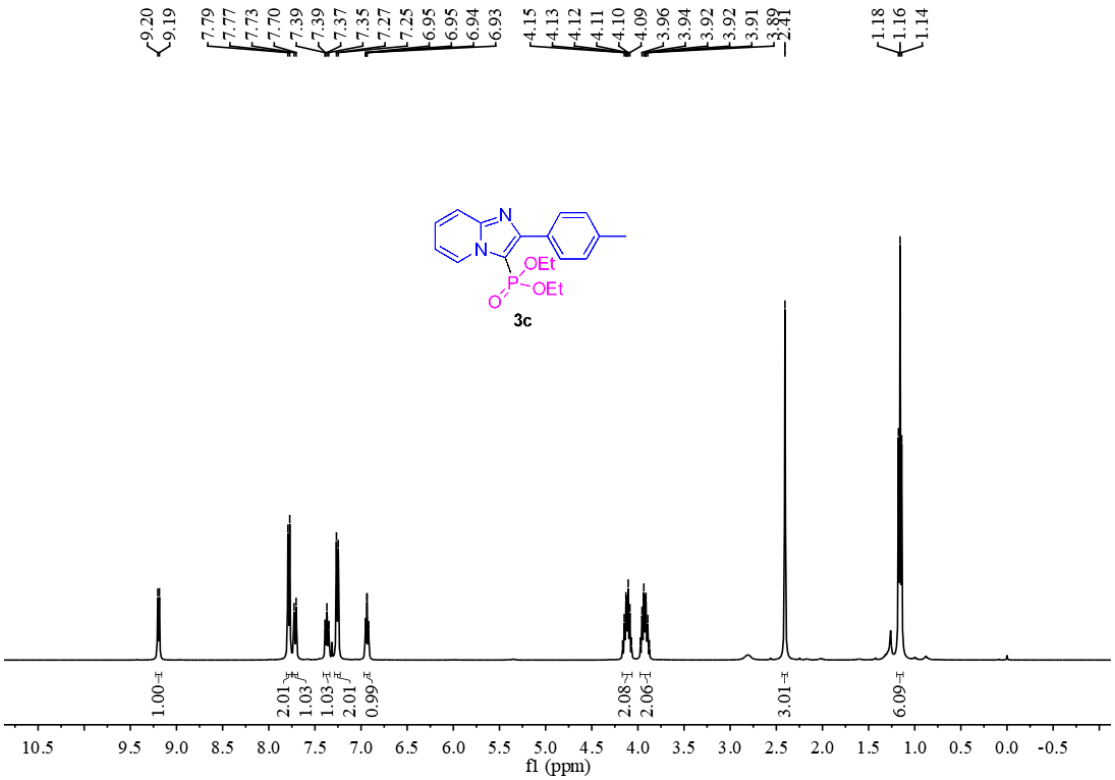

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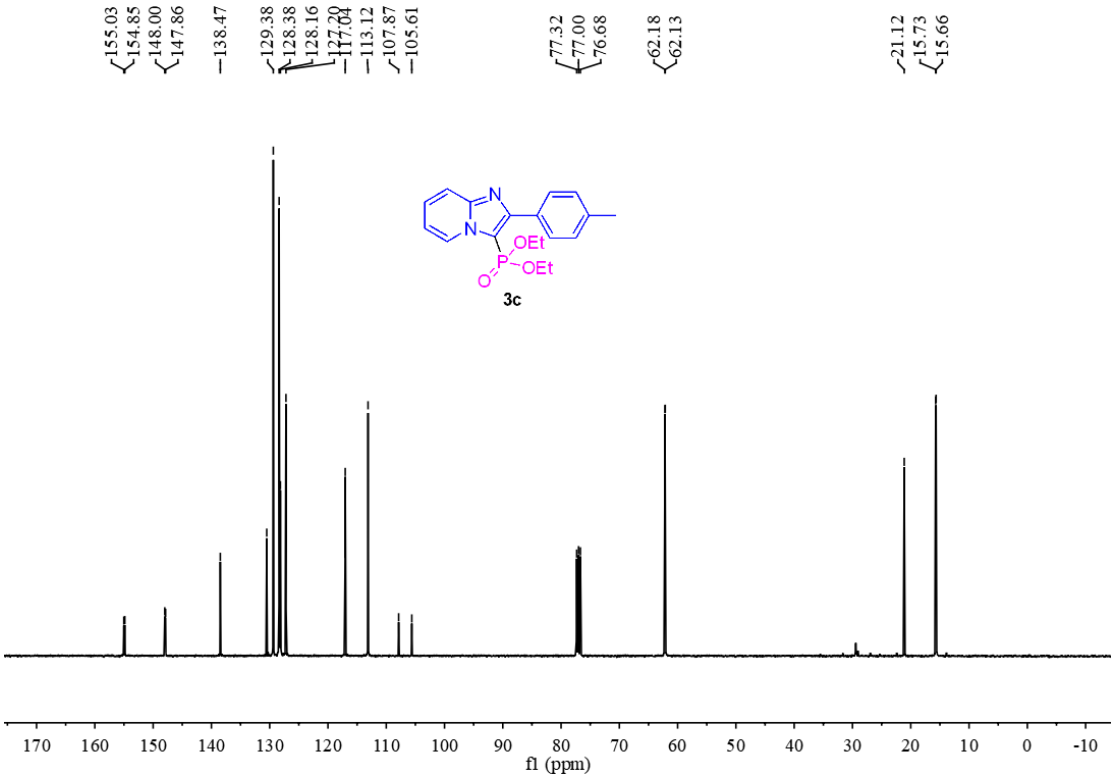
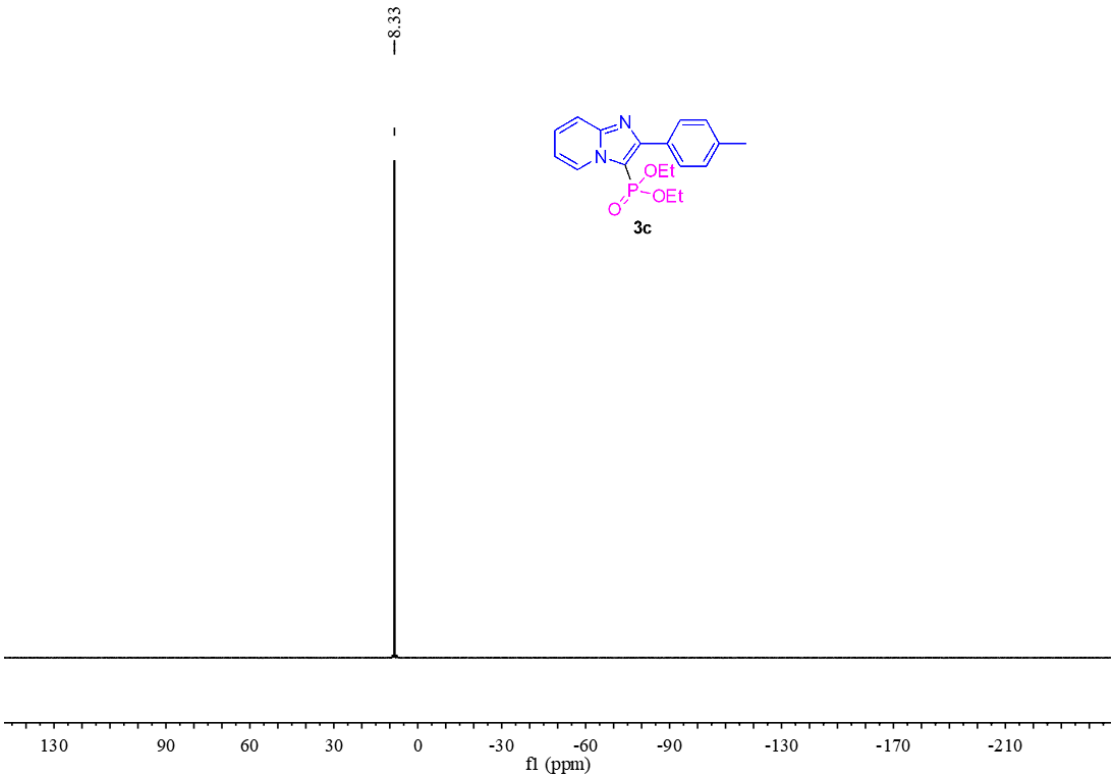


^{31}P NMR



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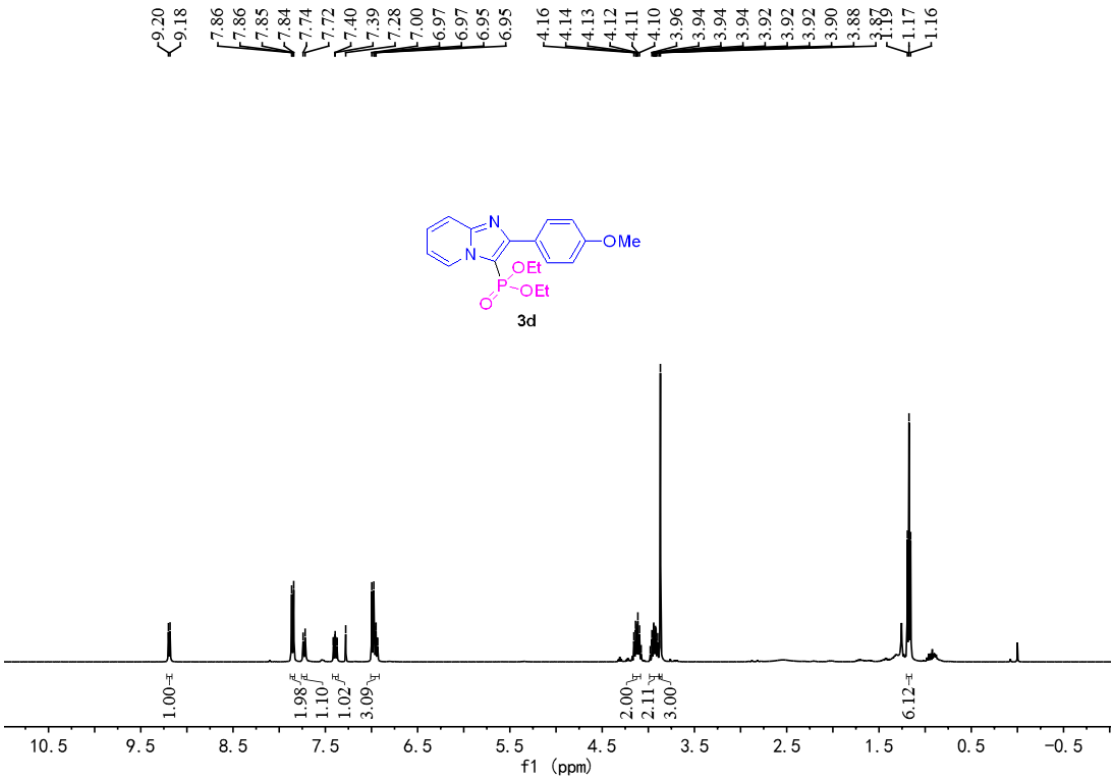
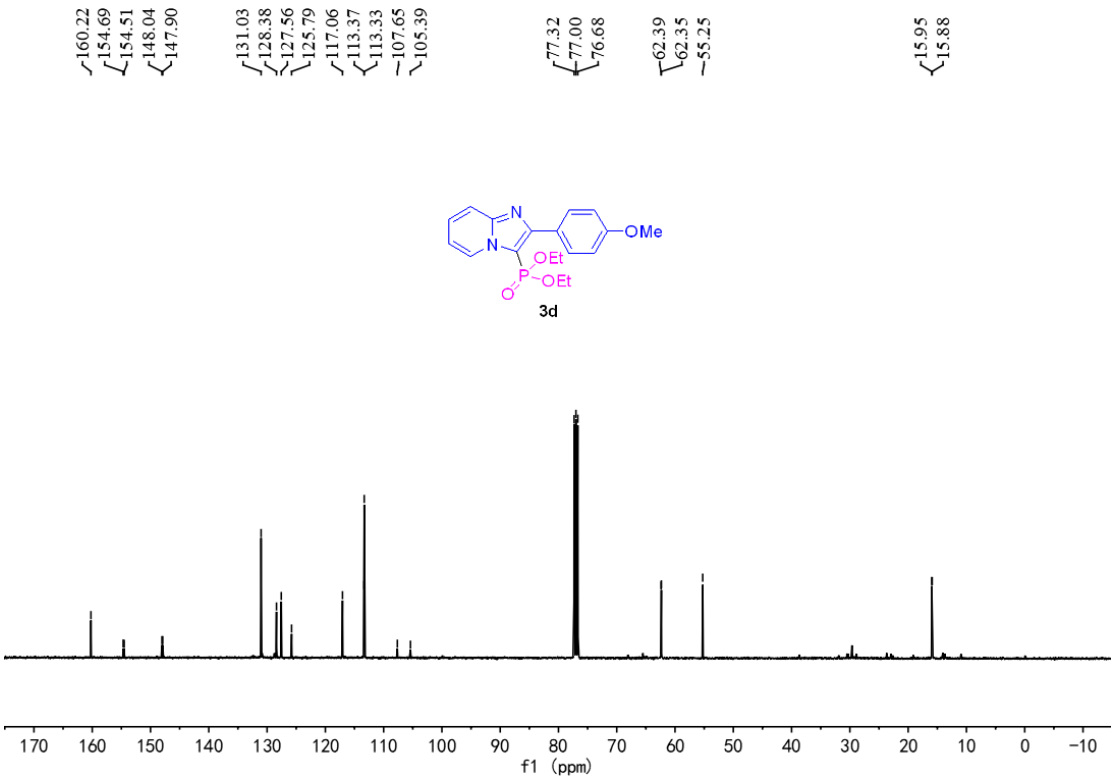
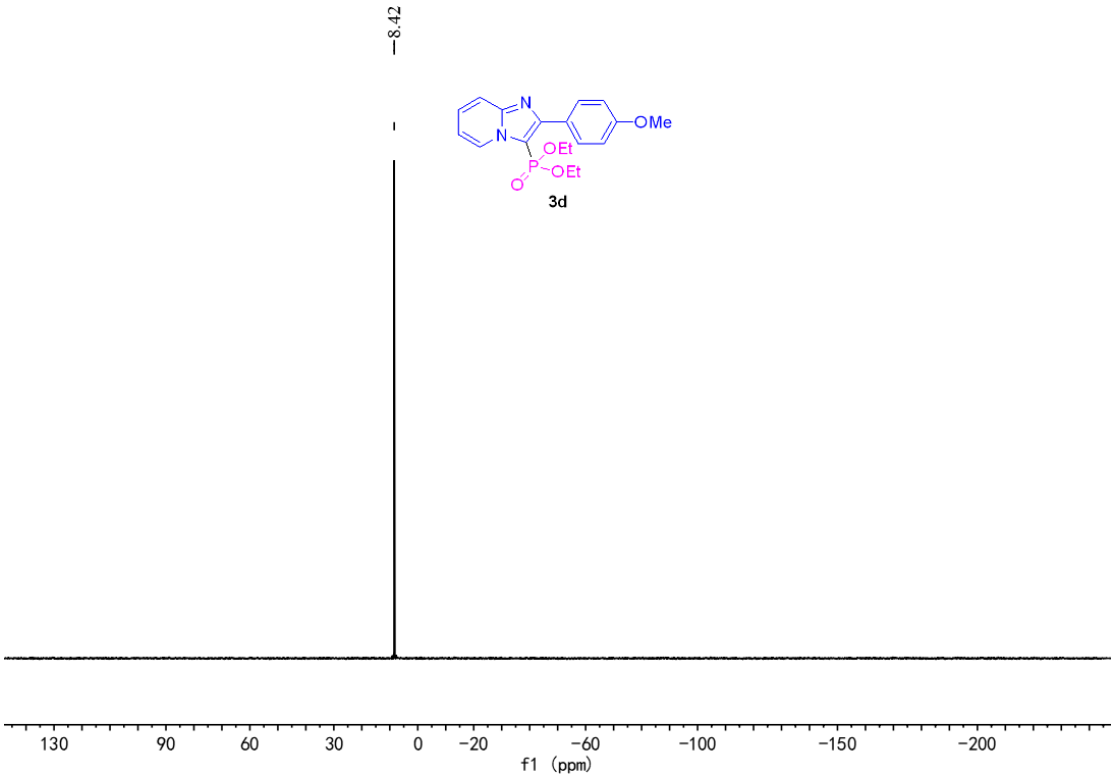


^{13}C NMR



^{31}P NMR



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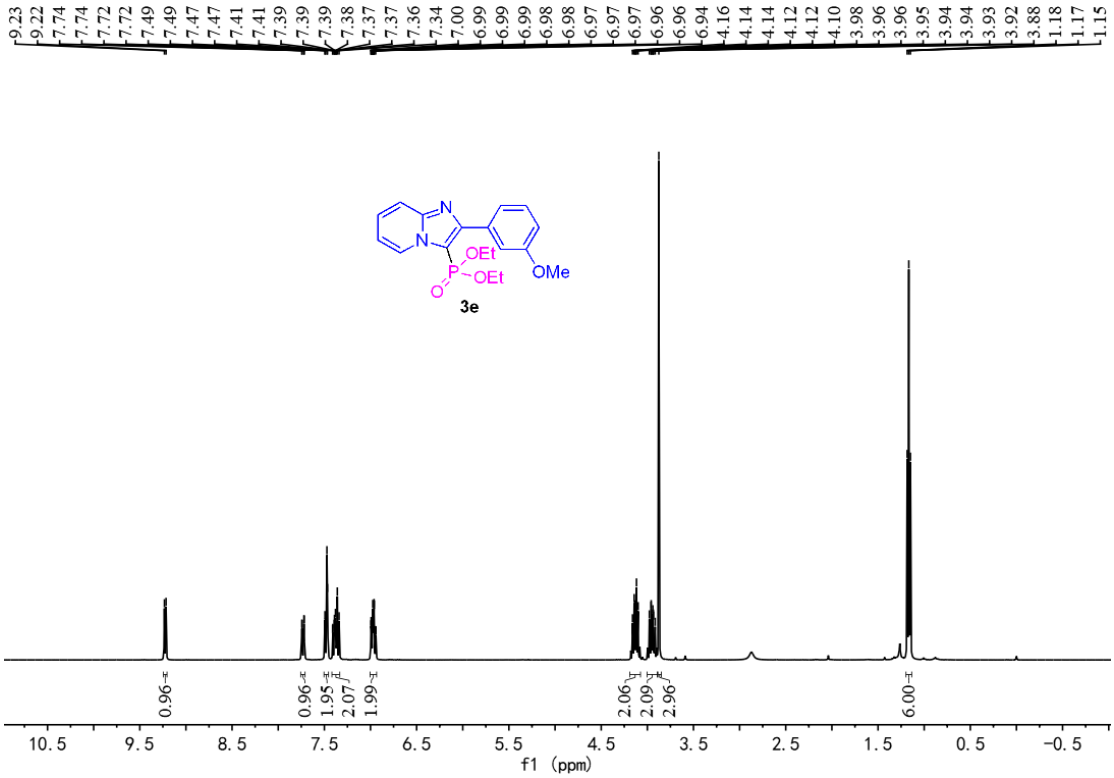

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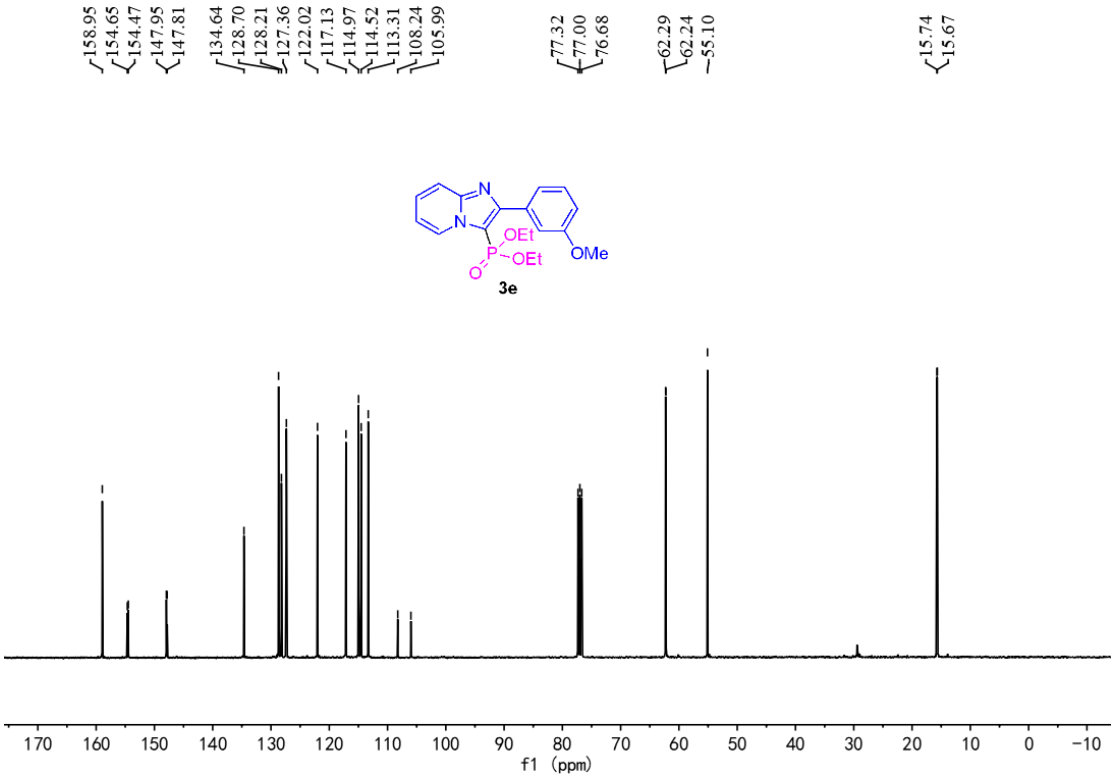

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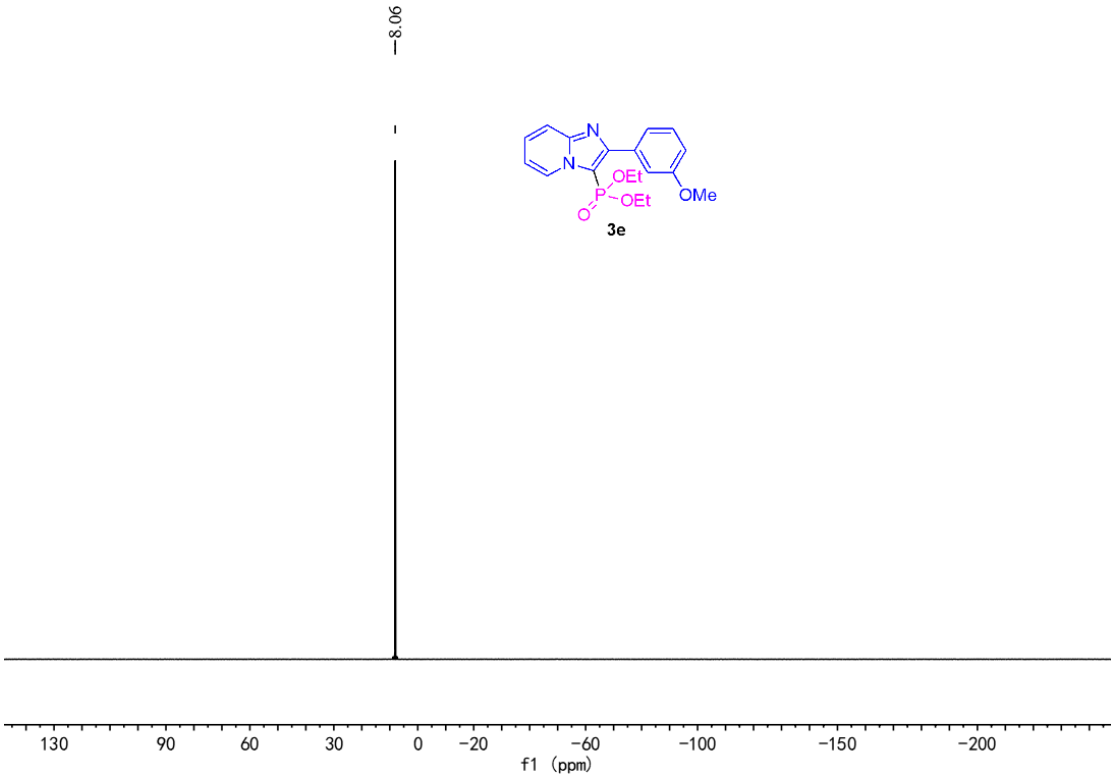

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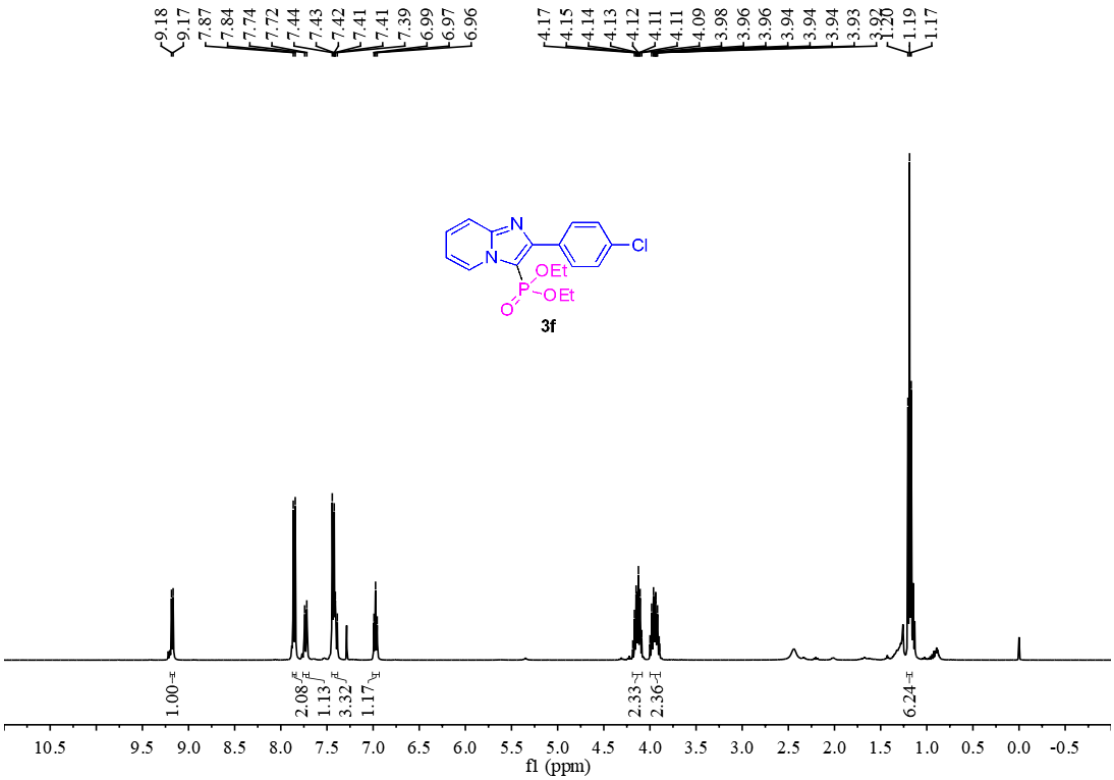

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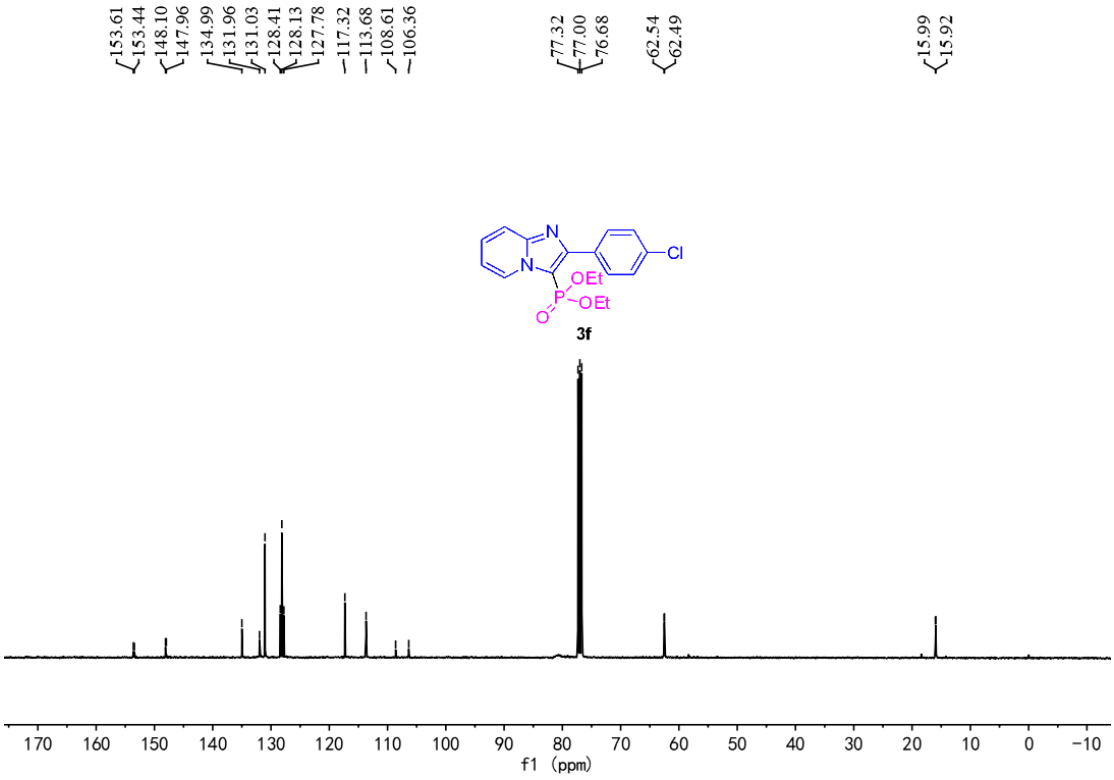

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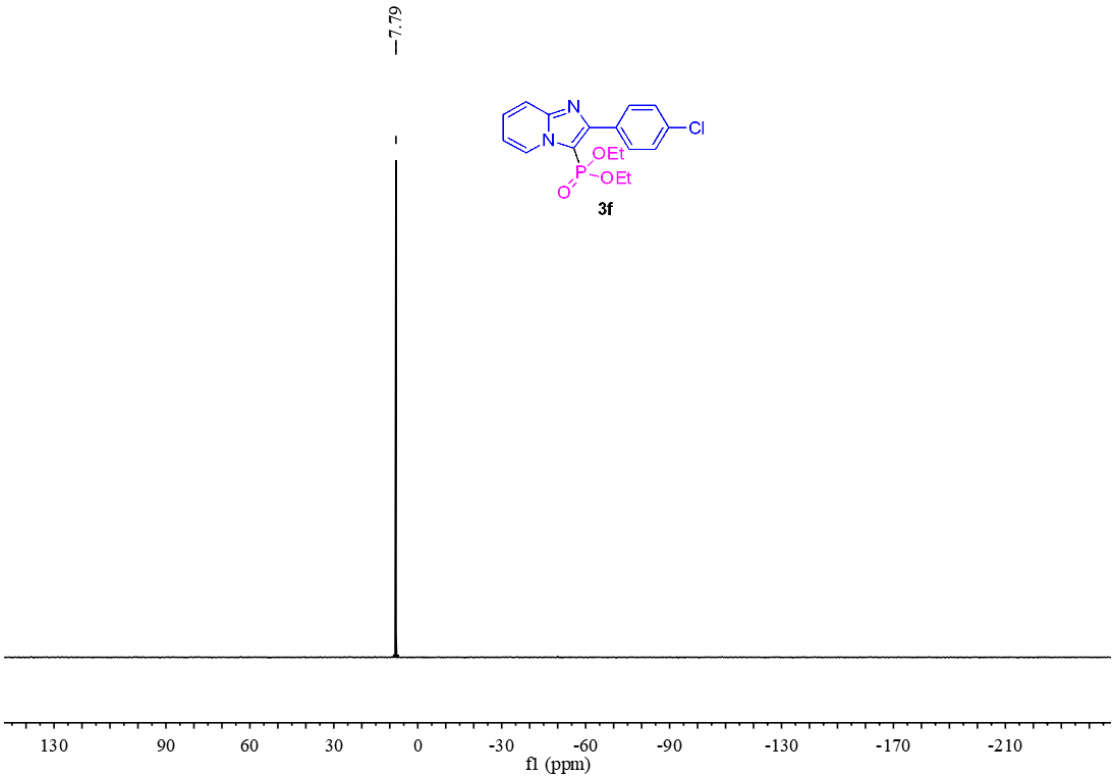

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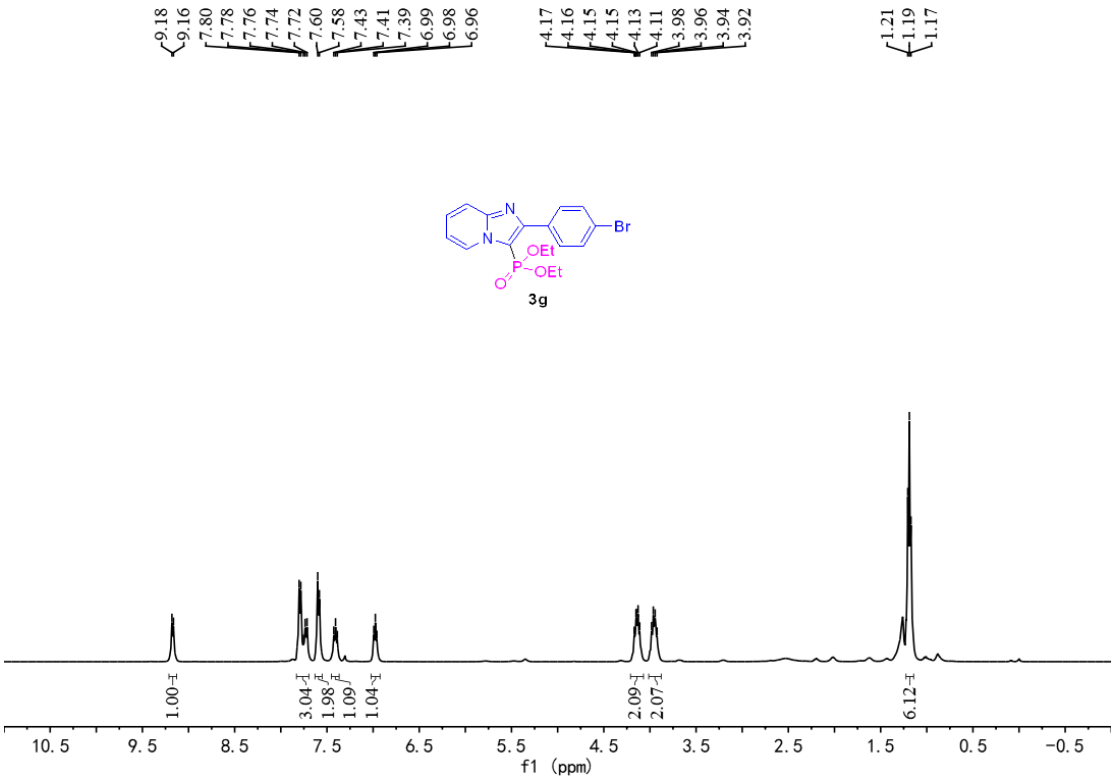

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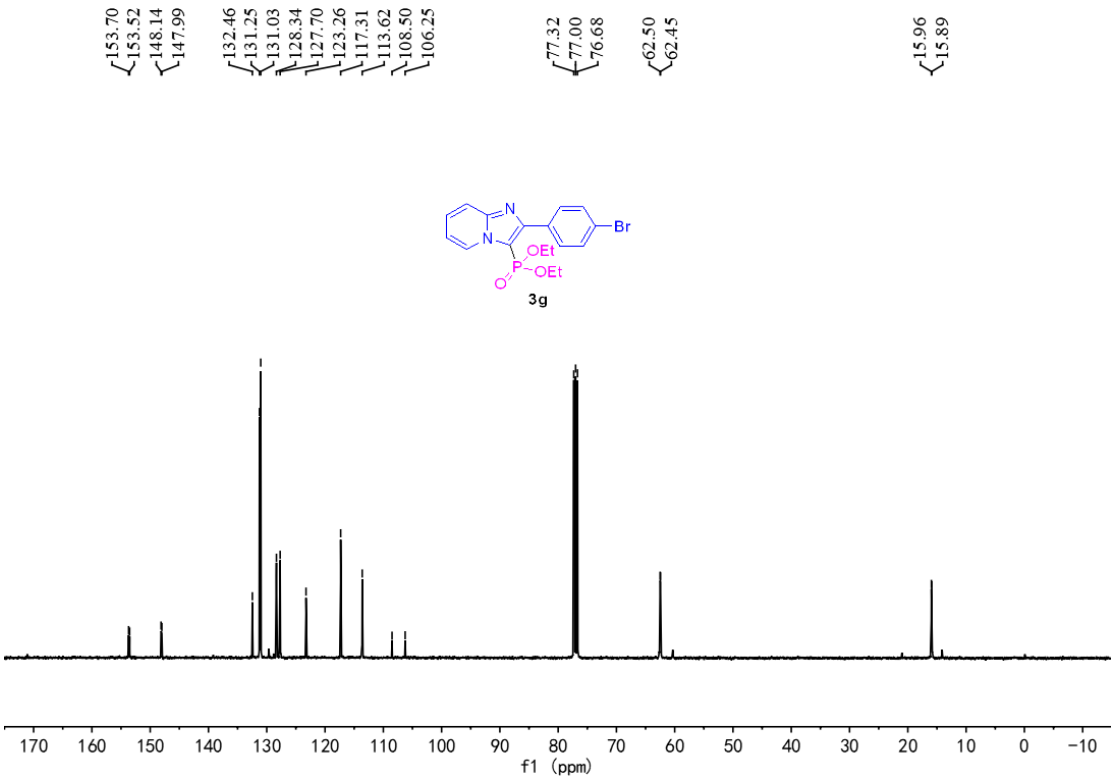

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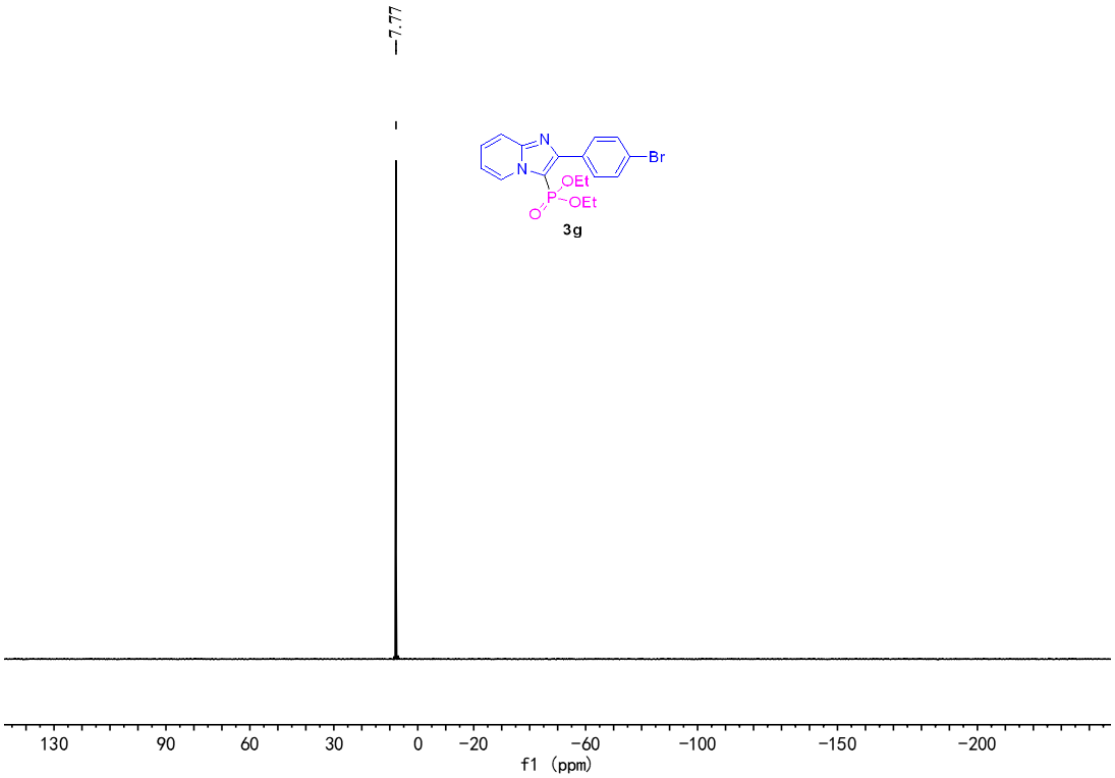

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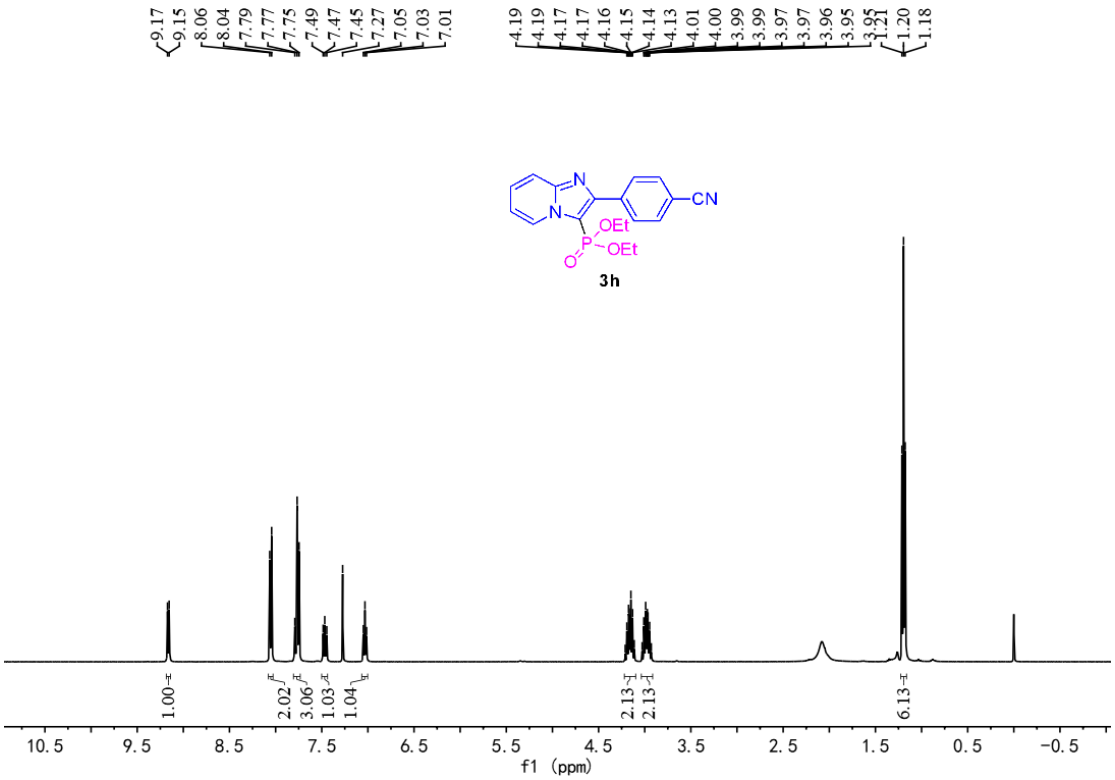

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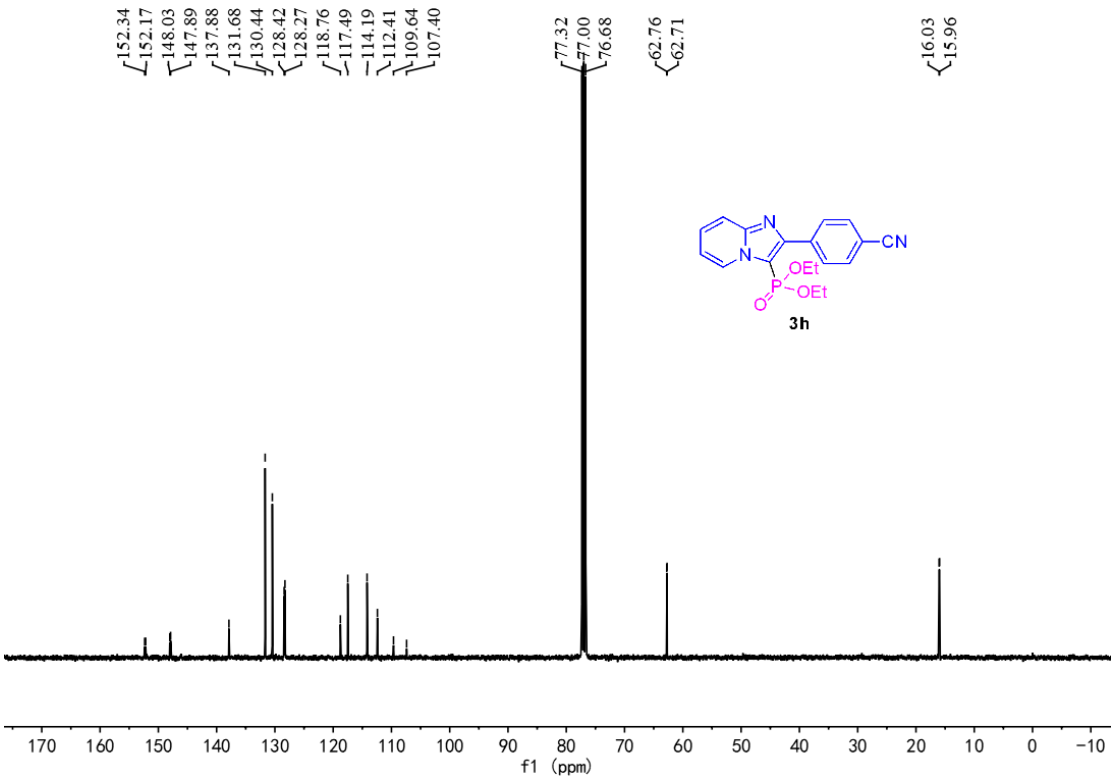

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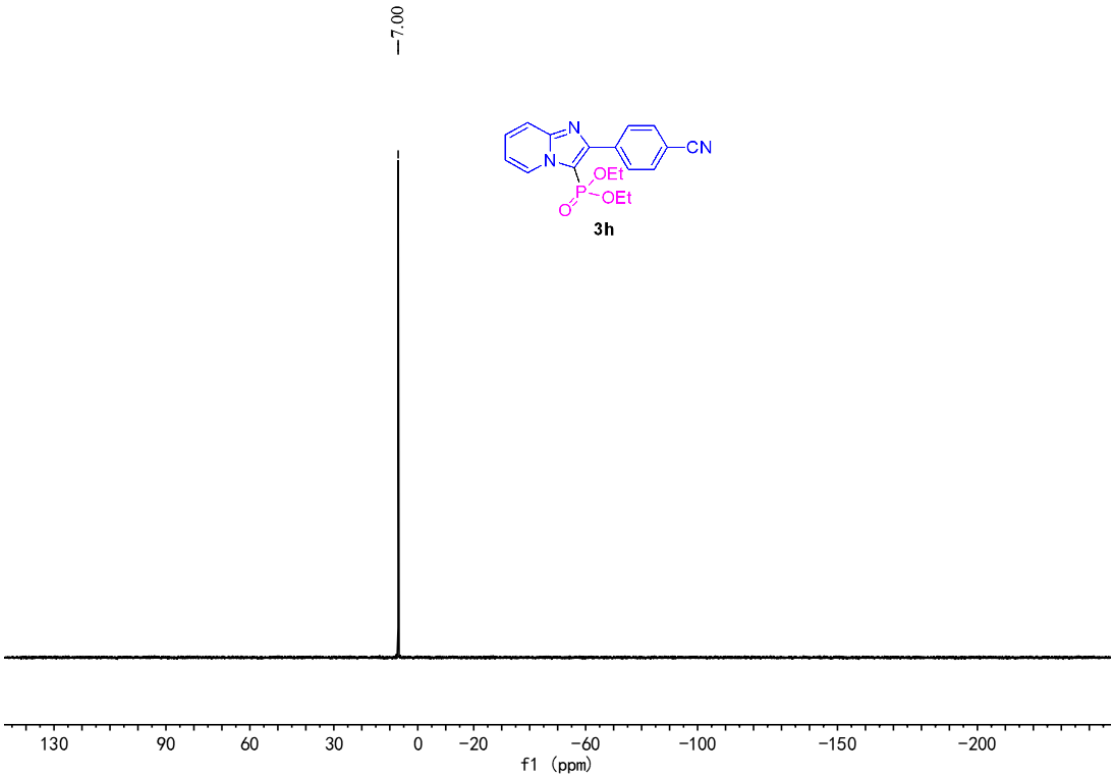

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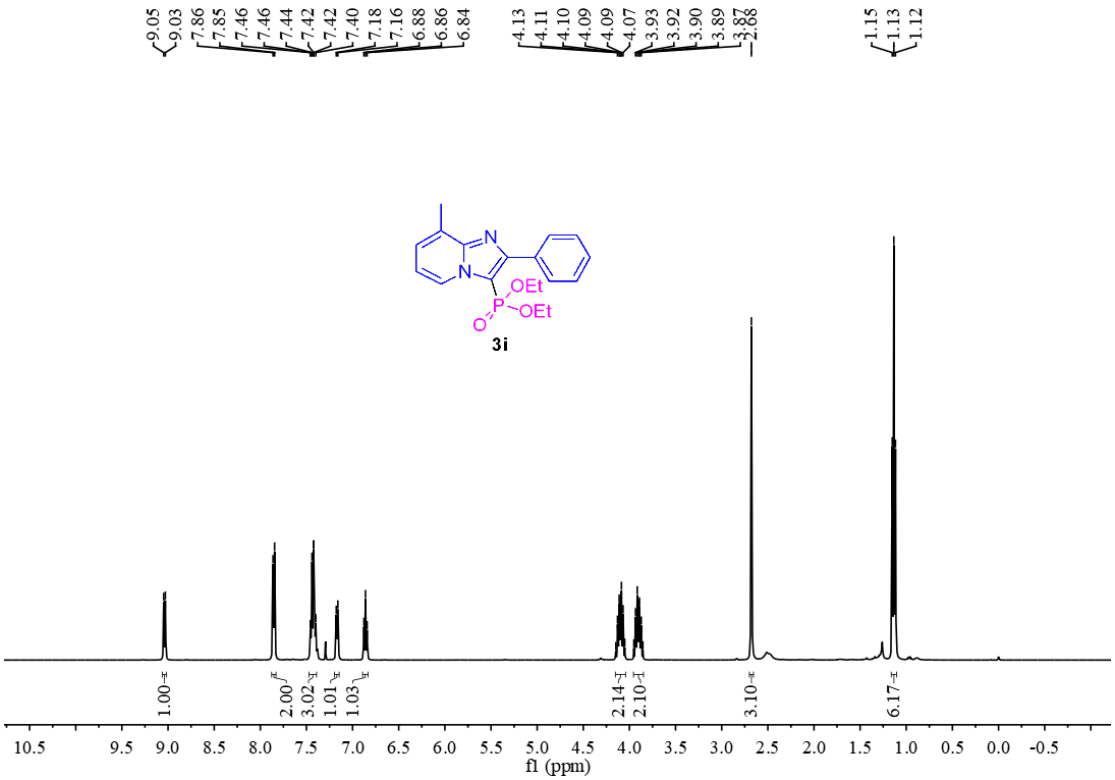

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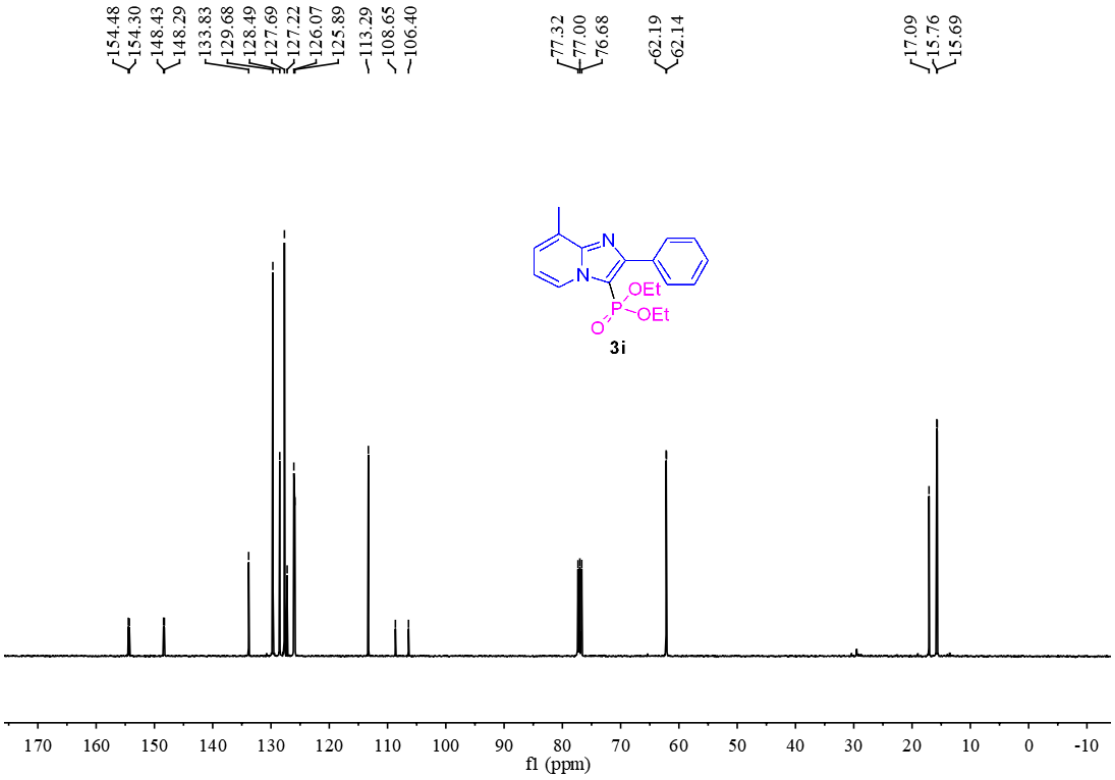

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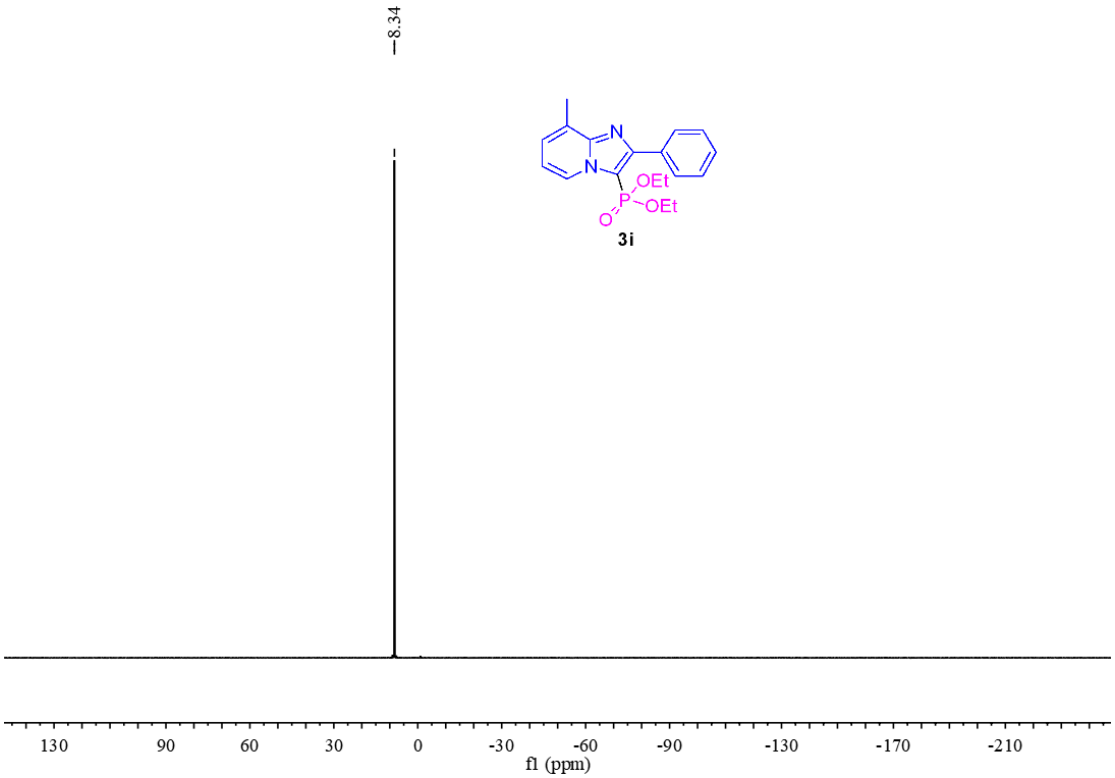

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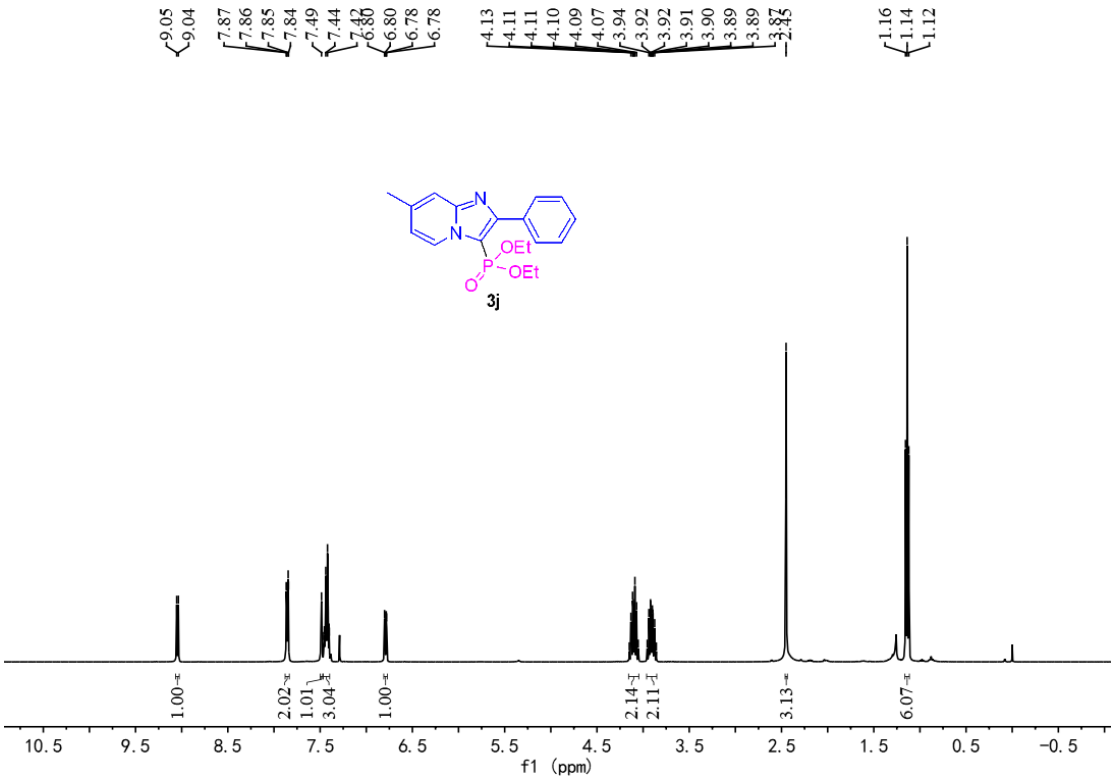

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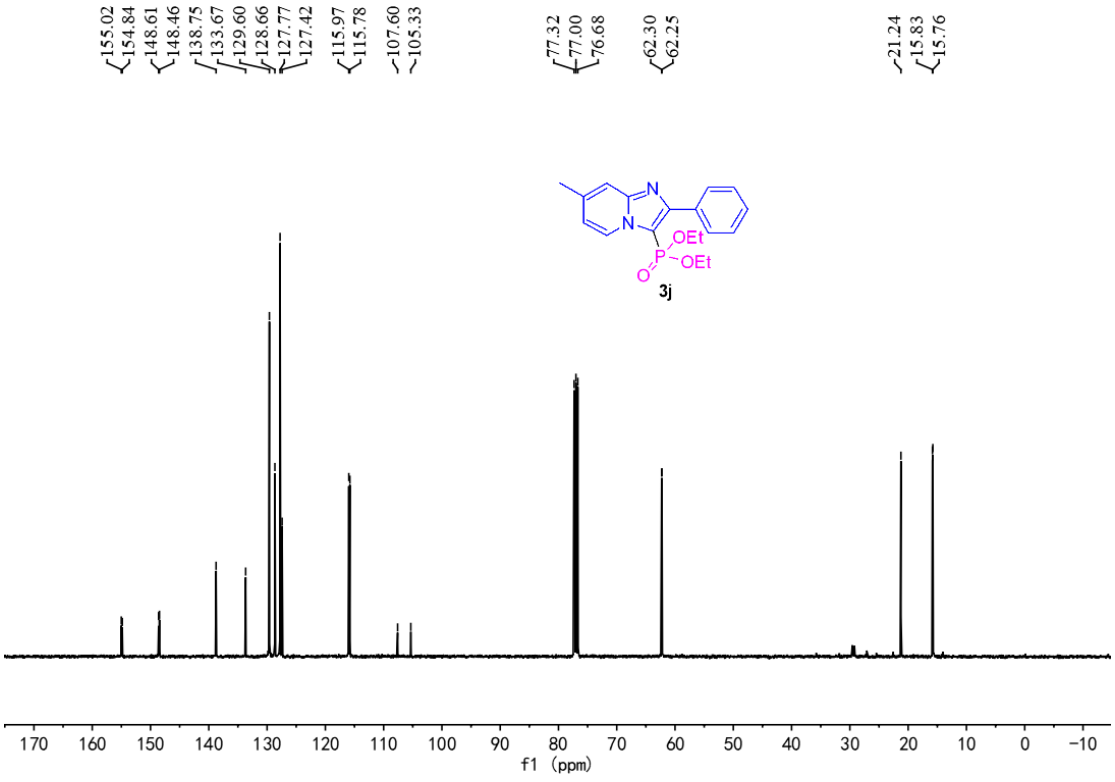

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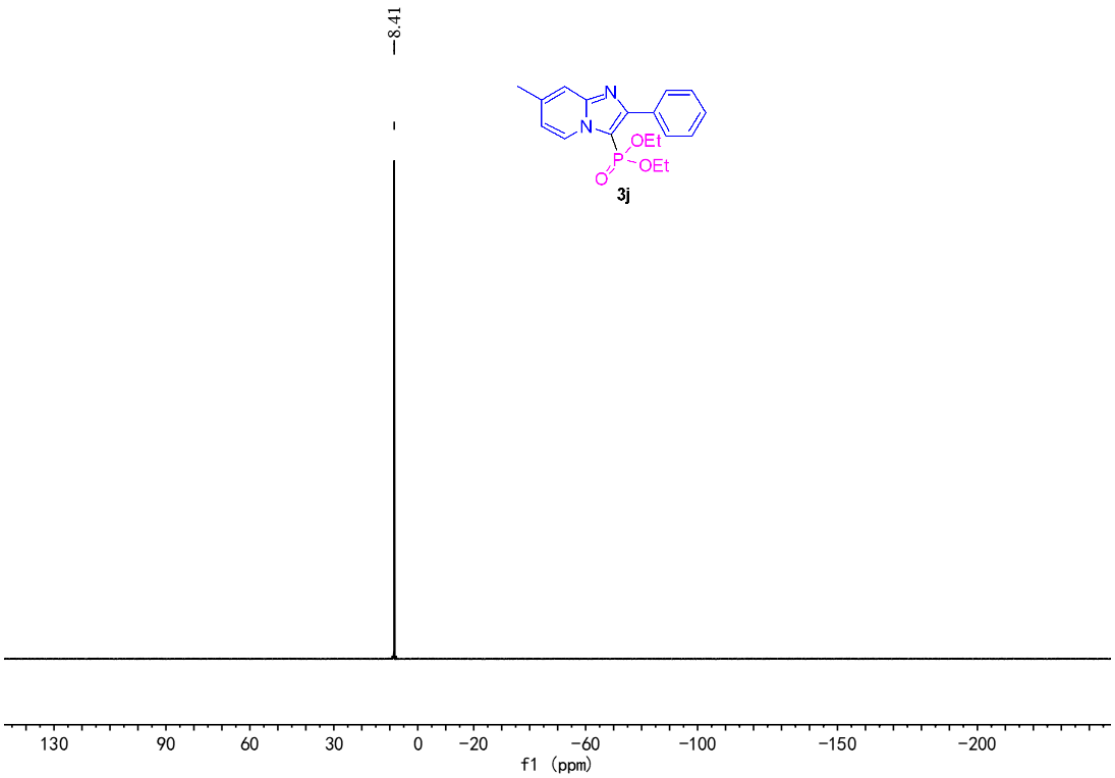

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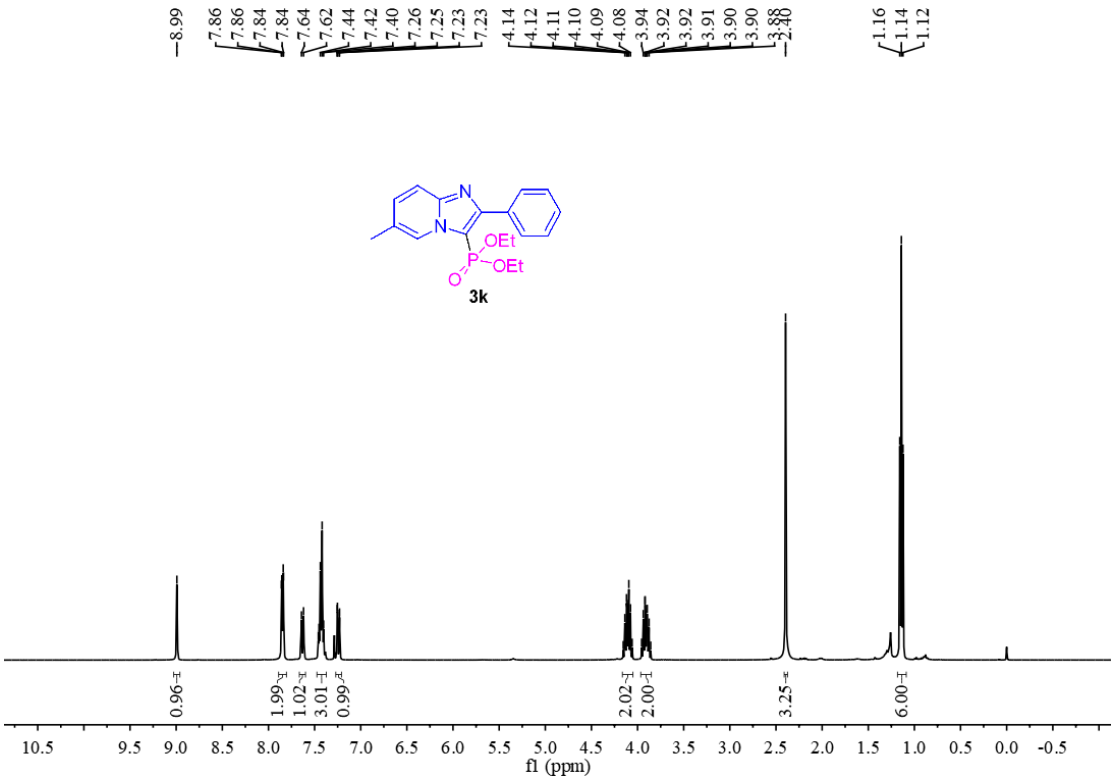

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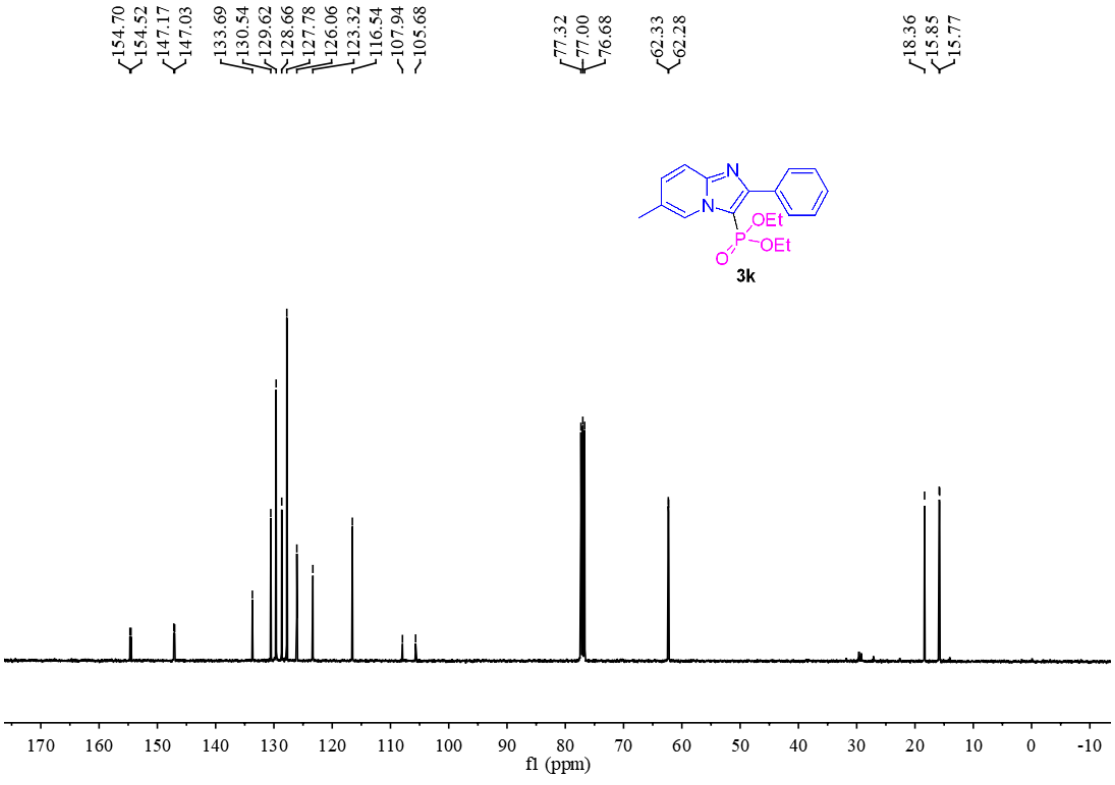

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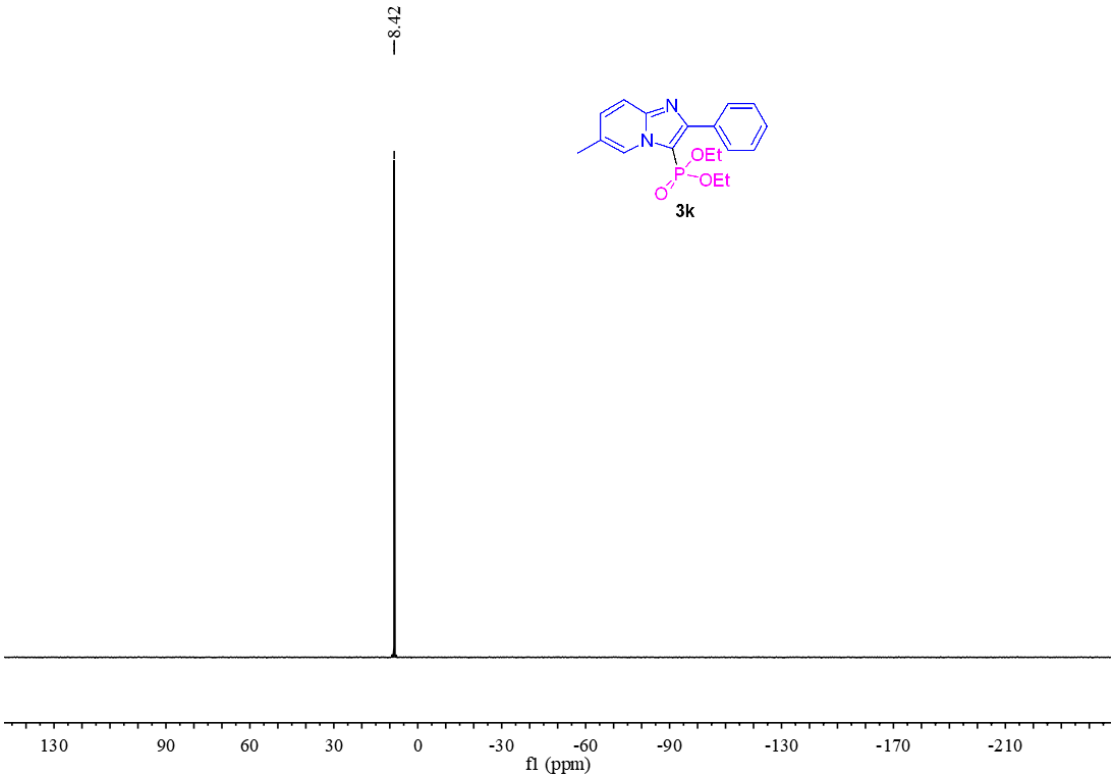

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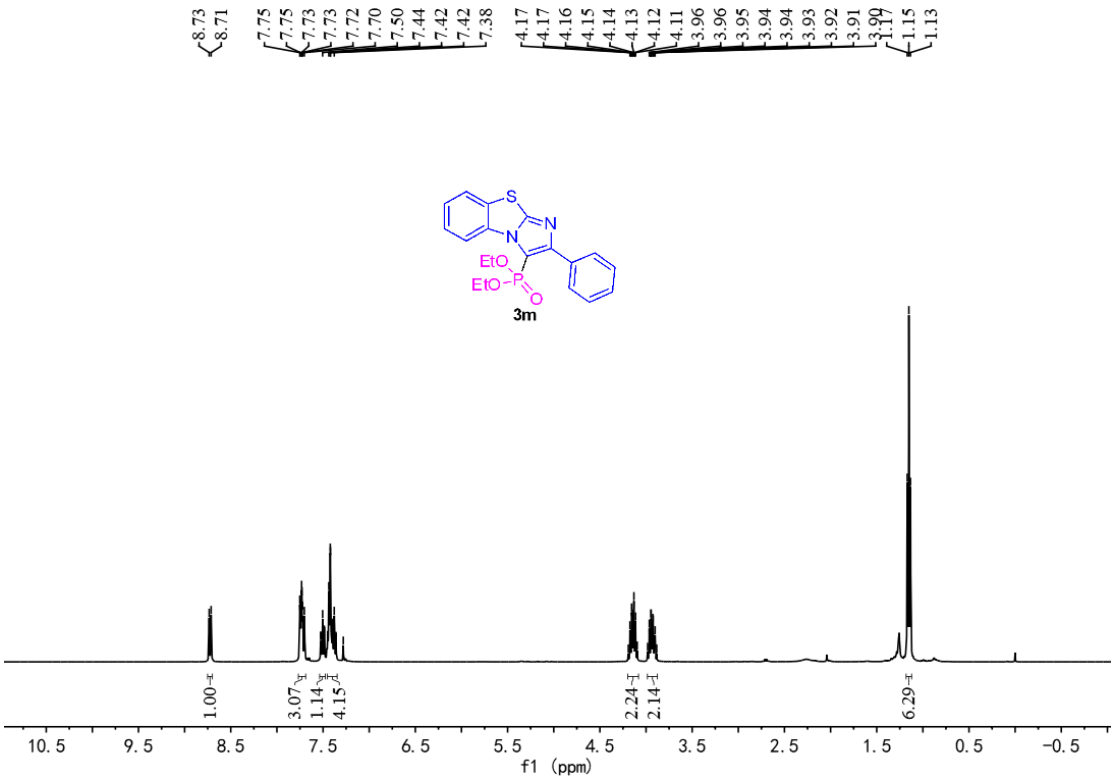

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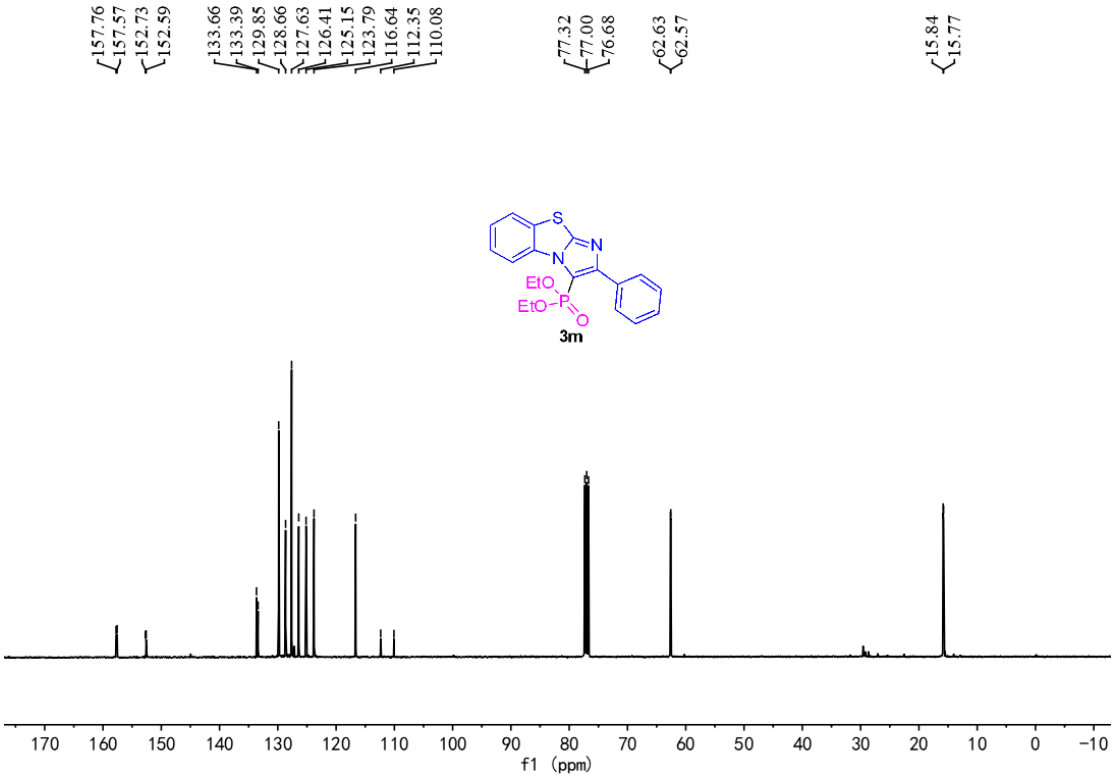

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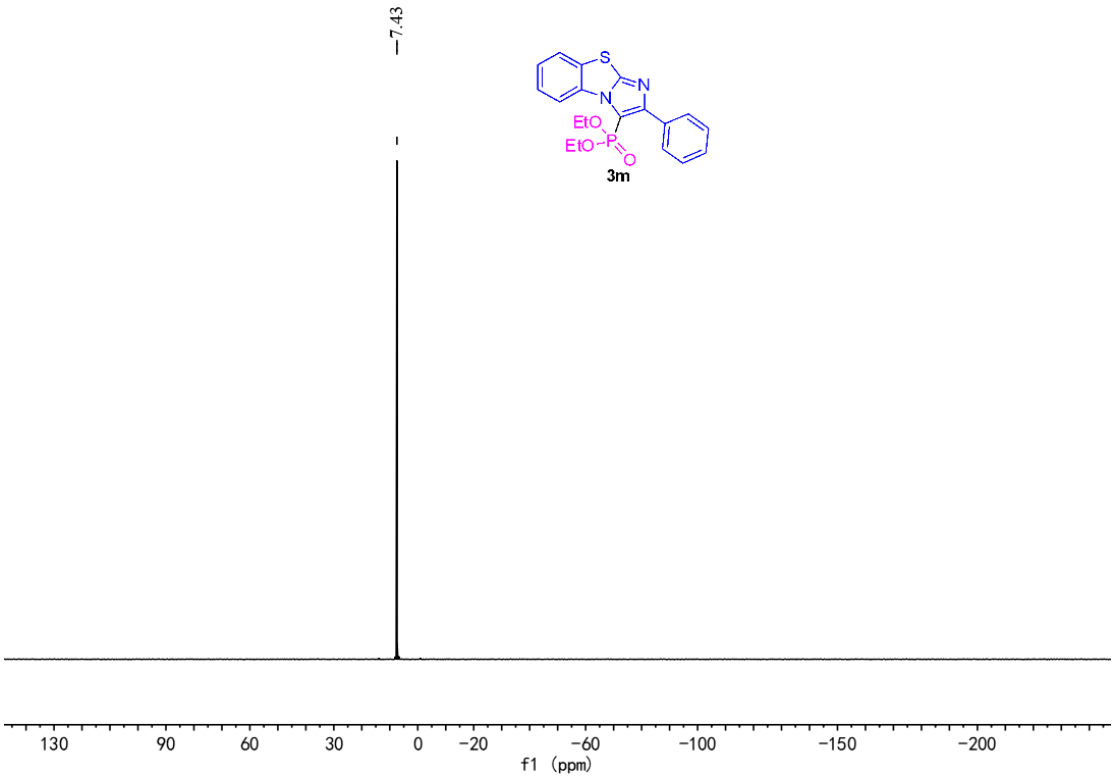

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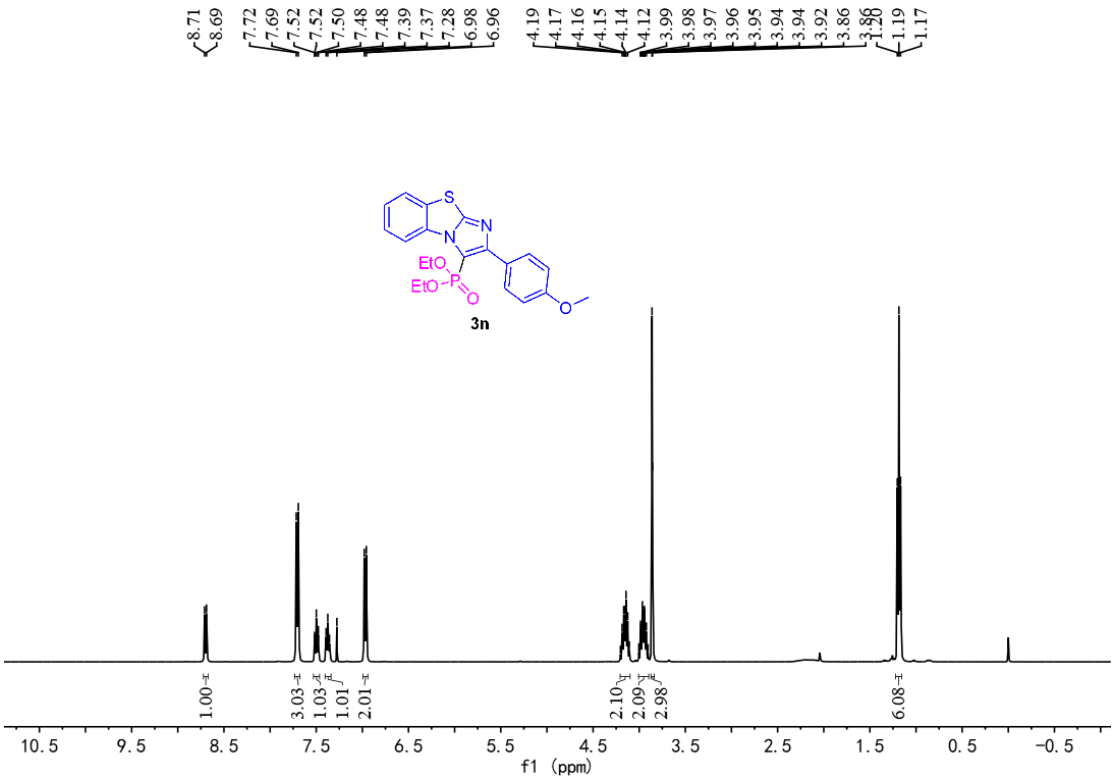

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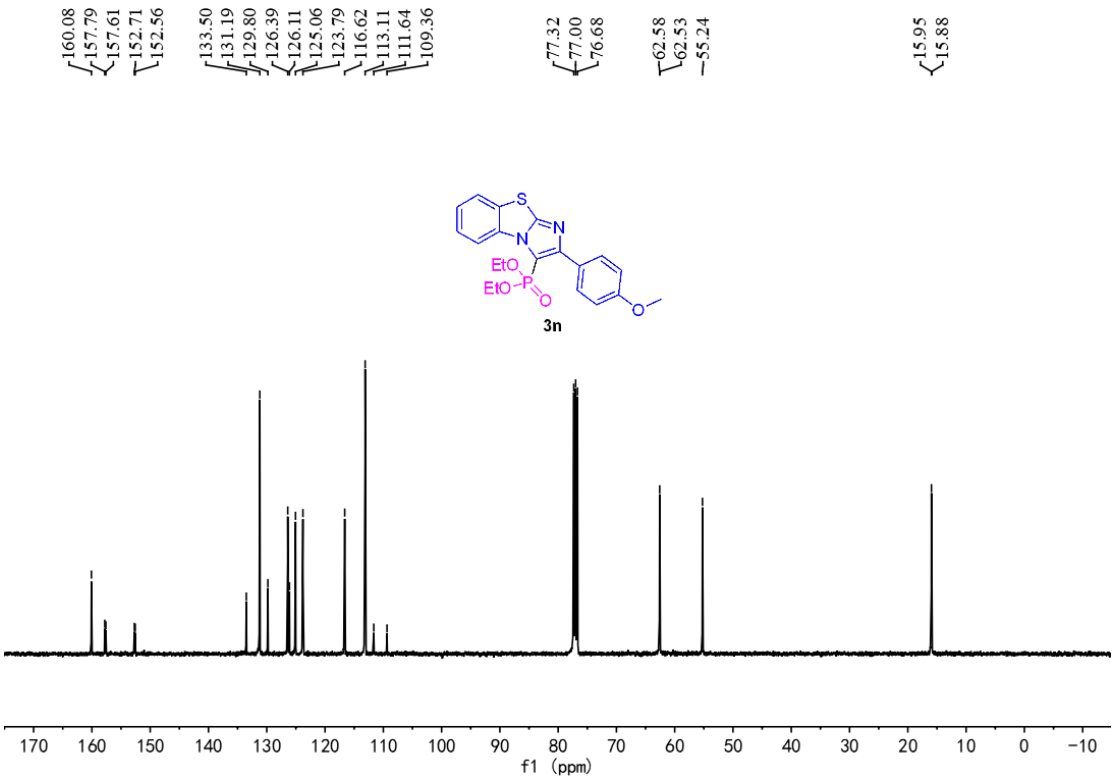

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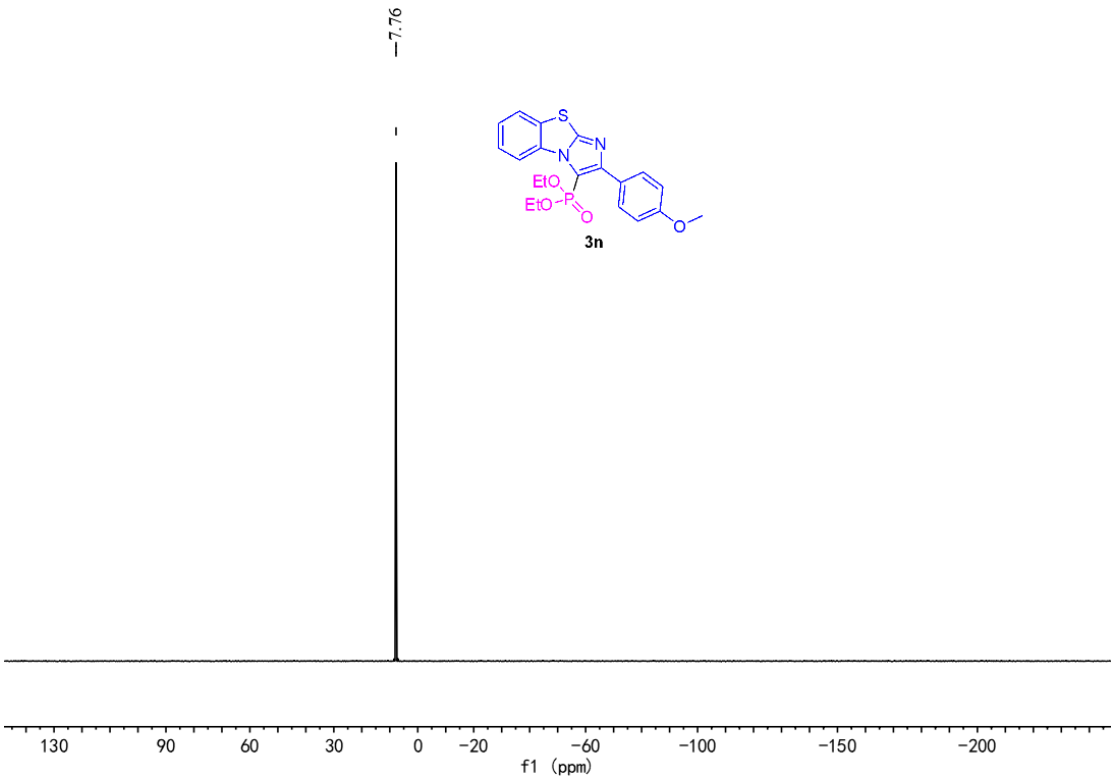

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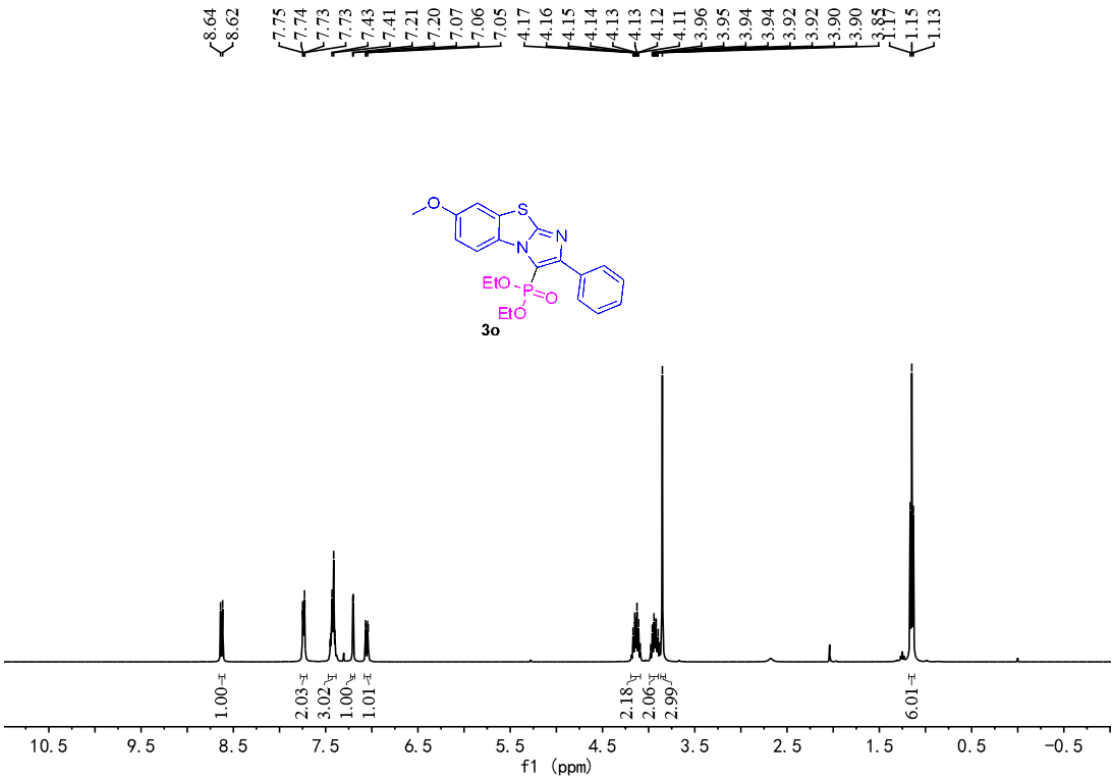

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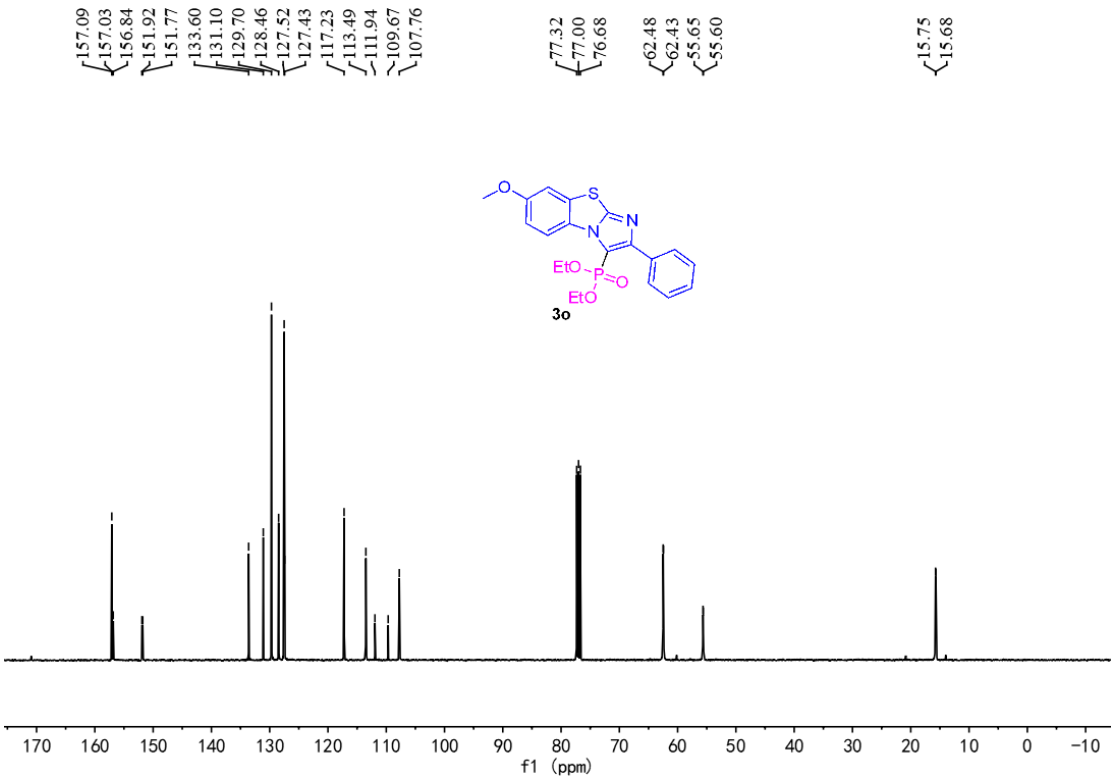

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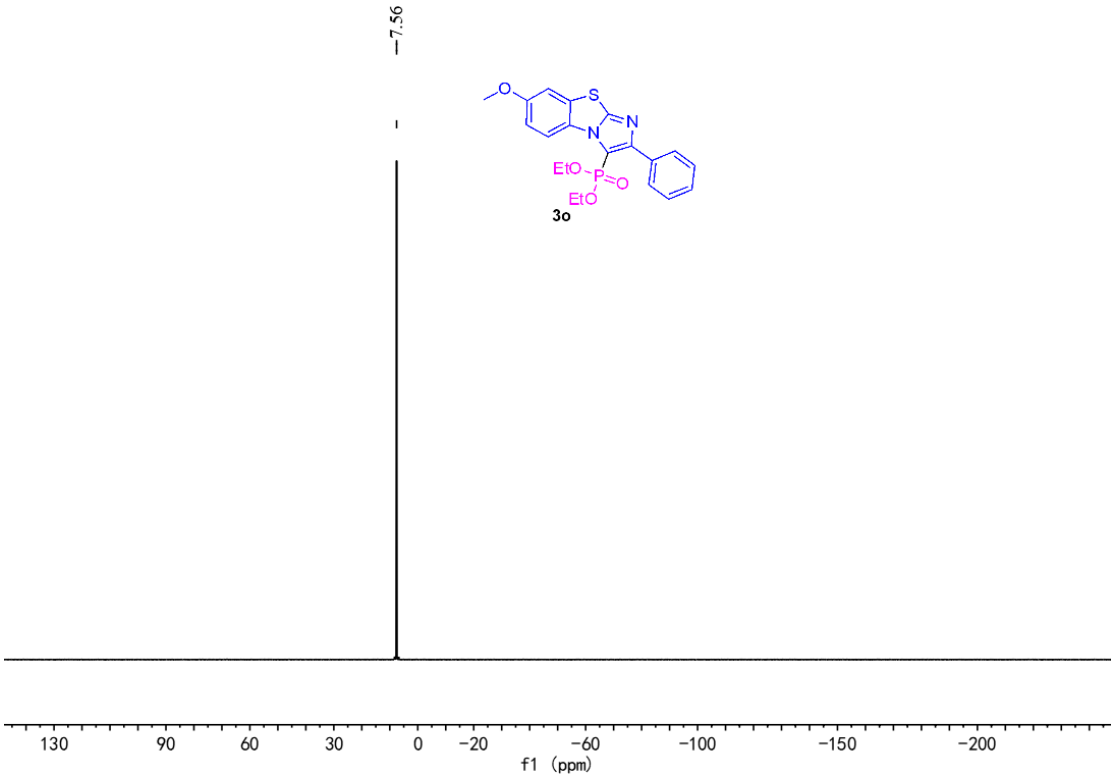

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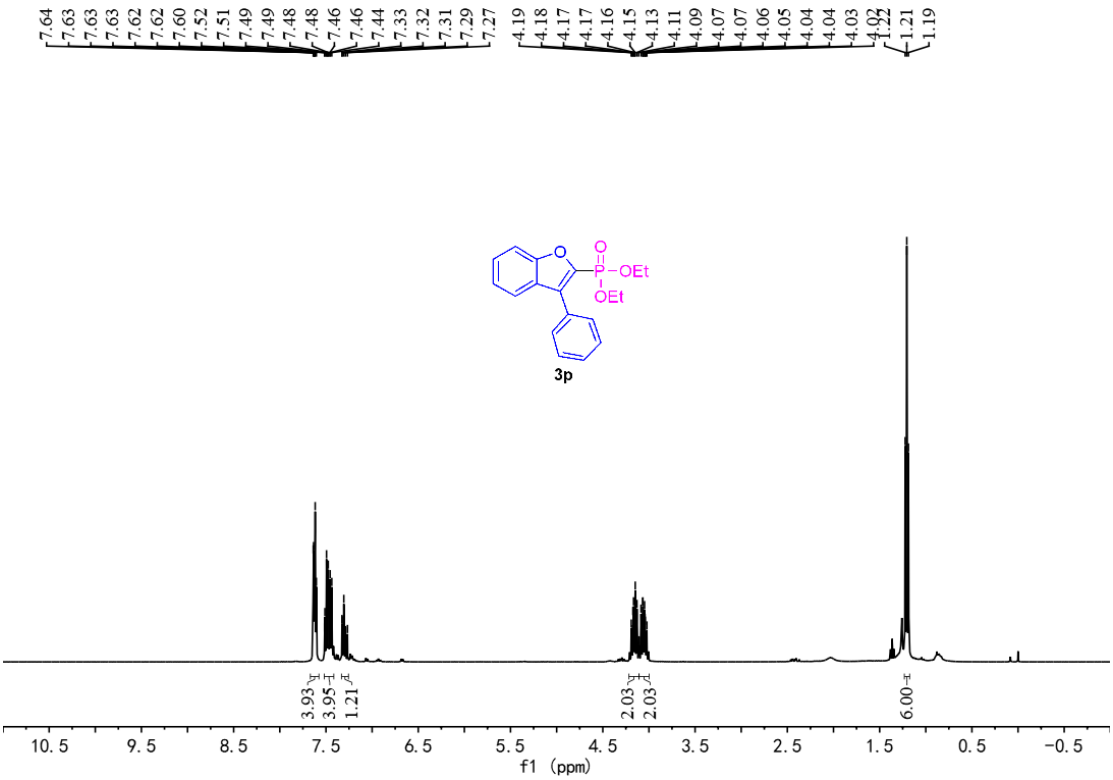

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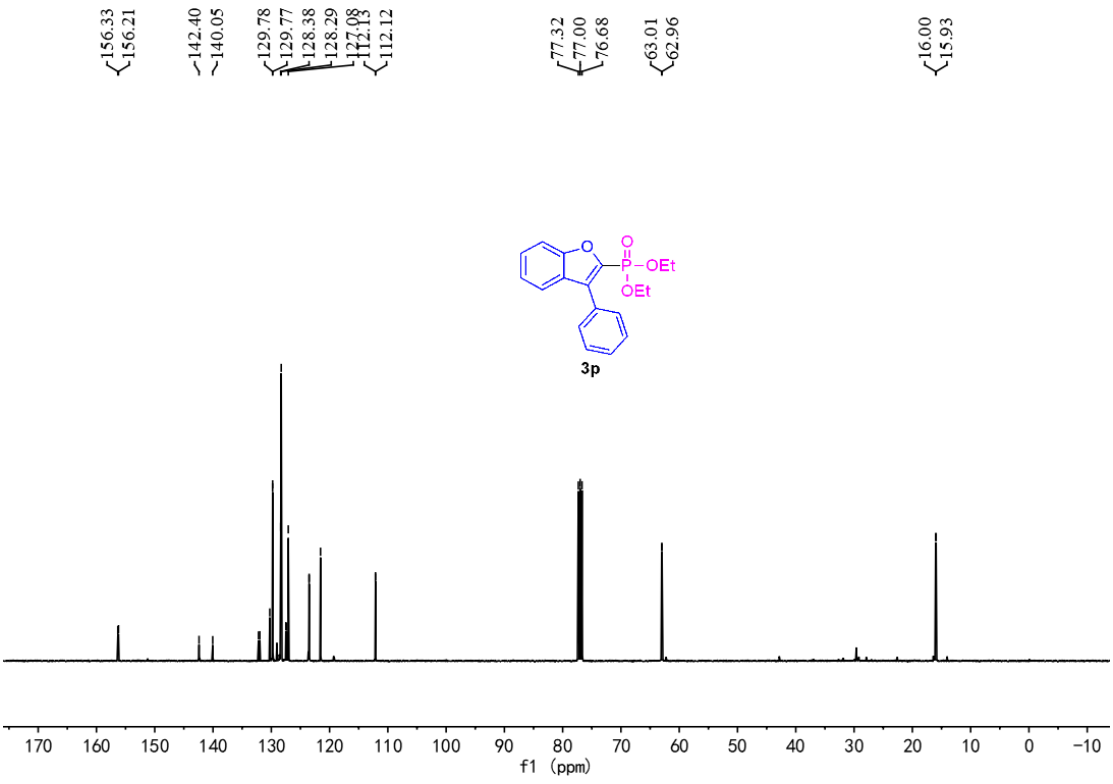

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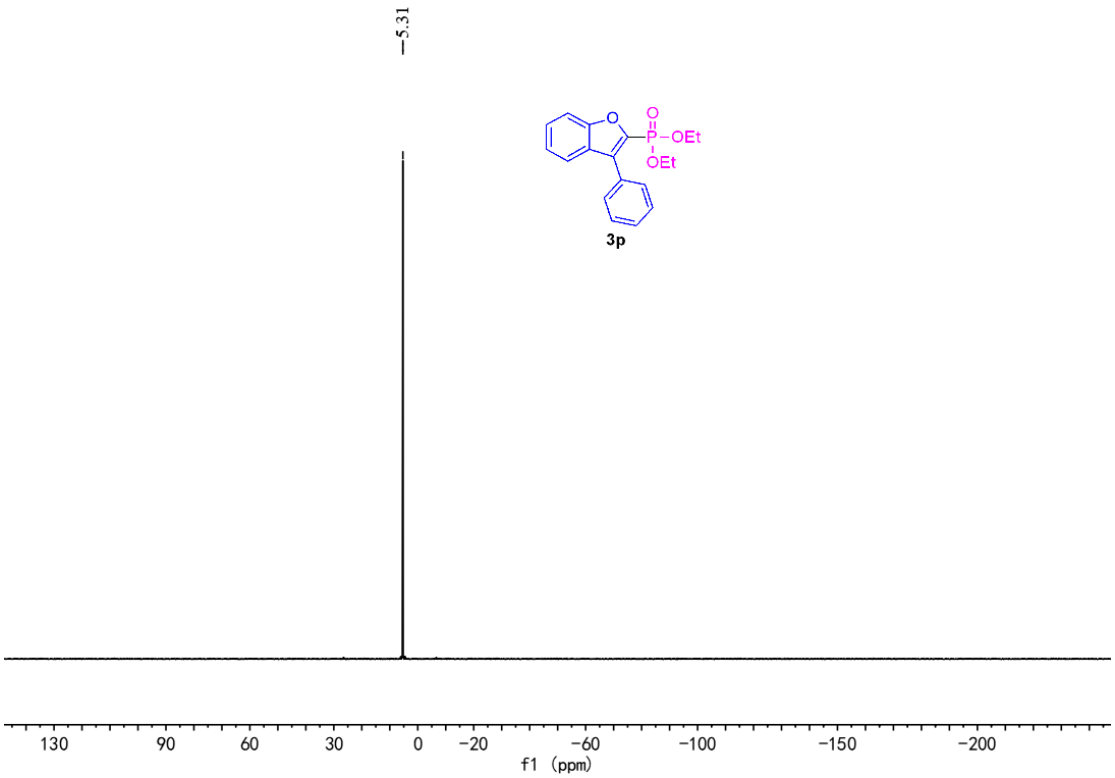

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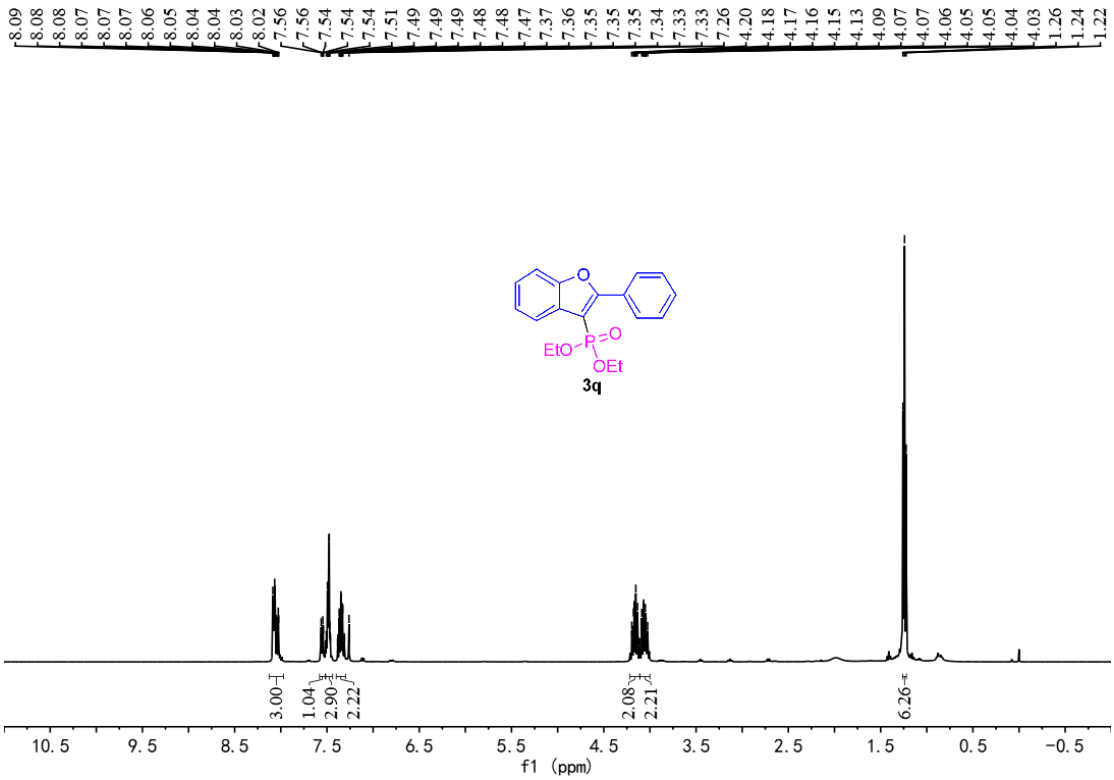

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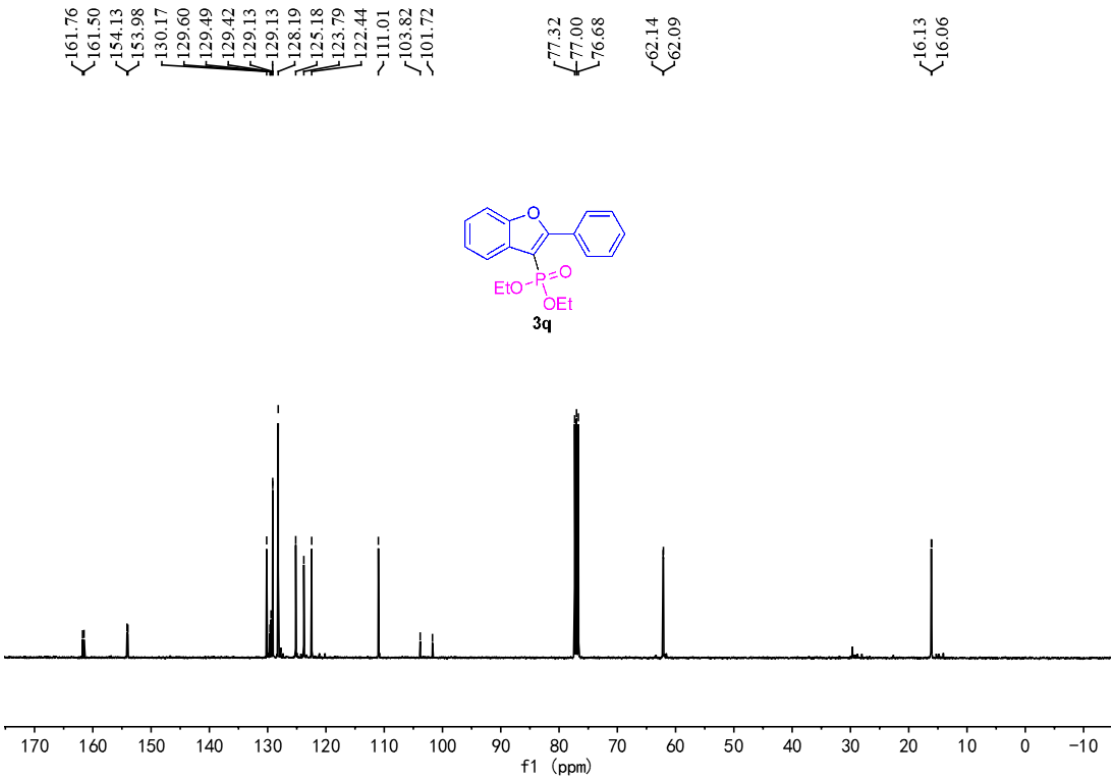

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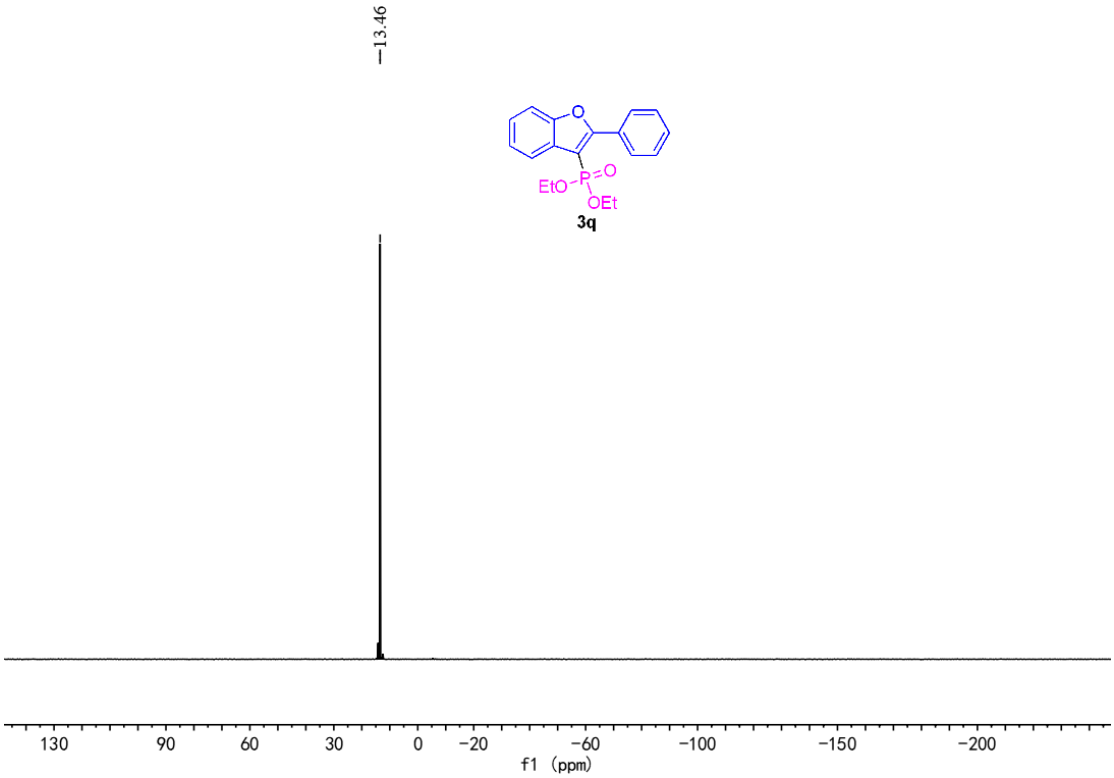

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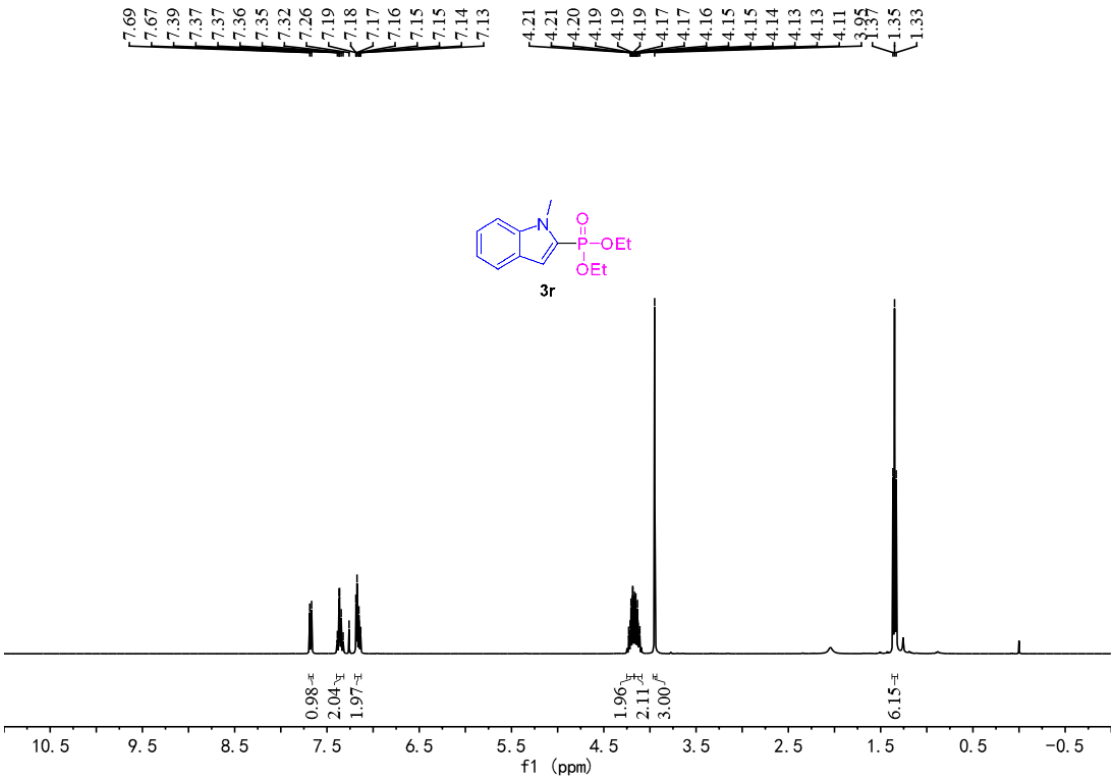
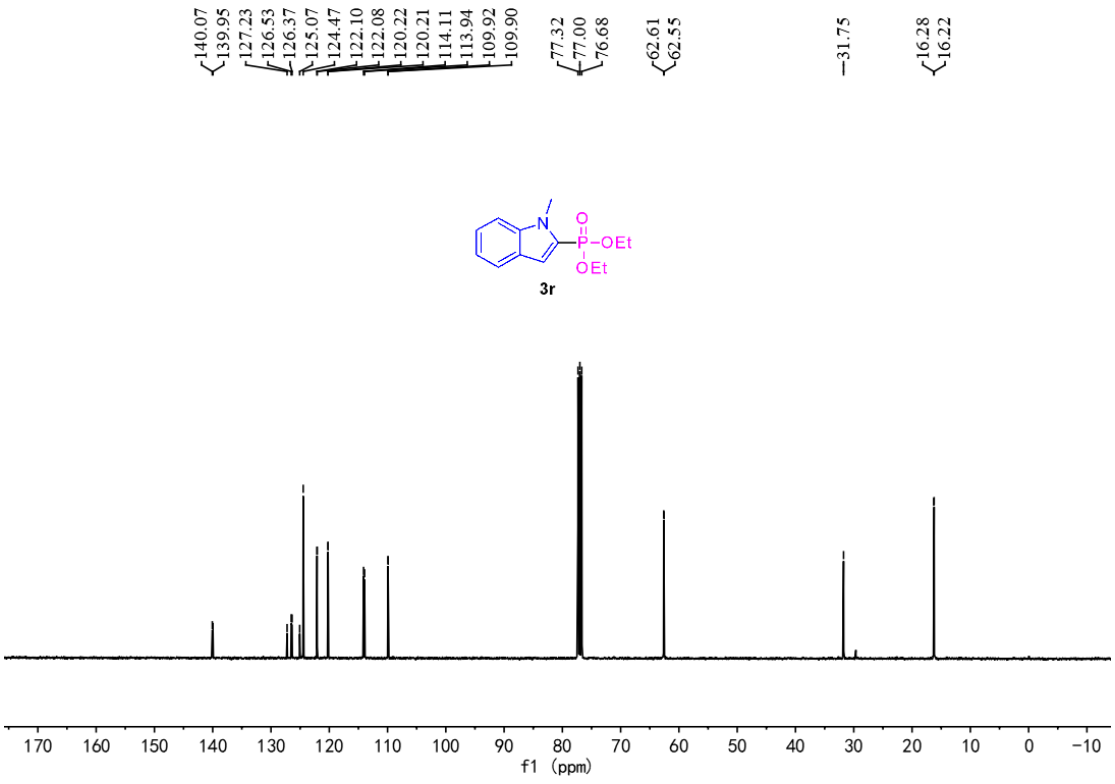


^{13}C NMR



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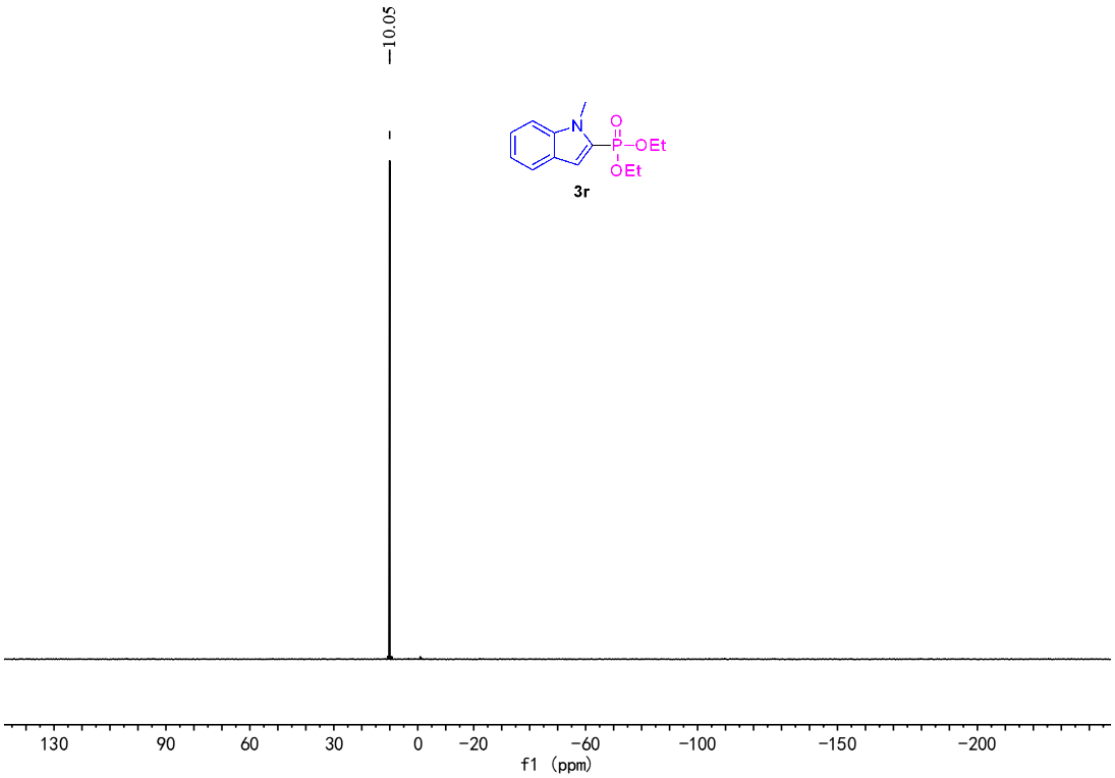
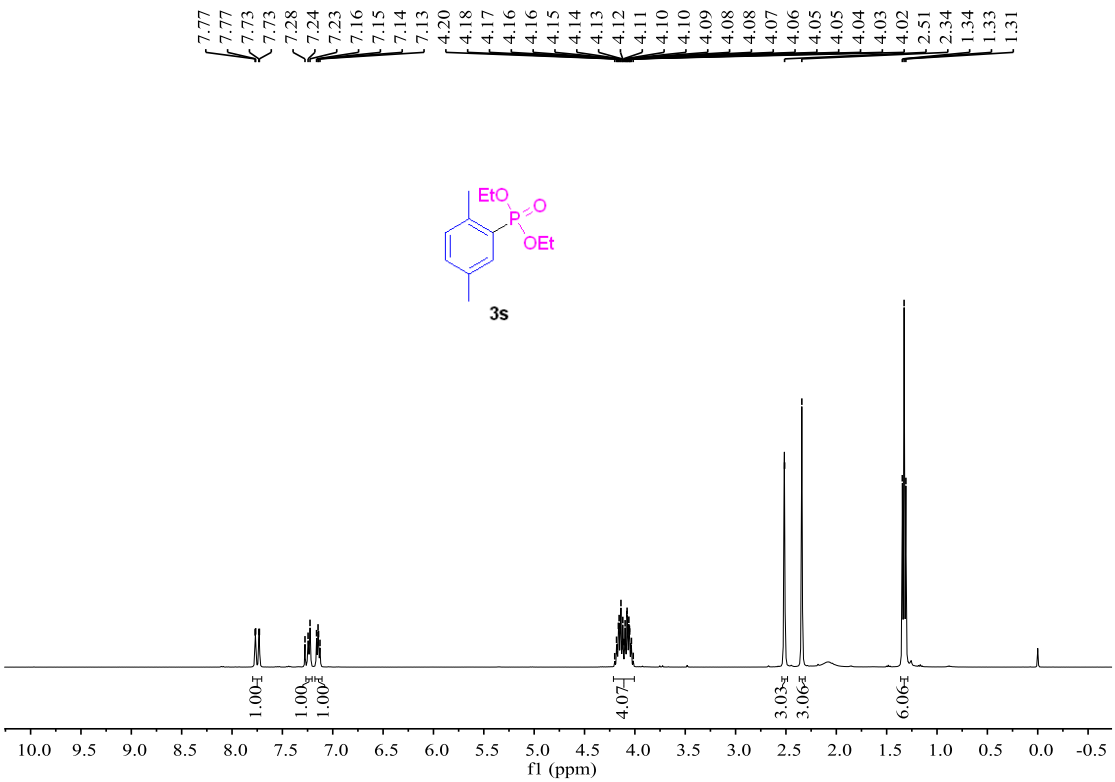


^{1}H NMR



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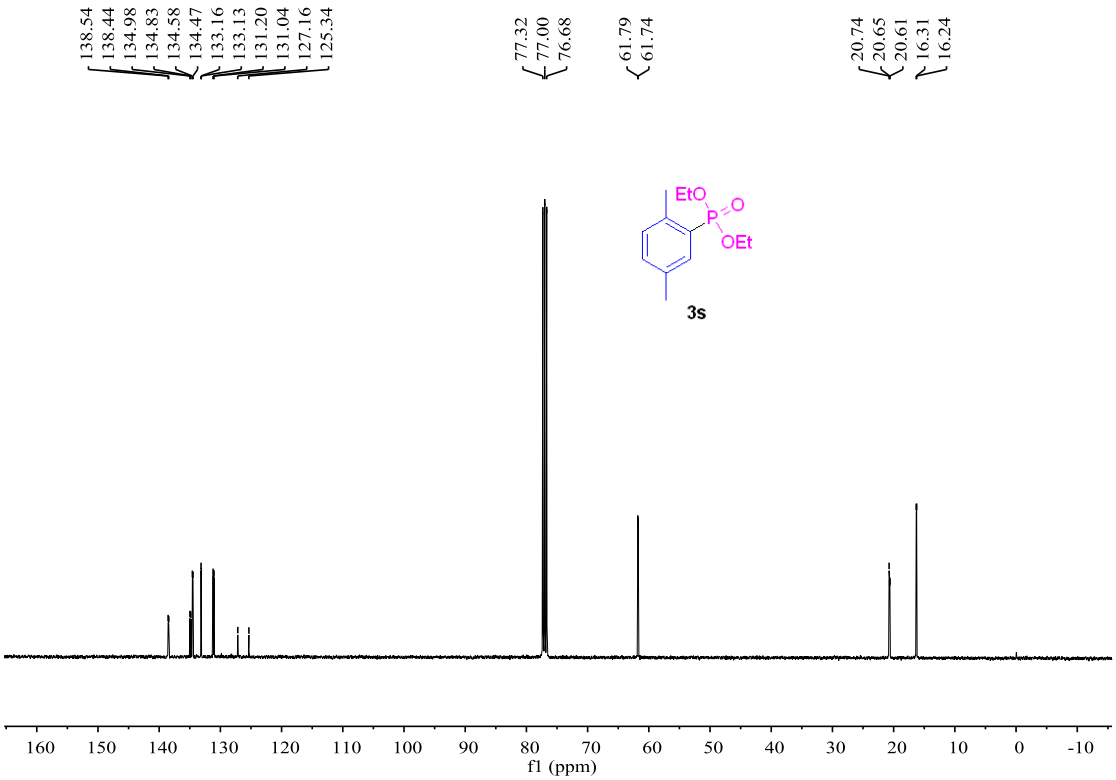
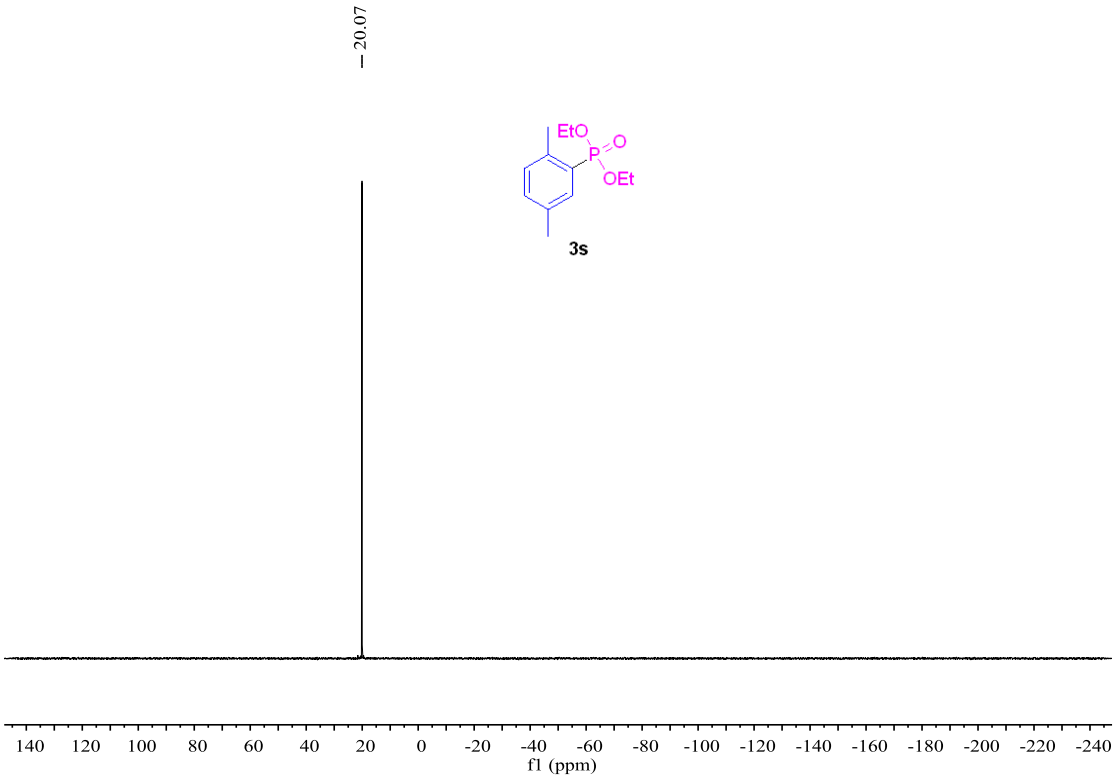
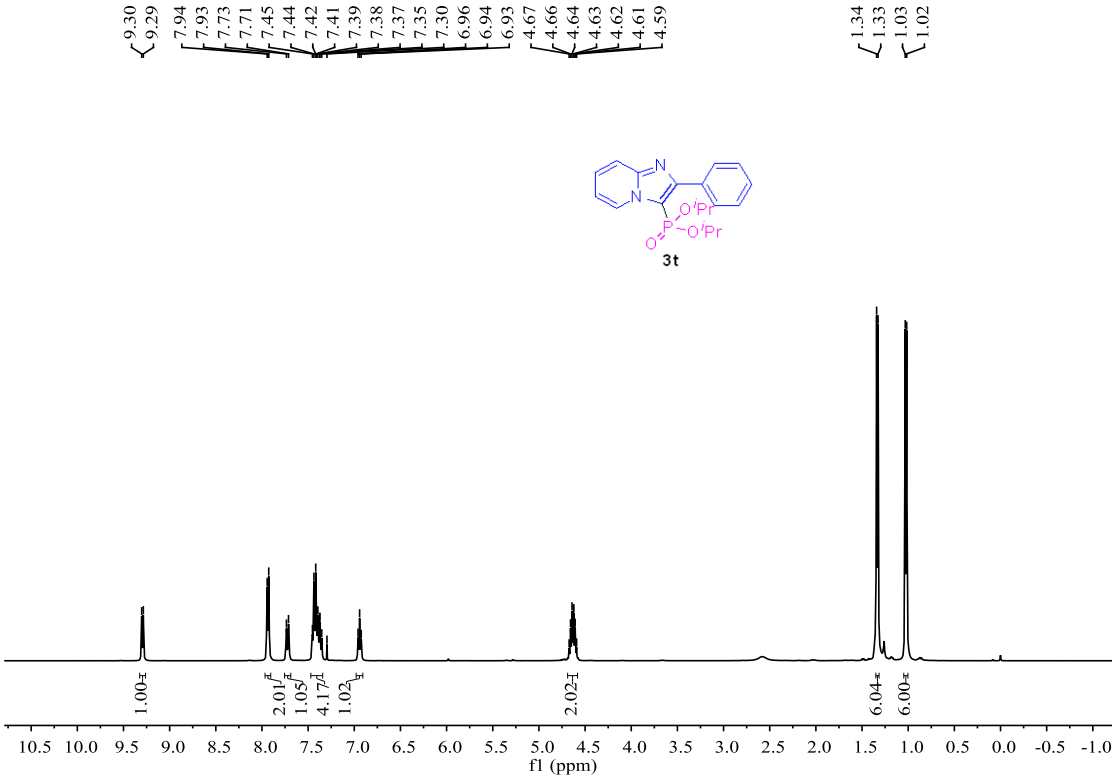


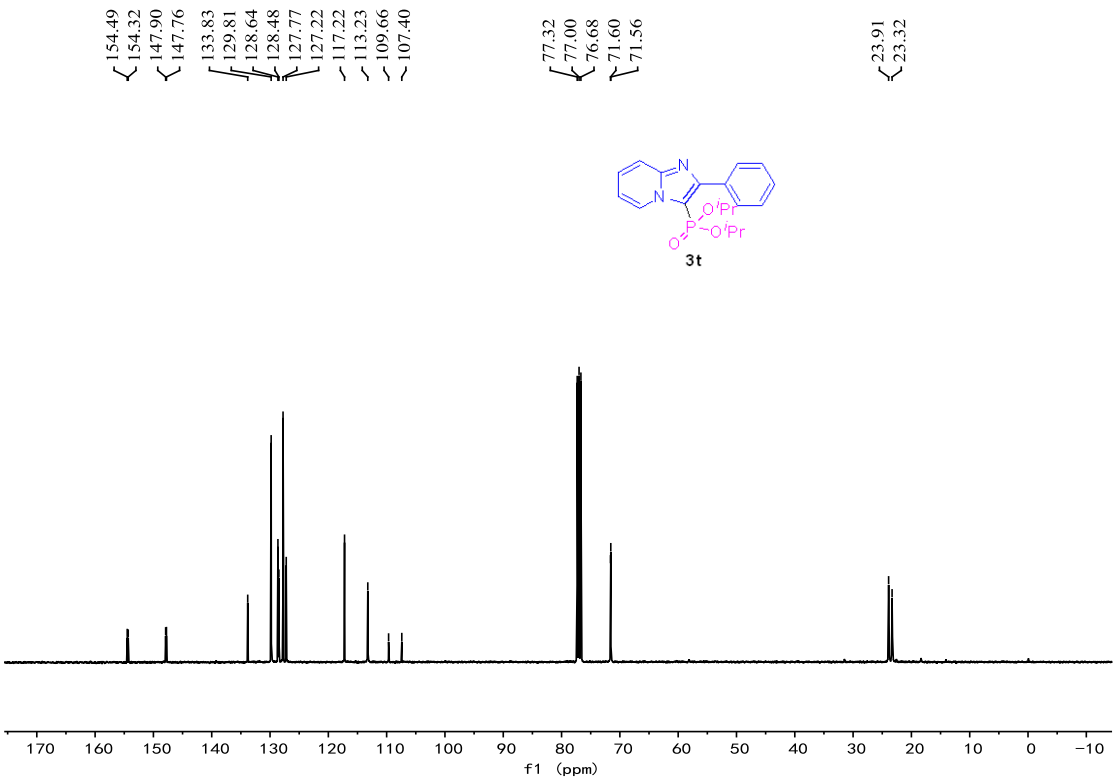
^{31}P NMR


20.07
EtO
P
O
OEt
3s
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

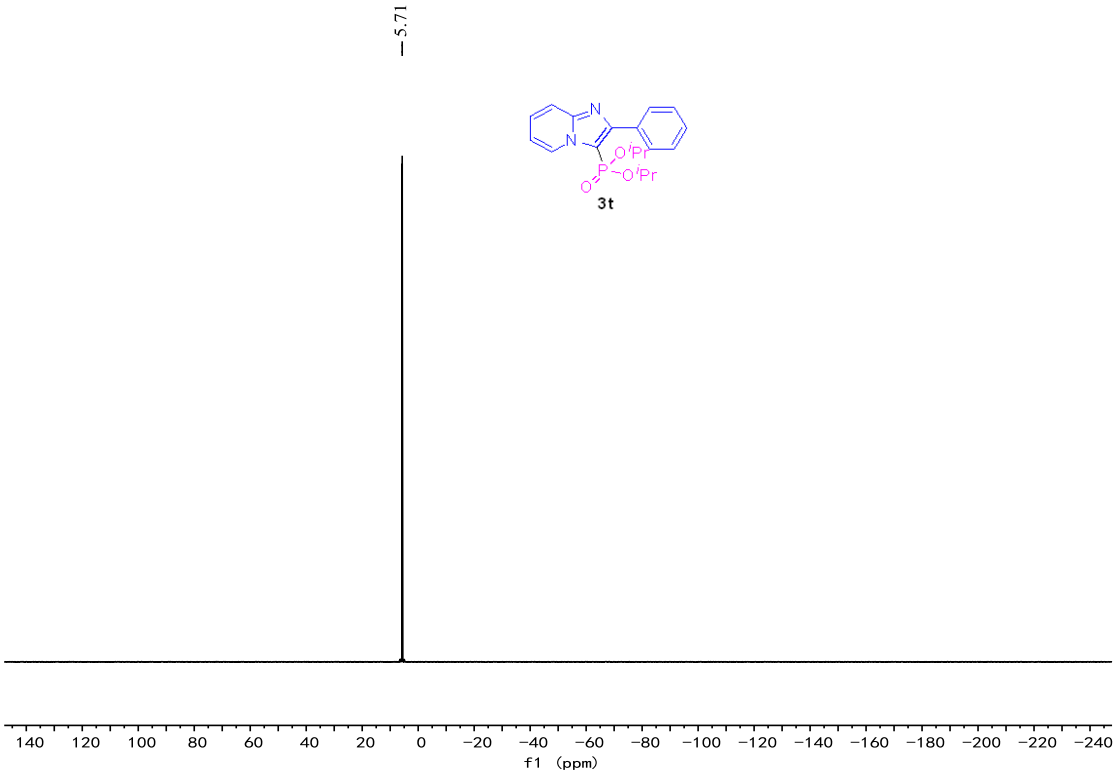
^{1}H NMR



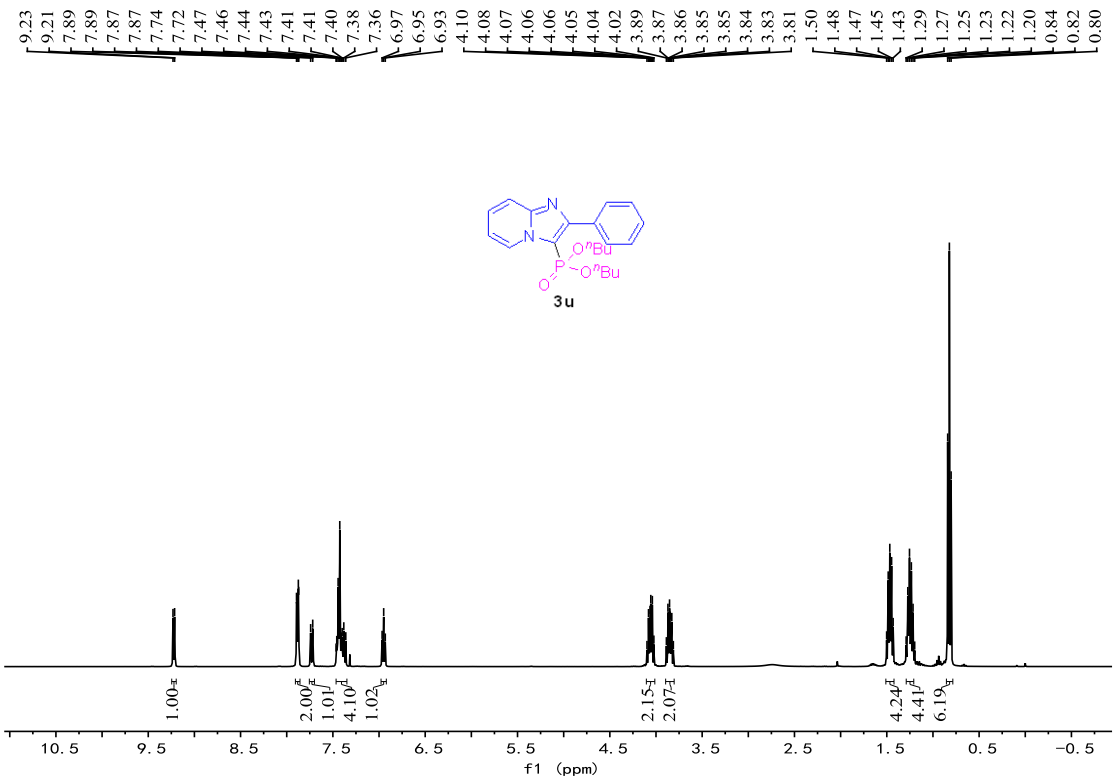
^{13}C NMR



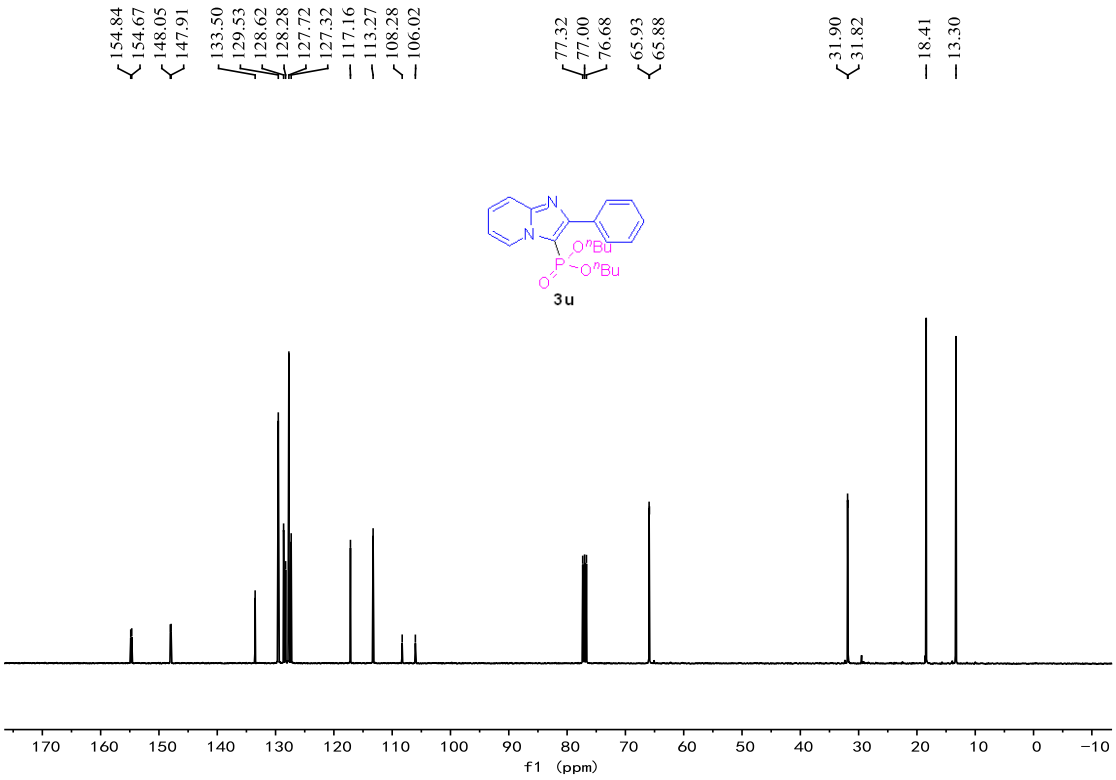
^{31}P NMR


5.71
N
N
O
P
O
O'Pr
O'Pr
3t
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)

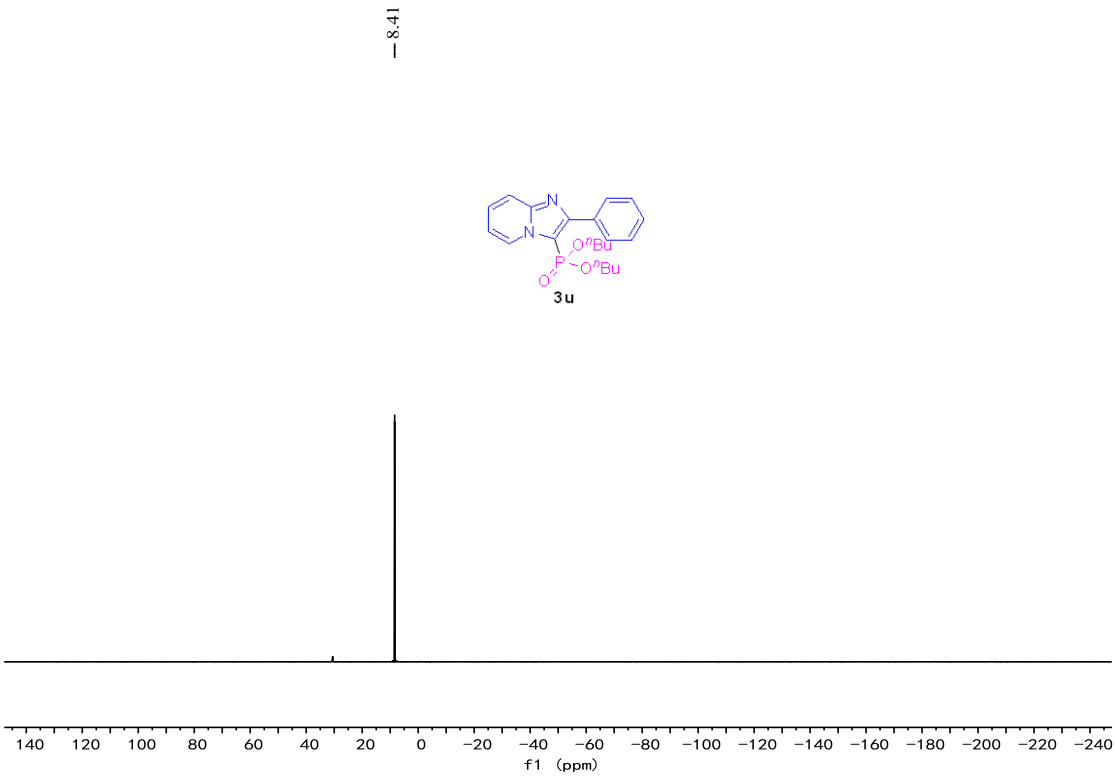
^{1}H NMR



^{13}C NMR



^{31}P NMR


8.41
N
N
O
P
O
O
nBu
nBu
3u
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
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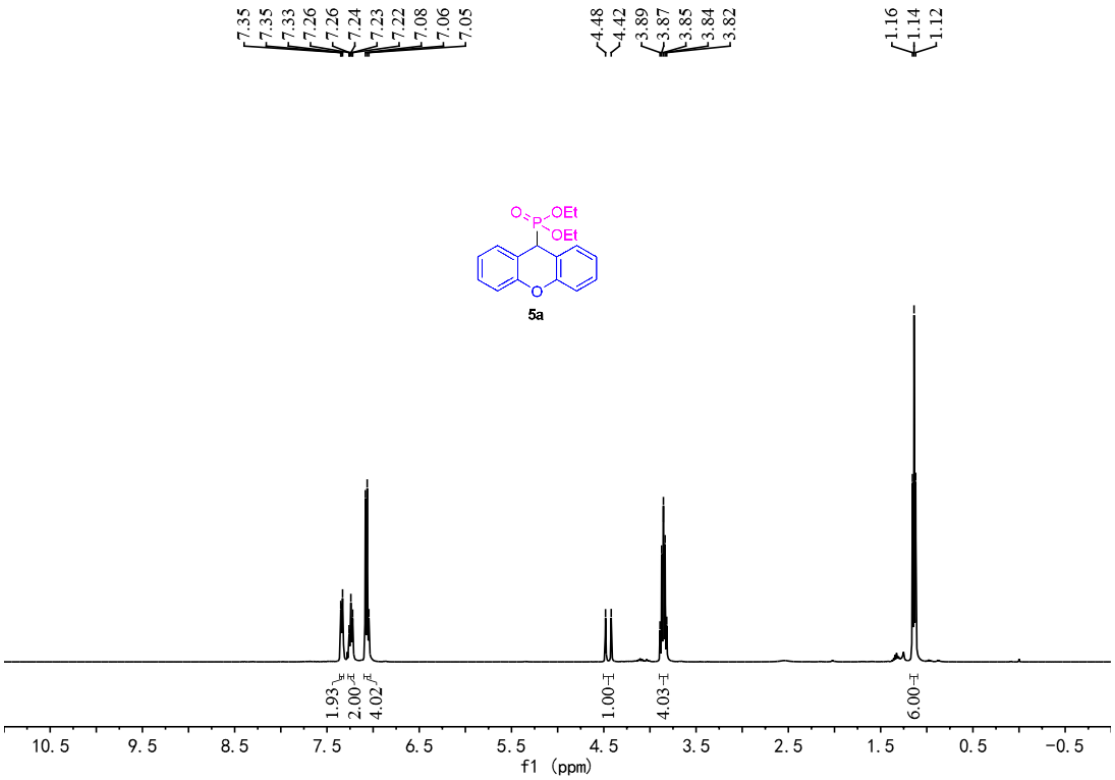
−180
−200
−220
−240
f1 (ppm)

^{1}H NMR



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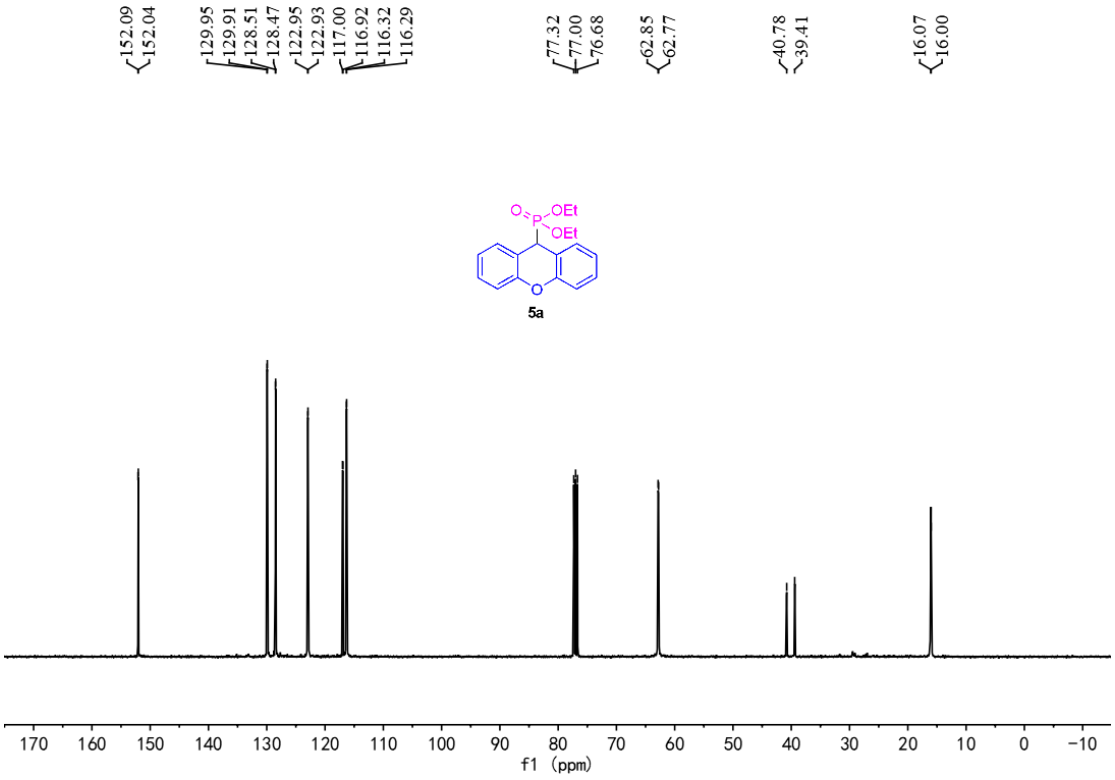
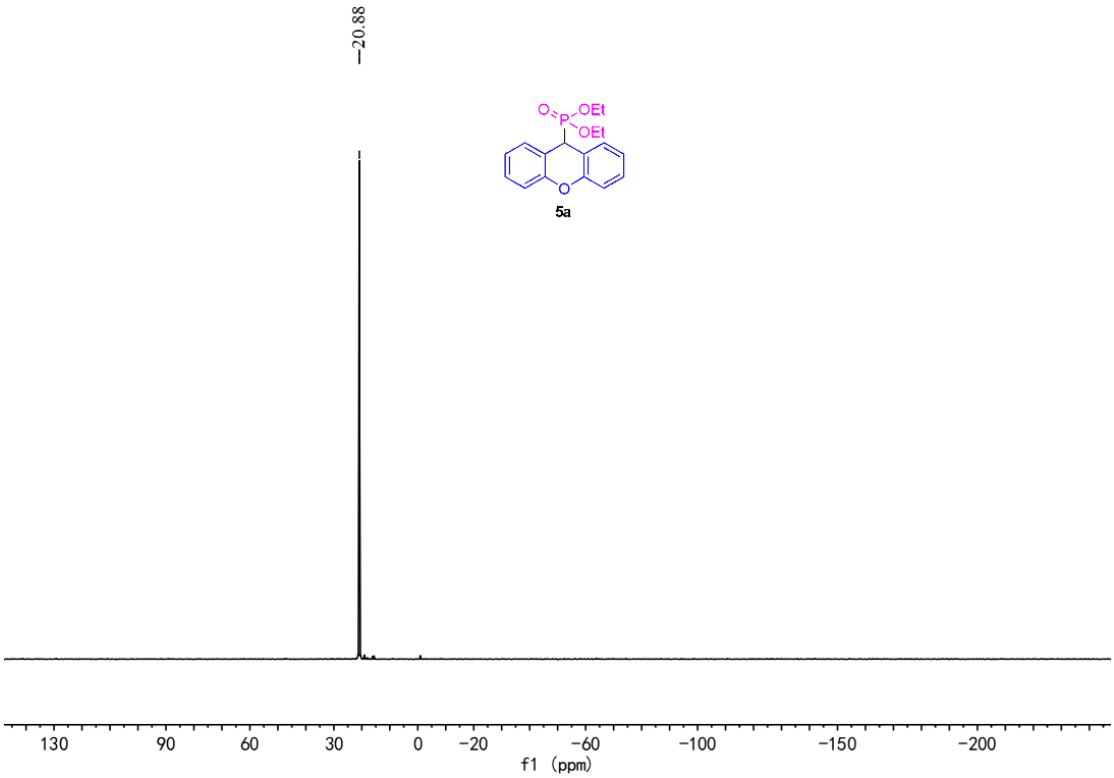
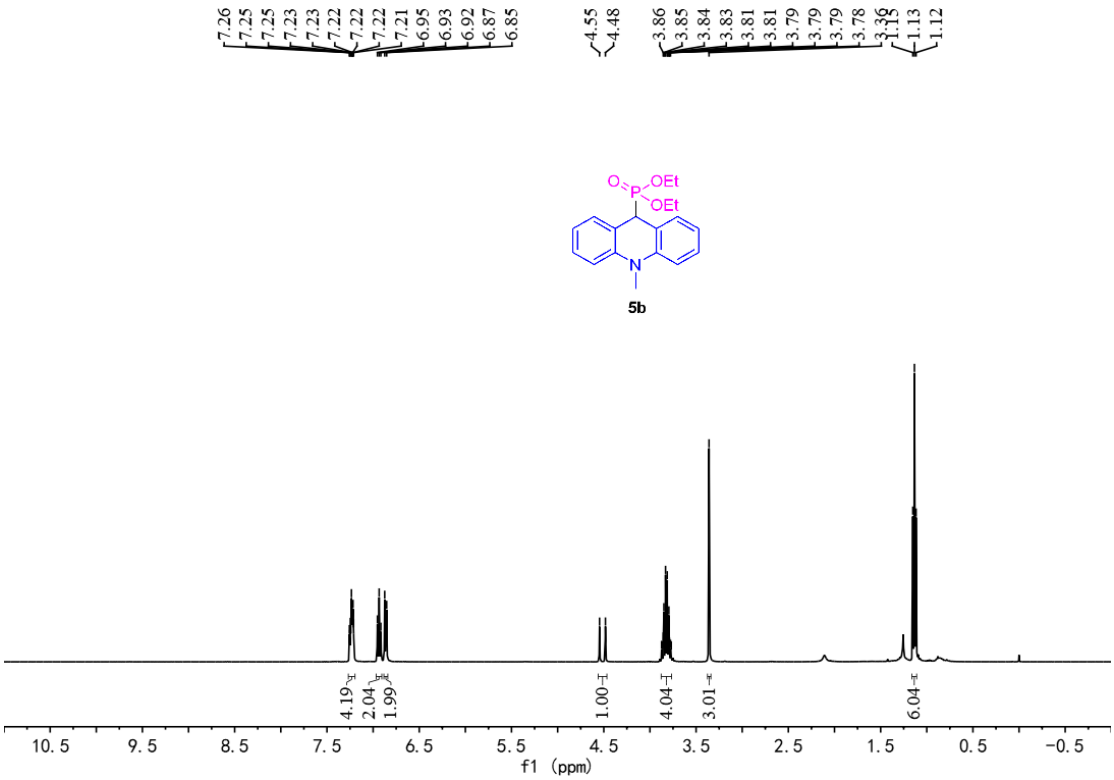


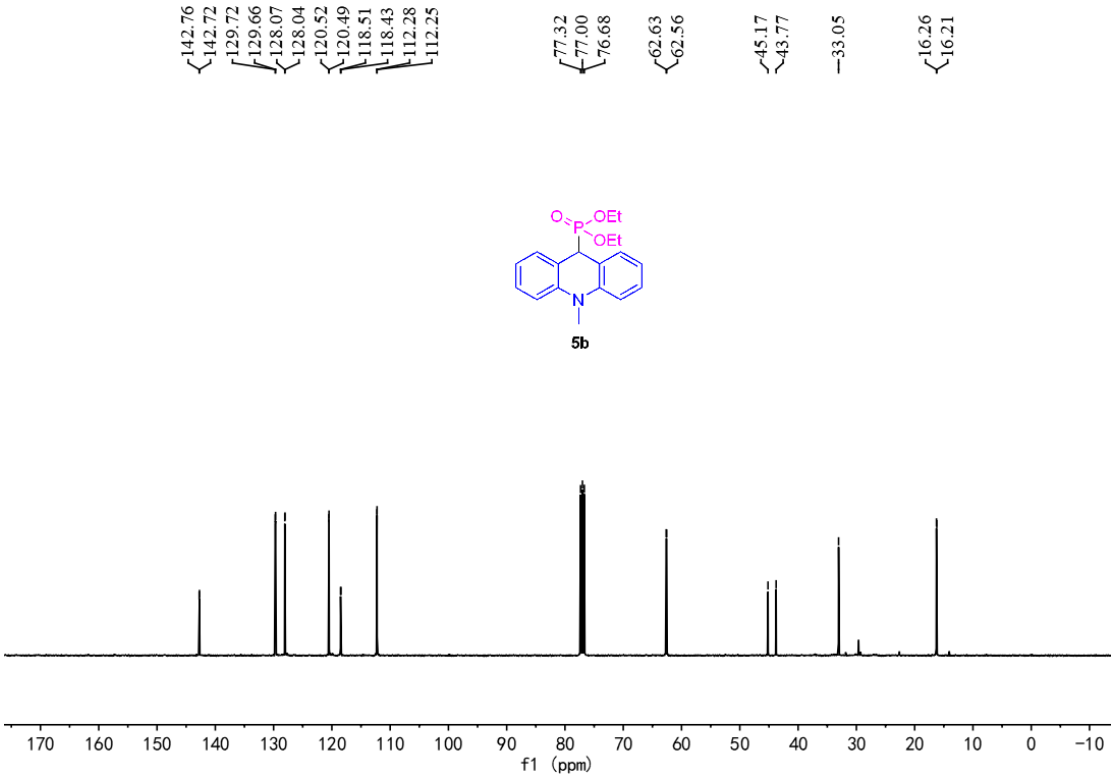
^{31}P NMR



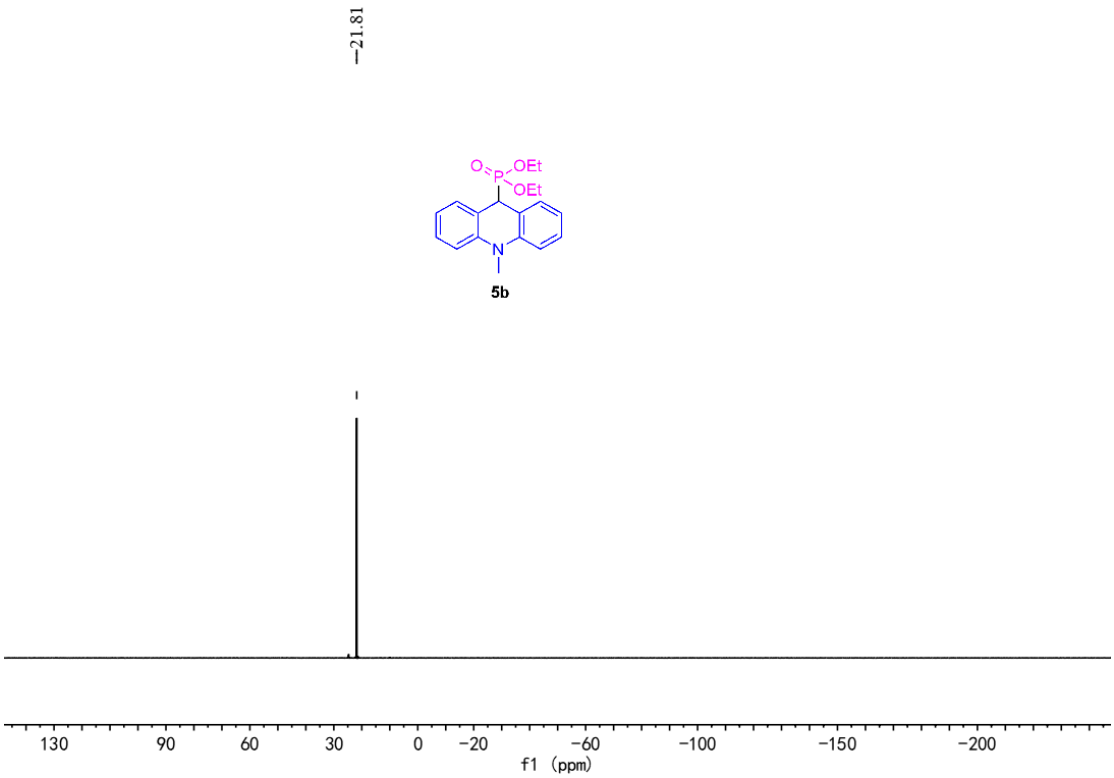
^{1}H NMR

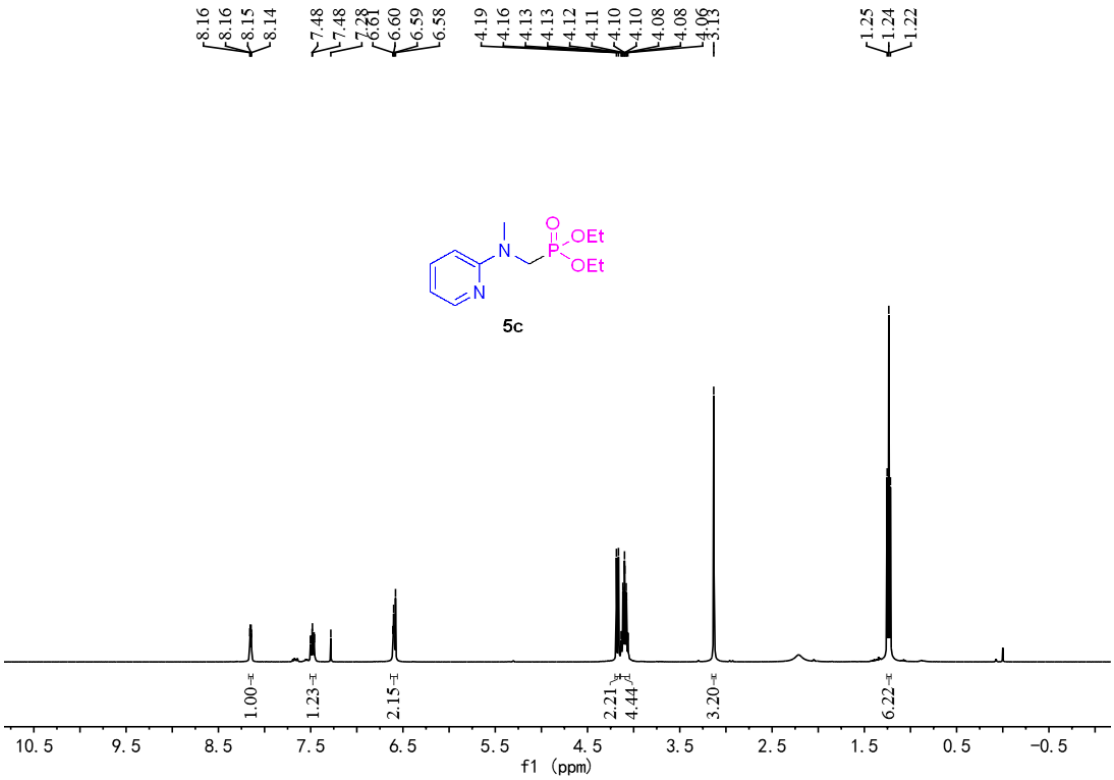


^{13}C NMR

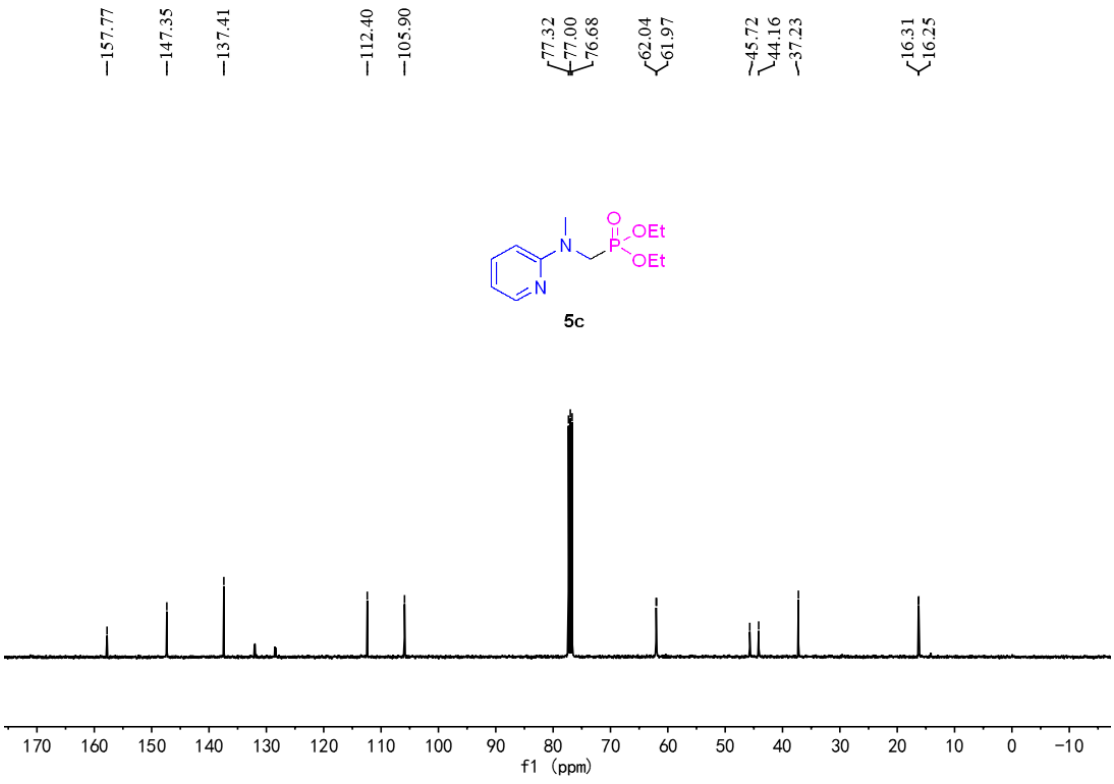


^{31}P NMR

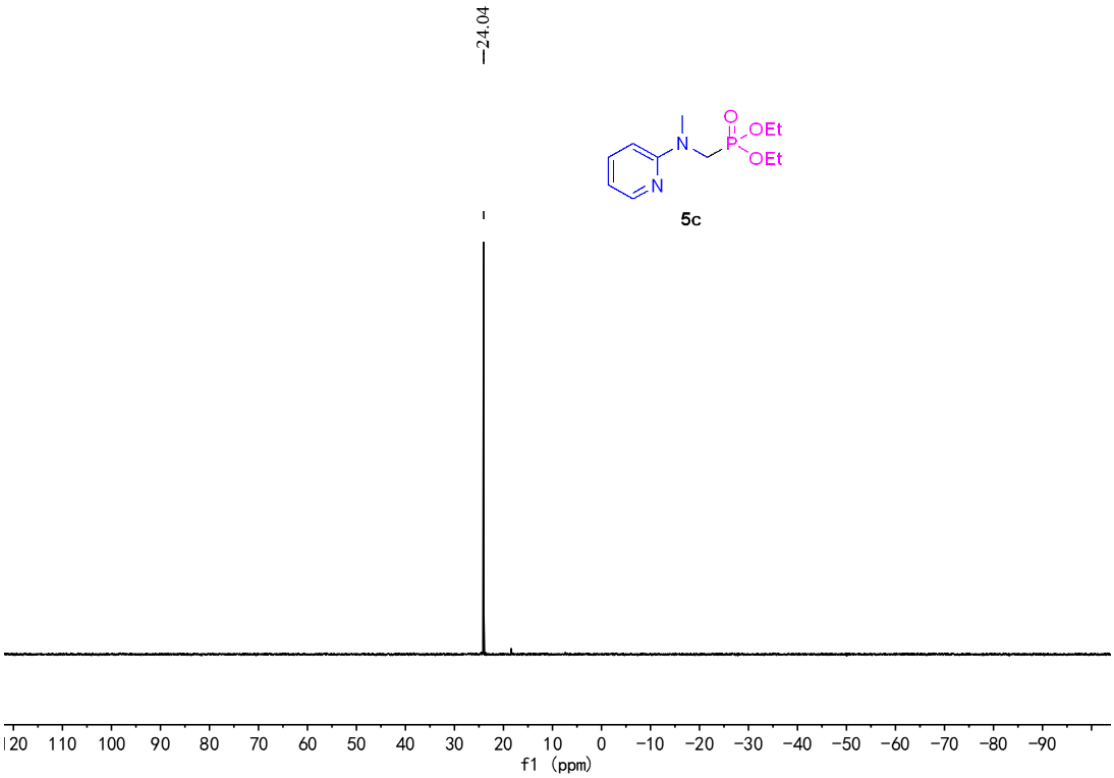




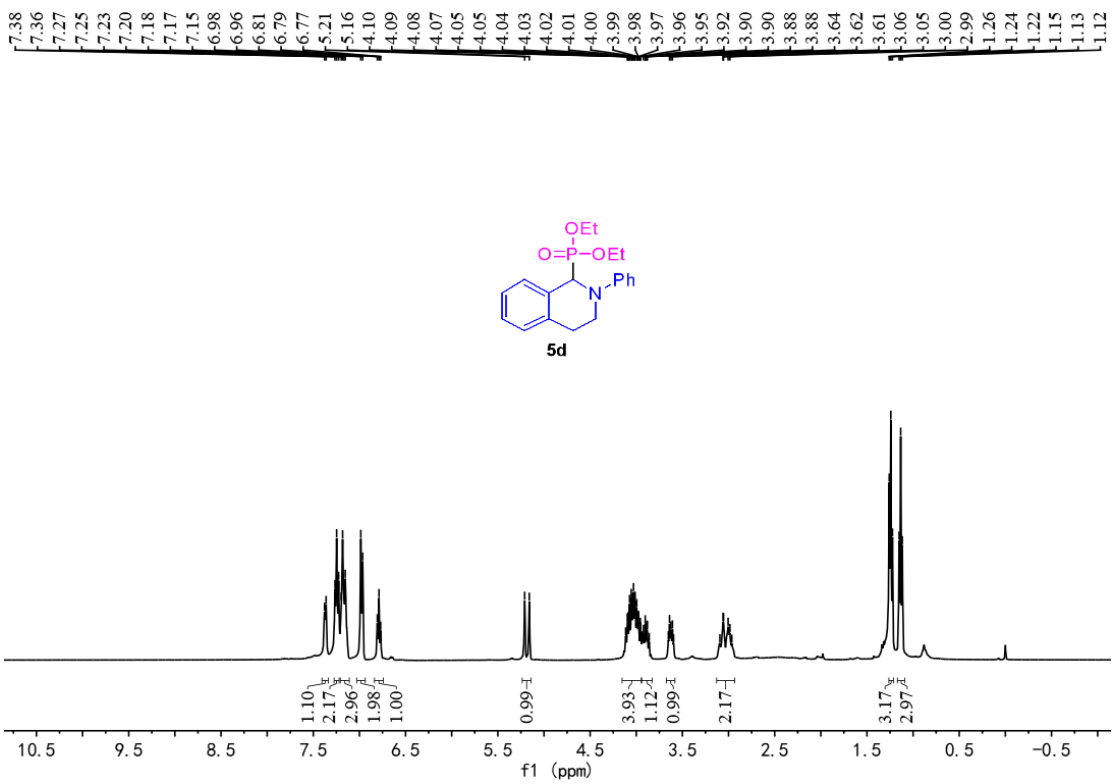
^{13}C NMR



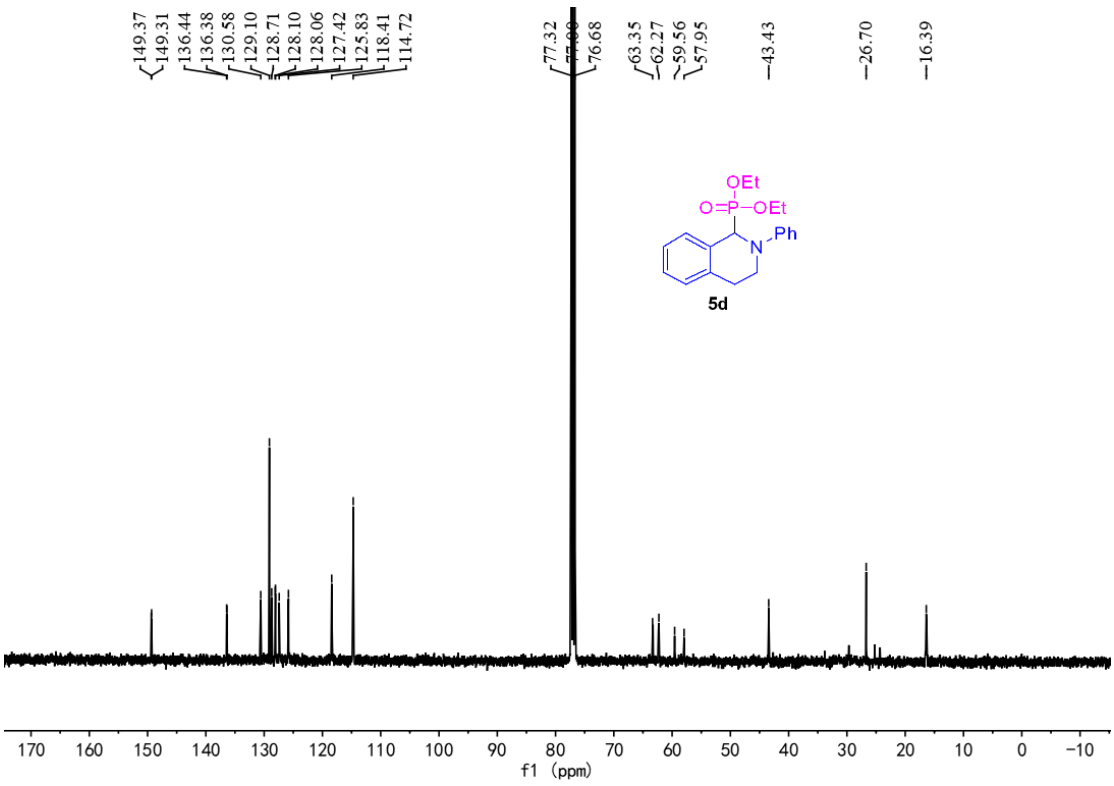
^{31}P NMR


24.04
OEt
OEt
5c
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

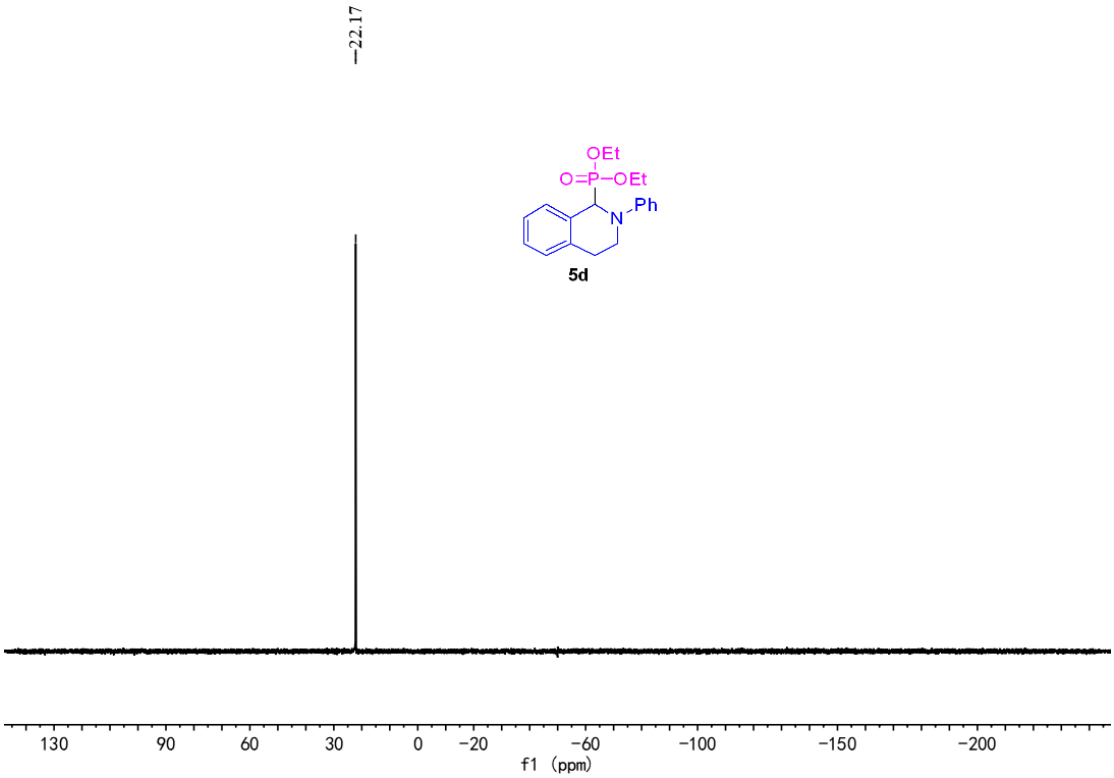
^{1}H NMR



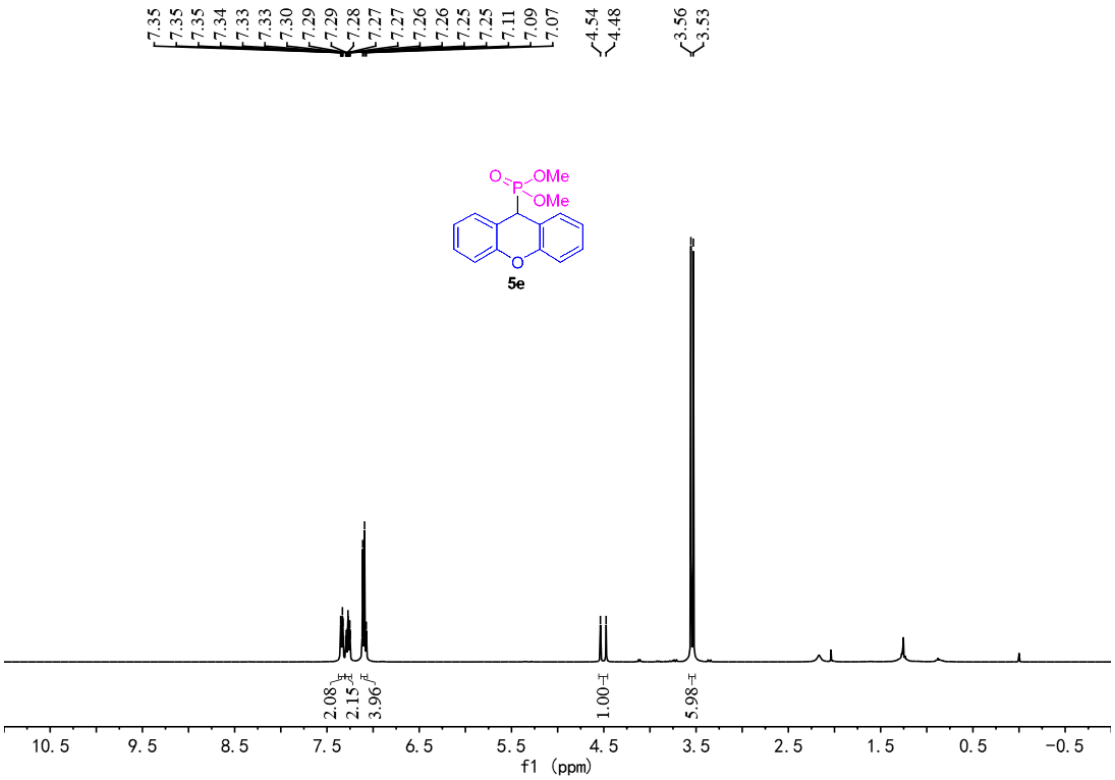
^{13}C NMR



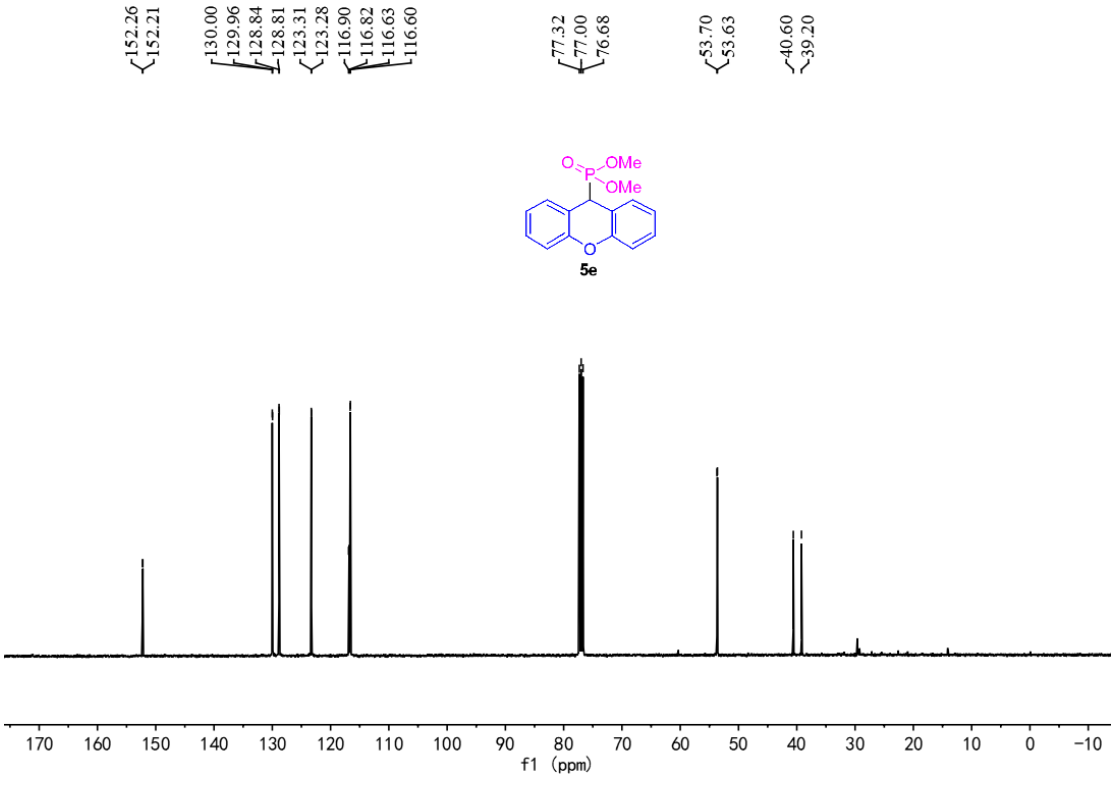
^{31}P NMR



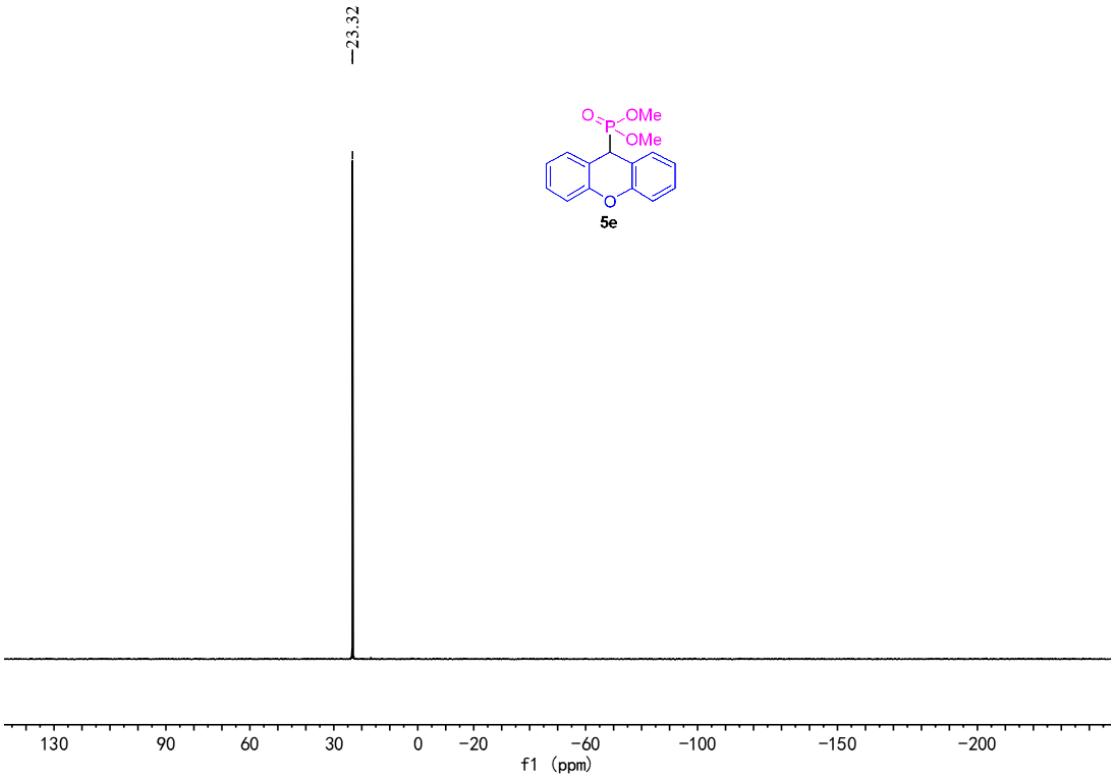
^{1}H NMR



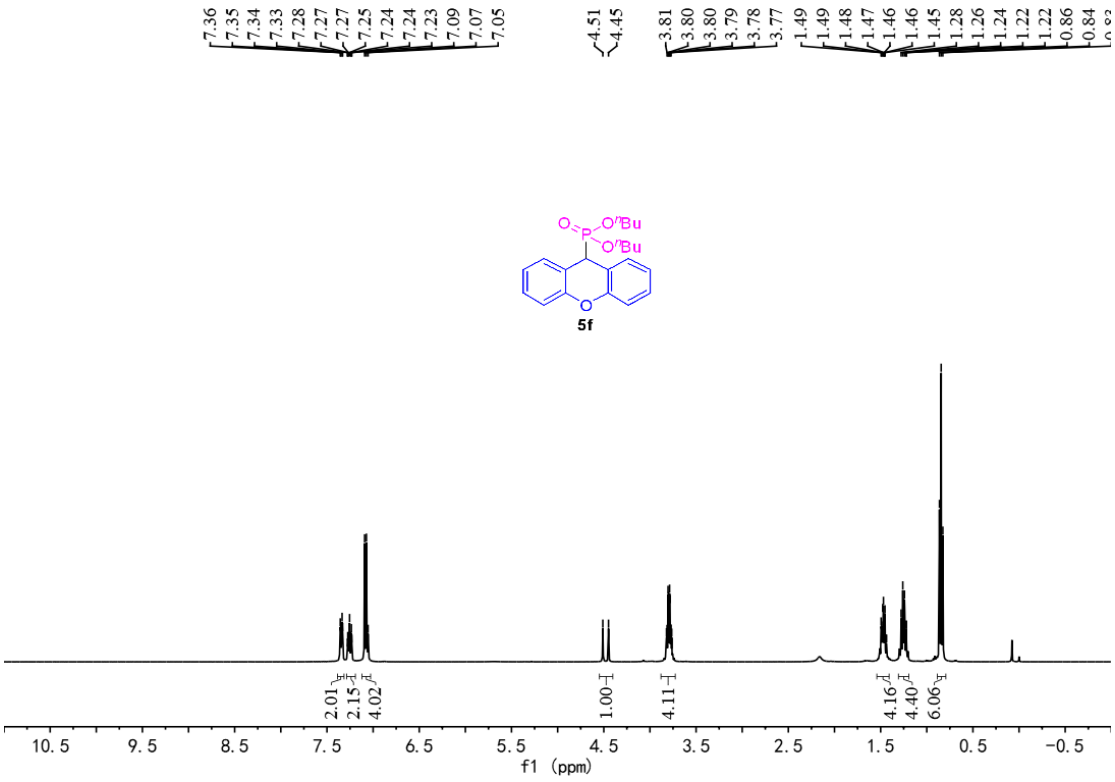
^{13}C NMR



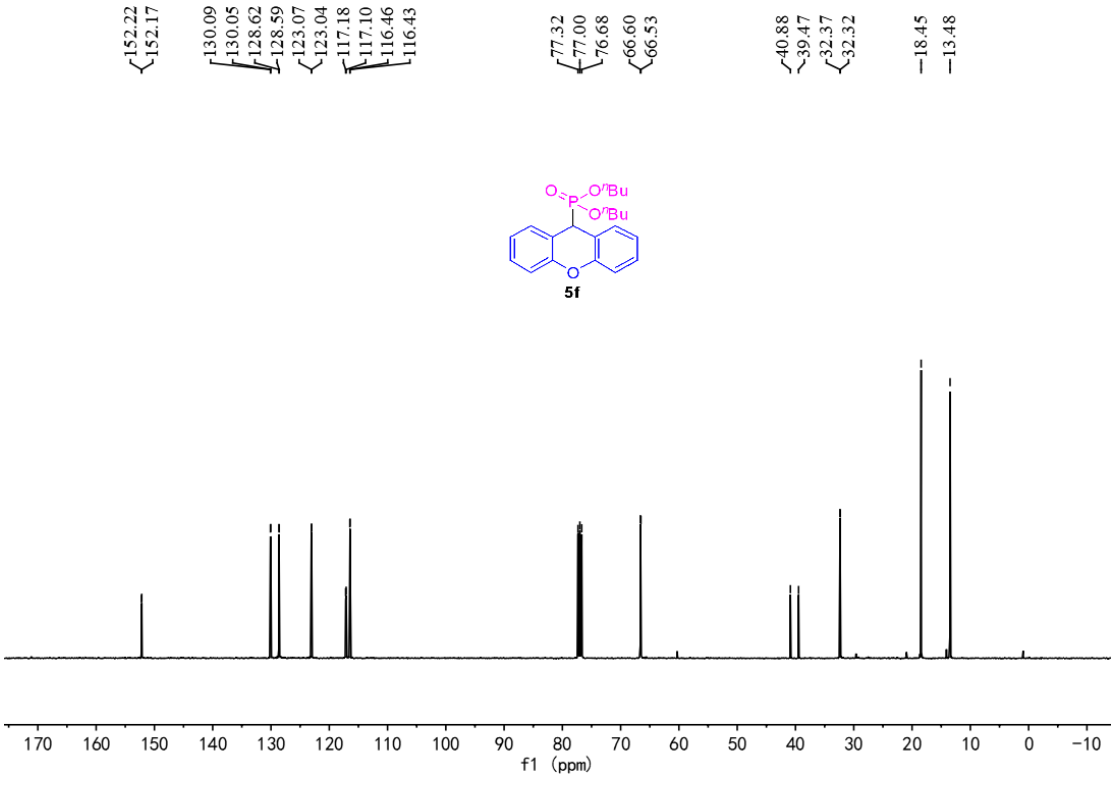
^{31}P NMR



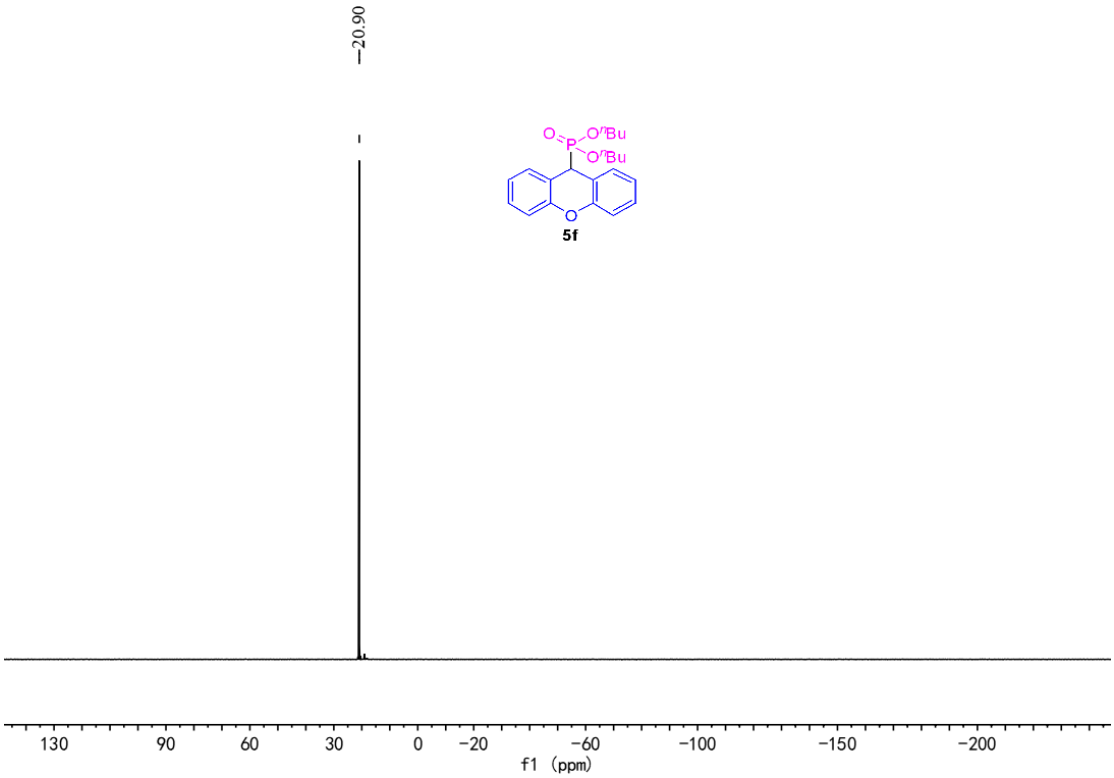
^{1}H NMR



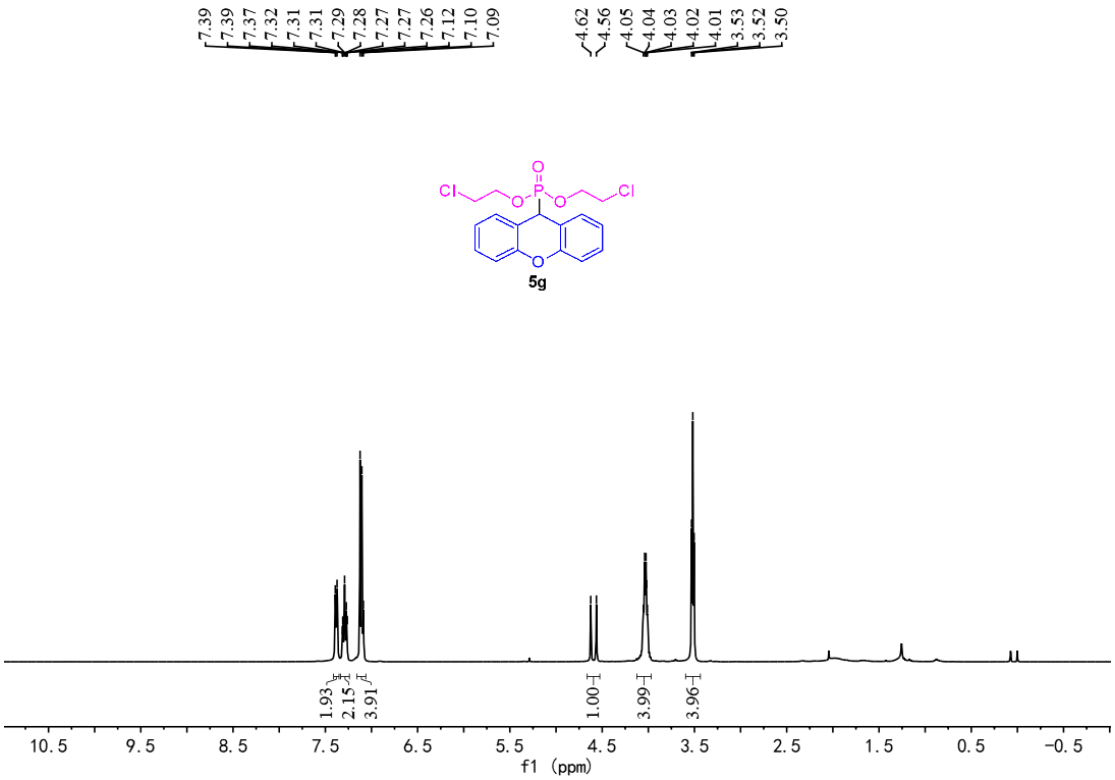
^{13}C NMR



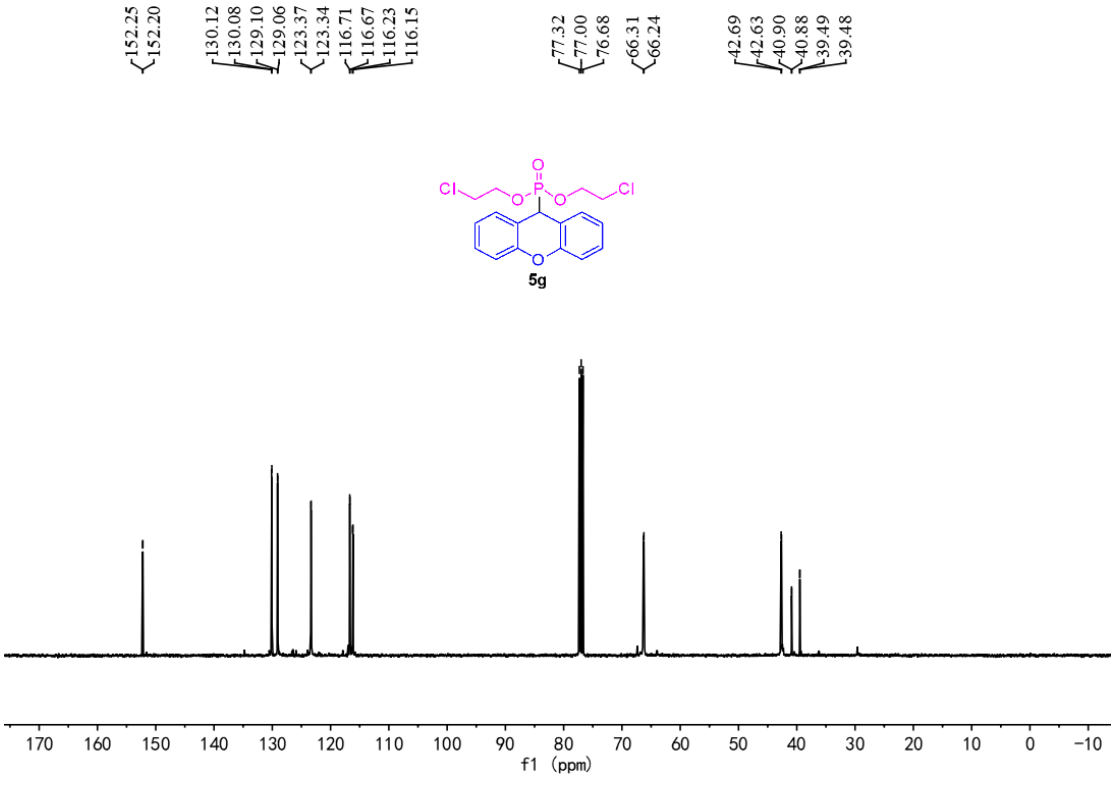
^{31}P NMR



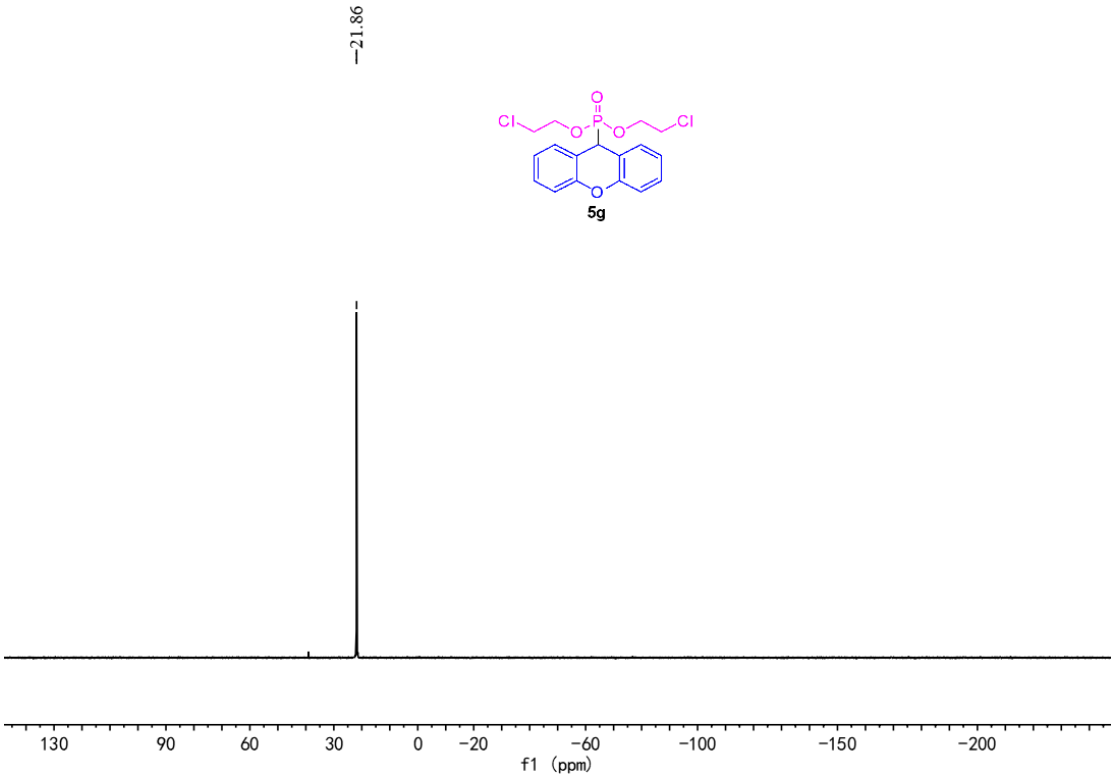
^{1}H NMR



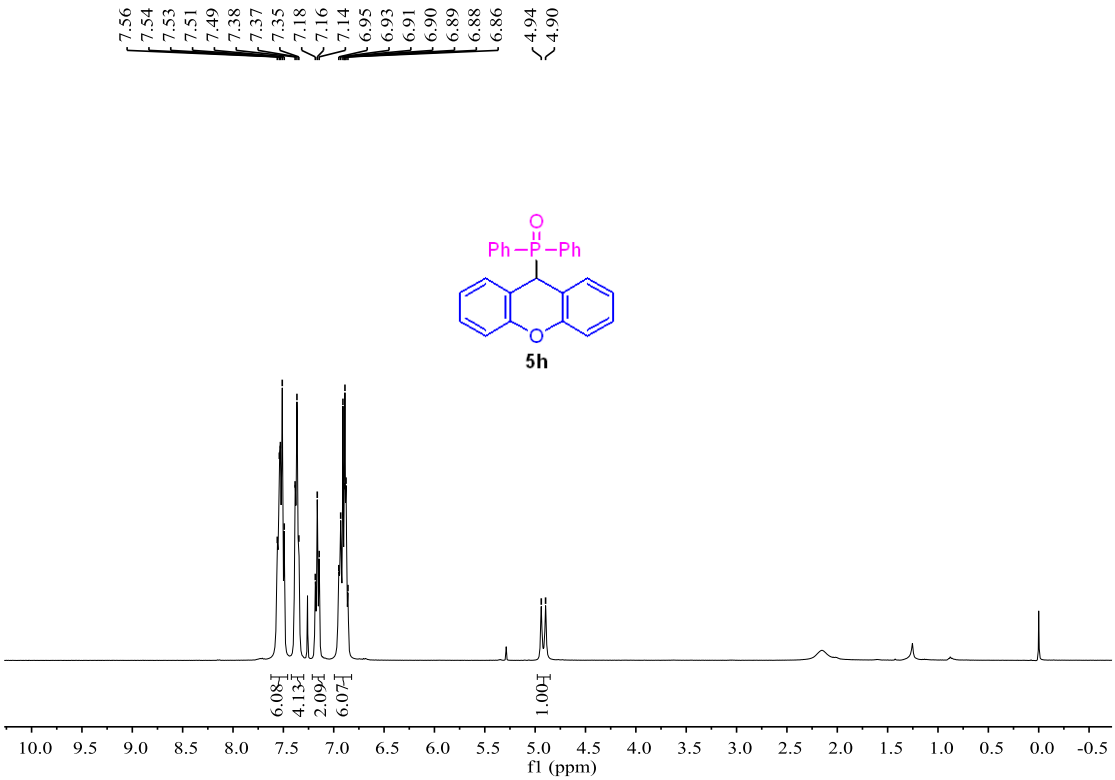
^{13}C NMR



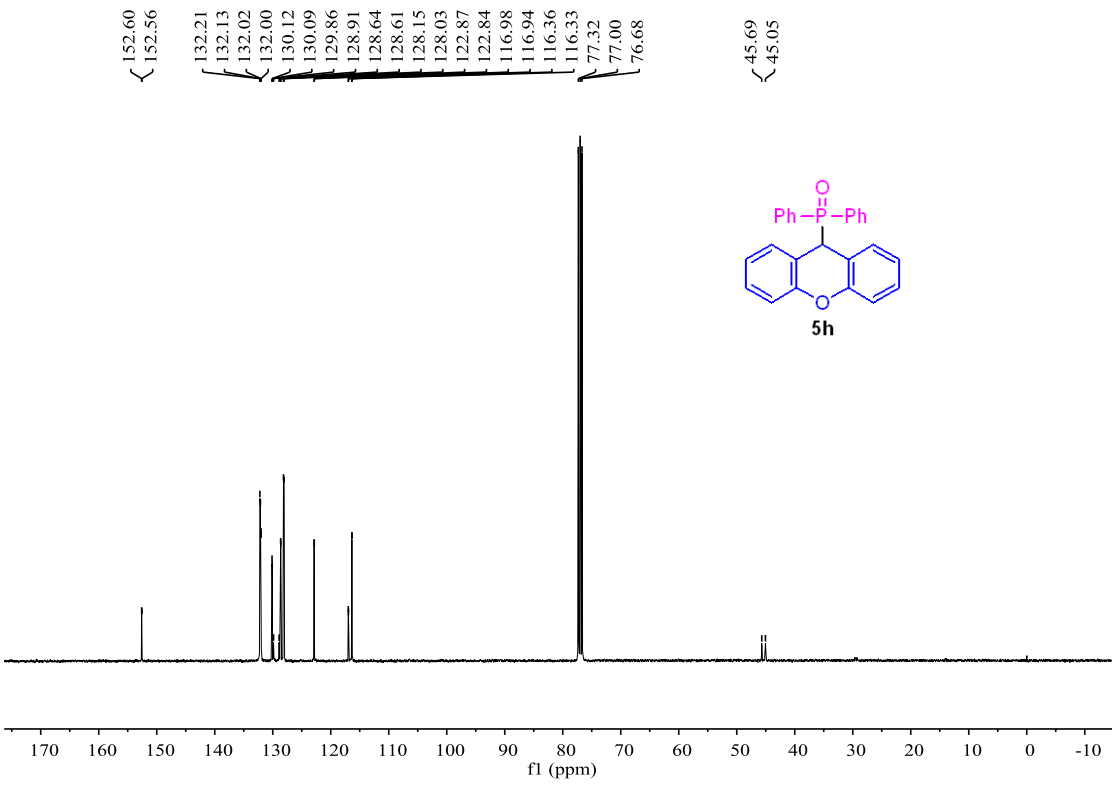
^{31}P NMR



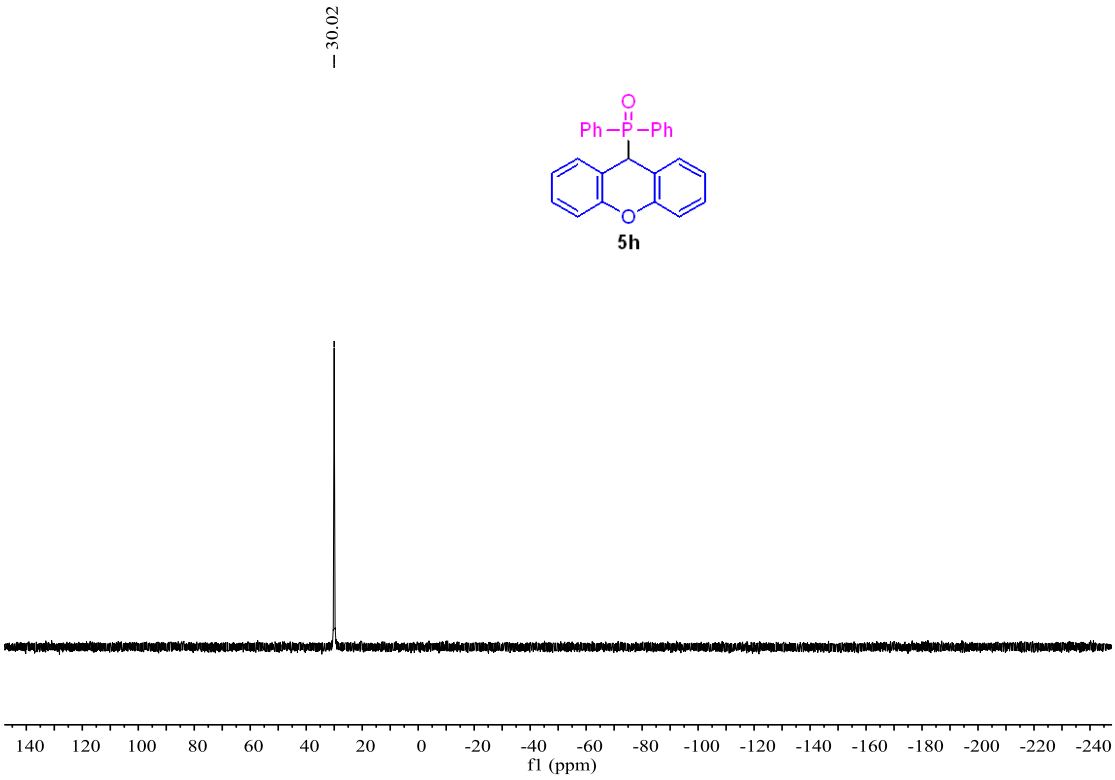
^{1}H NMR



^{13}C NMR



^{31}P NMR


30.02
O
Ph–P–Ph
O
5h
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)